NEE Exhibit B

STATE OF NEW MEXICO
BEFORE THE WATER QUALITY CONTROL COMMISSION

IN THE MATTER OF PROPOSED NEW
RULE 20.6.8 NMAC –
Ground and Surface Water Protection –
Supplemental Requirements For Water Reuse No. WQCC 23 - 84 (R)

NEW MEXICO ENVIRONMENT DEPARTMENT,
WATER PROTECTION DIVISION,

Petitioner.

DIRECT TECHNICAL TESTIMONY AND EXHIBITS

OF

JUSTIN NOBEL

ON BEHALF OF

NEW ENERGY ECONOMY

April 15, 2024

Background and Experience

Q. Please state your name and business address.

A. My name is Justin Nobel and my business address is 134 Round Top Rd, Germantown, NY 12526.

Q. On whose behalf are you testifying in this proceeding?

A. I am testifying on behalf of New Energy Economy ("NEE").

Q. Please summarize your educational background and your professional experience related to water regulation.

A. I have a dual master's degree in earth and environmental science and journalism, write regularly on issues of science and the environment for US magazines and investigative sites. In 2020, I published a lengthy story for Rolling Stone magazine entitled, "America's Radioactive Secret" on the issue of the radioactivity brought to the surface in oil and gas production and the many different pathways of contamination posed to the industry's workers, the public and communities, and the environment. This story won an award for narrative writing with the National Association of Science Writers. My book on this topic will be published April 24, 2024, "Petroleum-238: Big Oil's Dangerous Secret and the Grassroots Fight to Stop It." I have previously provided testimony at hearings of the Pennsylvania State Senate, Colorado Oil and Gas Conservation Commission and New Mexico Oil and Gas Commission. A more complete description of my qualifications is included at the end of my testimony as EXHIBIT 1.

Q. Have you appeared before the Water Quality Control Commission before?

A. I have not appeared before the Water Quality Control Commission ("Commission" or "WQCC"). In 2020, I provided public comment to the Oil Conservation Commission pertaining to the Matter of Proposed Amendments to that Commission's Rules on Produced Water, 19.15.2, 19.15.16, and 19.15.34 New Mexico Administrative Code.

Executive Summary

I have reviewed the Petition by the New Mexico Environment Department ("NMED") pending before the Water Quality Control Commission ("WQCC"), the First Amended Petition and Statement of Reasons, and its proposed new part ("Part 8") to Title 20, Chapter 6 of the New Mexico Administrative Code ("NMAC"). The proposed Part 8 is entitled "Ground and Surface Water Protection – Supplemental Requirements for Water Reuse" and will supplement the existing Ground and Surface Water Protection Regulations found at 20.6.2 NMAC.

In my expert opinion the WQCC should deny the Petitioner's proposal to adopt the Part 8, for the following reasons:

- **(I)** Part 8 fails to recognize that longstanding oil and gas industry documents provide an urgent warning on the very treatment and reuse processes proposed.
- **(II)** Part 8 fails to recognize that in multiple instances in other US oil and gas fields facilities attempting to treat and reuse produced water—even ones touted as industry gold standards—have failed, been shuttered and left a stunning and deeply alarming wake of contamination, for both adjacent communities and the facility's own workers.
- **(III)** Part 8 fails to recognize that permissive rules across other US oil and gas fields have enabled the oil and gas industry to create questionable products out of oilfield waste and led to situations that have unnecessarily exposed the public to radioactivity and other contaminants, as has been well document by academic and official state reports.
- **(IV)** Part 8 fails to recognize the significant health harms of the notorious radioactive element radium, well documented to be present in elevated levels in produced water of New Mexico's oil and gas fields, and furthermore Part 8 fails to

recognize important research which conveys that even minute upticks of radium in drinking water have led to increased cases of childhood bone cancer including the rare bone cancer Ewing sarcoma, which has emerged as an issue of concern in the Marcellus oil and gas field of Pennsylvania.

- **(V)** Part 8 fails to recognize that often included in the general category of produced water by industry workers and waste haulers is flowback, an entirely different waste stream consisting of fluids injected during fracking operations returned to the surface and including water, sand (the proppant), and also a spree of toxic fracking chemicals designed to lubricate and crack open rocks and whose ability to interact with other chemicals and contaminants in the waste streams and in treatment systems is still largely unexamined.

- **(VI)** Part 8 fails to address the significant body of research on uranium mill contamination to nearby croplands, which documents that even minute additions of naturally occurring radionuclides—such as those present in leftover piles at uranium mills and also oil and gas wastewater—to the environment have led to notable biomagnification responses, with radioactivity accumulating particularly in what is known as the "beef/milk pathway" and being found in several studies to accumulate at levels that may be deleterious in infant formula drawn from cow's milk.

- **(VII)** Part 8 fails to address the fact that facilities where oilfield wastewater is injected underground for disposal, typically referred to as injection wells or saltwater disposal wells (SWDs) and regulated by the State of New Mexico under the EPA's Underground Injection Control program, despite their copious use for disposal of oilfield wastewater across the state and nation rely on an outdated, scientifically unfounded, and dangerous disposal technique that puts waters of the state—both underground and surface—at risk of irreversible contamination, as is substantiated in important but overlooked decades-old industry and government reports and statements, and also present-day reports and incidents from other US oil and gas fields.

- **(VIII)** Part 8 encourages and allows for the recycling or reuse of produced water in a matter that may irrevocably lead to the contamination of waterways in New Mexico and generate a range of concerning potential health impacts on New Mexicans, their water resources, their wildlife, their air, water, soil and general ecosystems, and create a concerning and liability-stoked legal landscape due to aforementioned widespread contamination.

I. Part 8 fails to recognize that longstanding industry documents provide an urgent warning on the very treatment and reuse processes proposed.

Q. Why is oilfield wastewater a problem for the oil and gas industry?

A. The US oil and gas industry generates 3 billion gallons of oilfield wastewater a day, and over 1 trillion gallons a year. If a year's worth of this wastewater were filled into standard oil barrels and stacked atop one another they would reach the moon and back nearly 28 times. New Mexico alone generates 67 billion gallons of oil field wastewater a year, placing New Mexico behind only Illinois, Texas, Oklahoma and California when it comes to top oilfield wastewater producing states. Filling just New Mexico's yearly oilfield wastewater output in barrels would form a line to the moon, back again to earth, back again to the moon, and about half back again to earth.

The oil and gas industry often calls this wastewater "produced water", oilfield brine, or salt water, and in the 1820s in Kentucky and Tennessee it was actually mined, in order to make salt, with the oil considered an unwanted byproduct. Those roles were eventually reversed, the oil became the sought after product, the produced water became the waste stream. From day one, which in the United States was 1859, the US oil and gas industry has had no good idea what to do with this waste. And so began an extraordinary campaign to get rid of it all.

Throughout the industry's history drillers have directed produced water into unlined pits dug beside the well, or intentionally dumped it into ditches, streams, swamps, quarries, bayous, and in at least one instance, in Jackson, Mississippi in the 1930s, a wood-sided swimming pool for children—it was called Crystal Lake, and according to the book by veteran southern oilman Dudley Hughes, "Oil in the Deep South: A History of the Oil Business in Mississippi, Alabama, and Florida, 1859-1945," was "enjoyed by many Jacksonians for its balmy waters," although some complained of "the fumes, and the salt's burning children's eyes." Unfortunately for these children, and the oilfield workers who regularly get produced water soaked through their boots and into their skin, or splashed all over their faces and dripped into their mouth, nose and eyes, produced water may contain toxic levels of salt, benzene, a carcinogenic compound often associated with oil and gas deposits, toxic heavy metals like arsenic, lead, strontium and barium. Produced water can also be rich in the radioactive metal radium.

Presently, across the US, approximately 96 percent of produced water is disposed of at facilities known typically in the East as injection wells and out West as saltwater disposal wells or SWDs (for clarity I will stick with the term injection well in my testimony). In New Mexico, approximately 80 percent of produced water is disposed of at injection wells—the remaining 20 percent is reused by the industry. Injection wells have been linked to earthquakes across the nation, have been found to be leaking or alleged to be leaking in ways that threaten groundwater and enables wastewater to return to the surface and novel documents and little-known statements and reports on these issues will be discussed later in this testimony. Even in pro industry parts of the US, injection wells are often despised by communities, who are distrustful of this disposal method, and loathe the relentless truck traffic living near an injection well typically entails. Thus, given the water quality and environmental concerns, and also the social impacts, the desire to find an alternative disposal method for produced water is entirely understandable.

Q. What are the radioactivity levels in the oilfields of New Mexico?

Deep in the earth, radioactive elements like thorium, uranium and radium are in the formations that hold oil and gas, and water is present too. As oil and gas is tapped, this formation water flows to the surface as produced water, or oilfield brine. Uranium and thorium tend to remain in the formation, but radium can be moderately soluble, and generally, the saltier the formation water the more likely radium is to be displaced from the formation rocks, accumulate along with other metals in the brine, and travel with it up to the surface.

Radium has many forms, or isotopes, and the two most prominent in produced water are radium-226, with a half-life of 1,600 years, and radium-228, with a roughly 6-year half-life. This refers to the general amount of time it will take a radioactive element to decay, blasting off a tiny piece of itself—radiation—to become another element, known as a daughter, which may also be radioactive. Radium-226 and radium-228 will continue to decay to other isotopes of the radioactive elements' radon, polonium, lead and bismuth. While these radioactive elements have their own concerning suite of properties and health hazards, the radioactive isotopes typically measured in determining the radioactivity of produced water are Radium-226 and radium-228. Usually, radium-226 and radium-228 values are added together and the combined levels simply referred to as the radium levels.

The primary data source for produced water is the U.S. Geological Survey's National Produced Waters Geochemical Database, which lists levels of various salts and metals in produced water. Unfortunately, radium values are typically not provided in this dataset. In some oil and gas formations, such as the Marcellus in Pennsylvania, academic and government research has produced considerable data on radium levels. However, in other oil and gas formations, there are scant records or none at all. In New Mexico, the only records I have been able to locate of radium levels in produced water come from a 2022 research paper published in the journal, *Environmental Science & Pollution Research*, by researchers at the Carlsbad Environmental Monitoring & Research Centrt, the U.S. Department of Energy Carlsbad Field Office, and New Mexico State University. This paper shows that radium levels range from around 800 picocuries per liter (pCi/L) to more than 1500 pCi/L. While these radium levels place New Mexico produced water radium levels behind the Bakken formation in North Dakota, which according to 2014 research of the Energy & Environmental Research Center at the University of North Dakota can average 3,610 pCi/L and be as high as 6,490 pCi/L, the Antrim formation in Michigan which according to research published by researchers at the University of Michigan Department of Civil and Environmental Engineering can average 5,416 pCi/L and be as high as 22,358 picocuries per Liter, and the Marcellus formation in Pennsylvania which can the Pennsylvania Department of Environmental Protection can average 9,310 pCi/L and be as high as 28,500 pCi/L, the fact that one of the nation's most prominent oilfield states has such a dearth of data regarding radium in produced water is highly concerning and alone should raise pause on any projects attempting to try and manage, treat and reuse this waste stream.

Needless to say, levels of radium found in New Mexico produced water are still cause for concern, as they are far above various protective health-based limits EPA and the Nuclear Regulatory Commission have established for radium. For example, the Nuclear Regulatory Commission has a discharge limit of 60 pCi/L for both radium-226 and radium-228, meaning a nuclear power plant or any other facility overseen by the Nuclear Regulatory Commission would not be able to discharge a stream of fluids into the environment if either radium-226 or radium-228 are above 60 pCi/L. This is important to remember, as radium levels in New Mexico produced water, as evidenced by the above-mentioned 2022 *Environmental Science & Pollution Research* paper, are far above these levels.

The EPA has a specific level at which they define a liquid waste stream as "radioactive" and that level is also 60 pCi/L for both radium-226 and radium-228 and also 60 pCi/L for instances when both radium-226 and radium-228 are present in a waste stream, which in the case of oilfield produced water is almost always. Again, the above-mentioned 2022 *Environmental Science & Pollution Research* paper finds radium far above these levels, meaning in the eyes of EPA, produced water in New Mexico can legitimately be defined as "radioactive waste." It is important to note these researchers provided a range of radium readings they reported in New Mexico produced water, and radium levels were consistently well above the threshold for being defined by EPA as radioactive waste, and consistently well above Nuclear Regulatory Commission discharge limits. EPA's limits may seem complicated, but are laid out clearly in EPA's, "A Regulators' Guide to the Management of Radioactive Residuals from Drinking Water Treatment Technologies" which have included in my exhibits.

Furthermore, the diligent researchers of prior decades had concerns about the radioactive nature of Permian oil and gas formations. This, from the opening lines of a 63-page report produced in 1991 by the esteemed petroleum geologist John B. Comer, of the Bureau of Economic Geology at the University of Texas at Austin: "The Upper Devonian Woodford Formation is an organic-rich petroleum source rock that extends throughout West Texas and southeastern New Mexico and...is very radioactive." Thus, I offer the Department this important question—how can a regulatory agency possibly impose sound rules regarding a waste stream that they know so little about? Not only this, but they have virtually no data on one of the most concerning contaminants in that waste stream, a well-known human carcinogen known to the medical community as a bone-seeker because it has a similar chemical makeup as calcium and when accidentally inhaled or ingested into the human body tends to accumulate in bone.

I will get into details later on just how and why the radioactive elements in produced water can be of such concern to workers and members of the public but for now I will remind the Department of the important findings of the National Academy of Sciences 2006 Biologic Effects of Ionizing Radiation report, known among radiation experts as the BEIR VII report: “There is no threshold of exposure below which low levels of ionizing radiation can be demonstrated to be harmless...The health risks – particularly the development of solid cancers in organs – rise proportionally with exposure.” Essentially, the more radiation a population is exposed to, the more cancer we can expect in that population.

Q. What are the longstanding industry documents that provide an urgent warning on the very treatment and reuse processes being proposed?

A. The most straightforward warning when it comes to produced water treatment systems comes from the oil and gas industry. “Almost all materials of interest and use to the petroleum industry contain measurable quantities of radionuclides that reside finally in process equipment, product streams, or waste,” states an important 1982 report of the Department of Medicine and Biology, of the American Petroleum Institute. “Any control methodology proposed for radioactive materials must recognize the fact that radioactivity can not be modified or made inert by chemical means. It also must recognize that radioactivity dissipates at fixed rates through fixed sequences or series. Decay to daughter products cannot be guaranteed to reduce the hazard...” A few lines later the American Petroleum Institute report points out that any attempt to remove radioactivity is merely transforming, quote, “a very dilute source of radioactive materials into a very concentrated source of radioactivity.” Thus, encouraging the treatment of this complex radioactive waste stream, is nothing more than a free pass for industry to contaminate uninformed and inappropriately protected oil and gas workers.

It is important to note that the oil and gas industry has not promoted or publicized this important document, rather it has been hidden from the public and shielded from the industry operators looking to set up produced water treatment systems. Why the nation's most reputable industry advocacy group would not promote their own important warning, thereby putting communities and its own workers at risk is alarming. As you will soon learn from my testimony, the dangers are all too real and documented harms have already accrued.

It is important for me to inform members of the Department that this one damning 1982 American Petroleum Institute report is not alone. I read you the first two lines of a 1993 article published by the *Journal of Petroleum Technology*, which is produced by the oil and gas industry's flagship professional society, the Society of Petroleum Engineers: "Contamination of oil and gas facilities with naturally occurring radioactive materials (NORM) is widespread. Some contamination may be sufficiently severe that maintenance and other personnel may be exposed to hazardous concentrations." Later in this report it states, quote, "Much of the material wastes from a facility contaminated with NORM must be handled as low-level radioactive waste and disposed of accordingly." It would behoove the Department to familiarize themselves with these two reports and I am attaching them here as **EXHIBIT 2** ("An Analysis of the Impact of the Regulation of 'Radionuclides' as a Hazardous Air Pollutant on the Petroleum Industry" (Committee for Environmental Biology and Community Health, Department of Medicine and Biology, American Petroleum Institute, October 19, 1982)), and **EXHIBIT 3**, (P.R. Gray, "NORM Contamination in the Petroleum Industry" Journal of Petroleum Technology, Volume 45, Number 01 (1993)). I have also included the important 1991 report on Permian geology as **EXHIBIT 4**, (John B. Comer, "Stratigraphic Analysis of the Upper Devonian Woodford Formation, Permian Basin, West Texas and Southeastern New Mexico" (Bureau of Economic Geology, University of Texas at Austin, 1991)). **EXHIBIT 5**, Punam Thakur and Anderson L. Ward and Tanner M. Schaub, "Occurrence and behavior of uranium and thorium series radionuclides in the Permian shale hydraulic fracturing wastes," Environmental Science and Pollution Research, Volume 29 (2022). **EXHIBIT** 6, "A Regulators' Guide to the Management of Radioactive Residuals from Drinking Water Treatment Technologies," (EPA, Office of Water, July 2005).

II. The Stunning and Deeply Alarming Wake of Contamination Left By Facilities Across U.S. Oil And Gas Fields Attempting to Treat and Reuse Oilfield Waste

Q. What evidence do you have of alarming contamination at facilities across the US attempting to treat and process produced water?

A. I have spent the last seven years researching and documenting, among other things, instances of contamination at facilities attempting to treat or reuse produced water for to-be-released published book, "Petroleum-238: Big Oil's Dangerous Secret and the Grassroots Fight to Stop It." The book is a rigorous work of investigative science journalism and also features a number of important whistle-blowing oil and gas workers, including men who have worked at facilities attempting to treat and reuse produced water. In an effort to preserve the gravitas and impact of their words and stories, and the dramatic technical critiques of these facilities that they impart, I will quote directly from the book, and list several relevant and more accessible sources at the end as exhibits.

While my examples are from the Marcellus and Utica oil and gas fields of northern Appalachia, I think it is important to note that this is only because I spent significant time in the these oil and gas fields, and thus was able to make personal connections to communities and oilfield workers and determine the true scope of the problem. It is my firm belief that egregious contamination of this nature may already be occurring at New Mexico facilities attempting to treat and reuse produced water, but light has not yet been shed on the matter by regulators or journalists. They key word here is—yet.

"In June 2023, I am back in West Virginia with Jill Hunkler, Executive Director of Ohio Valley Allies, a grassroots group active in communities threatened by fracking across the Marcellus-Utica, a local filmmaker, and Dr. Yuri Gorby, the former Department of Energy scientist. I learn of another fracking waste treatment plant that had recently exploded, Fairmont Brine Processing, and we stop by to check it out. There are no gates, no "No Trespassing" signs and we waltz right in. The plant is set on a hilltop overlooking the city of Fairmont and has been abandoned. It is littered with random debris, including a mattress and also a speed boat, half-sunk in a moat of radioactive water that surrounds part of the charred main structure. A spew of odd brownish dirt has leaked or been ejected out of the burned-out building. We return with protective gear.

"This is all hot," Gorby exclaims, as he explores the site with a Ludlum 3000 Digital Survey Meter. As he approaches the brown dirt the unit issues a terrifying alarm—at around 2 milliroentgens per hour, and EPA later finds levels as high as 3 milliroentgens per hour. This is disturbing, as the facility's empty buildings are covered in graffiti and littered with beer cans and used condoms, indicating the place has become a local party spot. A man in town tells me scrappers have been visiting too, to swipe copper. "They would have been getting dosed," says Gorby. Behind a barbed wire fence, with gaps in it, is a pool of radioactive wastewater that in big rains spills right over the hillside and down toward town. And we find a bathing suit in the parking lot. “Oh my god, did they go swimming?” asks Jill.

We take samples across the facility and Gorby and Jill have them tested at a radiological analysis lab and discover the radioactive element radium to be 5,000 times general background levels, making these parts of the site more deeply contaminated with radioactivity than over 99 percent of the present-day Chernobyl Exclusion Zone.

In September 2023, Jill calls me. A former Fairmont Brine worker has gotten in touch with her and would like to speak about their experiences. A few weeks later I head out to southwestern Pennsylvania and meet Sean Guthrie. “I had been working in a state prison 12 years as a contract employee, and they lost the contract,” he tells me. Guthrie knew nothing about the oil and gas industry, but local employment had dried up and in 2009 he accepted an entry-level position at a Fairmont, West Virginia fracking waste treatment facility called AOP Clearwater. The year after he took the job the plant shuttered, and in 2013 it reopened as Fairmont Brine, under the ownership of a Pennsylvania firm called Venture Engineering & Construction and Guthrie signed on.

“I felt good about the job and thought we were doing something beneficial for the environment,” he says. He was promoted to operations manager but by 2017 the company was having trouble paying debts, and the following spring Fairmont Brine was shuttered. Two co-workers are now dead from cancer—stomach and brain—and Guthrie suffers a range of health issues that have sidelined him from manual labor jobs, led him to sell his possessions to pay expenses, and left him wondering if he has unknowingly clipped his own life short. “I would like to see some accountability,” he says.

“The facility was designed in accordance with the codes and regulations at the time,” Venture Engineering President and CEO Dave Moniot later tells me. “To our knowledge Fairmont Brine followed all regulations.” He says employees received a six-page explainer on radioactivity, but Guthrie and three coworkers I speak to deny ever receiving this document and say radiation hazards were not mentioned, and no one wore dosimeters, the simple radiation safety devices required in the nuclear industry and radiation medical field that measure a worker’s accumulated radiation dose. “Venture was very nonchalant,” says Guthrie. “They told us while there was radium in it, we weren’t concentrating it enough to have it be any kind of a danger.”

His story of what happened at Fairmont Brine is remarkable, and an important inside look at what may be awaiting workers and communities at dozens or even hundreds of fracking waste treatment facilities operating across America (amazingly, no agency or group I know of has accurately added them all up). Upon entering the Fairmont Brine facility brine trucks unloaded fracking wastewater, namely oil field brine and flowback, into a large pit—where we had found the half-sunk speedboat and soiled mattress. Workers would mix in material to help sediments in the brine clump together and settle as a sludge at the bottom. The leftover liquids went through a filtration system before being piped underground into the “brine pond”—that pool of wastewater we were worried people had been swimming in—then into the main processing building, where they went through a series of specialized tanks called vapor liquid separators that helped separate the salts from the water, which was piped into a second impoundment and after testing for certain contaminants under permitting known as the National Pollutant Discharge Elimination System or NPDES, discharged through a pipe into the Monongahela River.

But problems, Guthrie and his coworkers tell me, were many. Sludge that accumulated in the pits where brine trucks dumped their wastewater was too radioactive to take to local landfills. This led to a situation, reported in 2016 by the Kentucky Department of Environmental Protection, where sealed containers of radioactive oilfield waste were illegally disposed at a landfill across the road from an eastern Kentucky high school and middle school. The brine pond experienced issues too, Guthrie recalls an incident when a rip was detected in the liner and a worker was tasked with diving down to the bottom to make the repair. “They had to put weights on him to get him to go down,” says Guthrie, because the man was having trouble descending through the dense salty water.

In the main processing building the salt slurry being transported on conveyor belts between vessels routinely fell off and accumulated on the floor. This mess had to be shoveled away, and the task-soaked workers in the material. Salty dust in the air was so thick, they recall, the workspace often appeared as if trapped in a haze. With no face masks or respirators, the men were forced to breathe it in. “The ventilation in that entire building was shit,” says Guthrie. “Your clothes got encrusted in salt and it would eat through your boots. When I came into my office and sat down, I could taste salt in my beard. If you licked your lips, or took a drink, you could taste salt in your mouth.” This part of the facility was also uncomfortably hot, with temperature in some areas hovering “around 120 degrees,” he says.

The vapor liquid separators frequently broke down, which occasionally resulted in salty water that had not been fully treated being discharged to the Monongahela River. Guthrie alleged two more examples of waste being dumped into the river or local environment. On a Friday in 2017, he recalled, the brine pond had filled up with wastewater and Venture Engineering President and CEO Dave Moniot told him to take the weekend off and he’d fix the problem. Guthrie was suspicious. When he came back Monday the brine pond was significantly lower, but he saw no evidence of the 40 trucks Moniot claimed had drawn off the wastewater. What he did see was evidence someone had unhooked a hose, enabling wastewater from the brine pond to run directly into the Monongahela. “It looked like he hooked up the impoundment to run straight through the weekend,” says Guthrie, “and discharge the whole frigging thing into the river.”

In a second incident, Guthrie says, he was asked to dump fluids from a set of frac tanks into the parking lot. “I wouldn’t do it, so they got some knucklehead on the nightshift to do it,” he says. There was a pond rich in waterfowl, turtles and fish located downhill from this location. After the incident, “fish in the pond turned up dead,” remembers Guthrie. Still, proud of the facility and the energy he put into trying to make it run right, Guthrie insists that “under normal day-to-day operations, the standards for the NPDES permit were met.” Moniot has not replied to specific questions about these alleged incidents. He had previously told me: “All waters that were discharged were processed through the evaporation plant, according to the NPDES permit requirements.” The permit does not require testing for radioactivity.

Guthrie connects me, at the end of 2023, to Shannon Lutz, whose husband Michael was the worker who passed away from brain cancer. It was an aggressive form called glioblastoma, she tells me. Shannon remains convinced the causes were environmental and says Michael had his body donated to the West Virginia University School of Medicine’s Human Gift Registry, “so they could try and figure out what the problem was and keep this from happening to other people in the future.” She lost Michael earlier in the year and is still grieving. “This is not the plan I had for my life, to lose my husband at 45,” Shannon says.

She and Michael both grew up in northern West Virginia and met in the mid-1990s at a mall kiosk that sold batteries, Michael had helped interview her for the job, then fell in love with her, then she fell in love with him. “The movie Mallrats was our life,” says Shannon. They moved to Pennsylvania, taking office jobs in the same communications company, and followed the company to Buffalo, where they lived together in a large city for the first time and loved it. Then the stock market crashed, they moved back to West Virginia and in with her parents. They had a young child, and Michael got a job in fracking waste at AOP Clearwater to pay the bills.

“I just knew there was exposure,” she says. “His shoes and clothes got damaged, the bottom of his pants were crunchy and hard form the salt and chemicals, and the dust, the dust was crazy! Then there was the sludge pond. He would come home filthy and I would have to wash his clothes, I mean it was disgusting. I was like this can’t be good. We were educated enough to know there was something definitely not right. Michael wanted to get out as quick as possible, and he only worked there a year or two, but he made some of the best friends he ever had. They had a grill that stayed right there at the site, Michael liked to cook and would take a crock pot full of pork barbecue and feed everyone at work. They would bring rolls for sandwiches or Styrofoam bowls for soups. I know Michael grilled ribs at many different times. My son and I would drive up there and drop off dessert. Now when I look back I am like, Oh my god.”

I connect with the University of Pittsburgh geochemist, Dr. Daniel Bain, who interviews Sean Guthrie about the details of his job, amount of hours worked, type of clothing worn and level of exertion are all critical details in building a model to convey just what the radioactivity dose is that he and his coworkers would have received.

Bain's research could potentially challenge studies done by the Pennsylvania Department of Environmental Protection and Argonne National Laboratory, which conclude oilfield workers don't receive enough exposure to cause cancers. But these studies have failed to interview workers and truly understand the incredibly sloppy nature of the facilities where they work. The fallout from scientific evidence demonstrating that those working in oilfield waste indeed receive enough radiation exposure to cause lethal cancers would be explosive, as even if the industry keeps its exemptions, decking men out in hazmat gear and Geiger counters would make it a lot harder to put fracking waste treatment centers near homes and schools and in the heart of communities. And no worker I've met so far, no matter how much they love their country and believe in energy independence, wants to unknowingly be contaminated with radioactivity then get taken out by cancer and leave their spouse, perhaps a very special woman met decades ago at a kiosk in a mall, a widow.

And yet, these days the oil and gas industry has been boasting of their ability to treat, recycle and reuse oilfield waste. The most ambitious example may be a $255 million facility called Clearwater, located in Doddridge County, in northern West Virginia, and developed by the Colorado oil and gas extraction company, Antero Resources, and the multinational French waste, water and energy company, Veolia. At one point Yale University had nearly a quarter of a billion dollars invested in Antero, while Veolia is a $23 billion company and has branded itself as a compassionate corporation, fighting climate change and cleaning up pollution. They began as Compagnie Générale des Eaux, founded in 1853 by an imperial decree from Napoleon III, and have global headquarters in the Paris suburb of Aubervilliers in a building known as Le V that contains multiple interior gardens and is certified by various sustainable architecture alliances. Clearwater was built to process 600 trucks of oilfield brine and flowback each day.

“It’s the best project like this in the world. Bar none. Period,” one Antero official told a West Virginia newspaper in 2019. Project descriptions said Clearwater was going to transform 98 percent of the incoming fracking wastewater, “into clean products: salt and freshwater.” The water would be reused to frack new wells and the salt, said Antero engineer Conrad Baston at a 2015 community meeting in the Doddridge County courthouse, could be used as a deicer on roads, or even for food. “If anybody wants some I can get you a big bag of it,” he told residents. “I thought about calling it, Taste of the Marcellus.”

“This plant, if it works, it would be great,” stated the retired industrial electrician and self-taught radioactivity sleuth, Bill Hughes, at the 2015 meeting. “If it’s done poorly, if it’s not perfectly designed, installed the way it’s designed, operated in accordance with standard operating procedures, with a lot of failsafe features, we risk a massive amount of potential water contamination.” He reminded Baston, the Antero engineer, that he never addressed “the highly radioactive Marcellus Shale” and asked if this sort of project has “ever been done with Marcellus Shale quality produced water, ever, anywhere?” Baston did not directly answer the question. “Don’t lie, don’t shove it under the rug,” cried another resident. “We don’t want another Chernobyl.”

The balmy April morning in 2019 I visited Clearwater with Felicia Mettler from Torch CAN DO and Peter, the Ohio brine hauler, we approached the facility from the west on U.S. Highway 50 and immediately noticed a tremendous plume of grayish white steam rising off the plant’s cooling towers. It drifted over the highway and became one with the sky. Peter suggested flying through a drone or helicopter outfitted with a Geiger counter. This would have been a good idea, as Clearwater, which began operating in November 2017, by September 2019 had been idled. Whether or not the facility, during its 22 months of operation had drifted a curtain of radioactivity over the West Virginia countryside and locations downwind, like Baltimore and Washington D.C., remains an open question. When I ran the question by the Vermont-based nuclear physicist and radioactive waste specialist, Dr. Marvin Resnikoff, in 2019, he said the "steam should contain radioactive elements" and may "potentially mix with the hydrologic cycle and fall out as radioactive rain." Bill Burgos, the Penn State environmental engineer, has published several academic articles on Marcellus fracking waste and said the complex chemical makeup of oilfield brine and flowback, including the extraordinarily high salt levels, make it very difficult to treat, and very difficult to remove the radium. "The waste can be filtered with certain types of membranes," says Burgos, but to do this successfully can be expensive, and still may leave operators with a waste product, "rich in radium."

When I ask Carrie Griffiths, Executive Vice President and Chief Communications Officer for Veolia North America, in 2023, if radium from oilfield brine and flowback would have been released in the steam, she tells me, "Air testing was under Antero's responsibility." When I ask her if the steam was ever tested for radioactive elements commonly found in oilfield wastewater, such as radium, she says, "As previously stated, air testing was under Antero's responsibility." Antero has not replied to any of my questions, and I have been asking them questions on Clearwater since 2019.

When I ask the West Virginia Department of Environmental Protection, in 2019, whether Clearwater had a permit to release radioactivity into the air, and whether or not the agency was testing the steam being released for radioactivity, spokesperson Casey Korbini says the agency issues permits in accordance with federal and state air quality statutes, "and radionuclides are not a regulated pollutant under these statutes." He adds, "this does not mean that radionuclides are prohibited; they are simply not regulated."

Clearwater, and what really happened there, remains on my mind, and soon enough more information emerges. On March 13, 2020, Antero filed a lawsuit against Veolia in the District Court of Denver County, Colorado, accusing the company of fraud, breach of contract, gross negligence, willful misconduct, and demanding at least $457 million in damages. "Clearwater was a failure," reads the complaint, the legal document that lays out the lawsuit's allegations. "Veolia promised, a 'turnkey' facility" where Antero would "simply 'turn the key' and have everything function as intended" but "Veolia failed at every turn," the complaint alleges.

According to the complaint, the idling of the plant in September 2019 had nothing to do with a drop in natural gas prices, as Antero told the Pittsburgh Business Times, more, as the complaint alleges, "the facility simply did not work." Griffiths tells me: "Veolia has and continues to strongly disagree with Antero's allegations" and "in particular, Veolia emphatically denies that it committed fraud."

When I ask Griffiths in 2023 how radium was removed from the incoming waste, she said Clearwater's treatment process had three parts, a pretreatment system that treated solids and dissolved metals, a thermal system where salts were crystallized and separated from the water, and a post-treatment system where the remaining organic compounds were treated by a biological process. "The pretreatment process precipitated radium-containing constituents through a physico-chemical settling process," she tells me. "The radium-containing constituents exited the stream through the pretreatment system's sludge waste."

In reviewing project permits I learn that Clearwater, during its 22 months of operation, may have produced as much as 144 million liters of waste sludge, and 2.8 billion pounds of waste salt. Where did all this waste go? “The sludge was transported to several disposal sites in the United States,” Griffiths tells me. And were salts drawn from the fracking waste ever made into road salts or food? “To Veolia’s knowledge, all the salt was disposed of in the landfill adjacent to the Clearwater facility” and “Antero never produced commercially marketable salt,” says Griffiths. The West Virginia Department of Environmental Protection has not responded to my repeated questions on the whereabouts of this waste.

In early 2024 I hear from Nick Fischer, who had stumbled across my reporting. He operated a bulldozer at the Clearwater landfill, starting just after the plant came online and working through the day it was idled, burying the loads of soupy salt produced by Clearwater’s fracking waste treatment operations. This material, he says, was mixed with fly ash and delivered to him by dump truck. Nick tells me the Clearwater plant never really worked right, no one wore respirators and he was told radioactivity was not a problem he had to worry about. Recently, he has been having breathing difficulties, trouble holding down food, and is losing weight. “I am falling apart, I don’t know where to begin,” Nick tells me. “The companies are just fighting over the money, I’m stuck holding the radioactive bag at the end of this thing.”

Indeed, international and American corporations may battle it out in court over who is at fault, but nowhere does the complaint specifically mention the people and communities of West Virginia who were exposed to the plant’s emissions, and the workers who were exposed to its waste. “The oil and gas industry has succeeded in taking this enormous aspect of their operations and making it vanish,” says Carroll Muffett, President of the Center for

International Environmental Law, a nonprofit legal organization based in Washington, D.C. and Geneva, Switzerland. "Is this recognized in the European public? Almost certainly not, because it is not even recognized in the places where it is happening."

Q. Where does the waste from bench-scale or pilot projects go?

A. It is important to note that in its rulemaking the Department states, "Part 8 authorizes the Department to approve bench-scale or pilot projects involving produced water provided that the Department determines that there will be no discharge to groundwater or a surface water of the state." However, in my extensive reporting and research on this topic I have found that it is technically impossible to create a plant that truly has no "discharge" to the environment. The copious produced water waste stream cannot be made to simply disappear, and thus what I have find is that facilities that do not have a NPDES authorized discharge to waterways have find an alternate and perhaps even more concerning method to relieve them of their waste load, and that is by vaporizing the produced water stream and discharging it to the atmosphere. As noted in the above-cited passage from my book, this injects at least some percentage of the radioactivity and heavy metals inherent to produced water directly into our atmosphere, where it will inevitably be carried with winds and fall out on its own or with precipitation. Thus, rather be truly closed loop or zero discharge systems, these facilities could be more accurately described as active agents of radioactive fallout. For any facilities of this nature currently operating in the State of New Mexico, I would strongly recommend the Department to sample the emissions from these facilities for radioactive and heavy metals.

I am not including as exhibits nevertheless would recommend the Department read carefully the following materials: Justin Nobel, "Inside West Virginia's Chernobyl: A highly radioactive oil and gas facility has become a party spot in Marion County" Truthdig (Los Angeles, California, September 18, 2023);. Justin Nobel, "A Slow-Rolling Disaster in Fracking Country: Ex-employees at 'West Virginia's Chernobyl' speak out on lethal cancers, regulatory failure and contaminated drinking water" Truthdig (Los Angeles, California, December 7, 2023); Justin Nobel, "In West Virginia, Plan to Clean up Radioactive Fracking Waste Ends in Monster Lawsuit" DeSmog (Seattle, Washington, September 19, 2023); Justin Nobel, "Petroleum-238: Big Oil's Dangerous Secret and the Grassroots Fight to Stop It" (Hudson New York, Karret Press, 2024).

III. Permissive Rules Across Other US Oil And Gas Fields Have Enabled The Oil And Gas Industry To Create Questionable Products Out of Oilfield Waste And Led to Situations That Have Unnecessarily Exposed The Public To Radioactivity And Other Contaminants, As Has Been Well Document By Academic And Official State Reports.

Q. What evidence do you have that permissive rules across other US oil and gas fields have enabled the oil and gas industry to create questionable products out of oilfield waste and led to situations that have unnecessarily exposed the public to radioactivity and other contaminants, as has been well documented by academic and official state reports?

A. I will again draw on my seven years of research and reporting from this topic and in an effort to preserve the style and impactful tone of the material I have already crafted on this matter, quote from my upcoming book, "Petroleum-238: Big Oil's Dangerous Secret and the Grassroots Fight to Stop It."

AquaSalina is manufactured with brine from conventional gas wells by a company called

Nature's Own Source based in the Cleveland suburb of Brecksville. The product has been used along the Pennsylvania Turnpike, which runs from near Philadelphia past Pittsburgh, and in Ohio, from 2019 to 2021, 1.56 million gallons was applied by the Ohio Department of Transportation to state and US roads and interstates. Dave Mansbery, president of Nature's Own Source, and also the company that helps generate the product, Duck Creek Energy, tells me it's "400 million year old ancient seawater from the Silurian Age" that "contains a perfect natural balance of chlorides uniquely suited for snow and ice management." He told regional news station WKRC that he soaked his sore feet in AquaSalina.

Indeed, AquaSalina has been easily available for personal use. It comes in a plastic jug and has the fun blue-green color of a gas station slushy. The product's front label says it is "Safe for Environment & Pets" and recommends applying with a garden sprayer on driveways, walkways, and patios to melt ice and also before snowstorms. In 2004, the Ohio Department of Natural Resources issued Duck Creek Energy a Chief's Order to "produce AquaSalina as an alternate disposal method for conventional oil and gas production brine." Thirteen years later, on June 2, 2017, an official with the Ohio Department of Natural Resources entered a Lowe's in Akron, Ohio and purchased a jug of AquaSalina with the aim of testing it for radioactivity. They also purchased a jug from Hartville Hardware in Hartville, Ohio.

Samples were drawn from the jugs, preserved with nitric acid, a chain of custody was established, which is a legal record of the sample's movements, and they were delivered to Pace Analytical Laboratories in Dublin, Ohio. A set of radioactivity testing methods known as EPA Method 903.1 and EPA Method 904.0 were used. Samples are heated on a hot plate to evaporate away water, dried in a drying oven, then cooled in a desiccator. Radioactivity is tabulated by counting the energy different radionuclides release as they decay.

The results Pace delivered back to the Ohio Department of Natural Resources, when listed beside different government radioactivity limits, are striking:

Radium-226 levels in picocuries per liter

Nuclear Regulatory Commission discharge limit: 60

Level at which EPA defines a liquid as “radioactive”: 60

AquaSalina sample from Lowe’s: 1,059

AquaSalina sample from Hartville Hardware: 1,158

Radium-228 levels in picocuries per liter

Nuclear Regulatory Commission discharge limit: 60

Level at which EPA defines a liquid waste as “radioactive”: 60

AquaSalina sample from Lowe’s: 604

AquaSalina sample from Hartville Hardware: 1,333

Radium-226 and radium-228 combined levels in picocuries per liter

EPA Safe Drinking Water Act limit: 5

Level at which EPA defines a liquid waste as “radioactive”: 60

AquaSalina sample from Lowe’s: 1,663

AquaSalina sample from Hartville Hardware: 2,491

A number of researchers I’m in touch with are aware of AquaSalina. “If I had a beaker of that on my desk and accidentally dropped it on the floor, they would shut the place down,” says Dr. Yuri Gorby, the former Department of Energy scientist. “If I dumped it down the sink, I could go to jail.”

“Every time you put this solution onto your front steps you are basically causing a small radioactive spill,” says Dr. Avner Vengosh, the Duke University geochemist, who has examined AquaSalina.

The Youngstown Battalion Fire Chief Silverio Caggiano points out deer, horses and house pets love to lick salt. “What do you think Spunky the dog is doing to the AquaSalina after this stuff dries?” he says. “It is licking it up, then it licks you, it licks the furniture, it licks everything, and people will wonder why 10 years from now Spunky dies of doggy bone cancer.”

But the Ohio Department of Natural Resources made no public announcement in 2017 after learning Lowe’s and Hartville Hardware were selling a product in their stores containing worrisome amounts of radium.

In 2018, and again in 2019 and 2023, I ask Lowe's how many of their stores carried AquaSalina? If Lowe's outside of Ohio sold the product? If Lowe's was still selling it? Approximately how much AquaSalina they have sold? And if Lowe's has ever tested this product for radioactivity? The company hasn't replied to any of these questions.

Meanwhile, Nature's Own Source has continued producing their perfect blend of salts from "the Silurian Age." And it has kept on snowing.

Pacific Northwest Snowfighters may be the nation's most highly respected organization for evaluating deicers and runs products through a variety of tests to earn them a spot on its Qualified Products List. But the group "does not currently test products for radioactive elements," Jay Wells, a Pacific Northwest Snowfighers representative tells me in 2018. Nor does the group track product sources, making it impossible to determine just how many deicing products made from radioactive oilfield waste the organization has already approved. Their Qualified Products List, as of September 2023, had 158 products, and AquaSalina became one of them in 2013. When I ask Pacific Northwest Snowfighters in 2023 if AquaSalina is still on their Qualified Products List, they tell me that list is now managed by a group called Clear Roads. AquaSalina remains on it, and deicing products still are not being tested for radioactivity.

It is important to note that recently Ohio has had something of a reckoning. In August 2021, the Ohio Department of Transportation decided to stop purchasing AquaSalina. In 2022, the Ohio Department of Health analyzed the radiation risks posed by the continual application of a radium rich brine each winter in a residential setting and determined the dose received by an adult or child would be considerable. "Due to the increased levels of human exposure to radiation," the department concluded, "use of products derived from oil and gas production brine is not recommended."

IV. Part 8 fails to recognize the significant health harms of the notorious radioactive element radium, well documented to be present in elevated levels in produced water of New Mexico's oil and gas fields, and furthermore Part 8 fails to recognize important research which conveys that even minute upticks of radium in drinking water have led to increased cases of childhood bone cancer including the rare bone cancer Ewing sarcoma, which has emerged as an issue of concern in the Marcellus oil and gas field of Pennsylvania.

Q. What evidence do you have that even minute upticks of radium in drinking water have led to increased cases of childhood bone cancer including the rare bone cancer Ewing sarcoma, which has emerged as an issue of concern in the Marcellus oil and gas field of Pennsylvania?

A. I will again draw on my seven years of research and reporting from this topic and in an effort to preserve the style and impactful tone of the material I have already crafted on this matter quote from my upcoming book, "Petroleum-238: Big Oil's Dangerous Secret and the Grassroots Fight to Stop It." While the excerpt is lengthy, I advise the Department read it in full, as it contains important examples on how poorly crafted and permissive rules concerning oil and gas industry produced water can have significant ramifications and potentially devastating public health ramifications.

"In 2019 investigative reporters at the Pittsburgh Post-Gazette revealed that in the community of Cecil, in Washington County, five cases of Ewing sarcoma had been diagnosed since 2008. And across the four counties in the southwest corner of Pennsylvania, Washington, Greene, Fayette and Westmoreland, heart of the booming Marcellus Shale, from

2008 through 2018, 27 cases of Ewing sarcoma had been reported.

Six cases of Ewing's were diagnosed within the Canon-McMillan School District, the article reported, and several kids had attended the local high school together, known as Canon-Mac, in Canonsburg, Pennsylvania. One of them was Luke Blanock. Another was Mitch Barton, in 2018 he experienced pain in his right shoulder and a chiropractor found an unusual set of small bumps. An X-ray later revealed his clavicle had been mysteriously fractured. As kids, Mitch and Luke played baseball together. At Canon-Mac Luke was pitcher, and Mitch catcher.

Curtis Valent, also of Cecil, also a baseball pitcher, also played as a kid in the Cecil Township Youth Baseball Association was diagnosed with Ewing's in mid-2008. For him the cancer also began with a hurt shoulder, as well as a fever and chest pains. The disease spread to his lungs, liver, lymph nodes and spleen, and in 2011, at the age of 23, he passed away.

Alyssa Chambers of Cecil was diagnosed with Ewing's in late 2008 as an 18-year-old Canon-Mac senior. She survived.

Kyle Deliere was diagnosed in 2011. He had played in the Cecil Township Youth Baseball Association, and lived about a mile from Luke Blanock in Cecil. Kyle, according to the Pittsburgh Post-Gazette, "lost weight, had night sweats and fevers, and developed large tumors on his hip, femur and lungs," and died on November 15, 2013, at the age of 27.

There is also the case of David Cobb, diagnosed in June 2018 at the age of 37. "He found this cancer from a simple nose bleed," his wife Alison wrote on a patient support site. "And days later they were removing a tumor from his sinuses." It's a less common place for Ewing sarcoma to show up, but has been documented. At the time David was living in Cecil.

The Post-Gazette article described ten other cases of unusual cancer that were afflicting or killing the children and students of Cecil and Canon-Mac. They included one astrocytoma (brain and spinal cord); two osteosarcoma (bone); one liposarcoma (joint); one rhabdomyosarcoma (muscle); one Wilms tumor (kidney); one liver cancer and two cases of leukemia (blood).

David Spigelmyer, in 2019 president of the Marcellus Shale Coalition, the trade group representing fracking interests in Pennsylvania, had told the Post-Gazette that attempts to link the incidence of Ewing sarcoma to the industry were without scientific or medical support. His group cited a review of medical data by the American Cancer Society that had found “no known lifestyle-related or environmental causes of Ewing tumors.”

Indeed, the medical profession supports this conclusion. “Doctors have not identified any risk factors that make one child more susceptible than another,” says the American Academy of Orthopaedic Surgeons. “Parents should know that there is nothing they could have done differently to prevent their child’s tumor,” says the Academy, and the disease “does not develop as a result of any dietary, social, or behavioral habits.” There are about 75 million children and adolescents in the United States, and according to John Hopkins University School of Medicine, about 225 of them are diagnosed with Ewing sarcoma each year. “The exact cause of Ewing sarcoma,” says John Hopkins, “is not fully understood.”

But certain information is firmly known. Ewing’s primarily occurs in children and young adults. More males are affected than females. Ewing’s can develop in tissue near bone and also the sinus cavity but most often occurs in bone, and most regularly in the shin bone (tibia), thigh bone (femur), upper arm bone (humerus), hip bones, ribs, spine and skull. Initial symptoms include swelling and tenderness, a lump that may feel warm and soft, or a bone that breaks for no apparent reason. Parents may mistake Ewing's for a sports injury. And while Ewing sarcoma can occur at any time during childhood, it most commonly develops during puberty, when bones are growing quickly.

"In adults things sort of go in slow motion, but in children everything is rapidly replicating," says Dr. Larysa Dyrszka, an upstate New York pediatrician and co-founder of an advocacy group called Concerned Health Professionals of New York, which has repeatedly raised alarm about the health risks fracking poses to children. "Because children's organ systems and bones are still developing there is a lot more turnover of cells," says Dyrszka, "making them more likely to develop, say, a tumor." Every year her group, together with Physicians for Social Responsibility and the Science & Environmental Health Network, publish an epic report entitled, Compendium of Scientific, Medical, and Media Findings Demonstrating Risks and Harms of Fracking and Associated Gas and Oil Infrastructure. The latest volume cites from over 2,000 scientific studies and informs that radioactivity releases represent only one of the significant harms posed to workers and nearby communities. The release of benzene, heavy metals, and toxic drilling chemicals all pose cancer risks too.

In an area where a new toxic contaminant has been introduced to a community, children would naturally serve as the canary in the coal mine. And the first cancers expected to emerge would be the ones that tend to develop more quickly, like cancers of the blood, and bone.

If radium somehow did happen to be behind the Ewing sarcoma cases, then what exactly had gone wrong in southwestern Pennsylvania that could have led to the radioactive element entering the bones of teenagers?

“The corruption here was pathetic, there was major conflicts of interest,” says Ron Gulla, whose Washington County farm was one of the first places fracked in the entire state, in late 2004 and early 2005. He worked for a large company that supplied tools and equipment to the oil and gas industry. While initially enthusiastic about money and business the boom would bring, working in oil and gas and having wells on his farm enabled him to see the industry up close, and Gulla quickly became alarmed.

“The industry planted people on the county chamber of commerce, they hired off-duty police officers to work security, they showered gifts on the local fire departments, and they even wormed their way into agriculture,” he says. “I was like these motherfuckers are going to infiltrate everything, and they did. I told people, they are killing us without firing a bullet. And I said, Jesus Christ, this is going to cause cancer. Not because I am a scientist or Mr. Educated Scholar, it’s common sense”—a few years after Gulla and I first spoke, his wife was diagnosed with acute myeloid leukemia.

He describes how southwestern Pennsylvania, a patchwork of forests, industry, and sweeping fields and family farms, each with their own streams and cow ponds, and all of it woven together by larger creeks and rivers, became completely overrun by the oil and gas industry and its seemingly endless collection of tanks, trucks and impoundments. “People are going to fall over when they see how much waste this industry has produced,” says Gulla. The amount of chemicals necessary to drill and frack became apparent too, as residents saw vats and containers hauled regularly on their roads and set up at well pads. “I spoke to one trucker who hauled fracking chemicals and I was legitimately freaked out," says Gulla. "He said to me, you have no idea how much acid we dumped in these wells."

Among Gulla's biggest concerns were what it all meant for the creeks, and also the wild food many in southwestern Pennsylvania rely on, such as deer and fish. Early on, the son of a local science teacher he went hunting with was diagnosed with Ewing sarcoma. "Kyle Deliere was 25 years-old when he got it," says Gulla, and 27 when he died, in 2013. "Kyle suffered for two years," he continues, "it was a heart-breaking story, I went to the funeral. He played football, was on the wrestling team, and his father hunted on my farm, and Kyle liked to eat deer meat." That small things at the bottom of the food chain may take in minor amounts of an environmental contaminant, concentrate it in their bodies, and pass on much greater and potentially toxic concentrations to things that eat them is called biomagnification, and the concept niggled away at Gulla.

"Remember all the dead cattle," he says. "I know a lot of farmers who said they drilled on my farm and all is fine. Bullshit, who the hell went and did testing? These animals and wild game are exposed 24/7, and that's our food, so what the hell are we eating?"

Following radium from the fracking industry into things that can serve as food for humans has not been closely examined across Pennsylvania, but there has been some research. Dr. Nathaniel Warner, an environmental engineer at Penn State University, and his colleagues investigated freshwater mussels, which are common in Pennsylvania creeks and make their shells out of minerals pulled from the water. They found that in certain heavily drilled parts of the state, downstream of facilities that process oilfield wastewater and discharge back to waterways, the animals had taken in oilfield waste contaminants, including radium. “The mussels,” says Warner, “brought the radioactivity into their hard shells.”

He is currently assessing whether or not radium builds up in the organism’s soft tissue too, which would be worrisome, as most creatures eat the meaty part of the mussel and not the shell. This would suggest a route for the oilfield’s radium to travel out of creeks and up the food chain. Warner points out that catfish, muskrats, and humans all eat mussels—and humans eat catfish. “Unfortunately,” he says, “the literature is all over the place about how concerned we should be.”

Pennsylvania’s creeks have floodplains, and the floodplains hold things like baseball fields and town parks, and the creeks flood regularly. Videos of these events show violently rushing water and inundated fields. Everything ends up in the creeks, and when the creeks flood they can bring contaminants with them. Even good operators could lose material in an accidental spill. But early on in the Marcellus boom in southwestern Pennsylvania there was evidence emerging that massive amounts of waste were being spilled intentionally.

In Greene County, it was found that a company called Allen’s Waste Water Service had illegally dumped millions of gallons of fracking wastewater. They used dastardly methods, including discharging waste at night, in rainstorms, and pouring waste down a drain in the company garage that led into a stream that ran eventually to Dunkard Creek, a popular fishing hole. One local fisherman says a front of rusty brown contamination invaded the creek, and he observed thousands of fish die and stressed fish jumping out of the water—“you could tell they were being poisoned.” Allan’s Waste Water Service also dumped waste into an old coal mine shaft. “My theory,” one Greene County environmental leader told a reporter in 2013, in trying to describe the industry’s mindset, “is, whenever there’s a hole, you can use it. It's open season down here."

In adjacent Fayette County, it also must have been open season. In 2017, the Office of the Attorney General investigated local businessman John Ashley Joseph, who allegedly directed employees of a landscaping company he ran called Perry Stone and Supply to dump truckloads of fracking waste at locations across the county, including along a rural road just 50 feet from a cattle field, behind a Dairy Queen, and at a makeshift landfill on Joseph's own property that came to be known as the "Perry Pit." Investigators tested each location and detected diesel fuel, barium, and strontium, contaminants indicative of drill cuttings. Perhaps most outrageously, fracking waste was also allegedly dumped at the courthouse where John Ashley Joseph was eventually to appear. "A large former foundation and the parking lot," one driver testified, "are completely filled with drill cuttings."

The ecosystem was ripe for shady operators. An investigation in the early years of Pennsylvania's fracking boom conducted by ProPublica described spills of fracking fluids, drill cuttings and hydrochloric acid. In one 2009 incident, Texas-based Range Resources spilled nearly 5,000 gallons of waste—the equivalent of an entire truckload's worth—into a tributary of Cross Creek, a protected watershed. While the state reported numerous fish and other wildlife dead, Range Resources spokesman Matt Pitzarella said it amounted to less than a pound of minnows.

The U.S. Geological Survey research team that assessed the brine spill in Blacktail Creek in the Bakken oilfield in North Dakota found radium had traveled 4.5 miles downstream and built up in creek sediments and also the floodplain. Radium in the floodplain could be blown about by the wind and also indicated "a potential for animal exposures," the authors noted, and “radium exhibits characteristics similar to calcium and therefore can be deposited in bone and connective tissues surrounding organs.”

The idea that Pennsylvania creeks could have ferried a discharge of fracking waste downstream and spread the waste onto floodplains that residents interact with is certainly plausible. In Cecil, two youth baseball fields are in the floodplain of a creek that floods regularly called Millers Run. The fields, among other things, are downstream of the truckyard of Weavertown Environmental, a local oilfield waste hauling and environmental services company, and satellite images show the yard to be filled with, what appears to be, all sorts of waste trucks and containers. “In 2003, when Marcellus Shale discovered a promising flow of natural gas in Washington County, PA,” our business “jumped on the opportunity,” says Weavertown Environmental Group President Dawn Fuchs Coleman in a book she wrote about how to succeed in business. “We did not sit on the side lines like some companies did,” writes Coleman, and wait to “see if the Marcellus Shale opportunity was a winner, winner chicken dinner.” Her company, “seized the opportunity.”

I asked Weavertown Environmental about radium in the oil and gas industry waste they had hauled and disposed, just how much waste was kept on their site above Millers Run, what safeguards they installed to ensure runoff didn’t flow offsite, if they had ever tested this runoff for contaminants, and if any significant floods had occurred at the site, but I have not heard back.

It is not yet noon, and Ray Kemble has already taken shots of whiskey. He retreats to a chair at the head of the wooden table in his dining room, lights up a corncob pipe with Smoker’s Pride Black Cavendish tobacco, then pulls from beneath the wooden table a powerful handgun, which he has nicknamed the executioner, and shows it off to a visiting documentary filmmaker.

Ray lives in Susquehanna County, in northeastern Pennsylvania, directly atop a sweet spot of the Marcellus formation. “They’ve tried every possible way to shut me up,” he says. The former oilfield waste truckdriver has a long yellow beard and Harley-Davidson cap and holds what may possibly be an important clue to the Ewing sarcoma cases.

“All I know is we used to deliver to these wastewater treatment plants right on the river,” says Ray. “These places were slamming, they would take four brine trucks at a time. We hook up our hoses and are dumping 5,000 gallons of fucking frack waste into some vat, and I see it gets stirred around, and it gets rolled around, then it goes through the treatment plant and right into the river, schwoop!”

Oilfield brine in Pennsylvania was initially discharged to pits and streams. These practices were banned in the 1980s and more sophisticated options developed, such as spreading the waste on public roads to try and melt snow and ice or reduce dust. Pennsylvania has far fewer injection wells than other oilfield states, such as Ohio, which has hundreds, or Texas, which has thousands. Before the state’s fracking boom began, around 2005, Pennsylvania was still producing tens of millions of gallons of oilfield wastewater a year. Another tactic was needed for disposing of oilfield brine, and a custom developed of bringing this waste to sewage plants and places the state called centralized waste treatment facilities. They accept the waste, treat it in some way to remove contaminants, then discharge the treated waste back into a creek or river. In order for this discharge to be legal, the facilities need a National Pollutant Discharge Elimination System—NPDES—permit, which is supposed to ensure worrisome toxic elements aren't being shot back into rivers and the environment.

There was a problem with this system. According to the U.S. Geological Survey National Produced Waters Geochemical Database, even brine from conventional oil and gas wells in Pennsylvania can have levels of radium above 20,000 picocuries per liter, thousands of times higher than EPA's safe drinking water limit for radium, which is 5 picocuries per liter. But NPDES permits for centralized waste treatment plants didn't require operators to check for radium in the discharge they were putting back into Pennsylvania creeks and rivers.

"The problem started in 1859, with the first oil and gas well drilled in Pennsylvania," says David Hess, who led the Pennsylvania Department of Environmental Protection in the early 2000s and now runs the PA Environment Digest Blog, an invaluable site that keeps tabs on oil and gas and other environmental legislation in the Pennsylvania statehouse. "Every well from the time it is drilled until it is plugged produces brine/wastewater, day in and day out, and it has to be dealt with," Hess tells me via email in 2023. "Conventional well drillers never wanted to pay anything to get rid of this water so they just dumped it wherever, streams, holes they dug, spread it on roads they said to control dust (it doesn't, it's disposal)." He continues, "no one watches what's being shipped, what's being accepted, what's being cleaned up and reused, what's being discharged from these facilities. It's the wild west!" And while in 2010 the Pennsylvania Department of Environmental Protection added stricter discharge limits for salts and some metals at these treatment facilities, there were still no rules for radium.

By 2010, with the Marcellus Shale being intensively developed with the techniques of modern fracking, a massive new wave of oilfield wastewater was headed for the plants, 232 million gallons a year, according to a presentation by an oilfield wastewater treatment plant operator named Paul Hart. It included Marcellus flowback, with its largely unknown toxic cocktail of resurfaced frack chemicals, as well as Marcellus oilfield brine and all its salts, carcinogens, heavy metals, and radium.

In 2015, the environmental engineer Bill Burgos, along with a team of other researchers set out to examine whether they might be able to find places in Pennsylvania's environment where this oilfield radium was accumulating. They realized that 12 miles downstream of Paul Hart's oilfield wastewater treatment plant, on Blacklick Creek, was a reservoir called Conemaugh River Lake. Another oilfield waste treatment plant discharged into Blacklick Creek at a distance of six miles from the lake.

Burgos, and Penn State's Nathaniel Warner, the same geochemist studying the accumulation of oilfield radium in mussels, hypothesized that oilfield contaminants might be flowing all the way down the creek, to where it joins the Conemaugh River, then into the reservoir, which was formed by a dam. Because sediments accumulate regularly every year at the bottom of lakes, and a dammed lake is particularly good at trapping sediments, these mucky bottom layers can provide a detailed window into an area's pollution history. Indeed, the researchers found that coring down through layers of lake muck was like tracing back the years of the Marcellus Shale boom. A paper they published in the journal Environmental Science & Technology in 2017 reported that "sediment layers corresponding to the years of maximum" oil and gas wastewater disposal contained higher concentrations of salts and chemicals with the signature of oilfield waste.

Dr. Avner Vengosh, the Duke University geochemist who had studied brine spills in North Dakota and the liquid deicer AquaSalina in Ohio, sampled the point where an oilfield wastewater treatment plant discharged into Blacklick Creek, in western Pennsylvania. His research team found radium levels in the stream sediments at the point of discharge were about 200 times greater than the levels in the upstream and background sediments. The levels were so high, the researchers reported in 2013 in Environmental Science & Technology, that in certain states, Michigan for example, they "would require transportation…to a licensed radioactive waste disposal facility." (Nathaniel R. Warner, Cidney A. Christie, Robert B. Jackson and Avner Vengosh, "Impacts of Shale Gas Wastewater Disposal on Water Quality in Western Pennsylvania," Environmental Science & Technology, Volume 47 (2013))Oilfield wastewater treatment plants were clearly incapable of removing all the dangerous contaminants from the waste streams they were taking in.

The EPA knew this too, and in a little-publicized 2018 report on oilfield wastewater treatment plants in Pennsylvania, Ohio, and West Virginia, said there were "documented and potential impacts to both aquatic life and human health related to discharges from…facilities treating oil and gas extraction wastewater." EPA pointed out that, "multiple drinking water intakes are situated downstream of" these treatment plants. The Department of Energy also examined the issue, with a fieldtrip made by an Argonne National Laboratory scientist, and a report published in 2010. "As the Marcellus Shale development grew in popularity, operators sought permission to bring more truckloads of salty flowback and produced water to the treatment plants," they reported, resulting in an increased discharge of salts from the oilfield wastewater into waterways. (John A. Veil, "DOE Award No.: FWP 49462, Final Report, Water Management Technologies Used by Marcellus Shale Gas Producers" (Argonne

National Laboratory for U.S. Department of Energy, National Energy Technology Laboratory)) Argonne is one of the nation’s most sophisticated labs for analyzing radioactivity, but the report never once mentioned the word. I have asked Argonne why not, and not received a reply.

In 2016, the Pennsylvania Department of Environmental Protection published an expansive report on oilfield radioactivity in the Marcellus. The conclusion was, “there is little or limited potential for radiation exposure to workers and the public.” (Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM) Study Report, (Pennsylvania Department of Environmental Protection, 2016)) But the contents of the report revealed facilities treating Marcellus oilfield wastewater had an extraordinary radiological problem on their hands. At centralized waste treatment plants and also sewage plants, the state found concerning levels of radium accumulating in the sludge that settled out of the wastewater, the sediment at the point of discharge, and the treated wastewater the plants were discharging to waterways. Some plants were discharging radium back to the environment at levels thousands of times EPA’s safe drinking water limit. Radiation exposure rates for workers were occasionally at levels dozens of times what would be considered a contaminated workspace by US government health agencies, and radioactivity found on plant surfaces, according to the report, presented “a potential inhalation or ingestion hazard.” This raised the point that these workers should be treated more like nuclear workers than sewage plant workers.

Brett Jennings, Chairman of the Hallstead-Great Bend Joint Sewer Authority, in northeastern Pennsylvania, tells me he was against accepting the oilfield brine and flowback the fracking industry was seeking to dispose of at Marcellus area sewage plants like his. For one, says Jennings, sewage plants are not meant to process the complicated brew of chemicals, heavy metals and radioactive elements in fracking wastewater. He saw in real time what happened when his plant tried. In 2014, a pair of brine trucks were discovered near an abandoned railroad track, illegally discharging into one of the plant’s sewer lines. “They actually lifted the manhole up and dumped it right down,” says Jennings. The incident happened in the morning. By afternoon, his plant was dead.

But as the Marcellus boom came on and continued through the financial crisis in 2008 local governments were broke and desperate. In 2009, the ProPublica investigative reporter Joaquin Sapien reported that when Francis Geletko, financial director at a sewage treatment plant in Clairton, a city south of Pittsburgh located along the Monongahela River, learned drillers would pay 5 cents a gallon to get their wastewater processed at his plant his first thought was: “Cha-ching!” Pennsylvania had enabled a practice that was discharging a considerable yet largely unknown stream of additional radium into the same rivers Pennsylvanians relied on for drinking water.

And all roads lead to Pittsburgh, the city of three rivers. Here, the Monongahela meanders in from the south to meet the Allegheny, which enters from the northeast to form the Ohio, which exits toward the west. Water for downtown Pittsburgh is covered by the Pittsburgh Water & Sewer Authority. Much of the area north of Pittsburgh in Allegheny County is serviced by local municipalities. “And the whole southern part,” a former Pittsburgh Water & Sewer Authority water plant worker tells me, headed south along the Monongahela River and into Washington, Greene, Fayette and Westmoreland counties, the four counties where the Ewing sarcoma cases had occurred, “that’s mostly Pennsylvania American country.”

Pennsylvania American Water is a subsidiary of American Water, founded in 1886 as the American Water Works & Guarantee Company. “Our beginnings were humble,” says the company. “A small group of entrepreneurs and innovators spurred the nation’s industrial development by bringing a critical commodity - pure, abundant water - to towns and cities across the land.” Over the 20th century the company bought up smaller water providers and expanded. By 1999, American Water Works, as it was then called, served 345 billion gallons of water to more than ten million customers. “Today,” they say. “We work hard each and every day to supply our customers with something they cannot live without - high-quality water.”

But the oil and gas boom in Pennsylvania was so big it didn’t just swallow up local governments and fire departments and sewage plants and environmental protection departments, it swallowed drinking water providers too. “Private Water Companies Join Forces With Fracking Interests,” reads the 2012 headline of an article in the Colorado Independent. It detailed how “two of the country’s largest private water utility companies are participants in a massive lobbying effort to expand controversial shale gas drilling.” One was American Water. Apparently, because the practice drank up so much water, fracking was good for the drinking water business.

In 2011, Pennsylvania American Water joined the Marcellus Shale Coalition, the fracking industry’s powerful trade group. Annual associate membership dues at the time were $15,000. American Water will “continue to be stewards of the environment,” spokesman Terry Maenza told the Colorado Independent. In 2011 he told another investigative reporter that Pennsylvania American Water had at one point considered leasing its properties for gas drilling, but shelved the idea and instead decided fracking should be restricted to a distance of at least 1,000 feet from a reservoir relied upon for drinking water.

American Water's priorities are laid out in the company's 2012 annual report to investors. "Dear Fellow Stockholder," begins a message from Chairman of the Board President George MacKenzie and Chief Executive Officer Jeff Sterba (who previously worked as Chairman and CEO of PNM Resources). "We increased earnings per share from continuing operations by more than 12 percent to $2.11 per diluted share. Revenues, net margin and cash flow all increased, strengthening our balance sheet, while we improved our regulated operation and maintenance (O&M) efficiency ratio to 40.7 percent." And, the report continues, "we entered into agreements with two energy companies to construct pipelines for supplying water to support shale gas drilling operations."

By the beginning of 2012, American Water was selling water to the oil and gas industry at 34 different distribution points in Pennsylvania. We are "remaining vigilant in protecting our water sources," a March 2012 presentation to investors stated. And what exactly were their water sources? The company has three large drinking water intake facilities that serve customers in Washington County and southern Allegheny County, the E.H. Aldrich Water Treatment Plant, the Brownsville Treatment Plant, and the Hays Mine Water Treatment Plant. All three are located along the Monongahela River.

The Monongahela flows from south to north, starting as a series of rushing creeks in the mountains of West Virginia. While the eastern forks begin in largely undeveloped highlands in the Appalachian Mountains, one of the Monongahela's principal tributaries, West Fork River, flows through the heart of West Virginia fracking country before crossing the border into Pennsylvania, where the river continues to draw its water from smaller creeks and streams originating in some of the most heavily fracked land in Greene, Washington, and Fayette counties.

"One thing I think you need to keep in mind is the whole drinking water industry's formation was based primarily on microbiology," says Dr. Mike Domach, a chemical engineer at Carnegie Mellon University in Pittsburgh and also board member of the Pittsburgh Water & Sewer Authority. Initial water providers, he points out, were worried about things like cholera and dysentery, not oilfield salts and radium. "Chemistry and pollutants have been an add on," he says.

Domach also notes that drinking water systems are based on what's referred to as the barrier model. That is, a drinking water provider has a number of different barriers intended to keep contaminants or disease from entering their water supply. This might start with the protection of the water supply's watershed, include guidelines regarding the discharge of harmful waste into waterways, and treatment and disinfection at a drinking water plant before the water is passed on to the public. The establishment of a single industry across the landscape in a way that is pointed yet also diffuse and difficult to assess represents a significant challenge to the barrier model.

Several agencies and initiatives were monitoring water quality as fracking boomed across the area, including the U.S. Geological Survey, the Ohio River Valley Water Sanitation Commission, West Virginia University's Water Research Institute, and a group of water providers called the River Alert Information Network, or RAIN, which Pennsylvania American Water was a part of. But the release of oilfield waste into the Monongahela was so substantial that sophisticated techniques were not necessarily required, it appeared to be gumming up industrial machinery and household appliances, and contamination could even be tasted.

“Workers at a steel mill and a power plant were the first to notice something strange about the Monongahela River last summer,” Joaquin Sapien reported in his 2009 article for ProPublica. “The water that U.S. Steel and Allegheny Energy used to power their plants contained so much salty sediment that it was corroding their machinery. Nearby residents saw something odd, too. Dishwashers were malfunctioning, and plates were coming out with spots that couldn’t easily be rinsed off.” In the summer of 2008, people relying on the Monongahela had also begun complaining about a salty taste in their drinking water.

Dr. Jeanne VanBriesen, an engineer at Carnegie Mellon University, along with colleagues warned that the influx of salts from oilfield waste, or other industrial sources such as coal-fired power plants, could substantially raise levels of bromide in the Monongahela. The concern was that when bromide combined with the chlorine used by water plants for treatment substances called trihalomethanes would be produced. When consumed over long periods of time trihalomethanes have been associated with bladder cancer. “Especially during the low-flow conditions of 2008 and 2009,” VanBriesen and Dr. Jessica Wilson pointed out in 2012 in the journal Environmental Practice, “these loads would be expected to affect drinking water.”

A number of concerns with fracking had been documented by Pennsylvania residents and researchers, and in many instances not much seemed to change regarding the industry’s practices. But the Carnegie Mellon research had a profound effect, and this concern for drinking water led to action. In 2010 the Pennsylvania Department of Environmental

Protection had limited the discharge of salts and heavy metals at plants processing oilfield wastewater, but a loophole enabled the practice to continue at many facilities. In April 2011 the department issued a statement intending to close that and shutdown the practice altogether. “Basically, I see this as a huge success story,” Michael Krancer, the Acting Secretary of the Department of Environmental Protection, told the Associated Press. “This will be a vestige of the past very quickly.”

“We never thought that it was a good practice to begin with,” stated Range Resources spokesman Matt Pitzarella. John Hanger, Michael Krancer’s predecessor as Pennsylvania’s environmental secretary told the Associated Press that as early as 2008 he had been approached by Range Resources and another operator warning that the state’s permissive rules on oilfield wastewater treatment plant discharges had left rivers and streams at risk from the salts in oilfield waste. “They came to me,” Hanger explained, “and said, if this rule doesn’t change, there could be enormous amounts of wastewater…pouring into the rivers.”

Now the rules had changed, but just how much of the oilfield’s radium had made it into the area’s rivers? In 2010 and 2011, Ian Urbina, an investigative reporter at the *New York Times*, turned his attention to America’s fracking boom. The articles he produced were a deeply researched and sweeping indictment on the industry’s sloppiness, exemptions, and risks. The very first story he published, on February 26, 2011, focused on Pennsylvania and ran on the front page of the newspaper. It was titled, “Regulation Lax as Gas Wells’ Tainted Water Hits Rivers,” and lays out an apocalyptic scene.

“Drilling derricks tower over barns, lining rural roads like feed silos. Drilling sites bustle around the clock with workers, some in yellow hazardous material suits, and 18-wheelers haul equipment, water and waste along back roads," Urbina wrote. "The rigs announce their presence with the occasional boom and quiver of underground explosions. Smelling like raw sewage mixed with gasoline, drilling-waste pits, some as large as a football field, sit close to homes."

Urbina had visited oilfields across the nation and discovered many problems, but the lead story of his investigation focused on the issue of centralized waste treatment facilities and sewage plants discharging radioactivity into Pennsylvania's rivers. In memos he unearthed from EPA officials, the pollution the practice enabled was described as "one of the largest failures in U.S. history to supply clean drinking water to the public." Urbina honed in on the radioactive element radium. The oilfield waste being brought to these plants "contains radioactivity at levels higher than previously known, and far higher than the level that federal regulators say is safe for these treatment plants to handle," he wrote. Plants not designed to treat this radioactive load were then discharging right back "into rivers that supply drinking water."

Urbina pointed out plants had discharged not only to the Monongahela, but also the Susquehanna River, which feeds into Chesapeake Bay and provides drinking water to people in Baltimore, and the Delaware River, which provides drinking water for more than 15 million people in Philadelphia and across eastern Pennsylvania. In New York, oilfield wastewater was sent to at least one plant that discharged into Southern Cayuga Lake, in the Finger Lakes region, an area famous for its family-run dairy farms and vineyards.

"There is no way of guaranteeing that the drinking water taken in by all these plants is safe," wrote Urbina. "Sewage treatment plant operators say they are far less capable of removing radioactive contaminants than most other toxic substances. Indeed, most of these facilities cannot remove enough of the radioactive material to meet federal drinking-water standards before discharging the wastewater into rivers, sometimes just miles upstream from drinking-water intake plants." He noted, "the bigger danger of radioactive wastewater is its potential to contaminate drinking water or enter the food chain through fish or farming" and said, "once radium enters a person's body, by eating, drinking or breathing, it can cause cancer."

It was a major newspaper loudly ringing the alarm bell, and Pennsylvanians already skeptical of the industry and trying to hold it accountable now had new material. To quell the concern, the Pennsylvania Department of Environmental Protection and Pennsylvania American Water both conducted water testing. (Ian Urbina, "Drilling Down: Regulation Lax as Gas Wells' Tainted Water Hits Rivers" New York Times (New York, New York, February 26, 2011))

"The DEP tested water from the Monongahela River at Charleroi in Washington County; South Fork Tenmile Creek in Greene County; Conemaugh River bordering Westermoreland and Indiana counties; Allegheny River at Kennerdell in Venango County; Beaver River in Lawrence County; Tioga River in Tioga County, and the West Branch of the Susquehanna River in Lycoming County," the Pittsburgh Post-Gazette reported in March 2011. Radium levels were reported to be at or below normal background levels. "I'm pleased by it, of course, as all Pennsylvanians should be," John Hanger, the former secretary of the Pennsylvania Department of Environmental Protection told the paper. "The results demonstrate powerfully that the concerns raised by The Times articles were false and Pennsylvania runs a stringent oversight program for the gas drilling industry."

Pennsylvania American Water conducted tests of their own and say they found no radioactivity dangers. The results were widely broadcast across the state's media outlets, and also by the industry. "Following a full battery of tests at Pennsylvania American Water's raw water intakes along the Allegheny, Clarion and Monongahela Rivers and Two Lick Creek, in Indiana, PA, the company found no elevated or harmful levels of radiological contaminants, volatile organic compounds (VOCs) or inorganic compounds (IOCs)," the Marcellus Shale Coalition reported on May 18, 2011. The coalition condemned newspapers, such as the Philadelphia Inquirer, which had run editorials based on what they called "the debunked *New York Times* story," and said, "the results confirmed that the quality of the water supplied by Pennsylvania American Water's treatment plants has not been impacted by radioactive materials." ("New Tests Confirm Marcellus Development Not Impacting Pa. Waterways" (Marcellus Shale Coaltion, May 18 2011))

The EPA has enforceable rules on radium in drinking water. The limit, which adds together radium-226 and radium-228, is 5 picocuries per liter. ("Radionuclides Rule" (US EPA, 2023)) If radium is detected but remains below 2.5 picocuries per liter, then the facility must check for radium once every six years. If a plant finds radium at between 2.5 and 5.0 picocuries per liter, they must check every three years. If a plant finds no radium in their drinking water, what is known as a non-detect, they are required to test for radium once every nine years.

The ancient Greek philosopher Heraclitus famously said, you cannot step into the same river twice. Any waterway is continuously flowing and thus continuously changing, yet EPA's rules mean that for many drinking water plants, tests for radium were only being done once every 3,285 days, during a single moment of a single day. "To do radium once every nine years is ridiculous," says the former water plant worker from the Pittsburgh Water & Sewer Authority. "That is like you take a dart and shoot it into a huge room, well the radium could be anywhere in that room. It's like shooting blind." (Correspondence with Pittsburgh Water & Sewer Authority water plant worker, 2022-2024)

Even without industry putting additional radioactivity back into the environment, many parts of the US have naturally high radium levels in groundwater and drinking water, including parts of Illinois, Texas and North Carolina. But in southwestern Pennsylvania, a new radium-generating industry had established itself across the landscape. In his February 2011 story, Ian Urbina and the *New York Times* reviewed data from more than 65 drinking water intake plants downstream from some of the busiest drilling regions in Pennsylvania. "Not one has tested for radioactivity since 2008," he wrote, "and most have not tested since at least 2005, before most of the drilling waste was being produced."

When in 2021 I asked Pennsylvania American Water Government and External Affairs Director Gary Lobaugh to provide the results for radium testing going back to the beginning of the Marcellus Shale boom, in 2005, for the drinking water treatment plants his company uses to supply water to Washington County, where many of the Ewing sarcoma cancer cases were centered, he tells me: "All radium sampling results were non-detect between 2005 – 2019." Lobaugh has not yet provided me with actual results or details of the testing his company did after the *New York Times* article but in 2024 says: "To reiterate, the company found no elevated or harmful levels of radiological contaminants" and the results "confirmed that radioactive materials...from Marcellus Shale drilling wastewater had not impacted the water quality supplied by Pennsylvania American Water's treatment plants." I point out that in 2009 water in the Monongahela River experienced a large and concerning rise in salts and

Pennsylvania American Water was part of an effort to look into this matter. “The source of the total dissolved solids was never determined,” Lobaugh tells me.

As for my question of whether or not the company believes a drinking water provider providing water for the fracking industry represents a conflict of interest, Lobaugh tells me, “Pennsylvania American Water has worked with the natural gas industry since its inception in 1886” and state rules dictate “the company cannot discriminate against any water service applicant based on end-use.”

If the oilfield’s radium, in its path from wellhead to treatment plant to being discharged to a river could end up being concentrated in mud at the bottom of a reservoir, or the shells of a river mussel, then could the bones of kids who drank water run through the same set of rivers have concentrated radium in a similar manner?

Q. Please explain what you have learned about Ewing sarcoma and its distribution, patterns, and causes?

A. “When I started out with the field of pediatric epidemiology I figured environmental exposures would mostly be the cause of many of these rare cancers, and over the years I have learned that this is just not the case,” says Dr. Logan Spector, who directs the Division of Epidemiology and Clinical Research at the University of Minnesota and is one of the nation’s foremost experts on the distribution, patterns, and causes behind Ewing sarcoma. “It more has to do with genes, and lots of genes together creating a milieu that makes the cells more or less vulnerable. Sometimes people are disappointed to hear that, because we can clean up the environment, though it’s less easy to change someone’s genes—but it is what it is.”

"Ewing sarcoma has some very distinct patterns by your ancestry," he tells me. "Basically, European kids and also Pacific Islanders and maybe Middle Easterners have the highest rates. It is virtually absent among people with significant African ancestry, and east Asians have less risk too. Latinos have intermediate risk. If you were to map Ewing's in the US, I have zero doubt you would find lower incidence in the South, and we would find it highest in the whitest states. If a cluster were happening among Black children in rural Georgia that would blow my mind. But the fact that there is an alleged cluster of cases in southwestern Pennsylvania, among a very White population, is not very surprising."

Spector understands why a community might look to radiation as the cause for the disease. But, he says, "there are physiological hallmarks of radiation induced cancers, certain signatures of mutation, and to my knowledge Ewing's does not really exhibit them. Ewing's is very mutationally quiet, and that makes me think it is not caused by radiation." Still, Spector is concerned enough about the oil and gas industry's releases of radioactivity that he believes a nationwide study should be done to assess incidences of cancers like Ewing sarcoma in relation to the distance people live from oilfield waste treatment or disposal sites.

There is another way to learn potentially valuable information. "Analyzing the tumor of a kid with Ewing sarcoma would not be difficult and could provide the thumbprint for what might have caused it," says Spector. Though there are complications. Even something simple, like washing a tumor after removal could affect results. And profiling tumors is still a relatively young science. "They are good questions," he says, "and to my knowledge, no one is asking these questions, and nobody is looking to answer them. We all concentrate on different parts of the elephant, and these are studies for the young and enterprising who are willing to try something very different."

And yet, for me, the question remains—with thousands of researchers devoting their careers to studying cancer, why aren't more of them dissecting Ewing sarcoma tumors? Why aren't they probing more carefully the possibility that radioactivity may be a cause of the disease? It would seem incredible, Spector tells me, but "it is not incredible. These are not common cancers, and a lot of people don't want to stake their career on studying something rare." But there is one researcher who has.

During the 1990s, the Canadian epidemiologist Dr. Murray Finkelstein published a pair of studies on naturally occurring radium contamination in drinking water and the presence of Ewing sarcoma and osteosarcoma among Ontario youths. He wanted to know if there was an association between the amount of radium in home drinking water and the risk of death from these bone cancers. Finkelstein is still around, and one spring afternoon I reach him by phone.

For decades the radiation health community has abided by what is known as the Linear No-Threshold model. It acknowledges that scientific data points to a direct connection between cancer and radioactivity when levels are high. Turn up the radiation, and across a large population of individuals cancers increase. Although the data at low levels is inconclusive, the Linear No-Threshold model says there is no threshold at which this relationship breaks down, and even small amounts of radiation will somewhere in the population cause some cancer, and that it is appropriate for health officials to enact laws and policies accordingly. There have always been powerful critics of the Linear No-Threshold model, and they remain today. Finkelstein is not one of them.

"If you accept there is no threshold, then it is plausible that a small number of cases will arise at the low doses if the population exposed is large enough," says Finkelstein. The factors affecting any single human individual or community are inherently complicated, and he says the difficulty is that the signal of an exposure may often be hard to find. "You will never have a large enough population for this signal to easily be identified," he says. The work of an epidemiologist is to have a full enough view of the problem and its potential causes to at least be able to propose an elegant and precise way of examining the question.

On this note, Finkelstein was fortunate. While studying Ewing sarcoma he was working as an epidemiologist for the province of Ontario and had access to data. He was able to obtain a computer tape containing the death certificates for Ontario residents between 1950 and 1983 and identify people 25 years or younger who had died of bone cancer during this time. He then linked these people to their birth certificates and was able to obtain the patient's address at the time of death, and their mother's address at the time of birth. This meant water samples could be collected from the same drinking water source presumably used by the patient throughout their youth, and that water could then be sampled for radium.

Finkelstein's paper, published in 1994 in the Canadian Medical Association Journal and entitled, "Radium in drinking water and the risk of death from bone cancer among Ontario youths," reported the stunning result that even minute increases in radium in drinking water can lead to an increase in death from bone cancers, including Ewing sarcoma. There is a "statistically significant" relationship between levels of radium in drinking water and Ewing sarcoma, he wrote. Finkelstein co-published a follow-up paper in 1996, which found an association between risk of osteosarcoma, the more common form of bone cancer, and birthplace exposure to radium in drinking water. This paper did not find the same association for Ewing's, but it didn't negate his prior results. "The papers," says Finkelstein, "were generally ignored, and I don’t think the research had much impact or influence.” (Murray M. Finkelstein, "Radium in drinking water and the risk of death from bone cancer among Ontario youths," Canadian Medical Association Journal, Volume 151, Number 5 (1994) ; Murray M. Finkelstein and Nancy Kreiger, "Radium in drinking water and risk of bone cancer in Ontario youths: a second study and combined analysis," Occupational and Environmental Medicine, Volume 53 (1996) ; Correspondence and conversations with Canadian epidemiologist Dr. Murray Finkelstein, 2021)

Still, he has gained an extraordinary expertise on this little studied topic, and when I describe to him the Ewing sarcoma cases of southwestern Pennsylvania he is interested and clarifies information others had ignored. For example, Finkelstein provides an explanation on why some Ewing tumors may form in the sinus cavity, as was the case with 37-year-old David Cobb. “The radon gets into the bloodstream from its release in the bones and as the blood passes through the membranes in the sinus cavity radon outgases,” says Finkelstein. Sinus cancer is one of the cancers that occurred in uranium miners, he continues. “You need a blood air interface, like the lung—or the sinus.”

“I think the only ingestion pathway of any concern is drinking water,” he says.

I have again drawn on Justin Nobel, “Petroleum-238: Big Oil’s Dangerous Secret and the Grassroots Fight to Stop It” (Hudson New York, Karret Press, 2024).

V. Part 8 fails to recognize that often included in the general category of produced water by industry workers and waste haulers is flowback, an entirely different waste stream consisting of fluids injected during fracking operations returned to the surface and including water, sand (the proppant), and also a spree of toxic fracking chemicals designed to lubricate and crack open rocks and whose ability to interact with other

chemicals and contaminants in the waste streams and in treatment systems is still largely unexamined.

Q. What evidence and concerns do you have regarding other streams of oil and gas wastewater such as flowback?

One flaw I notice regularly in rulemakings is that while regulatory agencies may collaborate extensively with the oil and gas industry, they do not appear to collaborate with the workers on the ground doing the actual jobs that their rulemakings pertain to. I bring up this point, because I think the Department needs to be aware that the oil and gas industry is a trillion-dollar industry, and one of the most powerful and savviest industries on earth. When approaching regulatory agencies on issues such as produced water treatment and reuse it has been my experience that industry groups will convey to regulators a message that is in their best interest and that of their bottom line, but this may not necessarily be the truthful message of what processes and conditions are actually like on the ground in the oilfield. For that, it is best to speak with the workers, and particularly, the ones courageous to call out wrongs. This is what I am able to do regularly in my profession, and thus I am grateful to be able to pass along to you all. Again, quoting from my upcoming book, “Petroleum-238: Big Oil’s Dangerous Secret and the Grassroots Fight to Stop It”:

“The dirtiest stuff that I hauled on a regular basis was flowback,” says Tom. “As they frack the well is plugged, and all of the water, sand and chemicals used in the fracking process are held down in the borehole and under pressure. When they bring a well online they drill through that plug and everything surges back to the surface, and sometimes fountains into the sky and falls down on the workers at the well pad like rain. Flowback is frigging dirty, and it can be hot, like bathwater hot.”

Oil and gas companies try to capture flowback by piping it into a set of large and often colorful—red, blue, yellow, green—frac tanks. These resemble shipping containers and are on wheels so after use at one well they can be towed behind trucks and moved to the next. A full frac tank is too heavy to tow, and before being moved must be cleaned. It's a nasty job, as the tanks can be filled with toxic sludge settled out of the flowback, and a hydrovac will be called in. These look like brine trucks but have a powerful pump for sucking sludge, and they are expensive. To save time and money brine haulers like Tom may be asked to suck up any liquid lying on top of the sludge.

"I opened the manhole and stuck my head in," says Tom, remembering one time cleaning out frac tanks. He needed to guide a two-inch hose down to the bottom of the tank. "The end of that day, my head underneath the hard hat and above the neckline looked like I been down in Florida out in the sun," Tom says, "and the little spot between my gloves and where my shirt started, the only other part of my skin that was directly exposed to the tank, was all red like a sunburn."

An even worse job falls to swampers, who must crawl down into tanks. "Let's say your hauling brine for a month," says Tom. "Sludge builds up in the bottom of your truck's tank, and every time you haul it gets a little thicker. Back at our shop they'd pop the manhole and send these guys in with a shovel and pressure washer. Shovel the waste to the middle, then use the pressure washer to scrape down the sides and scour the bottom. A guy on the outside would be holding a bucket or big pan, you shovel the waste in there, then he would take that over and dump it in a hopper."

"Them guys on the inside would be exposed to anything in that brine or flowback. And you know how it is with some guys, they want to be tough, and could easily be in there over an hour, it was a challenge to them. Someone would get out, sit down and say, fuck it's killing me, and someone else would be like, you pussy. If you complain to the boss they'll say, shut up, don't like it go home. And you do shut up, because you need that job. Don't forget, it is crappy and gross, but none of us knew that sludge was radioactive."

Tom says swampers are supposed to wear standard oilfield PPE, FR's, steel toe boots and a hard hat. Some were supplied with, "these little yellow neoprene rain suits," a face mask, and a respirator. "But most of them don't wear the respirator," he says. "I seen guys go in there just a face mask, blue jeans, and a T-shirt, and they're made to do their own laundry. At home, in the hotel, or wherever. They're also instructed to bathe in Dawn dish soap, just like when the Exxon Valdez went down and the volunteers were cleaning off the little ducks, same deal."

People connected to the oil and gas industry will often point out that even bananas are naturally radioactive, but the statement is designed to mislead, and helps cloak the dangers posed by oilfield radioactivity. A banana's radioactivity comes from a radioactive isotope of potassium which has a half-life of over a billion years and in decay gives off a beta particle to become nonradioactive elements. The radioactive isotopes brought to the surface in oil and gas production decay to other radioactive isotopes, which decay relatively quickly to other radioactive isotopes, which continue to decay through a long list of other radioactive isotopes, blasting off radiation each time.

Sludge sitting in the bottom of a brine truck or tank, or scale stuck to the inside of an oilfield pipe would be giving off radiation in the form of gamma rays, beta particles and alpha particles. Gamma rays can travel several hundred feet through the air, go right through a human body, and even go through concrete and steel. Beta are minuscule particles and can go several feet through the air and penetrate human flesh. But of greatest concern are alpha particles, which are many thousands of times heavier than a beta particle and travel at a speed of 12,430 miles per second. The outer layers of human skin or a piece of paper are dead and act as shielding, absorbing an alpha particle's incredible energy. But the soft lining of an organ, the marrow of a bone, or the delicate tissue of the lung is very much alive. An alpha particle fired off here will smash about the cellular space, colliding with tens of thousands of different things. Any hit to the nucleus can break strands of DNA, usually killing the cell, or worse, leaving it genetically mutated, damage that can lead to cancer.

Oilfield waste happens to contain a number of radioactive isotopes that emit alpha particles as they decay, including radium-226, radon-222, and five different isotopes of polonium. Working in a contaminated workspace littered with piles of sludge or open pits of brine provides several pathways for workers to inhale or inadvertently ingest these elements. Even wearing some protective gear, workers cleaning out a tank can get their underclothes, faces, boots and bodies splattered in sludge, and also their hands. Because workers are uninformed, easily preventable actions can still lead to exposures, such as drinking a soda, smoking a cigarette, or not washing their hands then eating lunch.

And later on in the book, another whistle blowing worker provides important context:

In 2018 I meet an Ohio brine hauler who goes by the pseudonym Peter. He knows quite a lot about injection wells, as ever since 2014 when he began the job he has deposited waste there. Injection wells don't just receive oilfield brine, and flowback, Peter points out, but vats of chemicals, the refuse water that runs off a frack pad, impoundment and pit waste, various acids, a thick pungent liquid called sludge, and used frack sand that comes back up a well with the flowback and can be any color from "urine orange to jet black." Peter tells me about a set of hauls he made from a gas well in West Virginia that had started upchucking a vile glowing blue goo. That too, whatever it was, went down an injection well. "Any shit they have at the well pad they don't want any more and will fit in my brine truck," he says, "is taken to an injection well."

"Brine haulers," says Peter, "are considered the lowest of the low in the oilfield. We are replaceable. You can teach a monkey anything you want, and that is how they look at us."

"There is something in the frack mixture that is fucking with us," he continues. "I am not saying it is radioactivity, it could be any of the undisclosed chemicals. But I can tell you this, other drivers are getting scared. Guys are wanting to get tested."

Peter's health has declined since he took the job. "My fingertips and lower face is numb, like I been to the dentist," he says. "The joint pain is like fire, and my fillings are coming out." He knows some symptoms are hard to attribute, like the nausea, constant pressure on his temple, swelling of his lymph nodes, and blood that doesn't seem to clot as quickly. But what about the heart attack he had not so long ago at a well pad? He was transported to the Emergency Room. Maybe it's just stress, knowing the job's dangers and being incapable of preventing them, knowing the risks he's dumping upon the public and communities, knowing he too breathes air, drinks water and eats food like anyone else on earth yet also knowing he's pumping her insides full of toxic waste.

There are stranger things too, ones he is reluctant to mention.

"I am going to tell you a secret," says Peter. "My dick is numb. When I am with the wife I can't feel shit anymore. And I am not the only driver complaining of this."

He believes it's from his hands getting constantly splashed and soaked with fracking waste, then stopping on the road at a gas station or rest area a short time later and taking a pee. "Problem with gloves," he says. "They are not waterproof, and ones that are can't do the job right, so you got to take them off."

I ask Peter if he is worried about injection wells leaking and fracking wastewater getting in drinking water. "Of course it is going to get in drinking water, it's fucking everywhere," he snaps. "This is the cheapest known way to get rid of a cheap product, which if it's handled right is not a cheap product. Everything is contaminated, and it's never going to end until it hits the right person."

"I don't want to be any part of the story," Peter later tells me, "I just want to know, as I have wanted from the beginning, what have I been in? What have I gotten dripped on, splatted on, splashed on, splattered on, sprayed in, what have I been breathing in? What have I been involved with for the last 10 fucking years? What the fuck is inside of me?" But Peter, after years of trying to figure this out, has become jaded. "This country, until it gets a rude fucking enema from throat to ass, is not going to change," he says. "By the time the government gets off their asses, if they ever get off their asses, how much damage has been done that can't be undone? There is no reversing this, ever." So, he has taken things into his own hands.

He began filling up old antifreeze jugs and soda bottles with samples of the oilfield brine and flowback he was hauling and eventually packed a shed in his backyard with more than

40. “I cover my ass,” he says. “Ten or 15 years down the road, if I get sick, I want to be able to prove this.” In 2019, through a network of Ohio activists, Peter was able to transfer 11 samples to Dr. John Stolz at the Center for Environmental Research and Education at Duquesne University in Pittsburgh, who passed them on to Dr. Daniel Bain, a University of Pittsburgh geochemist. Testing revealed that radium-226 in four samples was above 3,000 picocuries per liter, and one was as high as 7,370. Any liquid waste bound for an injection well containing above 60 picocuries per liter of either radium-226 or radium-228 is considered “radioactive” by EPA. “So why the hell,” wonders Peter, “are we driving non-placarded trucks and given no training?”

While the descriptions may be crude, I think it is important for the Department to understand the general skill level of the workforce handling oilfield waste, the general lack of regard for their employees, and the manner in which already existent regulatory exemptions enable concerning and dangerous practices to compound. An important note here is that there is scientific backing to these worker’s concerns. Conversations with various academic sources of mine have expressed concern on the toxic or often unknown nature of chemicals in flowback, and how they may adversely interact with natural contaminants in produced water, such as salts or radioactive metals, be it in the setting of a treatment or reuse facility, an industrial facility that aims to use the supposedly treated produced water for critical and precise industrial processes, or in a disposal setting like an injection well. If the Department endeavors to discover the truth, it will learn that reputable government and industry sources expressed concern about this same matter decades ago.

I have again drawn on Justin Nobel, “Petroleum-238: Big Oil’s Dangerous Secret and the Grassroots Fight to Stop It” (Hudson New York, Karret Press, 2024).

VI. Part 8 fails to address the significant body of research on uranium mill contamination to nearby croplands, which documents that even minute additions of naturally occurring radionuclides—such as those present in leftover piles at uranium mills and also oil and gas wastewater—to the environment have led to notable biomagnification responses, with radioactivity accumulating particularly in what is known as the "beef/milk pathway" and being found in several studies to accumulate at levels that may be deleterious in infant formula drawn from cow's milk.

Q. What evidence is there that the same radionuclides found in oilfield wastewater environment have led to notable biomagnification responses, with radioactivity accumulating particularly in what is known as the "beef/milk pathway" and being found in several studies to accumulate at levels that may be deleterious in infant formula drawn from cow's milk?

A. Given that the Department's proposed rule explicitly sets up a regulatory pathway that would enable the discharge of supposedly treated produced water onto and for agriculture, irrigation, aquifer recharge, industrial processes, and for environmental restoration, I think that it is important to highlight research that has come up in my reporting. Again, quoting from my upcoming book, "Petroleum-238: Big Oil's Dangerous Secret and the Grassroots Fight to Stop It." This passage references the practice of land spreading in Oklahoma, in which drilling waste, which may contain harmful constituents like diesel fuel and potentially also elevated levels of heavy and radioactive metals, is applied to pastureland. This practice is common across Oklahoma, and also occurs in Texas and other oilfield states:

In 1966, British researchers published an article on "the metabolism of radium in dairy cows" that determined "radium might as a result of accidental circumstances enter food chains and constitute a radiological hazard by its transfer to milk." (B.F. Sansom and R.J. Garner, "The Metabolism of Radium in Dairy Cows," Biochemical Journal, Volume 99 (1966))

A 1978 research article published by Charles Garten Jr., a biogeochemist at Oak Ridge National Laboratory in Tennessee, stated one of the most important factors involved in the transport of radioactive elements like plutonium, uranium, and thorium into “terrestrial food chains” was the ability of crops to catch radioactive elements being blown about in the wind. Garten referred to this process as the “fractional interception of particulates by vegetation,” but it later came to be known as foliar deposition. .” (Charles T. Garten Jr., "A review of parameter values used to assess the transport of plutonium, uranium, and thorium in terrestrial food chains," Environmental Research, Volume 17, Number 3 (1978))

The oilfield waste being spread regularly on fields in Oklahoma is potentially elevated in radium from the brine-soaked drilling muds, uranium and thorium from the drill cuttings, and also the daughters of these elements, including radioactive lead and polonium. These are some of the same radioactive elements present in the waste left behind at uranium mills, where fuel for reactors and nuclear weapons is concentrated from naturally occurring uranium deposits. The U.S. Geological Survey, in a 2011 report, says “it is not known” whether research has been conducted on the uptake of the oilfield’s radium into crops and livestock, but the ways in which uranium mill waste can enter the human food chain has been assessed.” (E.L. Rowan, M.A. Engle, C.S. Kirby, and T.F. Kraemer, "Radium Content of Oil- and Gas-Field Produced Waters in the Northern Appalachian Basin (USA): Summary and Discussion of Data" (U.S. Geological Survey, 2011))

Argonne National Laboratory, a Department of Energy facility and one of the US’s premier radiological research centers has done significant research into human radioactivity exposure and in 1983 published a paper that assessed ways in which radioactive waste leftover from uranium mills could contaminate humans. “One of the major pathways of radiological exposure," states the report, "is through the beef/milk food chain." (**EXHIBIT 7:** Donald R. Rayno, "Estimated Dose to Man from Uranium Milling Via the Beef/Milk Food-Chain Pathway," The Science of the Total Environment, Volume 31 (1983))

It's simple. Radioactive metals in soil are taken up by plants just like the metals iron and zinc are taken up by plants. Radioactive elements may also be blown by wind off piles of uranium mill waste and deposited on plant leaves—foliar deposition. These contaminated plants are eaten by cows. While eating their meat can be a concern, drinking their milk may be more of a concern.

In one 2012 paper, Slovenian researchers examined a dairy farm located about one-third of a mile from piles of waste leftover from closure of the Žirovski Vrh uranium mine. The concern, said the researchers, was that radioactivity in the waste could be blown by the wind or carried by surface or groundwater to the farmer's fields, where it "can be transported via fodder into cow's milk, which is an important foodstuff for Slovenian people." (**EXHIBIT 8:** Marko Štrok and Borut Smodiš, "Transfer of natural radionuclides from hay and silage to cow's milk in the vicinity of a former uranium mine," Journal of Environmental Radioactivity, Volume 110 (2012))

The researchers tested the farm's soil, grasses the cows were eating, and their milk, and found the yearly amount of radiation infants would receive from drinking the milk would be about 40 millirem, the equivalent of four chest X-rays. "This study," state the researchers, "provides new data quantifying the transfer of natural radionuclides to milk." In 2017, another set of Slovenian researchers found detectable levels of radionuclides from the uranium-238 decay chain in infant formula made from cow's milk.

Unlike the leftover piles of uranium mill waste in Slovenia, the Oklahoma practice of land-spreading involves intentionally unloading waste directly to a field that beef or dairy cows will graze on. Land-spreading also occurs in Arkansas, Texas, and Colorado. The practice has not been thoroughly examined by US academic researchers. In fact, they have enabled it.

“Drilling fluids, including muds and liquids, can be applied to surrounding land,” states the press release for a 2013 article on the practice of land-spreading by researchers at Texas A&M University. “If done properly on soils that can accept these types of materials, no detrimental effects should occur.” (Kay Ledbetter, "Increased oil and gas drilling demands more land-applied fluid disposal" (Texas A & M press release, July 5, 2013))

When I speak to one of the co-authors by phone, the soil chemist Dr. Tony Provin, I ask him a number of questions on exactly what types of crops receive waste. He tells me that drilling waste is not regularly applied to row crops, like corn and beans, “simply because the timing issues don’t seem to work out.” Typically, it is Bermuda grass and other range food eaten by cattle that receive the waste, and there “is no requirement for testing of the Bermuda grass or the cattle to see if things are bioaccumulating,” says Provin. He says neither he nor his colleagues have ever actually tested the waste being applied to farm fields for heavy metals or radioactivity. When I ask how he can make a determination that a practice is safe when he has not examined all of the likely contaminants, Provin replies: “Fair enough.”

I ask if oilfield tank bottom sludge, well-known to be dangerously radioactive, could be put on farm fields too, he replies: “Oh yeah, if there is some nutrients in there we can put it out there.” He indicated radioactivity was the jurisdiction of Texas regulators, and says his lab openly suggests to landowners that full assessments of the liquids and solids be made before any discussion of land application. “Our testing aspects with Texas A&M AgriLife Extension Soil, Water and Forage Testing Laboratory,” says Provin, “is solely with the potential of salts and nutrients associated with these materials.”

I ask the Oklahoma Department of Agriculture, Food and Forestry just how much drilling waste is spread each year on fields, exactly what crops receive the waste, whether it is permissible to spread waste on fields where organic crops are grown, if the agency is monitoring for heavy metals and radioactivity in the waste and crops themselves, and whether or not some of the more highly radioactive oilfield waste streams like sludge and scale are also being spread, but my questions have gone unanswered.

One 2017 paper of Oklahoma State University’s agricultural extension does offer a certain clarity, stating, “little to no data is available” on the metals and radioactivity content of drilling mud. So, with no data, and no one gathering data, and no one interpreting data, the amount of radioactivity the spreading of drilling waste onto range and pastureland in Oklahoma has introduced into the American food system and our human bodies remains a mystery. (Chad Penn and Hailin Zhang, "An Introduction to the Land Application of Drilling Mud in Oklahoma" (Oklahoma State University press release, February 2017))

There has been at least one attempt to look into the matter. Argonne National Laboratory, the Department of Energy radiological lab, published a paper in 1996 that assessed radiation doses across the oil and gas industry. “Landspreading,” the paper determined. “Presents the highest potential dose to the general public.” But this paper remains hidden from the American public. As far as I can tell, Argonne National Laboratory never issued a press release, and they have not answered any of my questions on oilfield radioactivity. (K.P. Smith, D.L. Blunt, G.P. Williams, and C.L. Tebes, "Radiological Dose Assessment Related to Management of Naturally Occurring Radioactive Materials Generated by the Petroleum Industry" (Environmental Assessment Division, Argonne National Laboratory, U.S. Department of Energy, September 1996))

I have again drawn on Justin Nobel, "Petroleum-238: Big Oil's Dangerous Secret and the Grassroots Fight to Stop It" (Hudson New York, Karret Press, 2024). Other important sources include, **EXHIBIT 7**, Donald R. Rayno, "Estimated Dose to Man from Uranium Milling Via the Beef/Milk Food-Chain Pathway," The Science of the Total Environment, Volume 31 (1983), and **EXHIBIT 8**, Marko Štrok and Borut Smodiš, "Transfer of natural radionuclides from hay and silage to cow's milk in the vicinity of a former uranium mine," Journal of Environmental Radioactivity, Volume 110 (2012), and **EXHIBIT 9**, Miha Trdin and Ljudmila Benedik, "Uranium, polonium and thorium in infant formulas (powder milk) and assessment of a cumulative ingestion dose," Journal of Food Composition and Analysis, Volume 64 (2017).

VII. Part 8 fails to address the fact that facilities where oilfield wastewater is injected underground for disposal, typically referred to as injection wells or saltwater disposal wells (SWDs) and regulated by the State of New Mexico under the EPA's Underground Injection Control program, despite their copious use for disposal of oilfield wastewater across the state and nation rely on an outdated, scientifically unfounded, and dangerous disposal technique that puts waters of the state—both underground and surface—at risk of irreversible contamination, as is substantiated in important but overlooked decades-old industry and government reports and statements, and also present-day reports and incidents from other US oil and gas fields.

Q. What evidence do you have that injection wells rely on an outdated, scientifically unfounded, and dangerous disposal technique that puts waters of the state—both underground and surface—at risk of irreversible contamination?

A. While injection wells may not be the primary focus of Part 8, my reporting and research has discovered and documented notable information on the matter with alarming ramifications for the State of New Mexico and thus I believe it is appropriate to present my findings here to the Department in the context of this Testimony. Again, quoting from my upcoming book, "Petroleum-238: Big Oil's Dangerous Secret and the Grassroots Fight to Stop It." This passage references two sources, referred to in my book as Bob 1 and Bob 2. Both men operate conventional gas wells in eastern Ohio that have been contaminated with fracking wastewater leaking out of Class II injection wells. As you will see, this contamination pathway has been confirmed by the State of Ohio:

In June 2020 the Ohio Department of Natural Resources released a report on the Redbird injection well. It turns out the interior of the earth is not filled with tidy storage lockers waiting to accept endless truckloads of toxic waste. The agency found signatures of fracking waste, such as elevated levels of salts, in 8 different conventional gas wells in the area and identified the source as Redbird.

The state's report also mapped out the pathway of contamination. The Bobs were right. Fracking waste had traveled one-third of a mile vertically, and more than five miles laterally through the earth. "Naturally occurring fissures exist between the Ohio Shale formation and the Berea Sandstone formation," the report states, "allowing wastewater to migrate."

On a snowy winter morning in February 2021, I receive a phone call from Bob 1. He is upset and speaking quick. Between Dexter City and the village of Crooked Tree it appears that fracking waste from another Ohio injection well has found its way into an old gas well and is pouring out at the surface. “Brine is flowing down the hill, going a mile down into the creek, and killing fish,” says Bob 1. “I’ve got more people calling telling me their gas wells are filling up with brine, so this is happening all over Ohio now.”

In response to the event near Crooked Tree, in January 2023, the Ohio Department of Natural Resources issues a letter to a company called DeepRock Disposal Solutions, suspending operations at two of their injection wells in southern Ohio. “If the Wells continue to operate, additional impacts may occur in the future and are likely to contaminate the land, surface waters, or subsurface waters,” the state concludes. “Thus, the continued operation of the Wells presents an imminent danger to the health and safety of the public and is likely to result in immediate substantial damage to the natural resources of the state.”

In June 2023, the Ohio Department of Natural Resources issues another letter, this one suspending operations at the injection well near Felicia—her worst fears have been realized. Here too waste is leaking out from the injection zone and entering into nearby oil and gas wells then flowing back out at the surface, transforming them, essentially, into conduits of fracking waste. In August 2023, I learn of yet another problematic Ohio injection well.

These days, because the EPA formerly regulates injection wells under the Underground Injection Control program and has done so for more than 40 years, the takeaway for the American public is that our nation’s environmental protection agency is perfectly fine with the process and believes it to be an appropriate way to get rid of industrial waste. But knowledge that injecting waste underground posed tremendous risks has been there from the beginning.

“There is always the danger of subsequent contamination,” reads a 1929 report on the Disposal of Oil-Field Brines. “If this method is used,” states the report, authored by Ludwig Schmidt, a petroleum engineer, and John Devine, an organic chemist, both with the US Bureau of Mines Petroleum Experiment Station in Bartlesville, Oklahoma, “care must be taken that the brines are delivered to a reservoir formation from which migration can not take place with detrimental effect to sources of fresh-water supply.”

In the 1980s, EPA’s Environmental Research Lab in Ada, Oklahoma extensively researched injection wells. “Unfortunately, hazardous wastes are complex mixtures of materials,” states one of the lab’s reports on Injection of Hazardous Wastes into Deep Wells. “Making it difficult to predict exactly the action or fate of wastes after their injection.” A problem, note researchers, is when one hazardous waste stream is “combined with other mixed waste streams, the potential number of interactions increase factorially.” Because “subsurface environments often take many years to reach chemical and biological equilibrium, predicting exactly what will happen a priori may be nearly impossible.”

A report prepared by a collaboration between researchers at EPA and the Department of Energy and published in 1987 by the National Institute for Petroleum and Energy Research in Bartlesville, Oklahoma presented four main ways in which hazardous waste injected down injection wells might contaminate groundwater. One, an accidental spill at the surface. Two, old oil and gas wells that were never plugged or plugged incompetently provide “an escape route whereby the waste can enter an overlying potable ground water aquifer.” Three, waste is injected at such great pressure that it fractures the rocks deep in the earth, “whereby a communication channel allows the injected waste to migrate to a fresh water aquifer.” Four, the piping and cement that forms the injection well itself corrodes apart, enabling “the waste to escape and migrate” back up to an aquifer.

These early papers appear to fracture the notion that injection wells are a safe storage locker for industrial waste. But there is more. In October 1970, David Dominick, Commissioner of the Federal Water Quality Administration, which in two months would become part of the brand-new EPA, warned that injection was a short-term fix to be used with caution and “only until better methods of disposal are developed.” When EPA laid out its proposed policy on injection wells in 1974 the agency echoed Dominick’s concern, stating in an internal statement on the subject that EPA’s “policy considers waste disposal by [deep] well injection to be a temporary means of disposal.” The statement continues: “Should a more environmentally acceptable means of disposal become available, change to such technology would be required.”

But nothing of the sort has happened. Rather, injection wells have become so much a part of the American fabric they have been allowed to operate on the edge of a shopping plaza in Cambridge, Ohio, within eyeshot of a kitchen window in Vienna, Ohio, down the street from a daycare center for handicapped adults in Coitsville, Ohio. And one morning out in West Texas, I observe a food stand selling tacos in the dusty parking lot of an injection well.

In 2020, I ask Dr. Bill Alley, Director of Science and Technology at the National Groundwater Association and former Chief of the Office of Groundwater with the U.S. Geological Survey what eventually happens to all the injected waste. “I have never looked at it in detail,” he tells me. “It’s not a problem that I have any direct experience with beyond textbook type diagrams.”

Eventually I am led to a 1971 talk by Stanley Greenfield, Assistant Administrator for Research and Monitoring at the newly formed EPA, entitled, EPA—The Environmental Watchman. Deep-well injection, says Greenfield, is “a technology of avoiding problems, not solving them in any real sense…We really do not know what happens to the wastes down there. We just hope.”

Greenfield provides an analogy: “There may be another parallel with our current concern over dumping wastes at sea. Men have long assumed that, if you take the stuff out far enough and sink it deep enough, no harm will result—that the oceans are so voluminous they can dilute anything to innocuous levels. We know now that this assumption is wrong; the sea is soilable. The earth’s crust is soilable, too, and vulnerable to damage by man’s activities—not only in ways that we may predict and make allowance for, but also in unexpected ways.”

I find an old bound blue book with gold writing that contains Stanley Greenfield’s 1971 talk. It turns out, 53 years ago, the U.S. Geological Survey, together with the American Association of Petroleum Geologists organized a conference on the issue of injection wells and invited the nation’s leading experts. At the symposium on “Underground Waste Management and Environmental Implications,” held December 1971 in Houston, Texas, there are those who express optimism about the practice, such as Vincent McKelvey, Director of the U.S. Geological Survey and the symposium’s keynote speaker, who believes “natural pore space” in rock layers beneath the earth should be assigned value. “On the whole,” says McKelvey, “we are looking at an underutilized resource with a great potential for contribution to national needs.” But largely, the symposium’s speakers express concern, and lay out an eerily accurate prediction of the issues to come.

“It is clear,” says Theodore Cook, who is with the American Association of Petroleum Geologists and authored the forward to the book containing the symposium’s presentations, “that this method is not the final answer to society’s waste problems.”

Utah geologist Henri Swolfs explains that injecting chemical-filled waste deep into the earth could affect the strength of rocks and alter their frictional characteristics. “The result could be earthquakes,” he says, creating fractures that channel waste out of the injection zone.

Tsuneo Tamura, with the Department of Energy says the disposal of radioactive liquid wastes posed “a particularly vexing problem,” even in low concentrations.

“My message to you is not a cheerful one,” Frank Trelease, a Wyoming law professor, tells symposium attendees. “It is simply this: if you goop up someone’s water supply with your gunk; if you render unusable a valuable resource a neighboring landowner might have recovered; or if you ‘grease’ the rocks, cause an earthquake, and shake down his house—the law will make you pay.”

Robert Stallman, a Colorado research hydrologist with the U.S. Geological Survey presents potential consequences from injecting large amounts of liquid waste underground: Groundwater may become polluted, surface water may become polluted, the permeability of rocks may change, the earth may cave in, earthquakes could be triggered, and mineral resources—such as oil and gas—may become contaminated. The available theories on what happens to waste once injected, Stallman says, “are either so simplified that they do not represent the real system adequately, or they are so complex that they have not been tested.” Fast forwarding to the present, scientists at Stallman’s agency have indeed linked the practice of injection to earthquakes all across America.

But no one appears to have understood the lack of science behind the practice of injection as well as John Ferris, another U.S. Geological Survey research hydrologist.

For one, says Ferris, “the term ‘impermeable’ is never an absolute…all rocks are permeable to some degree.” So, the idea that any rock layer could act as a cork to seal off waste is simply wrong. Waste will always and inevitably escape the injection zone, says Ferris, and “engulf everything in its inexorable migration toward the discharge boundaries of the flow system.” Meaning, a water well, a spring, an old oil or gas well, a basement drain, even the roots of plants or a seep on the side of the road.

Interestingly, Ferris explains, wells, springs and basement drains might first surge with freshwater, which is being pushed out of the way by the advancing front of waste. But eventually “the sinister laggard—the waste cylinder” arrives, says Ferris. “In time,” he continues, this contamination “would become apparent at ever-increasing distances from the injection site.”

“Where will the waste reside 100 years from now?” asks Orlo Childs, the Texas petroleum geologist who closed the 1971 Underground Waste Management symposium. It is a rhetorical question, as Childs does not know. “We may just be opening up a Pandora’s box,” he says, and peers into the future. “Like ripples in a pond, the great question” is “how does man stop the process he has begun?’”

Since the 1971 symposium so much industrial waste has been shot down injection wells in the United States that if you had instead poured it into standard 42-gallon barrels and stacked them atop one another they would have reached Jupiter. And yet, shoved beneath America’s farm fields, forests, desert landscapes, and communities, where has all the waste gone?

My source here is as follows: “Underground Waste Management and Environmental Implications: Proceedings of the Symposium held December 6-9, 1971, in Houston Texas,” sponsored jointly by the United States Geological Survey and The American Association of Petroleum Geologists, edited by T.D. Cook (Tulsa, Oklahoma: The American Association of Petroleum Geologists, 1972).

VIII. In conclusion, Part 8 encourages and allows for the recycling or reuse of produced water in a matter that may irrevocably lead to the contamination of waterways in New Mexico and generate a range of concerning potential health impacts on New Mexicans, their water resources, their wildlife, their air, water, soil and general ecosystems, and create a concerning and liability-stoked legal landscape due to aforementioned widespread contamination.

Q. What are the principal sources you relied on, in addition to the ones you cited and are embedded in your testimony?

A. The Principal Source Used was the research for and content of my forthcoming book, “<u>Petroleum-238: Big Oil’s Dangerous Secret and the Grassroots Fight to Stop It</u>” (Hudson New York, Karret Press, 2024) slated for publishing April 24th, 2024 and Exhibits Are as Follows:

1. EXHIBIT 1: Justin Nobel’s resume
2. EXHIBIT 2: “An Analysis of the Impact of the Regulation of 'Radionuclides' as a Hazardous Air Pollutant on the Petroleum Industry” (Committee for Environmental Biology and Community Health, Department of Medicine and Biology, American Petroleum Institute, October 19, 1982)
3. EXHIBIT 3: (P.R. Gray, “NORM Contamination in the Petroleum Industry” Journal of Petroleum Technology, Volume 45, Number 01 (1993)
4. EXHIBIT 4: John B. Comer, "Stratigraphic Analysis of the Upper Devonian Woodford Formation, Permian Basin, West Texas and Southeastern New Mexico" (Bureau of Economic Geology, University of Texas at Austin, 1991)
5. EXHIBIT 5: Punam Thakur and Anderson L. Ward and Tanner M. Schaub, “Occurrence and behavior of uranium and thorium series radionuclides in the Permian shale hydraulic fracturing wastes,” Environmental Science and Pollution Research, Volume 29 (2022).
6. EXHIBIT 6: “A Regulators’ Guide to the Management of Radioactive Residuals from Drinking Water Treatment Technologies,” (EPA, Office of Water, July 2005).

7. EXHIBIT 7: Donald R. Rayno, “Estimated Dose to Man from Uranium Milling Via the Beef/Milk Food-Chain Pathway,” The Science of the Total Environment, Volume 31 (1983)
8. EXHIBIT 8: Marko Štrok and Borut Smodiš, “Transfer of natural radionuclides from hay and silage to cow’s milk in the vicinity of a former uranium mine,” Journal of Environmental Radioactivity, Volume 110 (2012)
9. EXHIBIT 9: Miha Trdin and Ljudmila Benedik, “Uranium, polonium and thorium in infant formulas (powder milk) and assessment of a cumulative ingestion dose,” Journal of Food Composition and Analysis, Volume 64 (2017).

Conclusion

Q. Does this conclude your direct testimony?

A. Yes, it does.

STATE OF NEW MEXICO
BEFORE THE WATER QUALITY CONTROL COMMISSION

IN THE MATTER OF PROPOSED NEW
RULE 20.6.8 NMAC –
Ground and Surface Water Protection –
Supplemental Requirements For Water Reuse No. WQCC 23 - 84 (R)

NEW MEXICO ENVIRONMENT DEPARTMENT,
WATER PROTECTION DIVISION,

Petitioner.

SELF AFFIRMATION

Justin Nobel, expert witness for New Energy Economy, upon penalty of perjury under the laws of the State of New Mexico, affirm and state: I have read the foregoing Direct Technical Testimony & Exhibits of Justin Nobel and it is true and correct based on my own personal knowledge and belief.

Dated this 15th day of April 2024.

/s/ *Justin Nobel*
JUSTIN NOBEL

Exhibit 1

JUSTIN NOBEL CV

EDUCATION

Columbia University: M.S. in Journalism & M.A. in Earth & Environmental Science. Courses in alternative energy, biodiversity, disease ecology, journalism. NY, NY 9/05-5/07

Duke University: B.S. in Earth & Ocean Sciences, Dean's List (2000-2003). Courses in marine biology, oceanography, atmospheric science, climatology, geology. NC & Australia 8/99-5/03

JOURNALISM

Freelancer: Reporting on oil & gas development across the US. Researching and writing book on oil & gas radioactivity. 2017-2024

Freelancer: Reporting from Nunavut, California, Florida, New Orleans, the Gulf Coast for publications such as Oxford American, Orion, Nautilus, Audubon. New Orleans 2010-2016

Freelancer: Received reporting grant from the Investigative Fund at The Nation Institute. Stories and photos on science and culture with TIME, Reuters AlertNet, Global Post. Micronesia 9/09-1/10

Freelancer: Stories and photos in Audubon, Meatpaper, The Daily Green and the Nunatsiaq News. Wrote weekly blog about death, http://blogs.funeralwise.com/dying/. Launched multimedia inauguration project featured in NY Times, www.januarythe20th.com. NY, NY 1/09-9/09

Audubon Magazine – Intern: Wrote science stories for mag. & web, fact checked, blogged. NY, NY 9/08-1/09

Freelancer: Stories & photos for the Nunatsiaq News, local Arctic paper. Award-winning photos of bowhead whale hunt. Story on Gourmet.com, photos in AP. Nunavik, Canada 7/08-9/08

Point Reyes Light: Pulitzer Prize-winning weekly newspaper, wrote science & environment stories, obits, features; photographer. Won breaking news writing award. Pt. Reyes, CA 6/07-6/08

Plenty Magazine – Intern: Environmental-lifestyle magazine, circ. 100,000; wrote science stories for website, research, fact-checking. NY, NY 1/07-5/07

American Museum of Natural History: Assistant to science writer; researched & drafted copy for website featuring multimedia science stories. NY, NY 2/05-8/05

SCIENCE

Columbia/U.N. development project: Surveyed birds in agricultural village in western Kenya for masters' in Environmental Science. Sauri, Kenya 5/06-7/06

Scripps' Research Vessel Melville: Research cruise assistant to Dr. Gabi Laske, deployed instruments to measure underwater earthquakes associated with the Hawaiian hotspot. Pacific Ocean 1/05

ECO (Env. Careers Org.) Field Biologist Intern for BLM: Surveyed endangered plants and lizards on the Mexican border in the Algodones Sand Dunes & Yuha Desert. El Centro, CA 2/04-8/04

Research Assistant to Dr. Paul Baker: Cored lakes on the Peruvian Altiplano and trees on the slopes of Bolivian volcanoes in the pursuit of paleoclimate data. Bolivia & Peru 5/03-6/03

AWARDS

- 2020 Rolling Stone magazine story on oilfield radioactivity, "America's Radioactive Secret," selected for Best Narrative Writing by the National Association of Science Writers.
- Story on Inuit ways of death selected for series, *Best American Travel Writing 2016.*
- Story on fire ants selected for series, *Best American Science & Nature Writing 2014.*
- Story on the Inuit Arctic selected for series, *Best American Travel Writing 2011.*
- Fellow at the 2009 Weather and Society Workshop (Boulder, CO; National Center for Atmospheric Research)
- Best Photo Essay at the Quebec Newspaper Awards (May 2009, Nunavik's 1st bowhead whale hunt in a century)
- Best 5 Web Travel Stories of 2008 by bravenewtraveler.com (60-hr bus trip from San Francisco to Mexico City)
- 2nd Place for Breaking News at California Newspaper Awards (2008, Obituary for 15-yr old car crash victim)
- Hechinger Award for Education Writing (May 2007, Expeditionary Learning at a Brooklyn Middle School)

163535

Exhibit 2

An Analysis of the Impact of the Regulation of "Radionuclides" as a Hazardous Air Pollutant on the Petroleum Industry

Prepared for the Committee for Environmental Biology and
Community Health, Department of
Medicine and Biology, American Petroleum Institute

October 19, 1982

Executive Summary

The impact of regulating "Radionuclides" as a hazardous air pollutant under Section 112 of the Clean Air Act is examined and is found to depend upon what is defined as an "acceptable level" of risk, and whether the regulation will be based upon committed dose equivalent to the general public, source characteristics, or individual radioisotopes.

Almost all materials of interest and use to the petroleum industry contain measurable quantities of radionuclides that reside finally in process equipment, product streams, or waste. In addition, groundwater used for waterflood and brine solutions from operating wells contain biologically significant quantities of Radium 226 and Radon 222. The mining, cleaning, and combustion of coal also add measurably to the burden of radioactive pollutants in ambient air.

Listing radionuclides as a hazardous air pollutant also brought radionuclides under the umbrella of CERCLA. Again, the impact of defining a "reportable quantity" depends upon the definition of "acceptable risk" and whether the standard is based upon a committed dose equivalent to a member of the general public or is established isotope by isotope.

Table 10 in the main body of the report summarizes the quantities of radionuclides found in products and raw materials of most concern to API member companies. Table 13 summarizes the EPA's estimate of risk associated with certain industry operations to a maximum exposed individual inhaling and ingesting radionuclides from products of combustions. Table 17 shows how the impact upon the industry expands as the level of acceptable risk is reduced, and Table 18 summarizes the combined potential impact of regulations under both the Clean Air Act and CERCLA.

It is concluded that the regulation of radionuclides could impose a severe burden on API member companies, and it would be prudent to monitor closely both regulatory actions.

What Radionuclides Should Be of Concern?

When the EPA listed "RADIONUCLIDES" as a hazardous air pollutant, they meant all radioactive materials without exemption for material concentration (specific activity), quantity, or material with which it is associated. There were no exemptions for the non-nuclear industries.

The general classification "Radionuclides" includes:

- By-Product Material - the material made radioactive through the use of special nuclear material or bombardment by radiations resulting from the use of special nuclear material (CFR, 1982).
- Special Nuclear Material - the fuel for reactors.
- Source Material - essentially the concentrated elements from which special nuclear material is separated.
- Naturally Occurring or Accelerator-Produced Radioactive Materials - those radioactive materials found in nature or made radioactive in a laboratory by an energetic ion beam. These are the materials that are present in our products in minute amounts.

While many petroleum companies use radioactive materials as tracers and in process control, these are carefully regulated by the U.S. Nuclear Regulatory Commission present little, if any, environmental hazard, and are of small concern. The API should be more concerned with the potential for naturally occurring radionuclides being in our raw materials. Naturally occurring radioactive material is either produced in the earth's atmosphere as a result of cosmic-ray bombardment, i.e. Carbon-14, or exists as primordial radionuclides, i.e. radionuclides present from the event of creation in the earth's crust, such as Potassium 40 and Uranium. The families of radionuclides or series of radionuclides that are of most significance are in this primordial grouping. These are the decay series of Uranium 238, Uranium 235, Thorium 232. Uranium 235 is the nuclear fuel. About 0.7% of natural uranium is Uranium 235. Uranium 238 and Thorium 232 are uniformly distributed in the earth's crust.

The Uranium 238 (Figure 1) series can be divided into some four subseries, all possessing significant exposure potential to man. These subseries are the decay of Uranium 238 and Uranium 234 to Thorium 230, the decay of Thorium 230 to Radium 226, the decay of the inert gas Radon 222 and its short-lived daughters to the long-lived daughter, product Lead 210, and finally the decay of Lead 210 to stable lead (NCRP, 1975). The elements in the Subseries Uranium 238 to Thorium 230 represent significant sources of internal exposure, primarily in the occupational environment. Radium 226 is a potent source of radiation exposure, both internal and external. Radon 222 and its short-lived progeny deliver significant population and occupational exposures to the upper tracheobronchial tree, while Lead 210 and its decay product contaminate much process equipment and can represent significant exposure to the bone in some occupational subgroups. Radon 222 and its daughters cause the most severe impact to the public health.

The Thorium series (see Figure 2) is characterized by the long-lived Thorium 232 at the head of the series and decay products that are relatively short lived. If no migration of the series members takes place, radio-equilibrium is established in about 60 years. In minerals and rocks of low permeability, the thorium series radionuclides are expected to be in equilibrium. In soils, natural waters, natural gas, crude oil and the atmosphere, the disparate chemical and physical properties of the series tend to cause disequilibrium. Certain parts of the world, Kerala in India and monazite mining districts in Brazil, are famous because of their high background levels of external radiation from the thorium series.

The Presence of Radionuclides in Crude Oil, Natural Gas (NG), Liquefied Petroleum Gas (LPG), Coal, Phosphate Rock, and Groundwater

It is well known that some naturally occurring elements, uranium for example, have an affinity for crude oil. The uranium that accumulates in crude oil, oil shale, coal, and phosphate rock is the residue remaining after the marine deposits have been consolidated. Petroleum is often assumed to have migrated to a position of minimum hydraulic potential in a "reservoir rock", which may or may not be derived from the same source deposits as the petroleum. Associated with the petroleum in widely ranging proportions are brine and natural gas. The radionuclides, particularly those of the uranium series (see Figure 1), distribute themselves among the three fluid phases and the crusty, solid lining of the intergranular spaces according to chemical affinity, sorption phenomena and the vagaries of radioactive recoil. The gaseous radon isotopes follow the temperature-pressure dependent Henry's Law in their portioning among the gas and liquid phases. The sites of major uranium-series nuclides in the Texas Panhandle gas field and adjacent areas have been studied extensively (Pierce, 1964). In the gas reservoir, uranium is resident mainly in the crude oil and in pellets of solid hydrocarbon, radium is found in the brine and in the solid crust, and radon distributes itself among the oil, gas and brine in that order. The series equilibrium is evidently disrupted continually by movement of decay products from one phase to another that is chemically or physically more compatible.

Crude Oil

Very little has appeared in the literature concerning the levels of radioactivity in crude oil, but it would be safe to assume that the actual levels of contamination would be between that found in coal and that found in sedimentary rock similar to that of the reservoir rock or where the petroleum was formed. Uranium in the earth's crust averages 4 parts per million (CRC, 1969). The NCRP (NCRP, 1975) reported the data shown in Table 1 for the various rock types.

TABLE 1 —*Summary of concentrations of major radionuclides in major rock types and soil*[a]

Rock Type	Potassium-40		Rubidium-87		Thorium-232		Uranium-238	
	percent total Potassium	pCi/g	ppm total Rubidum	pCi/g	ppm	pCi/g[b]	ppm	pCi/g[c]
Igneous Rocks								
Basalt (Crustal average)	0.8	7	40	0.9	3-4	0.3-0.4	0.5-1	0.2-0.3
Mafic[d]	0.3-1.1	2-9	10-50	0.2-1	1.6, 2.7	0.2, 0.3	0.5, 0.9	0.2, 0.3
Salic[d]	4-5	30-40	170-200	4-5	16, 20	1.7, 2.2	3.9, 4.7	1.3, 1.6
Granite (Crustal average)	>4	>30	170-200	4-5	17	1.9	3	1
Sedimentary Rocks								
Shale	2.7	22	120[e]	3	12	1.3	3.7	1
Sandstones:								
clean quartz	<1	<8	<40[e]	<1	<2	<0.2	<1	<0.3
dirty quartz	2?	10?	90?	2?	3-6?	0.3-0.7?	2-3?	1?
arkose	2-3	16-24	80-120[e]	2	2?	0.2?	1-2?	0.3-0.7?
Beach sands (unconsolidated)	<1	<8?	<40?	<1?	6	0.7	3	1
Carbonate Rocks	0.3	2	10[e]	0.2	2	0.2	2	0.7
Soils[f]	1.5	12	65[e]	1.4	9	1	1.8	0.6

[a] References cited in text unless otherwise noted; single values are averages; values estimated in absence of reference are followed by question mark.

[b] To obtain series equilibrium alpha, beta, or approximate gamma (excluding bremsstrahlung and x radiation) activity, multiply by 6, 4, or 2 respectively.

[c] To obtain series equilibrium alpha, beta, or approximate gamma (excluding bremsstrahlung and x radiation) activity, multiply by 8, 6, or 3, respectively.

[d] From Clark *et al.* (1966); for potassium and rubidium, the range of values for rocks within the class is given; for thorium and uranium, the median and mean value are given, respectively.

[e] Estimated by application of crustal abundance ratio with respect to potassium.

[f] In-situ gamma-spectral measurements at 200 locations by Lowder *et al.* (1964).

Table 2 (UNSCEAR, 1977) shows additional data.

TABLE 2. TYPICAL ACTIVITY CONCENTRATION OF ^{40}K, ^{238}U AND ^{232}Th IN COMMON ROCKS AND ESTIMATED ABSORBED DOSE RATE IN AIR 1 m ABOVE THE SURFACE

Type of rock	*Typical activity concentration (pCi g⁻¹)* ^{40}K	^{238}U	^{232}Th	*Absorbed dose rate in air (μrad h⁻¹)*
Igneous				
Acidic (e.g. granite)	27	1.6	2.2	12
Intermediate (e.g. diorite)	19	0.62	0.88	6.2
Mafic (e.g. basalt)	6.5	0.31	0.30	2.3
Ultrabasic (e.g. dunite)	4.0	0.01	0.66	2.3
Sedimentary				
Limestone	2.4	0.75	0.19	2.0
Carbonate	–	0.72	0.21	1.7
Sandstone	10	0.5	0.3	3.2
Shale	19	1.2	1.2	7.9

Sources: References 1, 353.

Gulf (Rhodes, 1972) has measured the amount of Lead 210 - a Uranium 238 daughter product - in light hydrocarbon streams. Their finding suggests concentrations as high as 1.2 ± 0.9 $pCig^{-1}$ in such streams.

Natural Gas

The quantities of radon contained in the natural gas of the Panhandle Field and at all other gas fields sampled for radon is of significance to radiation exposure estimates for the U.S. general population. Natural gas of the Panhandle field was found to contain an average radon concentration of about 100 pico curies per liter (pCi/ℓ). Maximum concentration as much as 1450 pCi/ℓ were observed after expansion to atmospheric pressure (Pierce, 1964). In-transit decay, processing of gas for pipelines, and storage decrease the radon contamination, but increase daughter (decay) product, i.e. Lead-210 (see Figure 1), contamination of lines, processing equipment, and storage tanks. This contamination can produce significant occupational exposures. Radon concentrations found in natural gas are summarized in Tables 3 and 4 (UNSCEAR, 1977).

TABLE 3. RADON CONCENTRATION IN NATURAL GAS AT THE WELL

Location of well	*Radon concentration ($pCi\ l^{-1}$)* *Average*	*Range*	*Reference*
Borneo			
Ampa field	...	1.5-3.2	352
Canada			
Alberta	62	10-205	302
British Columbia	473	390-540	
Ontario	169	4-800	
Germany, Federal Rep. of	...	1.0-9.6	352
Netherlands			
Slochteron	...	1.1-2.8	352
Other fields	...	3.7-44.7	
Nigeria			
Niger delta	...	0.9-2.9	352
North Sea			
Leman field	...	2.0-3.8	352
Indefatigable field	1.8	...	
United States			
Colorado, New Mexico	25	0.2-160	171
Texas, Kansas, Oklahoma	< 100	5-1 450	
Texas Panhandle	...	10-520	
Colorado	25.4	11-45	
Project Gasbuggy area	15.8	...	
California	...	1-100	
Kansas	100	...	
Wyoming	10	...	
Gulf Coast (Louisiana, Texas)	5	...	
California, Louisiana, Oklahoma, Texas	...	1-120	98

TABLE 4. RADON CONCENTRATION IN NATURAL GAS IN THE DISTRIBUTION LINE

Area	*Radon concentration ($pCi\ l^{-1}$)* *Average*	*Range*
Poland (Warsaw)	8	4-14
United States		
Chicago	14.4	2.3-31.3
New York City	1.5	0.5-3.8
Denver	50.5	1.2-119
West coast	15	1-100
Colorado	25	6.5-43
Nevada	8	5.8-10.4
New Mexico	45	10-53
Houston	8	1.4-14.3

Sources: Poland, 359; United States, 171.

Table 5 summarizes data from the USEPA.

Table 5. Radon-222 concentrations in natural gas at production wells

Area	Radon-222 level, pCi/l		Reference
	Average	Range	
Colorado New Mexico	25	0.2-160	1
Texas, Kansas, Oklahoma	<100	5-1450	2
Taxas Panhandle	---	10-520	3
Colorado	25.4	11-45	5-7
Project Gasbuggy Area	15.8-19.4	--------	7
Project Gasbuggy Area	29.4	12-59	8
California	---	1-100	10
Gulf Coast (Louisiana, Texas)	5	--------	11
Kansas	100	--------	11
Wyoming	10	--------	11
Overall average	37		

Liquefied Petroleum Gas

When natural gas is thermally fractionated to recover the heavier hydrocarbons, the radon tends to concentrate in the ethane and propane fractions (Gessell, 1975). These are sold in mixtures sometimes including butane, as liquefied petroleum gas (LPG) for use as a fuel. Typically, the concentration of Radon 222 in LPG is eight times the concentration in the natural gas before processing (Gessell, 1974). Subsequent storage allows the Radon 222 to decay, however, and there are indications that despite the higher initial Radon 222 concentration, LPG is no more important than natural gas as a pathway for population exposures to Radon 222.

An occupational external exposure situation can occur in gas processing plants where daughters of Radon 222 collect on the inside of processing equipment, especially pumps, and also create some disposal problems (Gessell, 1974).

Coal

Coal and its residues appear to be significantly contaminated with Radium 226. Table 6 (USCEAR, 1977) shows that U.S.-mined coal contains biologically significant quantities of Uranium 238, Radium 226, Bismuth 214, Thorium 228 and Thorium 232. Barber (Barber, 1977) also reported significant concentrations of Bismuth 214, Potassium 40 and Thallium 208. The U.S. Geological Survey Service (USCGS, 1959) has reported uranium concentrations in coal up to 0.2%.

TABLE 6. ACTIVITY CONCENTRATION OF RADIONUCLIDES IN COAL AND COAL RESIDUES

($pCi\ g^{-1}$)

Type of coal or coal residue and its origin	^{40}K	^{238}U	^{226}Ra	^{210}Pb	^{228}Ra	^{228}Th	^{232}Th	*Reference*
Coal								
Australia			0.8-1.3					23
Czechoslovakia (brown)			0.11, 0.35					165
Germany, Fed. Rep. of	< 2.5		< 0.7				< 0.6	307a
Hungary (bituminous)			0.04					165
Poland (bituminous)			0.048-0.94					165
Poland (brown)			0.90					165
United States								
Illinois	2.5		0.6[a]			0.04[b]		20
Montana	0.7		0.3[a]			0.07[b]		20
North Dakota	2.2		0.2[a]			0.02		20
United States		0.7					0.2	185
United States			0.014	0.28				175
Coal ash (laboratory processing)								
Australia			4.7-8.3					23
Germany, Fed. Rep. of			6.2[c]			2.6		172
	19		5.8				3.4	307a
Japan								
Central			0.10	19.8	1.15	15.3		257
Southern			0.98	8.16	0.46	2.35		257
Northern			0.63	105.0	1.45	6.79		257
United States (semi-bituminous)			3.8		2.4	2.6		79
Slag								
Poland	17.3		4.3[a]			1.2[b]		272
United States	26		4.5[a]			0.5[b]		20
United States		4.9					1.5	185
United States			0.55	1.0				175
Fly ash								
Australia			14.0					23
Hungary			0.6-15					204
Poland			1.0					165
Poland	22.5		6.4[a]			1.1[b]		272
Poland (bituminous)		1.5, 2.8	0.61, 4.18	4.4, 6.7			0.18, 0.22	166
Poland (lignite)			0.91					166
United States		10					2.6	185
United States			0.4	17.3				175
United States	11		3.1[a]			0.4[b]		20

[a] Assumed equal to activity concentration of ^{214}Bi.

[b] Assumed equal to activity concentration of ^{208}Tl.

[c] Including activity concentration of ^{224}Ra.

Solvent Refined Coal

Hittman Associates (USDC, 1978) have analyzed solvent refined coal for radionuclides in 1970 and noted concentration of uranium in the SRC particulates. These data are summarized in Table 7.

TABLE 7. RADIONUCLIDE CONCENTRATIONS

(ppm by weight)

Source	Uranium	Thorium
Coal		
Sample #1	1.3	4.74
Sample #2	1.4	4.24
SRC		
Sample #1	0.8	4.99
Sample #2	1.3	3.73
Coal Particulates		
Sample #1	2.6	14.99
Sample #2	1.9	20.50
SRC Particulates		
Sample #1	39	11.46
Sample #2	28	9.48

Phosphate Rock

Many of the American Petroleum Institute's members are also engaged in the peripheral activity of mining phosphate rock and manufacturing fertilizer. Table 8 (UNSCEAR, 1977) summarizes the presence of radioactivity of the rock and its products.

TABLE 8. ACTIVITY CONCENTRATION OF ^{226}Ra, ^{238}U, AND ^{232}Th IN PHOSPHATE ROCK AND IN PRODUCTS DERIVED FROM IT

Marketable rock produced in Florida (United States)

	Production in the United States in 1973[a] *(10^6 t)*		*Activity concentration ($pCi\,g^{-1}$)*		
Sample	*Amount*	*P_2O_5 content*	*^{226}Ra*	*^{238}U*	*^{232}Th*
Marketable rock	38	–	42	41	0.4
Wet process products					
Normal superphosphate	3.1	0.6	25	*b*	–
Triple superphosphate	3.4	1.6	21	57	0.4
Ammonium phosphate	5.3	2.4	5.7	63	0.4
Phosphoric acid	10.0	5.1	0.6	–	–
Gypsum	23.0	–	3.3	6.1	0.3
Electric furnace process products					
Slag	–	–	56[c]	–	–

Source: Reference 109.

[a] Florida accounts for 82 per cent of the marketable rock production of the United States.

[b] The activity concentration of ^{238}U in normal superphosphate is expected to be equal to that of ^{226}Ra.

[c] The ^{226}Ra activity concentration in the input feed ore was 60 pCi g^{-1}.

Groundwater

In groundwaters, such as those used for waterflood operations, Radon 222 is usually present in a concentration range of from several hundred to several thousand pico curies per liter. In North Carolina, where the geology is primarily sedimentary, Radon concentrations vary from 20 to 47,000 pCi/ℓ. Approximaately 33% of supplies tested had concentrations greater than 2000 pCi/ℓ (Sasser, 1978).

The groundwaters around Houston are probably typical of those associated with most petroleum operations. The radon concentrations shown in Table 9 (Prichard, 1981) are for water as it is delivered to Houston homeowners for consumption. In-ground levels are probably similar to the higher samples in North Carolina.

Table 9
Radon in Houston Homeowners' Water Supplies from Groundwater Sources (Prichard, 1981)

Tracts Included	Average Concentration of Radon (pCi/ℓ)
All	437
Tracts with Concentration greater than 500 pCi/ℓ	853
Tracts with Concentrations greater than 1000 pCi/ℓ	1722

Summary

Table 10 estimates the amounts of radioactivity contained in petroleum products in more familiar units. If we assume that a refinery processes one million barrels of crude per day, we find that we have handled some 1.46 curies per day or 533 curies per year of radioactivity, mostly in the form of naturally occurring Potassium 40.

If it is correct to assume that the uranium in the oil is at the same concentration as the host rock, then a one-million-per-day-capacity refinery could be throughputting some 480 lb of uranium per day (177,200 lb uranium per year).

TABLE 10

Quantities of Radionuclides in Normal Measurement Units Used by the Petroleum Industry

Item/Product	Units	Radioactive Contaminant						
		^{40}K	^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{222}Rn	Total
Crude Oil*	uCi/BBL	1.4	0.07		0.17	.04		1.46
Kuwait Oil	uCi/BBL				0.17			0.17
Natural Gas**	uCi/10^{6}ft^3						1400	1400
LPG	uCi/10^{6}ft^3						1400	1400
Coal-US	uCi/T	23.6	4.5	4.0	0.9	1.3	—	30.3
SRC-Product	uCi/T		0.6			100		100.6
Shale Oil	uCi/BBL	2.8	.17			.17		3.14
Shale Waste	uCi/T	17	1.0			1.0		19
Phosphate Rock (Marketable)	uCi/T		38	38		.36		76.36
Ground Waters	uCi/1,000 gal.						1.6	1.6

* Assumes Uranium in Oil is equal to Uranium in host Rock

** Assumes Average Concentration of 50pCi/l

Note: The USNRC regulates microcurie amounts of radioactive materials that are not naturally occuring.

Potential Public Health Effects of the Use of Materials and Products Important to the API and Its Member Companies

There are probably as many estimates of impact of radionuclides in air as there are individuals capable and incapable of making such estimates. Whether or not a radioactive material contained in petroleum, natural gas, or coal, is taken into the body depends upon a number of factors, including:

- amount originally present
- amount made airborne
- atmospheric phenomena and transport
- plate out and rain out
- routes of entry
- amount retained
- clearance mechanisms
- dietary sources
- dose contribution of "infinite cloud" and "infinite plane"
- and others

The EPA method of analysis assumed certain source characteristics and target populations (EPA, 1979), used a Gausian computer model to disperse the radioactive materials (BAES, 1981) and a second computer program to model intake, dose, and dose response based upon the linear non-threshold model (Begovich, 1981), (Sullivan, 1981), (Dunning, 1981). The first analysis by EPA concerning the naturally occurring radioactive materials is shown in Table 11 (EPA, 1979). Table 12 is a later analysis, currently in draft form, that expanded the original list (Teknekron, 1981).

Analysis of the data in both reports suggests that API companies should be concerned with operations described in Table 13. Table 13 suggests that the radioactive material emissions having the greatest potential impact on API member companies are Radon-222, followed closely by Uranium-238 and Radium-226. The two EPA analyses demonstrate that any operation involving the combustion of fossil fuels or the preparation of such fuels for use could be subject to regulation under the Clean Air Act.

Table 11. Summary of radiological impact caused by atmospheric emissions of natural radioactive materials

		Model facility									
				Exposure levels		Principal dose equivalent rates				Expected fatal cancers per year of operation	
										Population	
Source category	Number of sources	Principal radionuclide emissions (Ci/y)[a]		Maximum individual (WL)	Regional Population (Person-WL)		Maximum Individual (mrem/y)[b]	Regional Population (Person-rem/y)[c]	Lifetime risk to the maximum individual ($\times 10^{-6}$)	Regional (Fatal cancers)	U.S.
Uranium Mines (4.1) Underground	251	Rn-222	6700	0.006	1.3		-	-	10,000	0.03	0.03
Open pit	36	Rn-222	2000	0.0008	0.4		-	-	1,000	0.008	0.02
Uranium Mills (4.2)	20	Rn-222 U-238+d	2700 ~0.4	0.005	0.5	Lung Bone	350 360	3.4 3.9	10,000	0.01	0.03
Phosphate Industry (4.3) Mining and beneficiation	35	Rn-222	1300	0.0002	4.9		-	-	300	0.1	
Drying and grinding facilities	20	Rn-222 U-238+d	20 0.03	0.00005	0.08	Lung Bone	54 79	17 18	500	0.004	
Phosphoric acid plant	35	Rn-222 U-238+d	480 0.1	0.0007	2.0	Lung Bone	85 110	46 45	2,000	0.05	
Elemental phosphorus plant	9	Rn-222 U-238+d Po-210	490 0.15 7.4	0.0004	2.0	Lung Bone Kidney	740 570 1800	770 440 1400	6,000	0.1	
Coal-fired power stations[d] (4.4) New stations	145	Rn-222 U-238+d Th-232+d	1.9 0.3 0.07	<0.00001	<0.00001-0.024	Lung Bone	0.8-2.1 1.6-16	0.5-2600 1.5-1300	10-60	0.00008-0.2	
Existing stations	250	Rn-222 U-238+d Th-232+d	0.7 0.8 0.3	<0.00001	<0.00001-0.013	Lung Bone	6.7-15 8.3-62	2.7-19,000 7.1-11,000	60-700	0.0004-1.5	---

See footnotes at end of table.

Table 11. Summary of radiological impact caused by atmospheric emissions of natural radioactive materials--continued

		Model facility								
				Exposure levels		Principal dose equivalent rates			Expected fatal cancers per year of operation	
									Population	
Source category	Number of sources	Principal radionuclide emissions (Ci/y)[a]		Maximum individual (WL)	Regional Population (Person-WL)	Maximum Individual (mrem/y)[b]	Regional Population (Person-rem/y)[c]	Lifetime risk to the maximum individual ($\times 10^{-6}$)	Regional (Fatal cancers)	U.S.
Metal mining and milling[e] (4.5)	177	Rn-222	17 to 3000	<0.00001 to 0.001	0.005 to 0.8	-	-	20 to 2000	0.0001 to 0.02	
Nonmetal mining and milling[f] (4.5)	4,200	Rn-222	0.2 to 18	<0.00001 to 0.00004	0.0007 to 0.06	-	-	0.7 to 50	0.00002 to 0.001	
Geothermal power site (4.6A)	1	Rn-222	540	0.0004	1.5	-	-	700	0.03	
Ground water treatment plants (4.6B)	40,000	Rn-222	3.4	<0.00001	0.06	-	-	10	0.001	

[a] U-238+d emission rates are the sum of the individual release rates for uranium-238, and its daughter products uranium-234, thorium-230, radium-226, lead-210, and polonium-210. (For elemental phosphorus plants only, polonium-210 is not included in this sum.)

Th-232+d emission rates are the sum of the individual release rates for thorium-232 and its daughter products radium-228, thorium-228, and radium-224.

[b] The maximum dose equivalent rate an individual is likely to receive living near the facility.

[c] The maximum collective dose equivalent rate to the regional population. This is the maximum value expected to occur within 100 years following the start of facility operation.

[d] Ranges of impact values represent variations due to station siting.

[e] Includes iron, copper, zinc, and bauxite.

[f] Includes clay, limestone, fluorspar.

Table 12

SUMMARY OF RISKS FROM SOURCES OF AIRBORNE EMISSIONS OF RADIONUCLIDES

Source Category	Principal Radionuclide Emissions (Ci/yr)		Dose Equivalent Rates			Radon Daughter Exposure		Health Effects	
				Maximum Exposed Individual (mrem/yr)	Collective (person-rem/yr)	Maximum Individual (working level)	Regional Population (person working level)	Lifetime Risk to the Maximum Exposed Individual	Expected Fatal Cancers per Year of Operation to the Population at Risk
Ground Water Treatment Plant (3.1)									
Southeastern Site	Rn-222	8.1	Lung Bone	5.7E-3 1.9E-4	2.9E-2 9.3E-4	3.8E-6	1.9E-2	6E-6	5E-4
Southwestern Site	Rn-222	8.1	Lung Bone	9.6E-3 3.1E-4	0.15 4.9E-3	6.4E-6	0.10	1E-5	2E-3
Geothermal Power Plant (3.2)	Rn-222	5.5E+2	Lung	1.22	3.1	8.1E-4	2.1	1E-3	5E-2
Phosphate (3.3)									
Phosphate Mine: Stack	Rn-222 U-238	2.1E+1 1.8E-2	Lung Bone	3.5E+1 5.8E+1	8.8E+1 2.4E+2	9.7E-6	5.0E-2	1E-4	7E-3
Area Source	Rn-222 U-238	2.6E+3 4.0E-3	Lung Bone	1.7 5.5	9.2 0.3	5.9E-4	3.2	1E-3	2E-2
Phosphate Acid Plant: Stack	Rn-222 Ra-226 U-238	6.5E+1 1.8E-2 3.5E-2	Lung Bone	6.4E+1 1.0E+2	1.5E+2 3.5E+2	3.1E-5	0.16	2E-4	1E-2
Area Source	Rn-222	3.2E+2	Lung	0.22	1.1	1.4E-4	0.75	3E-4	2E-2
Elemental Phosphorus Plant: Stack	U-238 Ra-226 Pb-210 Po-210	2.2E-2 7.0E-3 3.3E-2 3.2E+0	Lung Liver Bone	2.1E+2 1.7E+1 7.0E+1	5.0E+2 2.6E+2 2.5E+2			7E-4	4E-2
Area Source	Rn-222	2.2E+2	Lung	0.15	0.78	1.0E-4	4.3E-2	2E-4	4E-2
Non-Uranium Metal Mining, Milling, Processing (3.4)									
Underground Mine. Area Source #1	Rn-222 U-Nat	2.1E+2 2.3E-5	Lung Bone	0.52 0.21	3.0E-2 7.2E-3	2.7E-4	1.8E-2	4E-4	4E-4
Area Source #2	Rn-222 U-Nat	2.3E+2 1.0E-2	Lung Bone	4.1E+1 6.7E+1	1.2 2.8	2.3E-4	2.0E-2	5E-4	5E-4
Open-Pit Mine	Rn-222 U-Nat	4.5E+3 5.0E-2	Lung Bone	3.6E+1 5.7E+1	2.6 6.1	7.2E-4	0.15	1E-3	4E-3
Copper Ore Mill	Rn-222 U-Nat	1.7E+3 2.0E-2	Lung Bone	7.3E+1 1.2E+2	6.5 1.6E+1	1.6E-3	0.38	3E-3	1E-2

Table 12 (Cont.)

SUMMARY OF RISKS FROM SOURCES OF AIRBORNE EMISSIONS OF RADIONUCLIDES

Source Category	Principal Radionuclide Emissions (Ci/yr)		Dose Equivalent Rates			Radon Daughter Exposure		Health Effects	
				Maximum Exposed Individual (mrem/yr)	Collective (person-rem/yr)	Maximum Individual (working level)	Regional Population (person working level)	Lifetime Risk to the Maximum Exposed Individual	Expected Fatal Cancers per Year of Operation to the Population at Risk
Non-Uranium Mining, Milling, Processing (Cont)									
Metal Smelter: Main Stack	Rn-222	8.0	Lung	5.3E+1	1.5E+1	Negligible		2E-4	2E-3
	Pb-210	1.0E+1	Liver	1.6E+1	2.4E+1				
	Po-210	1.0E+1	Bone	3.7E+1	4.0E+1				
	U-Nat	4.5E-2							
Area Source	Rn-222	1.7E+2	Lung	2.0E+2	6.3	1.5E-4	1.4E-2	9E-4	6E-4
	U-Nat	5.3E-2	Red Marrow	2.3E+1	1.1				
			Bone	3.2E+2	1.5E+1				
Non-Metal Mining (3.5) Kiln	Rn-222	4.3E-1	Lung	2.0E+1	1.1E+2	Negligible		7E-5	8E-3
	U-Nat	2.8E-4	Liver	1.8	8.3E+1				
			Bone	2.6	1.2E+2				
Area Source	Rn-222	4.3E-1	Lung	0.79	1.3	1.4E-6	6.3E-3	4E-6	2E-4
	U-Nat	5.1E-6	Bone	4.6E-2	1.2				
Coal Mining and Cleaning (3.6) Underground Mine	Rn-222	1.6E+1	Lung	2.6E-2	2.2	Negligible		9E-3	6E-4
	U-238	3.4E-6	Red Marrow	1.6E-2	2.2				
	Th-232	3.5E-6	Bone	3.1E-2	3.3				
Strip Mine	Rn-222	1.4E+0	Lung	1.1	2.3E+1	8.0E-7	3.1E-2	5E-6	2E-3
	U-238	3.6E-4	Bone	2.8	6.4E+1				
	Th-232	2.8E-4							
Coal Cleaning Plant	Rn-222	0.17	Lung	0.27	8.9	Negligible		1E-6	1E-3
	U-238	2.2E-4	Bone	0.69	3.0E+1				
	Th-232	2.2E-4							
Natural Gas Combustion Units (3.7) Natural Gas Boiler	Rn-222	2.4	Lung	2.9E-3	4.5E-2	1.9E-7	3.0E-2	3E-6	6E-4
Natural Gas Turbine	Rn-222	6.7E-2	Lung	5.2E-3	1.3E-2	3.5E-6	8.8E-2	4E-6	2E-4

Table 12 (Cont.)

SUMMARY OF RISKS FROM SOURCES OF AIRBORNE EMISSIONS OF RADIONUCLIDES

Source Category	Principal Radionuclide Emissions (Ci/yr)		Dose Equivalent Rates			Radon Daughter Exposure		Health Effects	
				Maximum Exposed Individual (mrem/yr)	Collective (person-rem/yr)	Maximum Individual (working level)	Regional Population (person working level)	Lifetime Risk to the Maximum Exposed Individual	Expected Fatal Cancers per Year of Operation to the Population at Risk
Coke Production (3.8)									
Northeastern Site	Rn-222	1.9E+0	Lung	1.8E+1	5.7E+2	Negligible		6E-5	3E-2
	Th-232	1.1E-3	Bone	4.3	1.9E+2				
	Po-210	6.2E-1							
	U-238	1.1E-3							
Midwestern Site	Rn-222	1.9E+0	Lung	1.9E+1	3.6E+1	Negligible		1E-6	3E-3
	Th-232	1.1E-3	Liver	7.1	2.8E+1				
	Pu-210	6.2E-1	Bone	5.9	1.7E+1				
	U-238	1.1E-3							
Coal-Fired Steam Electric Generating Stations (3.9)									
New CFSEGS: Midwestern Site	U-238	2.0E-2	Bone	4.2	2.9E+2			5E-5	3E-3
	U-235	1.2E-3							
	Th-232	7.3E-3							
Southeastern Site	U-238	2.0E-2	Bone	1.3E+1	2.2E+1			5E-5	2E-4
	U-235	1.2E-3							
	Th-232	7.3E-3							
Existing CFSEGS: Midwestern Site	U-238	2.9E-2	Bone	1.2+1	7.4E+2			9E-5	1E-2
	U-235	1.6E-3							
	Th-232	2.1E-2							
Southeastern Site	U-238	2.9E-2	Bone	3.1E+1	4.9E+1			5E-5	5E-4
	U-235	2.1E-2							
	Th-232	2.1E-2							
Coal-Fired Industrial Boilers (3.10)									
Eastern Site	U-238	4.5E-3	Lung	7.4	2.3E+2			3E-5	2E-2
	U-235	2.6E-4	Bone	1.0E+1	6.2E+2				
	Th-232	3.3E-3							
Midwestern Site	U-238	4.5E-3	Lung	8.0	1.5E+1			3E-5	1E-3
	U-235	2.6E-4	Bone	2.2E+1	5.2E+1				
	Th-232	3.3E-3							

TABLE 13

Summary of Operations Whose Regulation Will Impact On API Member Companies

Operation	Isotype of Interest	Lifetime Risk to the Maximum Exposed Individual
Ground Water Treatment		
Southeastern Site	^{222}Rn	6×10^{-6}
Southwestern Site	^{222}Rn	1×10^{-5}
Geothermal Power	^{222}Rn	1×10^{-3}
Coke Production		
Northeast	^{222}Rn	6×10^{-5}
	^{232}Th	
	^{210}Pu	
	^{238}U	
Southeastern	ditto	1×10^{-6}
Coal Fired Steam		
New Midwestern	^{238}U	
	^{235}U	5×10^{-5}
	^{232}Th	
Southeastern	ditto	5×10^{-5}
Existing Coal Fire Industrial Boilers		
Eastern	ditto	3×10^{-5}
Midwestern	ditto	3×10^{-5}
Coal Mining and Cleaning		
Underground Mining	^{222}Rn	9×10^{-3}
	^{238}U	
	^{232}Th	
Strip Mining	ditto	5×10^{-6}
Coal Cleaning	ditto	1×10^{-6}
Natural Gas Combustion	^{222}Rn	3×10^{-6}
Natural Gas Turbine	^{222}Rn	4×10^{-6}

Regulatory Options and Their Implications

As far as industry is concerned, the regulatory issues should be:

1. What is an "acceptable level of risk"?
2. Which approach will be followed in setting the standard, a generic "committed" dose equivalent approach or regulation isotope by isotope?

The EPA risk assessment in part evaluated the risk to a "maximum exposed individual". The risk to this person from sources of interest to the API ranged from 9 x 10^{-3} (underground coal mining) to 1 x 10^{-6} (coal cleaning) Risks for this individual resulting from the combustion of fossil fuels ranged in the 5 x 10^{-5} area (Teknekron, 1981). Table 14 (Wilson, 1981) gives an indication of how those risks compare with others "accepted" by United States residents.

The federal bureaucracy also has been pondering over the concept of acceptable and de minimis risk. Dr. Roy Albert has been supporting 1 x 10^{-5} excess lifetime risk of fatal cancer in the drinking water area. The FDA has accepted 1 x 10^{-6} excess risk as acceptable for acrylonitrile migration in food containers. The USNRC is considering in staff discussions 1 x 10^{-4} excess lifetime risk of death from occupational exposure and 1 x 10^{-6} excess lifetime risk of death or lower as de minimis. The EPA assessment lists the combustion of fossil fuels as lying between 10^{-4} and 10^{-5}.

In addition to the definition of acceptable risk, the method of setting the limits could have considerable impact. There are two methods available to the EPA: regulate population-committed dose equivalent to air pollutants, the generic approach; or limit the emission of specific radionuclides.

The generic approach specifies that the emissions of radionuclides will be controlled to a level such that the total committed dose equivalent received by an individual does not produce a risk of fatal cancer exceeding that of a preselected whole-body dose commitment (ICRP, 1977; ICRP, 1980).

Mathematically, this can be expressed as

$$\frac{H_d}{D} + \sum_j \frac{I_{i,j}}{(ALI)_{i,j}} + \sum_j \frac{I_{o,j}}{(ALI)_{o,j}} \leq 1$$

where H_d is the deep dose commitment or (whole body dose)

$I_{i,j}$ is the annual intake of radionuclide j by inhalation

$I_{o,j}$ is the annual intake of radionuclide j by the oral route

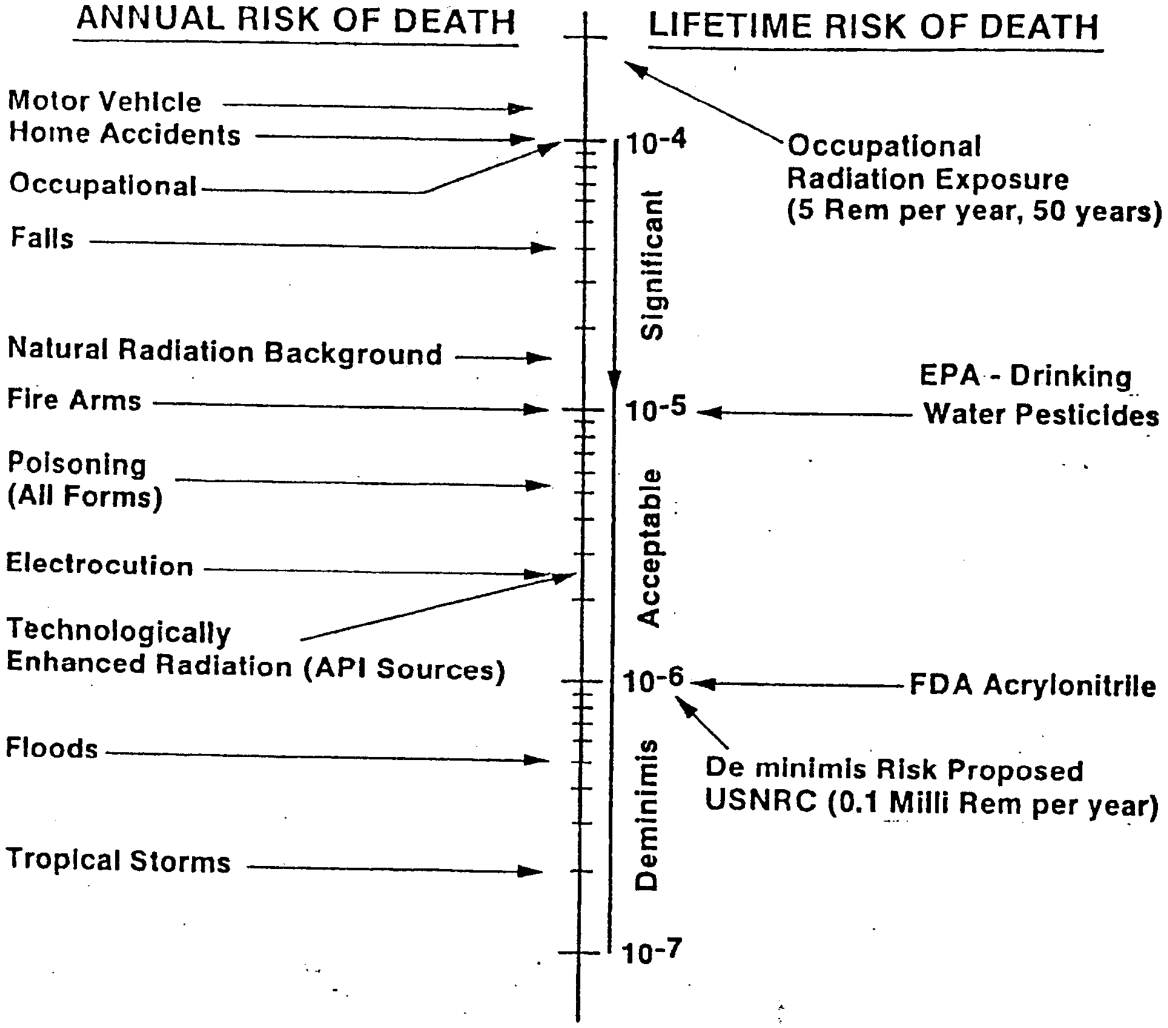
$ALI_{i,j}$ is the annual intake by inhalation which will provide a risk equal to a deep dose commmitment D

$ALI_{o,j}$ is the annual intake by the oral route that will produce a risk equal to a deep dose commitment D, and

D is the deep dose commitment resulting in an acceptable level of risk

TABLE 14

DEFINED LEVELS OF RISK



*Being considered in revision of 10CFR 20 Standards for Radiation Protection. This is not an agency position.

The risk factor for whole body radiation is about 1.65×10^{-4} fatal cancers per Rem (ICRP, 1977). If we calculate the committed whole body dose equivalent to produce an excess lifetime risk of 1×10^{-5}, we find

$$10^{-5}\left(\frac{\text{cancer death}}{\text{lifetime}}\right) = D\left(\frac{\text{rem}}{\text{yr}}\right) \times 1.6 \times 10^{-4} \ \frac{\text{cancer deaths}}{\text{rem}}$$

and that D, the whole body committed dose equivalent whole body, is 62.5 millirem for a single exposure. If we further average that exposure over a lifetime, as would be realistic for an air pollutant, the dose committed is 0.9 millirem/year. It could then be concluded that exposure to radioactive materials in combustion products of interest to the API plus all other sources should be less than 0.9 millirem per year.

The second approach, one based on a variant of derived air concentrations (DAC), is less complicated and perhaps more reasonable. It encompasses a bubble concept in that only that material leaving the plant confines is of interest. If the concentration of radionuclides, Uranium, Thorium, Radon, etc., is less than an established limit based on the Annual Limit of Intake (ICRP, 1980), the plant would be in compliance. It must be recognized that the current occupational DACs would have to be adjusted for 24-hour exposures and for the most susceptible exposed population. Compliance could be judged on an isotope-by-isotope limit or added in the manner of the TLV as below:

$$\frac{\text{Conc U}}{\text{DAC-U}} + \frac{\text{Conc Th}}{\text{DAC Th}} \cdots\cdots\cdots\cdots \frac{\text{Conc}\,^{210}\text{Pb}}{\text{DAC}\,^{210}\text{Pb}} \leq 1$$

where Conc is the concentration of the element of interest and DAC is the derived air concentrations for that environmental exposure.

The advantage of this system would be that each location could measure its own compliance without regard for air modeling, transport and dose response modeling. The disadvantage would be that the measurement is both difficult and expensive to make.

Table 15 compares the two methods and gives estimates of some limits. For either approach, 10^{-5} excess risk permits very small increases over the natural background.

Similar approaches as those suggested to regulate air pollutants are being applied to the development of the Reportable Quantity under CERCLA. Table 16 estimates the amount of raw material or product that will contain one reportable quantity of selected radionuclide for a weight, activity, or dose-equivalent approach. Depending on the mode of definition, very small quantities of petroleum products could easily contain reportable quantities of radionuclides.

Table 15
Estimate of Radioactive Material Concentrations to Produce 10^{-5} Lifetime Excess Risk of Fatal Cancer to a Maximum-Exposed Individual

Radioisotope	Solubility Class	Concentrations to Produce 10^{-5} Excess Risk in Target Population (curies per cubic meter)		
		At Stack	At Fenceline	
		Generic*	DAC**	MPC**
Uranium 238	D	2.6×10^{-8}	8×10^{-14}	6×10^{-15}(S)
	W		4×10^{-14}	1×10^{-14} (I)
	Y		2.6×10^{-14}	
Thorium 232	W	6.5×10^{-11}	6.5×10^{-17}	2×10^{-15}(S)
	Y		1.3×10^{-16}	2×10^{-15}(I)
Radium 226		3.9×10^{-8}	3.9×10^{-14}	(S) 6×10^{-15}
				(I) 4×10^{-15}
Radon 222		5.2×10^{-6}	5.2×10^{-12}	6×10^{-12}
Lead 210		1.3×10^{-8}	1.3×10^{-14}	8×10^{-15}
				1.6×10^{-14}

---

* Assumes 10^{-6} dilution factor, and the children (10-year old) as the target population, 15 m^3 air inhaled per day (ICRP, 1975).

** Assumes children (10-year) as target population.

TABLE 16

Amount of Product Needed to Assemble One Reportable Quantity of Uranium or Radon

Item/Product	Possible Form of Reportable Quantity			
	One Pound	One Milli Curie	One Micro Curie	5 Rem Committed Dose Equivalent
Crude Oil	2,162 Bbl	14,200 Bbl	14.2 Bbl	0.5 Bbl
Natural Gas	4.9×10^{16} MCF	714 MCF	714,000 CF	.017 MCF
LPG	4.9×10^{16} MCF	714 MCF	714,000 CF	.071 MCF
US Coal	33.6 T	222 T	0.2 T	.88 T
SRC Product	252 T	1,600 T	1.6T	.067 T
Shale Oil	890 Bbl	5,882 Bbl	5.8 Bbl	0.24 Bbl
Shale Waste	151 T	1,000 T	1 T	.04 T
Phosphate Rock	3.98 T	26.3 T	.026 T	.001 T
Ground Water	4.4×10^{16} Gals.	6.04×10^{9} Gals.	6.04×10^{5} Gals.	2.5×10^{4} Gals.

Control Options

Any control methodology proposed for radioactive materials must recognize the fact that radioactivity can not be modified or made inert by chemical means. It also must recognize that radioactivity dissipates at fixed rates through fixed sequences or series. Decay to daughter products cannot be guaranteed to reduce the hazard.

The control of emissions of naturally occurring radioactive materials can be accomplished by removing the radioactivity from the raw material or product, or by removing the radioactive materials after combustion. This removal can be accomplished by taking advantage of radioactive decay; by physically removing the radioactive material by washing, filtering, or by absorption; by chemically scrubbing the material from the product or combustion gas stream; or by combination thereof.

The removal of Radon 222 from natural gas could be accomplished by either decay or by absorption on a molecular sieve such as activated charcoal. Radon has a 3.83 day half-life. Storing natural gas for 5 half-lives approximately 20 days would change some 99.5% of the Radon in the influent stream to 21-year Lead 210, much of which will plate out in the storage tanks, pipeline, and process equipment. When one compares the derived air concentration for each, however, it appears that the relative health hazard may have been increased. The DAC for Radon plus daughters, target organ the lung, is 3×10^{-8} Ci per cubic meter, while that for Lead 210, target organ bone, is 1×10^{-10} (ICRP, 1980). Capturing the Radon on a molecular sieve and the Radon daughters on a high-efficiency (HEPA) filter cleans the product stream but changes a very dilute source of radioactive materials into a very concentrated source of radioactivity, presenting both an internal and external radiation hazard.

The removal of Radon from groundwaters can be accomplished by aeration (which releases the radioactive material to the ambient air) or through decay. The decay again introduces Lead 210 into the water which, again, is not totally free of hazard. The Lead 210 can be removed using bacterial filters; i.e., diatomaceous earth, with the resultant hazards associated with concentrating radioactive materials.

Uranium in crude oil presents a somewhat different dilemma. We estimated earlier in this paper that significant quantities of uranium potentially enter our refineries via crude oil. Little is known of its fate, however. Since the law of conversation of matter must apply, it can only end up in the product, the process waste, remain in the process equipment, or escape into the environment. The chemical properties of uranium suggest something concerning its ultimate fate. Uranium can be isolated by reducing uranium halides with alkali or alkaline earth metals or by reducing uranium oxides by calcium, aluminum or carbon at high temperatures. Strong acids can dissolve the metal, but it is relatively unaffected by alkali (CRC, 1981). It would seem likely to find most of the uranium plated out in the process equipment or concentrated in process wastes. Better understanding of the presence and fate of uranium in fuel oils is needed before a control scheme can be proposed.

The main contaminants in coal are members of the Uranium 238 decay series, primarily Radium, Radon, and Uranium. Cleaning the coal will remove much of the radioactive materials on the surface of the coal but will concentrate the material in the waste water. Pulverizing the coal will release much trapped radon to the atmosphere. Combustion will cause most of the radioactivity to be concentrated in the fly ash. High-efficiency scrubbers or filters may be required to reduce the health risks of such exposures to acceptable levels.

Impact of Regulation on API Members

The impact that the regulation of "radionuclides" under the Clean Air Act (CAA) will depend largely upon what the EPA decides is an "acceptable risk". The EPA has been forced to make this decision, and we will know the answer in 180 days.

What the EPA decides depends largely upon what society, as represented by its most vocal members, wants. Table 14 gives some indication of what we might expect, and it is likely that lifetime excess risks greater than one one-hundredth of that imposed by the natural background (1.5×10^{-5}) will be considered unacceptable. It is also equally likely that excess risks less than 10^{-7} will be considered <u>de minimis</u>. Table 17 summarizes candidates for regulation for different levels of acceptable risk.

Table 17
Operations Subject to Regulation as a
Function of Defined Acceptable Risk

Acceptable Risk Level
(Lifetime Excess Risk of Contracting Fatal Cancer)

1.5×10^{-5}	5×10^{-6}	1×10^{-6}
Geothermal Power	Groundwater Use (all locations) Geothermal Power	Groundwater Use (all locations) Geothermal Power
Coke Production (all locations)	Coke Production (Northeast only)	Coke Production (all locations)
Coal-Fired Steam	Coal-Fired Steam	Coal-Fired Steam
Coal-Fired Industrial Boilers	Coal-Fired Industrial Boilers	Coal-Fired Industrial Boilers
Underground Coal Mining	Underground Coal Mining Strip Mining (coal)	Underground Coal Mining Strip Mining (coal) Coal Cleaning Natural Gas Combustion Natural Gas Turbines

The impact of CERCLA on API members depends on the definition of reportable quantity. The data collected in this report appear to suggest that the CERCLA will place reporting requirements on many operating locations.

The impact of both regulatory actions is summarized on Table 18. It appears that regulation of radionuclides could impose a severe burden on API member companies and that both regulatory actions should be closely followed.

TABLE 18

Potential Impact of Regulation on API

Operation	Radio-Isotopes	Form	Potential For Regulation		Potential Impact
			CAA	CERCLA	
Production					
LPG/NG	^{222}Rn+d	Gas	X		Removal of Radon (20 day storage)
Gas Liquids	^{222}Rn+d	Liquid	X	X	Removal of Radon (20 day storage)
Crude Oil	^{238}U+d	Liquid		X	Reporting and Control
Water Flood	^{222}Rn+d	Gas	X		Control Release of Radon
Brine Disposal	^{226}Ra+d	Solid	X	X	Control Release of Radon
					Reporting and Control, Disposal Site
Disposal of	^{238}U+d	Solid		X	Reporting and Control
Scrap Equip.,	^{226}Ra	Solid		X	of Disposal Site
Pipe etc.	^{222}Rn+d	Gas	X	X	Control of Release of
	^{210}Pb	Solid		X	Radon
Manufacturing					
Process Heat	^{222}Rn+d	Gas	X	X	Control of Release of Radon
Power Generation					
Gas Turbine	^{222}Rn+d	Gas	X		Control of Release of Radon
Gas Furnace	^{222}Rn+d	Gas	X		Control of Release of Radon
Coal	^{238}U+d	Solid	X	X	Control of Release of Radioactive
	^{226}Ra+d	Solid	X	X	materials. Control of Release of Radon
		and Gas	X		Radon from Flyash Disposal Site.
Geothermal	^{222}Rn+d	Gas	X		Control of Release of Radon
Disposal of	^{238}U+d	Solid		X	Reporting and Control of Disposal
Process Equip.					Control of Release of Radon
Bottoms/Sludge	^{238}U+d	Liquid	X	X	Reporting and Control of Disposal
					Control of Release of Radon
Coal Mining					
Underground	^{238}U	Solid	X		Control of Release of Radioactive
	^{226}Ra+d	Solid & Gas	X		Materials and Radon
Strip Mining	ditto	ditto	X		ditto
Cleaning	ditto	ditto	X	X	Reporting and Control of Waste
					Disposal Site

References

(Baes, 1981), Baes, C. F. III, and Sharp, R. D.; A Directory of Parameters Used in a Series of Assessment Applications of the Air Dose-EPA and DARTAB Computer Codes, Oak Ridge National Laboratory, ORNL 5710, 1981.

(Barber, 1977), Barber, D. E., and Giorgio, H. R.; Gamma Ray Activity in Bituminous, Subbituminous, and Lignite Coals; Health Physics, Volume 32, February 1977, pp. 83-88.

(Begovich, 1981), Begovich, C. L., et al; DARTAB: A Program to Combine Airborne Radionuclide Exposure Data with Dosimetric and Health Effects Data to Generate Tabulations of Predicted Health Impacts, Oak Ridge National Laboratory, ORNL 5692, 1981.

(CFR, 1982) Code of Federal Regulations, Title 10, Part 20, Standards for Radiation Protection, Paragraph 20.3, April 23, 1982.

(CRC, 1969), CRC, Handbook of Chemistry and Physics, 49th Edition, PF144.

(Dunning, 1981), Dunning, D. E., et al; ORNL/TM-7105, A Combined Methodology for Estimating Dose Rates and Health Effects from Exposure to Radioactive Pollutants, Oak Ridge National Laboratories, 1980.

(EPA, 1973), EPA-520/1-73-004; Assessment of the Potential Health Effects from Radon in Natural Gas; Office of Radiation Programs, USEPA, 1973, p. 5.

(EPA, 1979, EPA 520/7-79-006; Radiological Impact Caused by Emissions of Radionuclides into the Air of the United States, Preliminary Report, Washington. D.C., 1979.

(FR, 1979), The Federal Register, Volume 44, NR 49, Thursday, December 27, 1979 (FRL 1292-8), pp. 76738-76746.

(Gessell, 1974), Gessell, T. F.; Radiological Health Implications of Radon in Natural Gas and Natural Gas Products, a report to the University of Texas, Health Science Center at Houston, School of Public Health, Houston, 1974.

(Gessell, 1975), Gessell, T. F., and Pritchard, H. M.; The Technologically Enhanced Radiation Environment, Health Physics, Volume 28 (April) 1975, pp. 361-366.

(ICRP, 1975), ICRP Publication 23; Report of the Task Group on Reference Man, Pergamon Press, 1975, p. 345.

(ICRP, 1977), ICRP Publication 26, Recommendations of the International Commission on Radiological Protection, Pergamon Press, New York, 1977.

(ICRP, 1980), ICRP Publication 30, Limits for Intakes of Radionuclides by Workers, Pergamon Press, New York, 1980.

(NCRP, 1975), Natural Background Radiation in the United States, National Council on Radiation Protection and Measurement, November 15, 1945, pp. 4, 47, 53, 54 and 57, and Figures 1, 2, and 3.

(Pierce, 1964), Pierce, A. P.; Gott, G. R; and Myton, J. W.; Uranium and Helium in the Pan Handle Gas Field, Texas, and Adjacent Areas; USGS Professional Paper 454-G, U.S. Government Printing Office, Washington, D.C., 1964.

(Rhodes, 1972), Rhodes, D. F.; Company Memo, Reference 6252PH00, Determination of Pb^{210} in Samples from Kuwait.

(Sasser, 1978), Sasser, M. K.; and Watson, J. E.; An Evaluation of the Radon Concentration in North Carolina Ground Water Supplies; Health Physics; Volume 34 (June), 1978, pp. 667-671.

(Sullivan, 1981), Sullivan, R. E., et al; Estimates of Health Risk from Exposure to Radioactive Pollutants; Oak Ridge National Laboratory, ORNL/TM 7745, 1981.

(Teknekron, 1981), "Draft", Technical Support for the Evaluation and Control of Emissions of Radioactive Materials into Ambient Air, Teknekron Research Corp., May 1981.

(UNSCEAR, 1977), United Nations Scientific Committee on the Effects of Atomic Radiation; Sources and Effects of Ionizing Radiation; United Nations, 1977, p. 12 and Annex B, Tables 35, 36, 38, 42 and 43.

(USCGS, 1959), Uranium in Coal in the Western United States, Geological Bulletin 1055, Washington, 1959.

(USDC, 1978), Analysis for Radionuclides in SRC and Coal Combustion Samples, Hittman Associates Inc., Columbia, Maryland, 1978, p. 11.

(Wilson, 1982), Wilson, R., and Crouch, E.; Risk/Benefit Analysis, Ballinger Publishing Company, 1982, Table 7-2.

Exhibit 3

NORM Contamination in the Petroleum Industry

P.R. Gray, SPE, Peter Gray & Assocs.

Summary. Contamination of oil and gas facilities with naturally occurring radioactive materials (NORM) is widespread. Some contamination may be sufficiently severe that maintenance and other personnel may be exposed to hazardous concentrations. Contamination with radium is common in oil-production facilities, whereas contamination with radon and radon decay products is more prevalent in natural-gas production and processing facilities. Although largely unregulated until recently, U.S. states, notably Louisiana and Texas, have or are enacting legislation to control NORM contamination in the petroleum industry.

Introduction

NORM contamination can be expected at nearly every petroleum facility. Some of it can be sufficiently severe that maintenance and other personnel may be exposed to hazardous concentrations. In addition, the industry must comply with new regulations. Mississippi and Louisiana have enacted legislation to control NORM; Texas will have regulations early in 1993; and other states, as well as Canada, can be expected to have similar regulations shortly.

Two general types of common NORM contamination will be controlled by these regulations.

1. Radium contamination of petroleum production facilities—specifically of pipe scale and sludge and scale in surface vessels. In addition, produced water may be radioactive from radium dissolved in underground water.

2. Radon contamination of natural-gas production facilities. This includes contamination with the long-lived decay products of radon. Facilities that remove ethane and propane from natural-gas facilities are especially susceptible to NORM contamination.

Naturally occurring radionuclides are widespread in the environment. In many geologic formations, radium, radon, and other radioactive elements are associated with oil and gas. When oil and gas are produced, traces of these radioactive elements also are produced. When the formation water contains traces of radium (radium-226, a decay product of uranium, and radium-228 from thorium), scale in the production pipe can become radioactive, sometimes containing several thousand picocuries of radium per gram of scale.[1,2] The radioactivity results when radium coprecipitates with barium and strontium sulfates in the scale formation.

Radium also can contaminate scale and sludges in surface equipment by similar mechanisms, including carbonate precipitates and sulfate deposits. Produced water may contain dissolved radium. This can lead to contaminated sludges in waste pits and radioactive water.

Contamination of gas wells, pipelines, and gas processing facilities results primarily from radon produced with natural gas.[3-6]

NORM Contamination

NORM contamination in the oil and gas industry commonly occurs as radioactive scale, films, and sludges.

Radium-Contaminated Scale and Sludge. Radioactive scale can contain uranium, thorium, radium, and associated decay products from the production of oil and associated brines contaminated with NORM. The radioactivity in the scale in production pipe originates mainly from radium, which coprecipitates with barium and strontium sulfate. Other isotopes in the uranium-238 and thorium-232 decay series also may be present. Contaminated scale may contain up to several hundred thousand picocuries of radium per gram of scale.

Radioactive scale may be found in surface processing and transport equipment and in downhole tubing. For example, piping, sludge pits, filters, brine disposal/injection wells, and associated equipment may be contaminated with radium NORM. Also, soils and equipment contaminated from well tubing workovers conducted to remove scale—both at the wellsite and at remote pipe cleaning yards—may be contaminated with NORM.

Films. Radioactive films, coatings, or plating can form from natural-gas production or processing. Often invisible to the naked eye, these films contain radon and its decay products, normally with no radon precursors (e.g., radium) associated with them. Because of radon contamination in natural gas, these radioactive films can be found at gas wellheads; in transport piping, headers, treater units, and pumps; and within natural-gas processing plants or other light-hydrocarbon facilities.

Sludge Contaminated With Decay Products of Radon. Radioactive sludges in pipelines, processing plants, natural-gas liquid (NGL) storage tanks and delivery facilities, pigging operations, and gas lines and other filter assemblies can be contaminated with

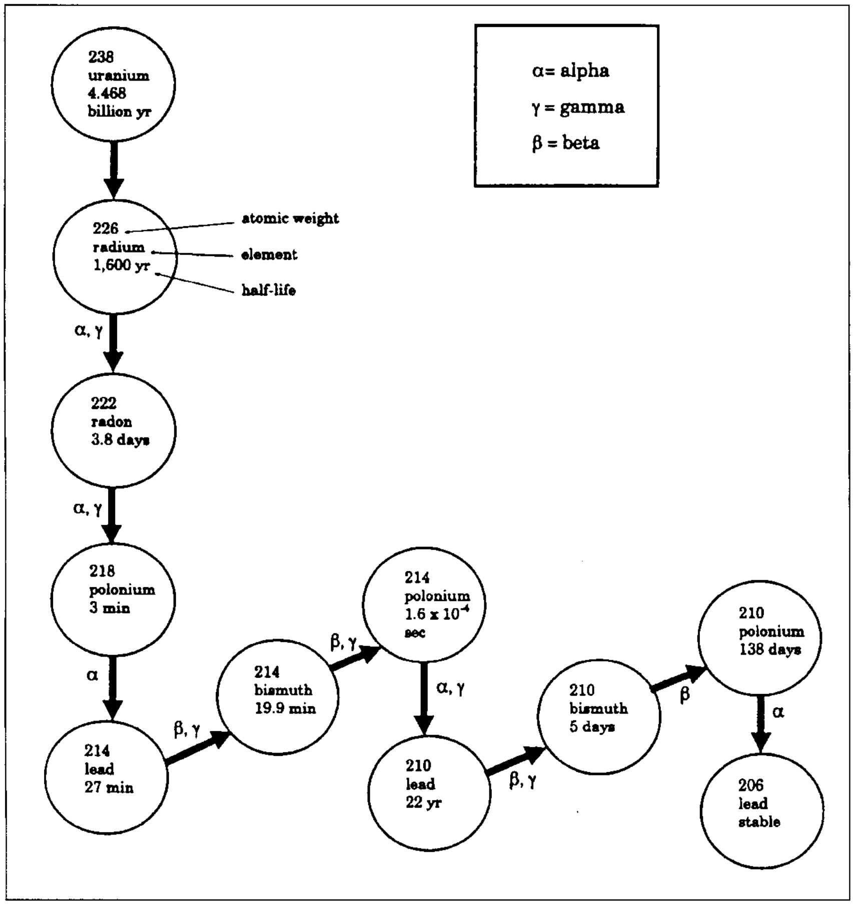


Fig. 1—Radioactive decay of uranium-238.

TABLE 1—RADON CONCENTRATIONS IN NATURAL GAS AT THE WELLHEAD*

Location of Well	Radon Concentration (pCi/L)
Borneo	1 to 3
Canada	
Alberta	10 to 205
British Columbia	390 to 540
Ontario	4 to 800
Germany	1 to 10
The Netherlands	1 to 45
Nigeria	1 to 3
North Sea	2 to 4
U.S.	
Colorado, New Mexico	1 to 160
Texas, Kansas, Oklahoma	1 to 1,450
Texas Panhandle	10 to 520
Colorado	11 to 45
California	1 to 100

*From *Radon Concentrations in Natural Gas at the Well,* U.N. Scientific Committee on the Effects of Atomic Radiation; Sources and Effects of Ionizing Radiation, United Nations, New York City (1977).

TABLE 2—BOILING POINTS AT 760-mm MERCURY

	°F
Methane	−258.0
Ethane	−124.0
Radon	−79.2
Propylene	−53.9
Propane	−44.4
Butane	+31.1

radon in the natural gas. Sludges also may be contaminated with several thousand picocuries per gram of the long-lived radon decay products (i.e., lead-210, bismuth-210, and polonium-210). These heavy-metal decay products may attach to dust particles and aerosols to become part of the sludge.

Filter assemblies in gas lines remove the radon decay products from the gas with other particulate matter and can become very radioactive.

History of NORM Contamination

Radium has been known as a trace contaminant of underground water for a long time but wasn't reported to be a contaminant of scale until the early 1980's, when the problem was first reported in the North Sea. Radon contamination of natural gas has been known for nearly 100 years.[7] However, it was only in 1971 that radon was found to concentrate in the lighter natural-gas liquids during processing and could present a serious health hazard to industry personnel, particularly maintenance employees.

Some radon was undoubtedly removed with the NGL's before 1971. However, deep extraction techniques developed to remove more ethane from the gas also extracted significantly greater concentrations of radon. The problem was discovered when the radon contamination in propylene became sufficiently high to interfere with liquid level sensors detecting slurry levels in a polypropylene plant.

The radioactive scale problem in the oil and gas industry has been reported in the literature.[1,2] With the notable exception of a 1975 report by Gesell[8] and a paper by Gray[9] in 1990, NORM contamination of gas facilities by radon and its decay products has not been as extensively reported.

Radium and Radon

Radium-226 is the fifth decay product of uranium-238, and radium-228 is the fourth decay product of thorium-232. Uranium and thorium are present in most soils and rocks in widely varied concentrations in the Earth's crust throughout the world. Some radium salts (e.g., radium chloride) are soluble in water, and underground water can dissolve the radium in the uranium and thorium formations. The radium may stay dissolved in the water as long as contact with sulfate and carbonate formations is limited. The radium-contaminated water may be produced with oil and gas.

Radon is a naturally occurring, highly mobile, chemically inert radioactive gas in the uranium-238 decay series. Radon-222 is produced by the radioactive decay of radium-226. Because radium is widely distributed in the Earth's crust, radon also is widely distributed. Recent reports of radon-contaminated buildings throughout the world attest to the wide distribution of radon in the environment. Radon is a noble gas, similar to helium and argon, and it is extremely unreactive chemically. Once formed by the radioactive decay of radium-226, radon is free to migrate as a gas or dissolve in water without being trapped or removed by chemical reaction. Migrating through rocks and soil, radon is produced with natural gas at the wellhead. **Table 1** shows that radon contamination of natural gas is a worldwide problem, and particularly high concentrations of radon are reported in the U.S. and Canada.

When radon-contaminated produced gas is processed to remove the NGL's, much of the radon is removed also. Radon's boiling (or condensing) point is intermediate between the boiling points of ethane and propane. Upon subsequent processing, radon tends to accumulate further in the propylene distillation stream. **Table 2** shows the boiling points of radon, the lighter NGL's, and propylene. As expected, radon usually is recovered more completely in plants with high ethane recovery. The radon is concentrated in the lighter NGL's and is detected relatively easily with radiation survey meters.

As long as it is contained and controlled within vessels, equipment, and piping, radon generally is not a health hazard to employees and the public. Even if radon-contaminated propane were released, the threat of fire or asphyxiation would far outweigh the hazard of a short-lived radiation exposure.

Although other radon isotopes exist [e.g., radon-220 (thoron)] from the decay of thorium-232, the only radon isotope of concern

TABLE 3—PRIORITY AREAS OF CONCERN FOR HIGH RADON AND RADON DECAY PRODUCT CONTAMINATION

- NGL facilities
  - De-ethanizers
  - Stills
  - Fractionators
  - Product condensers
  - Flash tanks
  - Pumps in liquid service
  - Piping in liquid service
  - NGL storage tanks
  - Truck terminals
  - Filter separators
  - Dessicants
  - Waste pits
- Pipelines
  - Filters
  - Pig receivers
- Machine shops
  - In-house
  - Contract

is the 3.8-day half-life radon-222. Radon-220 and other radon isotopes have very short half-lives and will have decayed before the gas is produced at the wellhead. Because the half-life of radon-222 is 3.8 days, 99% of the radon will decay to its long-lived lead-210 decay product in 25 days.

Radon Decay Products

Radon itself is not a particularly hazardous material. Because it is chemically unreactive, it does not accumulate in the body. The health hazards associated with radon exposure are from its decay products. These long-lived radioactive materials present a growing problem to the industry, especially to personnel who may be exposed to contaminated surfaces, sludges, and other waste materials. **Fig. 1** shows each atom of radon-222 eventually decays to an atom of lead-210 and subsequently to bismuth-210 and polonium-210 before decaying to stable lead-206. The half-life of lead-210 (a solid metal material) is 22 years. Therefore, the concentrations of radioactive lead, bismuth, and polonium will continue to increase in pipelines, gasoline plants, tank cars, and trucks for more than 100 years.

Contaminated facilities and waste-material problems must be recognized and addressed. The presence of the radioactive metals from radon decay cannot be detected on the outside of contaminated equipment and vessels. Unlike radon, the radiations that the decay products emit are easily absorbed by the walls of the equipment. If present in sufficiently high concentrations, radon can be detected externally to storage vessels, pumps, etc. Radon has moderately energetic gamma radiation in its decay that can be detected with gamma survey meters.

If an alpha/beta probe is held close to contaminated internal surfaces and concentrations are sufficiently high, survey meters may detect the presence of the radon decay products. However, laboratory analyses are usually required to determine concentrations of lead, bismuth, and polonium accurately.

These radioactive materials are not a health hazard unless they are ingested or inhaled into the body—e.g., during repair and maintenance on the facility. If inhaled, the dust and aerosols containing NORM can attach to the lung surfaces, where they emit alpha radiation into the tissue of the lung lining. Studies of uranium miners indicate that extended exposure to these radon decay products pose an increased risk of lung cancer.[10,11]

NORM in NGL Facilities

Although entire natural-gas and NGL systems may be contaminated with NORM, some facilities will be contaminated to the extent that they present significant decontamination and disposal problems. Gasoline plants and other NGL facilities will be among the most highly contaminated areas in a system.

During processing in a gasoline plant, the levels of external radiation from radon in propane 1 ft from a liquids pump may be as high as 25 milliroentgens (mR)/hr. Radiation levels up to 6 mR/hr have been detected at outer surfaces of storage tanks containing fresh propane. Sludges in gasoline plants are often contaminated with several thousand picocuries of lead-210 per gram.

Table 3 shows vessels and equipment in NGL service that may be significantly contaminated with NORM. Although NORM contamination will be general throughout an NGL facility, the contamination usually will be greatest in areas of high turbulence, such as in pumps and valves.

When employees open equipment and vessels, precautions must be taken to prevent exposure to radioactive contamination.[12] Maintenance procedures should include the use of respirators and good hygiene to prevent inhalation of radioactive dust. Grinding, if necessary, should be done wet to minimize dust.

Occasionally, a plant or other facility that has been processing light hydrocarbons, particularly ethane and propane, is taken out of service and the facility sold or dismantled. Any equipment with internal surface deposits of NORM must receive special consideration when scrapped, sold, transferred, or otherwise disposed of, particularly when the facility is being released for unrestricted use. Analyses for lead-210 usually will be required to verify the extent of contamination and to determine if special handling is needed. Particular care must be used to prevent employee exposure to NORM contamination.

There are potential liabilities involved if contaminated equipment, vessels, and other parts of the facility are released or sold for unrestricted use without first being cleaned and tested to be essentially free of NORM contamination according to state and federal regulations.

Much of the material wastes from a facility contaminated with NORM must be handled as low-level radioactive waste and disposed of accordingly. Contaminated wastes should be consolidated and separated from noncontaminated waste to keep radioactive waste volumes as low as possible. Consolidated contaminated wastes should be stored in a controlled-access area. The area should be surveyed with a radiation survey meter and, if required, should be posted according to state and federal regulations.

Other NORM Contamination

Besides vessels and equipment in NGL service, other facilities susceptible to significant contamination include pigging operations, machine shops, and filter assemblies.

Pipeline sludges can obtain small radium-226 concentrations together with a few hundred to several thousand picocuries of radon decay products per gram. These sludges require the same handling as low-level radioactive wastes. The pig itself may be contaminated. This may require handling the pig with gloves and storing it in an area with restricted personnel access.

Machine shops present a special NORM situation. For example, pumps in NGL service may be among the most highly contaminated equipment in a plant. Occasionally, these pumps may need to be checked for leaking seals or impeller balance. NORM contamination inside a pump is often chemically bonded to the pump structural metal and cannot be easily removed without scraping and grinding. Because rebalancing is usually done by grinding until balance is established, the grinding may generate significant quantities of radioactive dust that can contaminate personnel as well as the shop facility. This can pose a very serious problem if contract machine shops are used.

Although pipelines and equipment in dry-gas service may be only marginally contaminated, filter assemblies in dry-gas service may be contaminated with very high concentrations of NORM and require special handling to prevent inhalation of the radioactive dust and contamination of the environment during changing of the filters and other required maintenance.

Radiation Surveys

NORM contamination is detected by radiation surveys with Geiger-Mueller or scintillation probes on a suitable survey meter. The gamma radiation emitted by radium and radon are sufficiently energetic that they are detected relatively easily if present in high concentrations. The radiations emitted by the decay products of radon are not easily detected. The raditions from lead-210 (low-energy gammas), bismuth-210 (betas), and polonium-210 (alphas) will not penetrate vessel and equipment walls and are detected only with low efficiency when a suitable probe (e.g., an alpha pancake probe) is used directly on the contaminated surface. Because these radon decay products are detected, at best, with low efficiency, any reading on the survey meter above background indicates significant contamination.

Samples should be taken and submitted to a laboratory for analysis. The exempt concentration levels for these radionuclides are very low, and contamination above the exempt concentrations is common. Because the radiations are easily absorbed, areal surveys of the ground and soil around petroleum facilities for radon-decay-product contamination are generally not meaningful and samples must be taken for laboratory analyses.

Radium and radon emit sufficiently energetic radiation to make their detection somewhat easier. The gamma rays will commonly penetrate structure walls, making external radiation surveys with Geiger-Mueller or scintillation detectors meaningful. The exempt concentrations in the Louisiana and Mississippi regulations and in pending regulations in other states are so low, however, that concentrations of radium and radon near the exempt levels are very difficult to measure accurately. A well-trained technician is required to make such surveys with confidence. Again laboratory analyses may be needed to determine accurately the amount of contamination. Such analyses are probably required when the facility or property is being sold, abandoned, or otherwise released. Accurate records of contamination will be required to prevent future litigation.

Disposal of NORM Wastes

The disposal of NORM-contaminated wastes is a major problem with no completely satisfactory solution. The disposal of NORM wastes is regulated by Louisiana and Mississippi and will be regulated in all other states as their regulations become effective. Options are limited. For example, the NORM wastes must be separated from non-NORM wastes and cannot be disposed of by "ordinary" methods of waste disposal, such as landfills. Disposal of contaminated wastes with uncontaminated material in a landfill or by other methods of disposal is not allowed unless the contamination level is below exempt concentrations in state and federal regulations. The few facilities licensed to accept NORM wastes are expensive to use and require a complete paper trail.

Although individual states or groups of states are obligated to have low-level radioactive waste repositories by 1993, these facilities may not accept NORM wastes from the petroleum industry. This is the case in Texas, for example, where the Texas Low Level Radioactive Waste Repository is designed to accept radioactive wastes from medical facilities, educational institutions, and industrial non-NORM wastes. The cost of disposal will be expensive—Texas estimates that the cost of storing radioactive wastes in its low-level repository will be about \$175/ft^3.

Currently, the most economical and practical method may be to store the NORM wastes on the facility property in an area with controlled access. The revised Louisiana regulations address the disposal problem and require a proposed disposal plan be submitted to the state within 90 days of the NORM generation.

It sometimes may be possible to dilute the wastes sufficiently with noncontaminated material so that the NORM concentrations are below exempt levels. For example, moderately contaminated soil may be diluted with noncontaminated soil or radium-contaminated water may be diluted with "clean" water. If sufficiently diluted, the resulting wastes may possibly be disposed of by ordinary methods.

Reinjection of radium-contaminated water is a possible solution to the disposal of such water. Injection of other NORM wastes (e.g., contaminated scale) in a Type II injection well may be the best possible disposal method for these wastes when allowed by the regulations.

The high cost of disposing of NORM wastes is opening new opportunities for R&D in methods and techniques for reducing waste volumes. For example, production waste may be contaminated above exempt levels with radium-226 and radium-228. If the radium could be removed from the water economically, the costs of disposing of the contaminated water would be reduced significantly. There are R&D efforts in progress to do this, such as using resins and membranes to absorb or separate the radium from water and other corrosive liquids. Similar efforts are being applied to concentrate radium and lead-210 and its radioactive daughters from organic and inorganic sludges. If successful and economical, this may be a solution to the disposal of large volumes of NORM-contaminated wastes.

"The high cost of disposing of NORM wastes is opening new opportunities for R&D in methods and techniques for reducing waste volumes."

Decontamination of facilities by sandblasting can generate large volumes of NORM wastes. Novel methods of "sandblasting" with materials that will minimize the solid wastes are being explored. Reaming out scale from production pipe can generate large quantities of NORM wastes. Because only a fraction of the scale, possibly as low as 5% to 10%, may be contaminated above exempt concentrations, preliminary gamma surveys of the pipe to locate NORM sites can be used to guide reaming operations and to reduce NORM-contaminated scale wastes. Contaminated scale may be spotty (i.e., not uniform within the pipe), so the total joint should be surveyed on all sides. External scale on the pipe also can be contaminated with radium, necessitating careful handling to prevent ingestion or inhalation of NORM dust and contamination of the environment.

As an alternative to reworking or cleaning of contaminated production pipe, the pipe can be left in place in the ground. It is not required to pull the pipe and remove the contaminated scale.

The trend in U.S. state regulations is toward more regulation and control of NORM wastes. NORM disposal will undoubtedly become very expensive.

Regulations

Radium and radon in oil and gas operations produce radioactive waste materials that contaminate facilities and equipment, exposing employees to hazardous materials and creating waste disposal problems. Such wastes and facilities should be treated as much as possible like other facilities and equipment covered by the U.S. Atomic Energy Act (e.g., soil contamination limits, criteria for facilities and equipment released for unrestricted use, and rules for proper handling and disposal of contaminated materials).

Several state and federal agencies have potential jurisdiction over NORM, but their application to NORM is unclear. NORM does not fall under the definition of source, special nuclear, or by-product material as currently defined in the Atomic Energy Act. Therefore, NORM is not subject to the Nuclear Regulatory Commission regulations. States have laws and regulations governing the use, possession, handling, and disposal of radioactive materials, but their application to NORM is still unclear. Except for Louisiana and Mississippi, no specific state regulations for the control of NORM contamination exist. Texas and several other states are expected to have NORM regulations in 1993. Louisiana specifically exempts the wholesale and retail distribution, possession, use, and transportation of oil and natural gas and NGL's from the regulations. The exemption, however, does not apply to contaminated facilities, such as pipelines, gasoline plants, and other physical facilities.

The Louisiana and Mississippi and other proposed state regulations are very specific regarding disposal of contaminated wastes and sale, abandonment, or release of facilities that may be contaminated. Companies doing production pipe cleaning and workovers must be specifically licensed, as do contractors supplying decontamination services. Louisiana has required radiation surveys of every petroleum facility in the state. As proposed, the Texas regulations will not require such extensive surveys. Texas will require surveys only of specific licensed facilities.

To ensure compliance, companies must be familiar with the regulations as they evolve. Although only Louisiana and Mississippi have regulations in effect, Texas, other states, and Canada are expected to have regulations soon for the control of NORM in the petroleum industry. The U.S. Environmental Protection Agency (EPA) is also

Author

Peter Gray is a consultant on NORM contamination in the petroleum industry. He retired in 1985 from Phillips Petroleum Co. where he was the principal investigator in Phillips' NORM control program. Gray holds BS and MS degrees from Michigan Technological U. and a PhD in nuclear chemistry from the U. of California at Berkeley.

considering enacting NORM regulations on the federal level.

Regulatory developments must be monitored as current knowledge of the NORM issues evolves. Where possible, industry input should be directed to minimize an overregulation of NORM contamination in the industry.

Suggested Program for the Control of NORM

The following are suggestions for use in establishing a program for the control of NORM contamination.

1. Determine whether there is a NORM contamination problem.
2. Determine areas of potential NORM exposure and contamination.
   A. Make gamma radiation surveys of facilities and equipment.
   B. Make wipe tests on accessible interior surfaces of selected equipment and vessels, especially any in NGL service.
   C. Obtain samples of sludges and scale and analyze for radium and lead-210.
   D. Obtain samples of other waste materials, such as dessicants and filters.
   E. Analyze produced water and waste pond water for radium.
3. Establish programs to ensure personnel safety, product quality, customer satisfaction, and protection of the environment.
   A. Establish policy on periodic surveys, inspection and maintenance procedures, product controls, and record keeping.
   B. Provide safety-manual material that informs employees and details required procedures, particularly for maintenance personnel.
   C. Recommend a management and audit system.
   D. Develop plans and procedures for the disposal of contaminated waste materials, equipment, and facilities.
   E. Prepare a public relations release to use if questioned by employees, customers, the public, and the media.
4. Inform facility personnel of the possibility of NORM contamination.
5. Review governmental regulations to ensure regulatory compliance.

Conclusions

1. NORM contamination can be expected at nearly every petroleum facility.
2. The presence of NORM in oil and gas production facilities, gas processing plants, pipelines, and other petroleum equipment and facilities is not, in general, a serious technical problem.
3. The concentrations of NORM contamination and the energies of the radiation are relatively low and do not usually present a health hazard to the public or to most personnel in the industry. Some facilities may be more highly contaminated, however, and may be hazardous to maintenance personnel in particular.
4. Radium contamination of pipe scale can be a serious problem requiring special procedures for the removal and disposal of contaminated scale to prevent contamination of personnel and the environment.
5. Produced water may be contaminated with radium, requiring special procedures for the protection of the environment.
6. Surface equipment and facilities at production sites also may be contaminated with NORM, requiring special repair and maintenance procedures and the disposal of NORM-contaminated wastes.
7. The buildup of long-lived radon decay products (specifically lead-210) in gas pipelines, gasoline plants, and refineries requires that specific procedures be implemented for inspection and maintenance personnel to ensure their safety when working on the internal parts of equipment and facilities where radon may have been present.
8. A serious problem that must be addressed is the disposal of radioactive materials and equipment. Options available for the disposal of NORM and NORM-contaminated wastes are limited.
9. Although only Louisiana and Mississippi have enacted regulations for the control of NORM, Texas will have regulations early in 1993, and other states and Canada can be expected to enact similar legislation. The U.S. EPA is considering enacting NORM regulations on the federal level.
10. The industry must comply with the regulations.

Although potentially hazardous to personnel and the environment, NORM contamination is controllable.

References

1. Smith, A.L.: "Radioactive-Scale Formation," *JPT* (June 1987) 697-706.
2. Nancollas, G.H.: "Oilfield Scale, Physical Chemical Studies of its Formation and Prevention," Chemistry Dept., State U. of New York, Buffalo (1984).
3. Bunce, L.A. and Sattler, F.W.: "Radon-222 in Natural Gas," U.S. Public Health Service, Farmington, NM, Radiological Health Data Report (1986) 441-44.
4. Tunn, W.: "Investigation on the Trace Elements in Gases from German Natural Gas and Petroleum Fields," *Compens-Dtsch. Ges. Mineraloelwiss Kohlechem 75-76* (1975) 96-111.
5. Kolb, W.A. and Wojcik, M.: "Enhanced Radioactivity Due to Natural Gas and Gas Production," Sixth Radiat., Risk, Prot. Int. Congress (1984) **1,** 93-96.
6. Pierce, A.P., Gott, G.R., and Myton, J.W.: "Uranium and Helium in the Panhandle Gas Field, Texas and Adjacent Areas," Professional Paper 454-6, U.S. Geological Survey, U.S. Government Printing Office, Washington, DC (1964).
7. Satterly, J. and McLennan, J.C.: "The Radioactivity of Natural Gas of Canada," *Trans. Royal Canada* (1918) **12,** 153.
8. Gesell, T.F.: "Occupational Radiation Exposures Due to Radon-222 in Natural Gas and Natural Gas Products," *Health Physics* (1975) **29,** No. 5, 681-87.
9. Gray, P.R.: "Radioactive Materials Could Pose Problems for the Gas Industry," *Oil & Gas J.* (June 25, 1990) 45-48.
10. Whittmore, A.S. and McMillan, A.: "Lung Cancer Mortality Among U.S. Uranium Miners: A Reappraisal," *J. Natl. Cancer Inst.* (1983) **71,** 489-99.
11. Svec, J., Kunz, E., and Placek, V.: "Lung Cancer in Uranium Miners and Long-Term Exposure to Radon Daughter Products," *Health Physics* (1976) **30,** 433-37.
12. Summerlin, J. Jr. and Prichard, H.M.: "Radiological Health Implications of Lead-210 and Polonium-210 Accumulations in LPG Refineries," *J. American Industrial Hygiene Assn.* (1985) **46,** No. 4, 202-05.

SI Metric Conversion Factors

curie × 3.7* E+10 = Bq
°F (°F−32)/1.8 = °C
ft × 3.048* E−01 = m
ft^3 × 2.831 685 E−02 = m^3
R × 2.58 E−04 = C/kg

*Conversion factor is exact.

Provenance

Original SPE manuscript, **NORM Contamination in the Petroleum Industry,** received for review Oct. 6, 1991. Revised manuscript received Oct. 29, 1992. Paper accepted for publication Jan. 15, 1992. Paper (SPE 22880) first presented at the 1991 SPE Annual Technical Conference and Exhibition held in Dallas, Oct. 6-9.

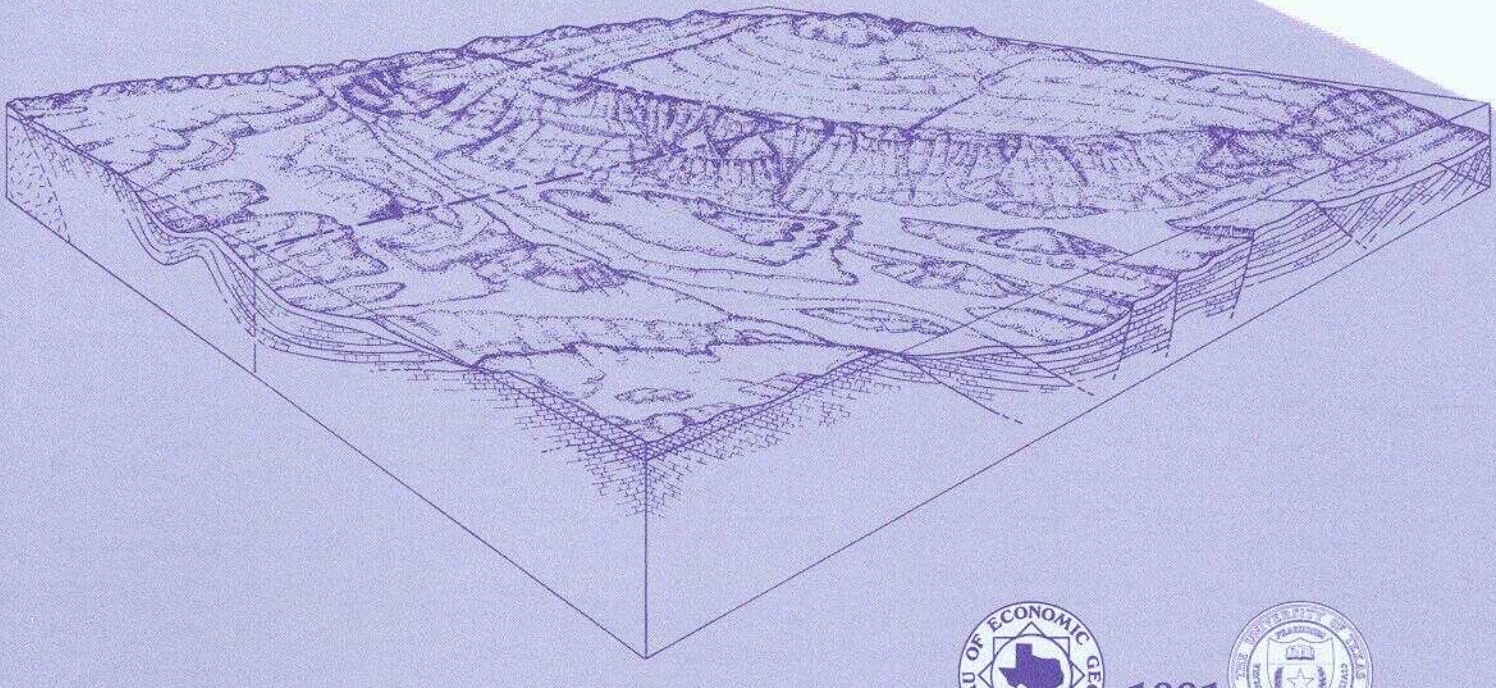
JPT

Report of Investigations No. 201

Exhibit 4

Stratigraphic Analysis of the Upper Devonian Woodford Formation, Permian Basin, West Texas and Southeastern New Mexico

John B. Comer



1991

Bureau of Economic Geology • W. L. Fisher, Director
The University of Texas at Austin • Austin, Texas 78713-7508

Report of Investigations No. 201

Stratigraphic Analysis of the Upper Devonian Woodford Formation, Permian Basin, West Texas and Southeastern New Mexico

*John B. Comer**

*Current address
Indiana Geological Survey
Bloomington, Indiana 47405

1991

Bureau of Economic Geology • W. L. Fisher, Director
The University of Texas at Austin • Austin, Texas 78713-7508

Contents

Figures

Plates (in pocket)

Abstract

The Upper Devonian Woodford Formation is an organic-rich petroleum source rock that extends throughout West Texas and southeastern New Mexico and currently is generating oil or gas in the subsurface. The Woodford is a potential hydrocarbon reservoir in areas where it is highly fractured; the most favorable drilling targets are fractured siltstone or chert beds in densely faulted regions such as the Central Basin Platform, southernmost Midland Basin, and parts of the Northwestern Shelf. Stratigraphic analysis was undertaken to determine how the Woodford was deposited and why its petroleum source potential is so great.

The Woodford consists of two lithofacies, black shale and siltstone. Black shale, the most widely distributed rock type, is very radioactive and contains varvelike parallel laminae, abundant pyrite, and high concentrations of marine organic matter. Siltstone, typically a basal facies, in deep basin and proximal shelf settings, exhibits disrupted stratification, graded layers, fine-grained Bouma sequences, and a subequal mixture of silt-sized quartz and dolomite. Black shale is mostly pelagic and represents an anaerobic biofacies, whereas siltstone is the result of bottom-flow deposition and represents a dysaerobic biofacies.

The depositional model developed herein for the Woodford was based on stratigraphic sequence, patterns of onlap, and lithologic variations, together with published information about global paleogeography, paleoclimate, and eustasy. During the Late Devonian, the Permian Basin was a low-relief region located on the western margin of North America in the arid tropics near 15 degrees south latitude. Worldwide marine transgression caused flooding of the craton and carried water from a zone of coastal upwelling into the expanding epeiric sea. Strong density stratification developed, due partly to accumulation of hypersaline bottom water that formed locally in the arid climate. Anaerobic conditions resulted from poor vertical circulation and from high oxygen demand, which was caused by the decay of abundant organic matter produced in the nutrient-rich surface waters. Continuous, slow deposition of pelagic material was interrupted by episodic, rapid deposition of silt and mud from bottom flows generated during frequent tropical storms.

This report documents the composition, distribution, and structure of the Woodford Formation in a major hydrocarbon-producing basin. Petrologic and organic geochemical data helped explain the origin of the unit and provided information necessary for predicting potential locations and lithologies of commercial petroleum reservoirs within the Woodford. Combining comprehensive stratigraphic, petrologic, and geochemical data was useful for developing a depositional and exploration model of Devonian black shale in West Texas and New Mexico. Similar studies should be conducted elsewhere to enable discovery of unconventional hydrocarbon reserves in black shales.

Keywords: Upper Devonian, Woodford, black shale, siltstone, source rocks, unconventional reservoirs, depositional model, paleogeography

Introduction

This report presents a stratigraphic analysis of the Woodford Formation (Upper Devonian) in the Permian Basin of West Texas and southeastern New Mexico (fig. la, b). The study is part of a larger project undertaken to determine how and why these enigmatic, organic-rich marine rocks were deposited and to document their petroleum-generation history. The part of

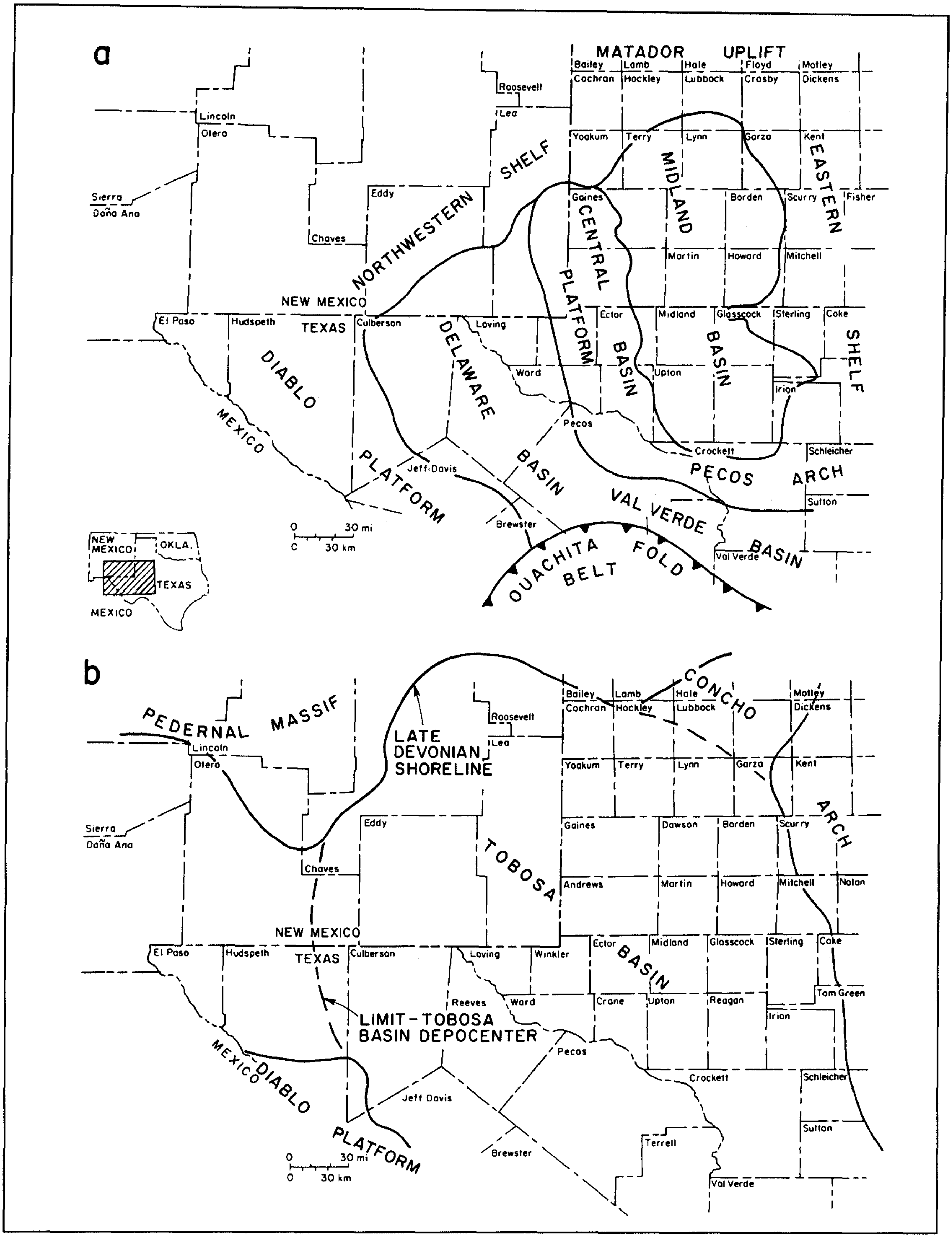


FIGURE 1. Index maps showing structural provinces in the Permian Basin, (a) Late Paleozoic to Recent. After Walper (1977) and Hills (1984). (b) Late Devonian. After Galley (1958) and Wright (1979).

the project involved in this study entailed mapping, conducting lithologic studies of cores and outcrops, and reconstructing paleogeography and depositional environments.

The Woodford Formation has long been recognized by geologists working in the region as an important stratigraphic marker because of its black shale lithology, anomalously high radioactivity, and widespread distribution (Ellison, 1950; Wright, 1979). The organic-rich formation typically yields shows of oil from cuttings and cores and produces a gas response on mudlogs. The Woodford, acknowledged as a principal petroleum source rock in the Permian Basin (Galley, 1958; Jones and Smith, 1965; Horak, 1985), contains some intervals of "oil shale" as well (>10 gal of retortable oil per ton of shale). It is also a low-grade, subeconomic uranium and heavy metal deposit (Swanson, 1960; Landis, 1962; Duncan and Swanson, 1965).

The economic potential of black shales has prompted several studies of shale deposition. Previous publications describe and interpret the origin of Devonian black shales in the eastern United States (for example, Cluff, 1980; Ettensohn and Barron, 1981; Broadhead and others, 1982; Schopf, 1983; Ettensohn and Elam, 1985; Pashin and Ettensohn, 1987), but no comparable work has been published on equivalent strata in the southern Midcontinent. Developing a comprehensive depositional model of the Woodford was complicated in that no modern analog is available for comparison. During the Late Devonian a euxinic sea, in which broad expanses of marine black shale had been deposited, occupied most of the Midcontinent of North America. However, virtually no large euxinic epeiric seas on stable cratons and passive continental margins adjacent to the open ocean exist in the modern world. Why cratonic euxinic seas developed must be understood before the origin of the Woodford can be fully explained. Although global controls, such as deglaciation and ocean ridge expansion (Heckel and Witzke, 1979; Johnson and others, 1985), can account for the worldwide transgression in the Late Devonian, regional controls must be used to account for the strongly stratified water columns and widespread bottom anoxia that developed in North America. The depositional model described later herein shows that it was the unique relationship among geography, geomorphology, tectonics, climate, and oceanography that produced the uncommon environment and unusual lithology of the Woodford Formation.

Methods

Data for the project were obtained from 558 well logs, 13 cores, and 3 measured sections. Well control is plotted on the structure and isopach maps (pls. 1, 2), and the location of cores, measured sections, and cross sections is shown in figure 2. An index of well names and locations is on open file at the Bureau of Economic Geology, and the core and measured section localities are listed in appendix A.

Plates 1 and 2 were contoured using the well data shown on each map. In areas of poor control, elevation of the Woodford (pl. 1) was inferred using the *Tectonic Map of Texas* (Ewing, 1991), which was contoured on top of the Ellenburger Formation (Lower Ordovician) in West Texas and on top of the Silurian-Devonian carbonate section in southeastern New Mexico. Faults mapped in this report were redrawn from Ewing's map.

Outcrops in the Hueco, Franklin, and Sacramento Mountains were described to compare these well-studied measured sections in the west with the poorly known rocks in the subsurface. Outcrops were chosen that had been mapped previously and for which paleontological analysis had established relative ages.

The Woodford Formation was identified from well logs, primarily by high radioactivity on the gamma-ray log (pls. 3 through 7), and by its stratigraphic position between carbonates. Although other highly radioactive strata lie in the Permian Basin, the Woodford is the most laterally persistent and typically exhibits the strongest radioactivity anomaly.

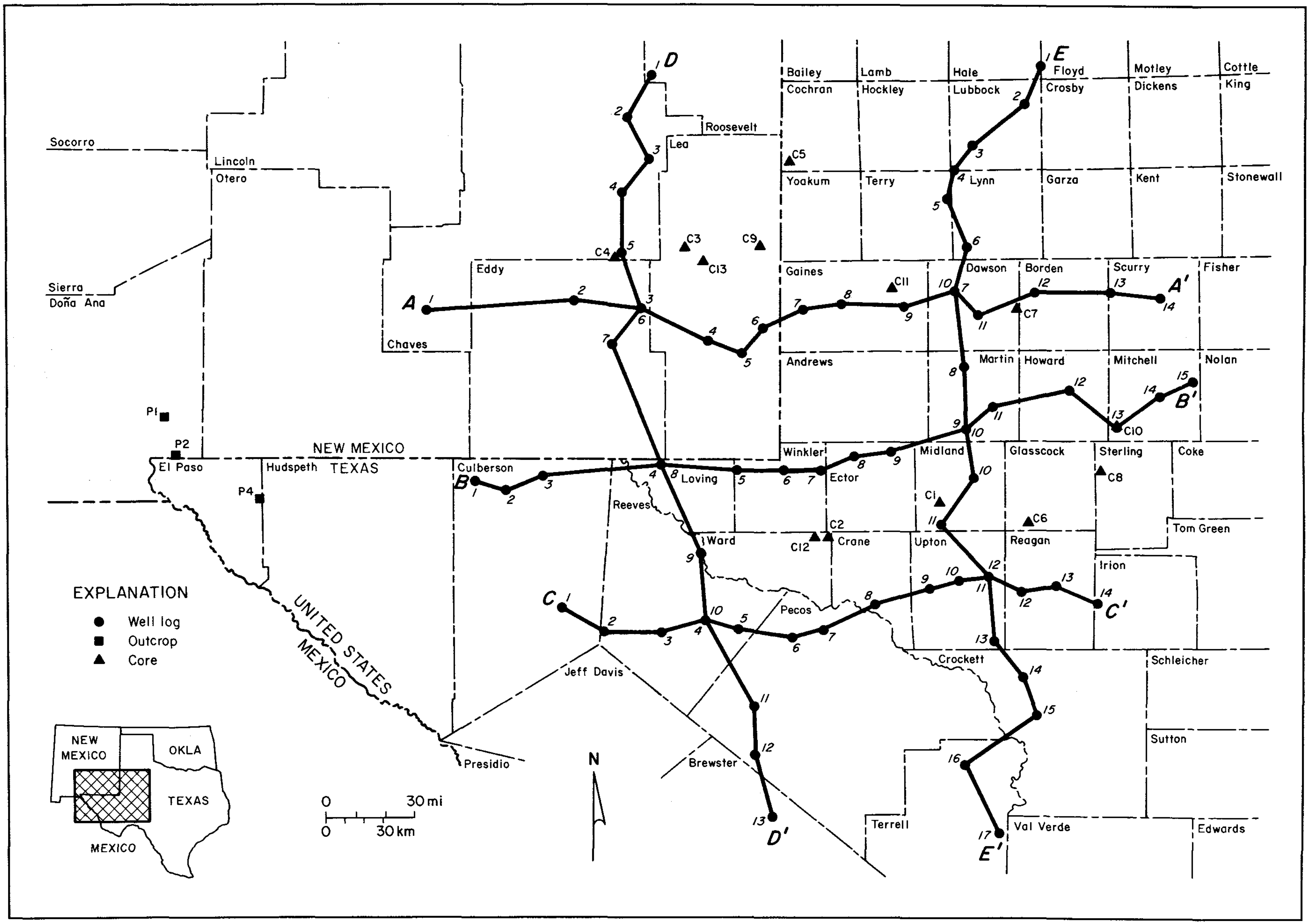


FIGURE 2. Map showing lines of cross sections (pls. 3 through 7) and locations of cores and measured sections (app. A).

The Woodford was more difficult to identify where it is overlain by radioactive, fine-grained carbonates or shales (for example, pl. 5, logs 9 through 14; pl. *6,* logs 9 through 13; pl. 7, logs 10 through 12 and 16, 17) and where the lower part of the formation is much less radioactive than the upper part (for example, pl. 4, logs 9, 11; pl. 7, logs 7, 8). In such sections, the upper and lower contacts were picked from cores, if available, or on sonic, resistivity, and neutron logs. Typically the Woodford Formation exhibits low sonic velocity, low resistivity, and low neutron-induced radiation.

In cores and outcrops, the Woodford and correlative formations were identified by their high radioactivity and unique lithology. A radioactivity profile (counts per second [CPS]) was made for each core and outcrop using a hand-held scintillometer (Ettensohn and others, 1979). Discrepancies between log depth and core depth were corrected by comparing the radioactivity profile and the wireline gamma-ray log. Lithologically, Woodford black shale contrasts sharply with the light-colored Silurian-Devonian carbonates below and Mississippian carbonates above. Where differences in color and composition are less obvious, continuous, varvelike parallel laminae and abundant pyrite distinguish the Woodford.

Petrologic analysis was conducted using slabbed cores, outcrops, slabbed hand specimens, and thin sections (app. B). Uncovered thin sections were X-rayed to identify the clay minerals and to distinguish calcite and dolomite, and selected thin sections were point counted (app. C).

Woodford lithofacies were correlated in the subsurface using gamma-ray logs (pls. 3 through 7). The two dominant lithofacies, black shale and siltstone, are readily identified because siltstone is markedly less radioactive than black shale (app. B; C5, C9).

Total organic carbon (TOC), vitrinite reflectance (% R_o), and kerogen morphology data (app. D) were valuable in interpreting the sediment provenance, paleogeography, climate, and oceanography during Woodford deposition. Recognition of pelagic and terrigenous sediment was aided by distinguishing between amorphous kerogen, which derives from organic matter of aquatic origin, and structured kerogen, which is mostly the debris of land plants (Hunt, 1979; Tissot and Welte, 1984). Large concentrations of organic matter, recorded in the rocks as high TOC values, indicate high primary productivity, rapid sedimentation, or anoxic conditions; kerogen type records relative influences of terrigenous, paralic, or marine sources and indirectly reflects depositional processes, paleosalinity, paleoclimate, and proximity to land (Byers, 1977; Hunt, 1979; Demaison and Moore, 1980; Tissot and others, 1980; Tissot and Welte, 1984; Stein, 1986; Pedersen and Calvert, 1990). Vitrinite reflectance, which records maximum paleotemperature (Dow, 1977; Hunt, 1979; Tissot and Welte, 1984), allows inferences to be made about structural evolution, thermal events, and burial history of the basin during and after the Late Devonian and constrains models of mid-Paleozoic tectonics and paleogeography.

Stratigraphy

Nomenclature

The name Woodford was first used by Taff (1902) to describe exposures of chert and black shale along the southern flank of the Arbuckle Mountain anticline in Carter County, Oklahoma. Both Woodford Chert and Woodford Shale are established as formation names (Keroher and others, 1966), but the term Woodford Formation also appears in the literature. In this report, "Woodford Formation" is used because of the wide variety of lithologies that compose the interval in the southern Midcontinent. The most readily apparent and dominant lithology is black shale; however, chert, dolostone, sandstone, siltstone, and light-colored shale are common (Harlton, 1956; Amsden and others, 1967; Amsden, 1975, 1980).

Correlation and nomenclature of Devonian and Mississippian formations are well known regionally (fig. 3), but within the Permian Basin, stratigraphy and correlation of Silurian, Devonian, and Mississippian strata are poorly known. Throughout this report, therefore, carbonate rocks underlying the Woodford are referred to as Silurian-Devonian (undifferentiated), and those overlying the Woodford are referred to as Mississippian (undifferentiated), unless faunal or lithologic data indicate a specific system, series, or stage.

Age and Correlation

The Woodford Formation is mostly Late Devonian (Frasnian-Famennian) in age, although beds of latest Middle Devonian (Givetian) and earliest Mississippian (Kinderhookian) appear at some localities (Hass and Huddle, 1965; Amsden and others, 1967; Amsden and Klapper, 1972; Amsden, 1975, 1980). Ellison (1950) found Late Devonian conodont assemblages but no Mississippian fossils in the Woodford Formation in the Permian Basin, and he documented the correlation between the Woodford in the Permian Basin and the Percha Formation in southeastern New Mexico and West Texas (fig. 3). The Late Devonian age of the Percha and Sly Gap Formations (fig. 3) has been established by faunal analysis (Stevenson, 1945; Laudon and Bowsher, 1949).

The Woodford is stratigraphically equivalent to several Devonian black shales in North America, including the Antrim Shale in the Michigan Basin, the Chattanooga and Ohio Shales in the Appalachian Basin, the New Albany Shale in the Illinois Basin, the Bakken Formation in the Williston Basin, and the Exshaw Formation in the Western Canada Basin (Meissner, 1978; Cluff and others, 1981; Roen, 1984; Burrowes and Krause, 1987). Correlative rocks exposed in uplifts in the southern Midcontinent include the Houy Formation in the Llano Uplift of Central Texas; the Chattanooga Shale in the Ozark Uplift of northeastern Oklahoma, southern Missouri, and northern Arkansas; the middle division of the Arkansas Novaculite in the Ouachita Mountains of southeastern Oklahoma and west-central Arkansas; the upper part of the Caballos Novaculite in the Marathon region of West Texas; the Percha Formation in the Hueco and Franklin Mountains of West Texas; and the Sly Gap Formation in the Sacramento Mountains of southeastern New Mexico (King and others, 1945; Stevenson, 1945; Laudon and Bowsher, 1949; Graves, 1952; Cloud and others, 1957; Huffman, 1958; Hass and Huddle, 1965; Amsden and others, 1967).

Previous Work

Western Outcrop Belt

Throughout the Franklin, Hueco, and Sacramento Mountains, Middle and Upper Devonian rocks unconformably overlie massive beds of the Lower Silurian Fusselman Dolomite (King and others, 1945; Stevenson, 1945; Laudon and Bowsher, 1949; LeMone, 1971; Lucia, 1971). In the Franklin and Hueco Mountains and at Bishop Cap, New Mexico, the Fusselman is overlain by the upper Middle to lower Upper Devonian Canutillo Formation, which is overlain conformably by the Upper Devonian Percha Formation (King and others, 1945; Rosado, 1970) (app. B; P1, P4). The Canutillo consists of dark cherty and noncherty dolostone (Rosado, 1970), and the Percha is black, fissile, nonfossiliferous shale (Stevenson, 1945). The Canutillo-Percha contact is sharp, and the lithologic transition abrupt.

In the Sacramento Mountains, the Fusselman is overlain by the upper Middle to lower Upper Devonian Onate Formation, which is overlain by the lower to middle Upper Devonian Sly Gap Formation (Stevenson, 1945; Laudon and Bowsher, 1949; Kottlowski, 1963; Rosado, 1970; Bolton and others, 1982). Locally, rocks assigned to the Percha overlie the Onate or the Sly Gap (Pray, 1961; Bolton and others, 1982). The Onate-Sly Gap contact was found to be conformable by Stevenson (1945) but locally eroded and disconformable by Pray (1961). Kottlowski (1963) suggested that the Onate may be a basal facies of Sly Gap because the contact is gradational or only slightly erosional. The Onate consists of interbedded gray-brown shale, siltstone, fine sandstone, and carbonate (Stevenson, 1945), and the most common lithology is dolomitic siltstone (Kottlowski, 1963). The Sly Gap is fossiliferous and consists of thinly interbedded, mostly tan to pale-yellow shale, siltstone, and limestone, along with a few dolomitic beds (Stevenson, 1945; Rosado, 1970). The Sly Gap is distinguished from the Onate in the field by color; and the Sly

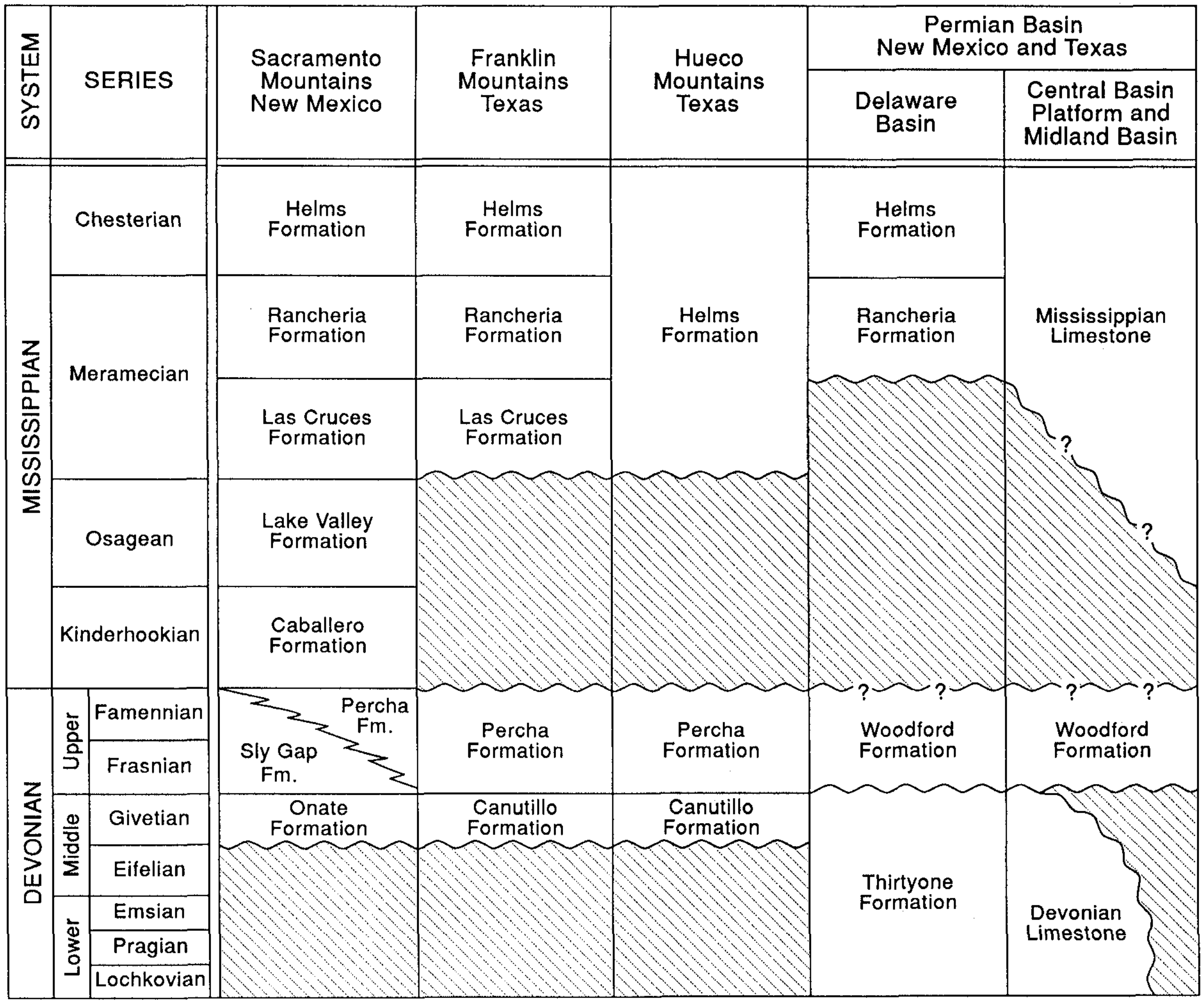


FIGURE 3. Correlation chart for Devonian and Mississippian Systems in West Texas and southeastern New Mexico. Adapted from Rosado (1970), LeMone (1971), Hoenig (1976), Bolton and others (1982), Lindberg (1983), and Hills (1984).

Gap has more shale and fewer massive, resistant beds than does the Onate (Stevenson, 1945). In the Sacramento Mountains, the Sly Gap gradually thins to the east and south and contains more black shale than do exposures farther west (Stevenson, 1945), reflecting a facies relationship with the Percha (Rosado, 1970).

At most localities in the Franklin, Hueco, and Sacramento Mountains, the Percha and Sly Gap Formations are overlain disconformably by Mississippian limestones (King and others, 1945; Rosado, 1970) (app. B; P2, P4). At Bishop Cap, New Mexico (app. B; Pl), and locally in the Sacramento Mountains, Upper Devonian rocks are overlain conformably by the Kinderhookian Caballero Formation (Rosado, 1970; Bolton and others, 1982) (fig. 3).

Central Texas

In the Llano region of Central Texas, the Houy Formation disconformably overlies rocks of Early to Middle Devonian and Early Ordovician age (Cloud and others, 1957). Rocks below the unconformity are carbonates, and most are cherty. In upward succession, the Houy consists of a lower or basal chert breccia (Ives Breccia Member), black shale (Doublehorn Shale Member), and an upper, unnamed phosphatic unit. The Ives Breccia consists mostly of angular fragments and unbroken nodules of chert and locally contains angular blocks of dolostone, all of which appear to be little-moved lag deposits (Cloud and others, 1957). The Doublehorn Shale is fissile, radioactive, spore-bearing black shale, and the upper phosphatic unit contains phosphatic debris such as fish bones, pellets, and conodonts. The Houy is predominantly Late Devonian, but locally the lowermost Houy may be Middle Devonian and the upper phosphatic unit partly Early Mississippian (Kinderhookian) (Cloud and others, 1957).

The Houy is conformably overlain by the Kinderhookian Chappel Limestone (Cloud and others, 1957). However, the upper Houy has thin beds, interrupted faunal zones, and intervals containing mixed Mississippian and Devonian fossils, all of which make correlation, age, and vertical continuity difficult to determine (Cloud and others, 1957).

Northeastern Oklahoma and Northern Arkansas

In the Ozark Uplift, the Chattanooga Shale rests disconformably on rocks ranging in age from Devonian to Ordovician (Huffman, 1958). The Sylamore Sandstone Member constitutes the lower part of the formation at many localities, and its age is late Middle Devonian to late Kinderhookian (Freeman and Schumacher, 1969; Pittenger, 1981). The black shale interval, sometimes called the Noel Shale Member (Huffman and Starke, 1960), is predominantly Late Devonian but ranges in age from early Late Devonian to Kinderhookian (Amsden and others, 1967). The Sylamore is submature to supermature quartzarenite that contains minor phosphate, glauconite, and locally abundant dolomite (Pittenger, 1981). Quartz was reworked from contemporaneous exposures of the Middle Ordovician Bergen Sandstone (Pittenger, 1981). Locally the basal layer of the Sylamore is chert breccia (Amsden and others, 1967). The Noel is black, fissile, radioactive shale and is the most abundant Chattanooga lithology. The Chattanooga is overlain disconformably by limestones and cherts of the Mississippian Boone Group. The Boone is predominantly Osagean but ranges in age from middle Kinderhookian to early Meramecian (Sutherland and Manger, 1979).

Ouachita Fold Belt

The middle division of the Arkansas Novaculite in Oklahoma and Arkansas is from Late Devonian to Kinderhookian age and represents, at least partly, a lateral facies of the Woodford (Hass, 1951; Amsden and others, 1967). Likewise, the upper Caballos Novaculite in West Texas is a Late Devonian (Graves, 1952) lateral facies of the Woodford. Faunal data are scarce and contact relationships problematic, but vertical lithologic continuity suggests that the Woodford-equivalent interval in the novaculite formations is bounded conformably by the underlying and overlying beds. The upper Caballos contains mostly white novaculite, and the middle division of the Arkansas Novaculite contains interbedded dark-gray and greenish-gray shales and dark-gray novaculite (Hass, 1951; Amsden and others, 1967).

Central and Southern Oklahoma

In central and southern Oklahoma, the Woodford Formation rests disconformably on rocks of late Early Devonian to Ordovician age (Amsden, 1975, 1980). The Woodford is mostly Late Devonian but ranges in age from Givetian to Kinderhookian (Hass and Huddle, 1965; Amsden and others, 1967; Amsden and Klapper, 1972; Amsden, 1975, 1980). A basal clastic unit, the Givetian to early Famennian Misener Sandstone, is present in some areas (Amsden and Klapper, 1972). Woodford black shale is Frasnian to Kinderhookian (Hass and Huddle, 1965; Amsden and others, 1967).

Rocks underlying the Woodford are predominantly carbonates, and some are cherty. In southern Oklahoma, the Misener is sandstone, siltstone, green shale, dolostone, or chert breccia, whereas in north-central Oklahoma it is mostly mature quartzarenite containing minor glauconite and phosphate and locally abundant dolomite (Harlton, 1956; Amsden and others, 1967; Amsden and Klapper, 1972; Amsden, 1980; Francis, 1988). Quartz was derived with little transport from Middle Ordovician Simpson sandstone in north-central Oklahoma and from the Ouachita province in southern Oklahoma (Amsden and Klapper, 1972). Black shale is the most widespread Woodford lithology. It is fissile, spore-bearing, and highly radioactive, and in the Arbuckle Mountains it is interbedded with chert (Amsden and others, 1967; Amsden, 1975, 1980). Woodford chert is dark and rich in radiolarians and marine organic matter (Comer and Hinch, 1987). The Misener-Woodford sequence is stratigraphically equivalent to the

Sylamore-Chattanooga sequence in the Ozark Uplift, and the lower boundary of both sequences is diachronous, onlapping parts of the northern Oklahoma shelf and the Ozark Uplift (Freeman and Schumacher, 1969; Amsden and Klapper, 1972; Amsden, 1980).

In the Arbuckle Mountains, the Woodford is conformably overlain by the Sycamore Formation. The Sycamore consists of poorly fossiliferous, fine-grained, silty limestone interbedded with dark shale, and its age spans the Early to Middle Mississippian (Kinderhookian to Meramecian) (Ham, 1969). In the subsurface, the Woodford is overlain by Mississippian rocks (mostly limestones), but the stratigraphic relationship is problematic. In basinal regions, evidence of unconformity is obscure, although the contact is probably disconformable (Ham and Wilson, 1967; Frezon and Jordan, 1979). Locally the contact appears to be gradational, and the unconformity, if present, represents only a minor stratigraphic break (Frezon and Jordan, 1979).

Permian Basin

In the Permian Basin, lithologic, electric-log, and sparse faunal data indicate that the Woodford unconformably overlies rocks ranging in age from Devonian to Ordovician (Lloyd, 1949; Ellison, 1950; Peirce, 1962; McGlasson, 1967, Munn, 1971; Hoenig, 1976). The Woodford is overlain disconformably by Mississippian limestone (fig. 3) and locally by rocks as young as Early Permian (Lloyd, 1949; Wright, 1979). Lloyd (1949) assigned the Mississippian limestone section in the subsurface to the Meramecian Rancheria Formation on the basis of a few fossils and lithologic similarity to rocks exposed in the Sacramento Mountains. Older, Osagean and Kinderhookian rocks have not generally been recognized in the basin, although Kinderhookian strata were postulated to exist in a small area of eastern Chaves, southwestern Roosevelt, and northwestern Lea Counties, New Mexico, on the basis of lithologic similarity to the Caballero Formation in the Sacramento Mountains (Lloyd, 1949).

Ellison (1950) divided the Woodford Formation into three units using radioactivity, log response, and lithology. The lower unit was calcareous and cherty, and it had the lowest radioactivity; the middle unit had the most resinous spores and the highest radioactivity; and the upper unit had few spores and intermediate radioactivity (Ellison, 1950). The middle unit was the most widespread, comprising the black shale lithology characteristic of the Woodford throughout the basin, and the lower unit was the most areally restricted. A correlation may exist between Ellison's lower Woodford unit and the Ives Breccia Member and between the middle Woodford unit and the Doublehorn Shale Member of the Houy Formation in Central Texas (Wright, 1979).

Formation Boundaries

The lower boundary of the Woodford and its stratigraphic equivalents represents a major regional unconformity that extends across the southern Midcontinent and records a major period of uplift and erosion that is at least partly Devonian (Galley, 1958; Amsden and others, 1967; Ham and Wilson, 1967; Ham, 1969). During this regressive episode, older Devonian and Silurian strata were removed over broad areas of the Midcontinent, and rocks below the unconformity became locally deeply eroded (Ham and Wilson, 1967; Ham, 1969; Amsden, 1975). In basinal regions, such as the Anadarko Basin, the unconformity marks the end of early Paleozoic shallow-water carbonate sedimentation and the beginning of deep-water carbonate and clastic deposition (Ham, 1969). The Woodford and correlative formations are diachronous and represent onlapping sediments (Freeman and Schumacher, 1969; Amsden and Klapper, 1972) deposited during worldwide Late Devonian marine transgression (Johnson and others, 1985). The coarse sandstone and breccia occurring locally above the unconformity are lag deposits derived from older formations (Cloud and others, 1957; Amsden and others, 1967; Amsden and Klapper, 1972; Amsden, 1975, 1980; Pittenger, 1981), and the black shale represents strongly reduced mud laid down on the anoxic floor of an epeiric sea (Ellison, 1950; Wright, 1979).

The upper boundary of the Woodford represents only a minor stratigraphic break (Ham and Wilson, 1967; Frezon and Jordan, 1979; Click, 1979; Mapel and others, 1979). It is disconformable at some localities (for example, the

Ozark Uplift and parts of the western outcrop belt and Oklahoma subsurface) and conformable at others (for example, Central Texas, the Arbuckle Mountains, and the Ouachita Fold Belt). The local occurrence and minor stratigraphic expression of disconformities indicate low-lying land masses in the latest Devonian or earliest Mississippian and an episode of minor epeirogenic uplift, slight sea-level fluctuations, and brief interruption of marine sedimentation (Stevenson, 1945; Ham and Wilson, 1967; Frezon and Jordan, 1979; Mapel and others, 1979).

Distribution

Distribution of the Woodford Formation in the Permian Basin is illustrated in plates 1 through 7. The area contoured in plates 1 and 2 was not extended to the western outcrop belt because of limited well control in Chaves, Eddy, Otero, and Lincoln Counties, New Mexico, and Culberson, Hudspeth, and El Paso Counties, Texas.

Relief on the present-day Woodford surface is more than 20,000 ft in the subsurface (pl. 1) and more than 25,000 ft if elevations in the western outcrop belt are included. Most of the relief in the basin developed as a result of deformation during the late Paleozoic Ouachita orogeny (Galley, 1958; Muehlberger, 1980), whereas relief in the outcrop belt and Diablo Platform was strongly influenced by later Laramide deformation (Muehlberger, 1980).

The Woodford Formation ranges in thickness from 0 to 661 ft (pl. 2) and is thickest in structural lows and thinnest or absent on structural highs. Thicknesses shown on plate 2 were not corrected for dip and do not everywhere represent true stratigraphic thicknesses. The Woodford is more nearly flat-lying in basin and shelf settings farthest from major faults (for example, on the Eastern Shelf and in most parts of the Midland Basin and Northwestern Shelf).

Northwestern Shelf and Matador Uplift

The Woodford Formation is present at most localities on the Northwestern Shelf but is absent on and north of the Matador Uplift (fig. la; pls. 1, 2, 7) (Ellison, 1950; Wright, 1979; Dutton and others, 1982; Ruppel, 1985). In northern Lea County, New Mexico, elevation of the Woodford increases northward, but the pattern is broken by several faults (pl. 1). These faults trend north-south or northwest-southeast, generally parallel to the Central Basin Platform and the axis of the Delaware Basin.

The Woodford thins northwestward across Eddy County, New Mexico, away from the Delaware Basin (pls. 2, 6), the gradual thinning coinciding with the increase in elevation (pl. 1). In eastern Chaves and northern Eddy Counties, New Mexico, thin and thick areas are irregularly distributed and are not clearly related to structure (pl. 2). In the northernmost part of the map, Woodford thickness appears to be structurally controlled because isopach contours are oriented east-west, parallel to the structural trend of the Matador Uplift (pl. 2).

Eastern Shelf

The Woodford Formation was previously thought not to extend onto the Eastern Shelf (Ellison, 1950; Wright, 1979), but in the present study no clearly defined eastern limit for the Woodford was found (pls. 1, 2). The formation is absent in northeastern Crockett County, in most of western Irion County, and in a large area that includes parts of Scurry, Borden, and Garza Counties. However, the formation is present across Sterling, Mitchell, and most of Scurry Counties.

The wide spacing of structural contours in the eastern part of the map (pl. 1) documents a gradual increase in elevation of the Woodford from the Midland Basin onto the Eastern Shelf. The Woodford also thins gradually in the same direction (pls. 2 through 5). On the Eastern Shelf, the Woodford is thin, and the distribution is somewhat irregular and patchy (note thicknesses in Scurry, Mitchell, and Sterling Counties, pl. 2). These structural and isopach trends are uninterrupted except in southern Irion and northern Crockett Counties, where large-scale faults cut the section.

Central Basin Platform and Pecos Arch

The Central Basin Platform and Pecos Arch are the diverging structural highs in the center of the map that meet in Crane and northeastern Pecos Counties (fig. la; pls. 1, 2). Faults bounding the Pecos Arch trend east-west, whereas those along the Central Basin Platform trend northwest-southeast. Some of the largest faults, those having throws of a few thousand feet, are normal or high-angle reverse faults, although some show evidence of strike-slip motion (Galley, 1958; Walper, 1977; Muehlberger, 1980; Hills, 1984).

The Woodford is absent from the Pecos Arch and from many of the faulted structures on the Central Basin Platform (Ellison, 1950; Galley, 1958) (pls. 1, 2, 7). Elevations of the Woodford or the unconformity representing the Woodford range from 980 ft below sea level in northern Pecos County to more than 7,000 ft below sea level in eastern Winkler County. The Woodford thins over the Central Basin Platform in most places, but in some areas, such as southern Ector and Winkler Counties, the thickness steadily increases westward (pl. 2).

Delaware Basin

The Woodford Formation reaches its maximum thickness of 661 ft in the Delaware Basin structural low in western Winkler County (pls. 1, 2). The Woodford is more than 600 ft thick in central and southwestern Winkler, southeastern Loving, and northern Ward Counties. The top of the deepest Woodford is more than 16,000 ft below sea level in eastern Loving County and more than 15,000 ft below sea level in east-central Reeves County (pl. 1). Several isolated thick areas whose distribution is fault controlled appear in Reeves County (pl. 2); in the north-central part of the county, thickness locally exceeds 500 ft, and in central and southeastern areas, 400 ft.

Midland Basin

The axis of the Midland Basin is approximately outlined by the closed -9,000-ft structural contours east of the Central Basin Platform in Texas (pl. 1). The deepest Woodford is nearly 9,800 ft below sea level in northeastern Gaines County (pl. 1). Within the basin thickness trends are subtle (pl. 2); the Woodford at its thickest is 135 ft in north-central Martin County. Two thick areas are indicated by the closed 100-ft isopach contours in Dawson, Gaines, Andrews, and Martin Counties. Between the thick areas lies an east-west trend of relatively thin Woodford (50 to 100 ft). Another narrow thin trend (<50 ft) lies in southern Martin and southeastern Andrews Counties. These trends parallel structural and isopach trends along the Matador Uplift and Pecos Arch and are at a high angle to those along the Central Basin Platform immediately to the west.

Val Verde Basin

The Woodford is present in the Val Verde Basin of southern and southeastern Pecos, southern Crockett, northern Terrell, and northern Val Verde Counties (fig. la; pls. 1, 2, 7). In northern Brewster and southern Pecos Counties, the Woodford Formation, along with a carbonate sequence typical of the Paleozoic section of the craton, lies beneath allochthonous rocks of the Ouachita Fold Belt (pls. 1, 2, 6 [D–D′, well 13]).

Two structural trends are present in the Val Verde Basin (pl. 1). In south-central Pecos County, faults and structural contours trend northwest-southeast, and elevation of the Woodford Formation increases from central Pecos County south westward and westward. In Terrell, southern Crockett, Val Verde, and eastern Pecos Counties, faults trend east-west, and elevation of the Woodford increases northward from the Ouachita Fold Belt to the Pecos Arch.

In central Pecos County, the Woodford was inferred to be more than 21,000 ft below sea level (pl. 1) on the basis of the elevation of the Ellenburger Formation (Ewing, 1991), and it was inferred to be more than 300 ft thick (pl. 2) on the basis of nearby thickness trends. In central Terrell County, the Woodford was inferred to be more than 20,000 ft below sea level, and even deeper burial is likely beneath the Ouachita overthrust (pl. 1). Thicknesses in this part of the basin locally exceed 400 ft and may be 300 ft or more in central Terrell County beneath the Ouachita allochthon (pl. 2).

Diablo Platform and Western Outcrop Belt

The Diablo Platform (fig. la, b) is a major structural boundary between the Permian Basin to the northeast and the Chihuahua Tectonic Belt to the southwest that has been strongly affected by Laramide deformation (Muehlberger, 1980). Most of the faults along the platform trend northwest-southeast and follow Proterozoic basement faults (Walper, 1977; Muehlberger, 1980).

The Woodford is absent in the southeastern part of the Diablo Platform, southwest of the map area (Wright, 1979), but it is present in the northeastern part (Rosado, 1970) (pls. 1,2). The highest observed subsurface elevation (128 ft below sea level) is in northwestern Culberson County (pl. 1). The highest overall elevation (>5,000 ft above sea level) is in the western outcrops. From the Delaware Basin, elevation of the Woodford gradually increases westward across Reeves and Culberson Counties toward the Diablo Platform (pl. 1), and the formation gradually thins in the same direction (pl. 2).

Lithofacies

Two lithofacies were identified in the Woodford Formation—black shale and siltstone. Black shale is pyritic and has parallel laminae; siltstone, a hybrid rock composed of silt-sized quartz and dolomite grains, is medium to dark gray and has discontinuous and disturbed bedding. Distinguishing between lithologies can be difficult because differences in color may be slight, and many layers contain subequal mixtures of silt- and clay-sized grains. Contacts between lithofacies may be sharp, particularly at the base of the siltstones, or gradational; and lithologies are commonly interbedded and interlaminated.

Lithofacies were defined and described from cores because weathering had severely oxidized the pyrite and organic matter in outcrop. Outcrops are medium to light shades of gray or brown, whereas cores are black (black shale) or light to dark gray (siltstone). Textures were found to be comparable in outcrop and core, and the mineralogy of the silicate and carbonate fraction was similar. Hence, lithofacies analysis was possible at all localities.

Black Shale

Characteristic Features

Parallel laminae are the most characteristic feature of black shale (fig. 4a, b). Other distinguishing features include abundant pyrite, fine grain size, black color, and high radioactivity. The black color is caused by high concentrations of pyrite (as much as 13 vol %; app. C) and organic carbon (as much as 35 vol % [app. C] or 12 wt % TOC; app. D), and high radioactivity is caused by uranium bound in the organic matter (Swanson, 1960, 1961; Leventhal, 1981).

Bedding and Sedimentary Structures

Continuous parallel laminae predominate (fig. 4a), but other stratification types include discontinuous, wavy, and lenticular laminae and thin beds. Most laminae have no internal structure but can be distinguished by subtle differences in color that result from differences in composition (for example, unequal amounts of detrital quartz, clay, pyrite, dolomite, and organic matter and different numbers of spores and radiolarians). These laminae typically have a varvelike appearance in slabs and thin sections (fig. 4a). Thin graded siltstone-shale couplets were found in some intervals, mostly in shelf regions (app. B; C3, C4, C13). Most graded couplets have sharp bases, and some exhibit primary sedimentary structures such as fading ripple forms.

Burrows are scarce but commonly cause disrupted or distorted layers (fig. 4a through c). Most burrows are confined to, or start in, siltstone laminae (fig. 4a, b), but a few were found exclusively in shale (fig. 4c). Flattened horizontal burrows were the most common type observed, and vertical burrows (fig. 4b, c) were found only locally. Burrows are filled by silt, secondary silica, carbonate, and pyrite in varying proportions, and some contain scattered remnants of anhydrite (fig. 4d).

Syneresis cracks (fig. 4e) were found locally on the Central Basin Platform in organic-rich, pyritic black shale. They are short, wide vertical fractures, linear in plan view and wedge shaped in cross section. Syneresis cracks are found in the middle of the black shale section and not at lithologic or formation contacts (app. B; C2). They are highly compacted and thus are inferred to be syndepositional or very early diagenetic. The cracks are filled mostly by secondary silica (including quartz, chert, and chalcedony) and locally contain carbonate, along with patchy remnants of anhydrite. Filling must have occurred shortly after the cracks formed because cementing phases are deformed, and the surrounding black shale is differentially compacted (fig. 4e). Subaerial exposure is not indicated because pyrite and organic matter in the host shale are unoxidized.

Texture

Black shale consists of more than 50 percent clay-sized material and less than 50 percent silt-sized particles (fig. 4a through c). Silt-sized grains may be randomly scattered (fig. 4c) or concentrated in laminae (fig. 4a, b). Lighter colored laminae will typically contain greater proportions of silt-sized particles than will the darker laminae.

Median grain sizes of the silt fraction are between 0.01 and 0.05 mm. Sand-sized grains are rare. A few large (as much as 5 cm long) greenish shale clasts exhibiting parallel laminae (fig. 4f) were found locally on the Central Basin Platform.

Composition

Clay-sized material consists of organic matter and illite, and the silt-sized fraction consists of mostly dolomite, quartz, pyrite, mica, feldspar, glauconite, biogenic pellets, spores, and radiolarians. Other types of fossils, including conodonts, brachiopods, trilobites, sponge spicules, and vertebrate debris, were found locally, but only rarely.

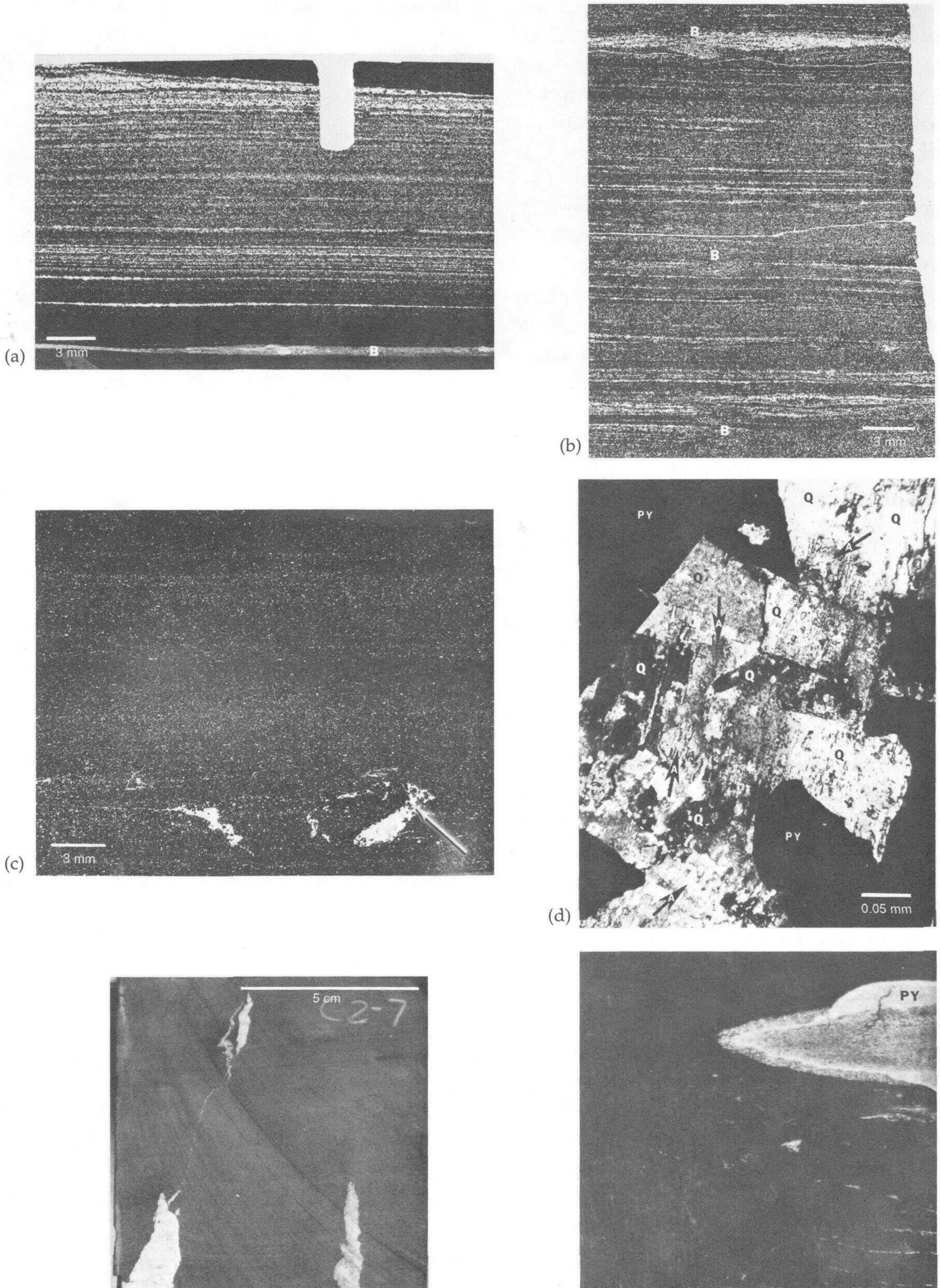
Organic carbon content in core samples ranges from 1.4 to 11.6 weight percent TOC (mean = 4.5 ± 2.6 wt % TOC for 72 samples), or from roughly 4 to 35 volume percent organic matter. Outcrops contain much less organic carbon than do the cores (<0.1 to 2.3 wt % TOC; mean = 0.8 ± 0.6 wt % TOC for 25 samples) primarily because of oxidation during weathering. Average TOC concentration in each core ranges from 2.2 to 9.0 weight percent and in each outcrop from 0.1 to 1.1 weight percent (app. D).

Organic matter most commonly appears as fine-grained, disseminated, amorphous material (app. D), an oil-generating type. Woody particles were rare in thin sections and in separated kerogens. Large plant fragments appeared on a few bedding surfaces in cores from the Northwestern and Eastern Shelves. Recycled vitrinite occurs only in black shale from the Central Basin Platform, Eastern Shelf, and southern Midland Basin (app. D). The mean reflectance values of primary vitrinite in cores and outcrops range from 0.54 to 1.92 percent R (app. D) and represent hydrocarbon generation stages between early oil generation and late wet-gas generation (Hunt, 1979).

Illite is abundant in the black shale. Volume percentages range between 34 and 79 percent and average 59 ± 3 percent (app. C). The coarse clay mineral fraction (1 to 2 μm) is detrital illite, whereas the fine clay mineral fraction (<0.2 μm) is diagenetic illite (Morton, 1985).

Dolomite and quartz are the most common silt-sized components. They occur randomly mixed in subequal proportions, and they have the same grain-size distribution. Dolomite grains in shale have no overgrowths—most are subhedral to anhedral and appear to be abraded (fig. 4g). Euhedral dolomite grains are abundant only locally in cores from the Central Basin Platform, Midland Basin, and Northwestern Shelf. Scattered silt- to sand-sized poikilotopic dolomite patches cement clay- or fine silt-sized particles in some samples.

Pyrite is ubiquitous in cores and can be found in a variety of forms: (1) large (as much as 8 cm) nodules (some possessing cone-in-cone fabric), (2) irregular elongate patches, (3) thin streaks, (4) smooth elliptical masses having stromatolite-like or oncolitelike fabric, (5) scattered fine grains, (6) framboids, (7) aggregates (silt sized or finer), (8) fillings or replacements of minute organisms (for example, spores and radiolarians), (9) cement or replacement in burrows, and rarely, (10) fracture fillings. Weathering has altered pyrite in outcrop to various oxides and sulfates. Locally, gypsum lines joints and bed-


(a)
3 mm
B
(b)
B
B
B
3 mm
(c)
3 mm
(d)
PY
Q
Q
Q
Q
A
Q
Q
A
Q
Q
PY
A
0.05 mm
(e)
5 cm
C2-7
(f)
PY
V
5 mm

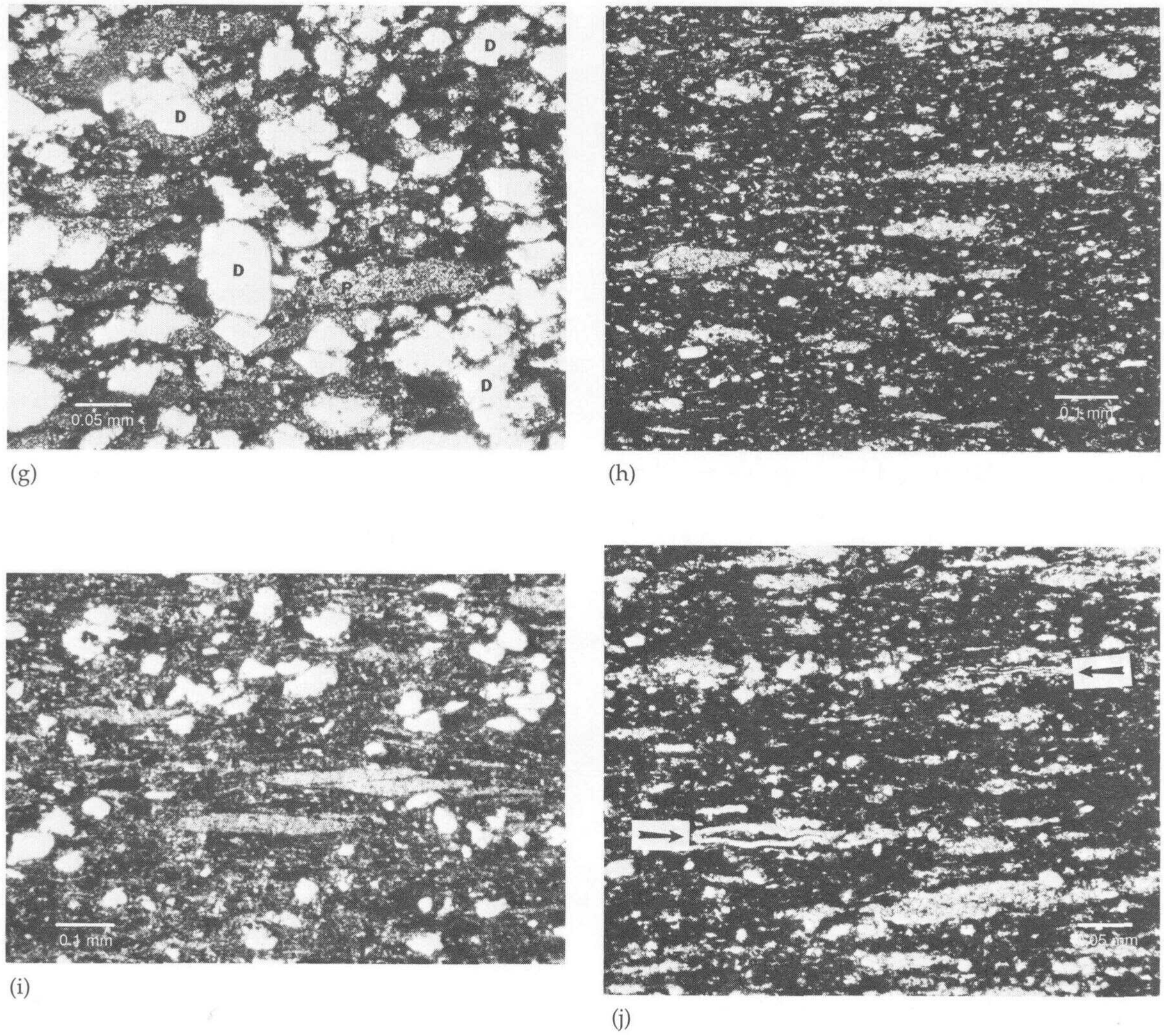


FIGURE 4. Photos of Woodford black shale. (a) Black shale exhibiting continuous parallel laminae at 11,555 ft in the No. 1918 Parks (app. B; C1, sample C1-10). Note cyclic change from black shale at base, siltstone laminae increasing upward, and abrupt return to black shale at top. Silty lamina at base, B, is burrowed. TOC = 4.2 wt %. (b) Disrupted parallel siltstone laminae in black shale at 10,914 ft in the No. 1 Champeau Federal (app. B; C4, sample C4-4). Disrupted areas, B, are burrows. TOC = 5.0 wt %; R_o = 1.03%. (c) Black shale exhibiting parallel laminae, scattered silt, and burrows at 12,228 ft in the No. 5 Pacific Royalty (app. B; C9, sample C9-2). TOC = 3.2 wt %. (d) Enlarged view of burrow in photo (c) (see arrow in photo [c]). Burrows are filled mostly by quartz, Q; pyrite, PY; and patchy remnants of anhydrite, arrows marked A. Rectangular habit indicates quartz is pseudomorph after anhydrite. Crossed nicols. (e) Syneresis cracks filled mostly by silica and carbonate and locally containing anhydrite at 7,179 ft in No. 43 Yarborough & Alien (app. B; C2, sample C2-7). Note differential compaction of black shale laminae and compactional deformation of syneresis structures. TOC = 8.5 wt % in host shale. (f) Shale clast in black shale at 7,177 ft in No. 43 Yarborough & Alien (app. B; C2, sample C2-6). Clast has parallel laminae, and the outer edge was pyritized, PY. Oblique calcite veins and ptygmatic veinlets, V, reflect shearing. TOC = 11.2 wt % in host shale. (g) Silty shale at 7,172 ft (app. B; C2, sample C2-3). Silt is exclusively dolomite, D, and most grains are angular, broken, or abraded. Pellets, P, are elongate fine-grained aggregates and probably biogenic. Plane-polarized light. TOC = 8.5 wt %. (h) Pellets containing silt particles at 7,404 ft in the No. 1 Sealy Smith (app. B; C12, sample C12-4). Plane-polarized light. Dolomite/quartz ratio = 1.3/1.0; TOC = 10.2 wt % ; R_o = 0.55%. (i) Pellets composed mostly of clay at 11,639 ft in the No. 1 Walker (app. B; C5, sample C5-2). Silt grains are dolomite and quartz. Plane-polarized light. Dolomite/quartz ratio = 1.3/1.0; TOC = 2.8 wt %. (j) Pellets and flattened spores at arrows from same thin section as those in photo (h). Spores are *Tasmanites*. Plane-polarized light.

ding planes, and iron oxide appears as pyrite pseudomorphs, indicating that these rocks were highly pyritic before weathering. Elsewhere, disseminated ferric oxides record the former abundance of pyrite in the Percha and Sly Gap Formations.

Muscovite flakes appear in all samples. Mica flakes and illite typically are well oriented parallel to bedding. In biogenic pellets, however, illite may comprise domains of differing orientations. Locally some mica flakes lie at high angles to bedding, a few flakes being oriented 90 degrees to bedding. Such flakes appear to be part of larger clumps of organic-bound sediment.

Feldspar (microcline) and glauconite are rare in black shale. Feldspar appears mostly in samples from the Northwestern Shelf, Central Basin Platform, and western Midland Basin (app. C; Cl, C2, C4, C13). Glauconite occurs as an isolated grain or two in many thin sections.

Biogenic pellets are common (as much as 11%; app. C) in many black shale samples. They appear as flattened silt sized to fine sand sized aggregates and impart a microlenticular fabric to the rock when viewed in thin section (fig. 4h through j). Pellets are easily distinguished from burrows in plan view because pellets exhibit no trail-like patterns on bedding surfaces or in cross section because pellets show no cross-cutting contacts or internal stratification. Most pellets consist of illite, but some consist of silt-sized grains of quartz and dolomite (fig. 4h). Silty pellets commonly are cemented by carbonate and are flattened slightly less than clay pellets.

Spores are minor components in black shale, but they are widely distributed. Generally spores are flattened as a result of compaction (fig. 4j). However, in some intervals spores have been replaced by pyrite or infilled by pyrite, chert, or carbonate. Locally, early infilling is indicated by spores that are uncompacted or only slightly flattened.

Radiolarians also are a minor but widely distributed component. They are composed mostly of chert or chalcedony, but some have been partly or completely replaced by pyrite or carbonate. Spores and radiolarians may be randomly scattered throughout a laminated sequence or concentrated in laminae or thin beds. Radiolarian chert layers were observed locally on the Central Basin Platform and in the southern Midland Basin (app. B; C2, C6).

Trilobite fragments are sparsely scattered in some intervals and locally occur alongside pellets. Most are carbonate, but a few have been partly replaced by chert. Trilobite fragments locally are common at the top of the formation along the disconformity with the Mississippian limestone (app. B; C10).

Brachiopods are scarce in the Woodford. Inarticulate brachiopods *(Lingula)* were recognized on bedding surfaces in cores from the Central Basin Platform and the Northwestern Shelf (app. B; C2, C4, C9). One silicified articulate brachiopod was found in black shale on the Central Basin Platform (app. B; C2). Elsewhere, articulate brachiopods are abundant only locally at the top of the formation (app. B; C10).

Phosphatic fossil debris is a minor component in black shale. Conodonts are scarce but widely distributed, and bone and teeth fragments and fish scales also are rare. Phosphatic debris sometimes is concentrated in the siltier shales and in interstratified siltstones.

Sponge spicules were found only locally in one core from the Central Basin Platform where monaxons were scattered parallel to stratification (app. B; C2). All of the spicules had altered to chert.

Secondary silica is the major constituent in some layers and sedimentary structures. Secondary silica in the form of chert, chalcedony, and megaquartz fills or replaces fossils and cements or replaces burrows and syneresis cracks (fig. 4c through e). Megaquartz that has pseudomorphic rectangular cleavage after anhydrite was found locally associated with anhydrite (fig. 4d). Also, some of the chalcedony in burrows and syneresis cracks is length-slow, suggesting that it replaced evaporites (Folk and Pittman, 1971).

Siltstone

Characteristic Features

Siltstone in the Woodford Formation is a hybrid siliciclastic-carbonate rock in which dolomite and quartz are the dominant silt-sized framework grains. Compared with black shale, siltstone has coarser grain size, lighter color, more disrupted or discontinuous strata, and lower radioactivity. Siltstone, unlike the carbonate lithologies of bounding formations, has a more uniform silt-sized texture, abundant quartz grains, no chert, no large body fossils, and higher radioactivity.

Bedding and Sedimentary Structures

Stratification ranges from thin laminae to thin beds. Continuous, discontinuous, and wavy parallel laminae commonly are preserved, but stratification typically is disrupted by burrowing (fig. 5a, b) or, more rarely, contorted by soft-sediment deformation (fig. 5b, c).

Interbedded and interlaminated dark-gray to black shale, fine-grained dolomite grainstone, fine-grained lime grainstone, and lime mudstone locally are common (app. B; C9, C11). The interbedded shales and mudstones typically exhibit continuous, discontinuous, or wavy parallel laminae, and the grainstones, discontinuous and disturbed layers.

Most siltstones and grainstones have sharp lower contacts (fig. 5d through f), and many form graded couplets with shale (fig. 5e, f). Others have gradational upper and lower contacts (fig. 5g). Cores containing well-developed siltstone lithofacies commonly consist of vertically stacked couplets in which siltstone beds as thick as 10 to 15 cm grade upward into shale layers as thick as 5 cm (fig. 5a, b, e). Primary sedimentary structures include normal grading (fig. 5a, b, e, f), fading ripple forms (fig. 5e), climbing ripple cross-stratification (fig. 5d), horizontal stratification, soft-sediment deformation (fig. 5b), and flow-sheared laminae (fig. 5c). The vertical succession of structures typically comprises a partial or complete Bouma sequence (fig. 5e). Siltstone sequences such as these constitute a basal facies of the Woodford in the Northwestern Shelf and northern Midland Basin (app. B; C5, C9, C11).

Texture

Median grain sizes of siltstone are between 0.01 and 0.05 mm. Typically, little or no sand-sized material is present, although sand grains as. large as the medium-sized grade were encountered locally. Clay-sized material ranges from 0 to almost 50 percent by volume. Siltstone is moderately to poorly sorted and rarely well sorted.

Composition

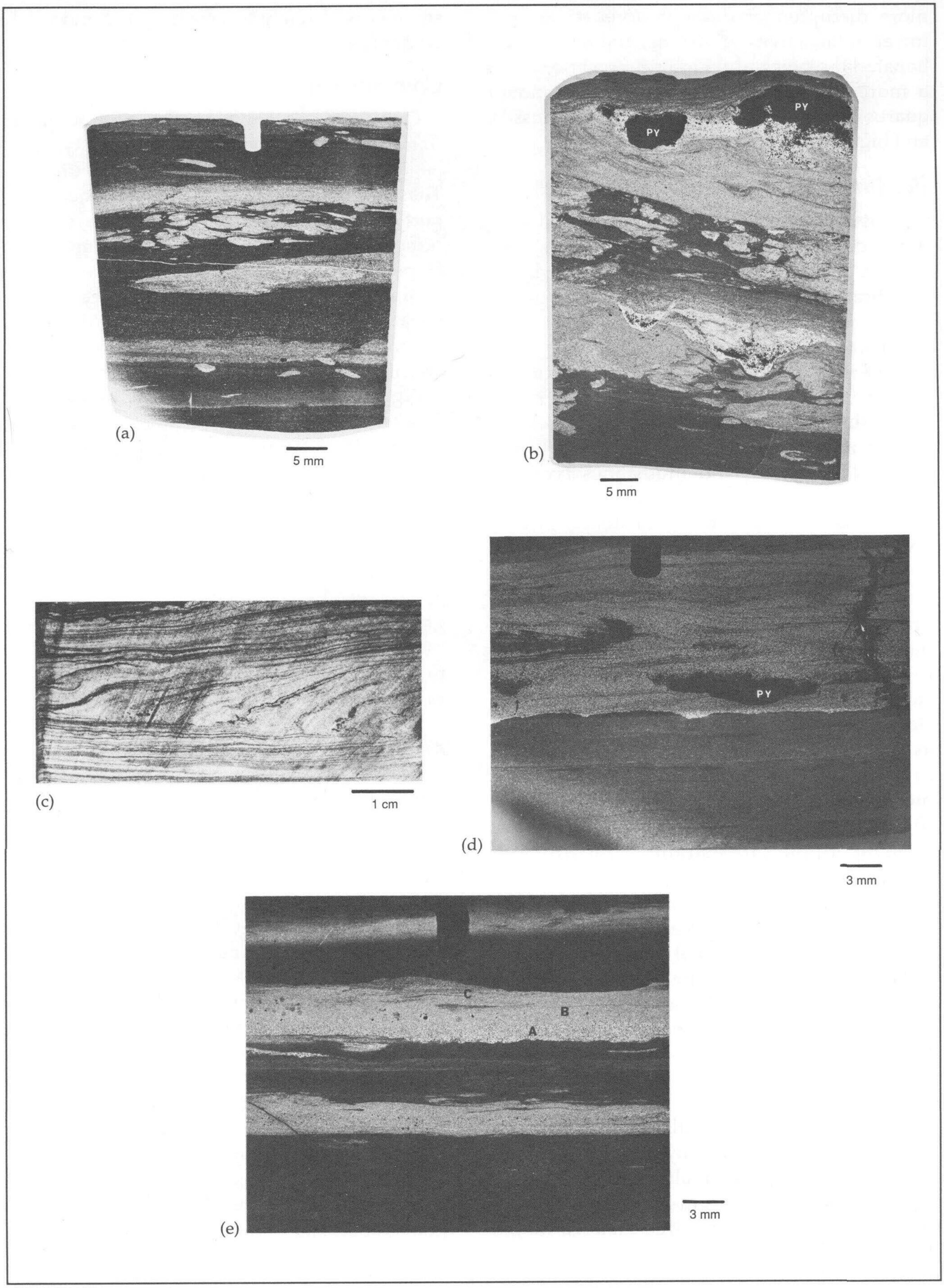
Quartz and dolomite are the most abundant framework grains in siltstone, and they typically have the same grain-size distribution (fig. 5h). They are commonly present in subequal proportions and are mixed with a variety of other components so that neither constitutes more than 50 percent of the rock. Dolomite is mostly subhedral or anhedral, and such grains commonly have an abraded appearance (fig. 5h). Euhedral grains were found locally, but many have anhedral or subhedral cores rimmed by euhedral overgrowths. In most siltstones, dolomite forms an interlocking mosaic with quartz, yet dolomite is rarely poikilotopic, even in dolomite grainstones. Locally, poikilotopic patches of dolomite cement a few angular silt-sized grains.

Other silt-sized constituents are pyrite, mica, feldspar, glauconite, phosphatic debris, and rare zircon and tourmaline. Pyrite is common and appears as nodules, euhedral crystals, irregular grains, aggregates, and framboids. In some beds, pyrite has subhedral and anhedral shapes similar to those of quartz and dolomite (fig. 5f, h) and may be reworked.

Mica (muscovite) was observed in all quartz-dominated siltstones and most dolomite-dominated siltstones; however, it is rare in carbonate mudstones and grainstones. Feldspar (microcline) is a minor component mostly in quartz-dominated siltstone. Both mica and feldspar are more abundant in the Northwestern Shelf and northern Midland Basin (app. B and C; C5, C11) where they occur along with minor amounts of the ultrastable silicates zircon and tourmaline.

One or two grains of glauconite were seen in many samples, but glauconite is concentrated only locally at the top of the formation (app. B; C10, C13). Many core samples contained minor amounts of phosphatic debris, mostly conodonts and fish debris.

Illite and organic matter compose the fine fraction of siltstones, and in some samples the clay constitutes almost 50 percent of the rock. Illite is abundant in wispy laminae, in the upper part of graded layers, and in gradational shaly


PY
PY
(a)
5 mm
(b)
5 mm
PY
(c)
1 cm
(d)
3 mm
C
B
A
(e)
3 mm

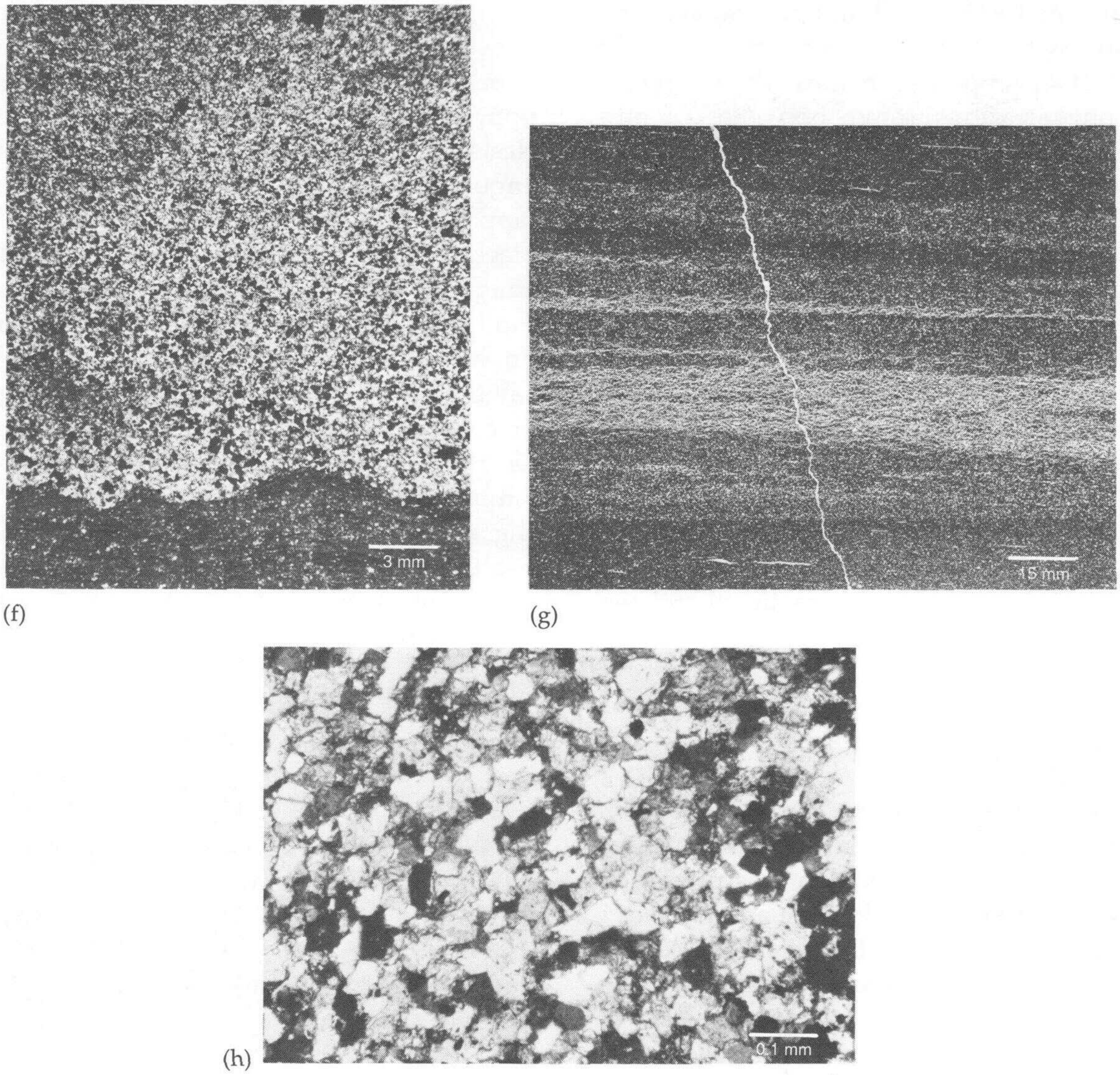


FIGURE 5. Photos of Woodford siltstone. (a) Burrowed quartz-dominated siltstones and interlaminated shale in No. 1 Walker at 11,681 ft (app. B; C5, sample C5-12). Mean TOC of interlaminated interval = 0.2 wt %. (b) Quartz-dominated siltstone in No. 1 Williamson at 13,064 ft (app. B; C11, sample C11-10). Note soft-sediment deformation fabric just below pyrite, PY, nodules. Mean TOC of interlaminated interval = 0.7 wt %. (c) Core chip showing fine-grained dolomite grainstone in No. 1 Federal Elliott at 14,638 ft (app. B; C13, sample C13-6). Contorted laminae record flow shear during rapid deposition in a bottom flow. Dolomite/quartz ratio = 40/1. (d) Very thin dolomite-dominated siltstone bed in No. 1 A. E. State at 13,771 ft (app. B; C3, sample C3-6). Bed contains small-scale climbing ripple cross-laminae and grades into silty shale at top. Dark patches, PY, are pyrite. TOC in underlying shale bed = 2.3 wt %. (e) Dolomite-dominated siltstone laminae in No. 1 A. E. State at 13,768 ft (app. B; C3, sample C3-5). Middle lamina shows Bouma sequence that has graded, A; flat, B; and rippled, C, intervals. Ripple crests are spaced roughly 1.5 cm apart. Mean TOC in shale laminae = 1.6 wt %. (f) Enlarged view of graded interval, A, in photo (e). Silt is a subequal mixture of dolomite, quartz, and pyrite. (g) Dolomite-dominated siltstone laminae in No. 43 Yarborough and Alien at 7,172 ft (app. B; C2, sample C2-3) having indistinct contacts and lacking internal structure. (h) Magnified view of quartz-dominated siltstone shown in photo (b). White and dark-gray grains are quartz, pale-gray grains are dolomite, black grains are pyrite. Note angular and abraded appearance of some dolomite grains. Dolomite/quartz ratio = 0.95/1.0. Crossed nicols.

intervals between black shale and siltstone (fig. 5a, b, d through g).

Organic matter is not abundant, and siltstone cores and outcrops average less than 1 weight percent TOC (app. D). In individual samples TOC concentrations range between 0.1 and 1.1 weight percent (mean = 0.5 ± 0.3 wt % TOC for 20 samples), which roughly corresponds to 0.3 to 3 percent organic matter by volume. The types of organic matter include amorphous particulate material, spores, and wood, but amorphous organic matter greatly predominates in all samples. Spores are rare, and only a few wood fragments were found on bedding planes. Siltstones contain only small amounts of primary vitrinite and no recycled vitrinite (app. D), suggesting that terrigenous source areas had minimal plant cover and few carbonaceous rock exposures. Reflectance values range from 0.8 percent to 1.3 percent and are directly related to present-day burial depth (app. D).

Formation-Boundary Lithologies

Lower Contact

In the Permian Basin, contact between Silurian-Devonian carbonate rocks and the overlying Woodford Formation was preserved in two cores, the No. 1 A. E. State and the No. 1 Walker (app. B; C3, C5). In the No. 1 Walker core, the Woodford disconformably overlies Silurian-Devonian limestone that consists of mottled fine-grained grainstones and brachiopod grainstones (fig. 6a, b) that contain scattered chert lenses and nodules. The upper surface of the limestone is irregular, and locally it is bored. The basal Woodford layer is conglomeratic chert arenite that contains glauconite and phosphatic debris (fig. 6a, b) and is texturally and compositionally similar to the basal chert breccia in the Arbuckle Mountains described by Amsden (1975, 1980). Phosphatic debris includes conodonts, assorted fragments (bone, teeth, fish scales, *Lingula),* aggregates (fecal material), and ooids that exhibit both radial-fibrous and concentric fabric. Basal Woodford chert arenite is unsorted and has no current-induced primary sedimentary structures; thus it appears to be a residual lag produced by dissolution of the underlying cherty limestone. The fossils, glauconite, and phosphatic ooids indicate open-marine conditions and slow sedimentation.

In the No. 1 A. E. State core (from Lea County, New Mexico) brecciated, cavernous limestone is overlain disconformably by black shale. The uppermost 1 ft of limestone contains black shale clasts, and the basal Woodford contains scattered angular fragments of black shale and limestone (app. B; C3). The transition from limestone to black shale is abrupt; however, the contact is irregular and penetrative, and infiltration of mud tens of feet downward into the underlying limestone has occurred. Some of the solution cavities and fissures in the limestone are partly or completely filled by black shale that either has no structure or contains deformed, contorted laminae indicative of soft-sediment deformation (fig. 6c). The shale-filled cavities and fissures at Lea County, New Mexico, are similar to those in Andrews and Terry Counties, Texas, described by Peirce (1962).

Upper Contact

Contact between the Woodford and the overlying Mississippian limestone was preserved in two cores, the No. 1 Brennand and Price and the No. 1 Federal Elliott (app. B; C10, C13). In the No. 1 Brennand and Price, the uppermost Woodford contains articulate brachiopods, trilobite fragments, black shale clasts, dolomite grains, glauconite, and phosphatic debris (fig. 6d). The overlying Mississippian limestones are mostly laminated fine-grained grainstones along with some lime mudstones, sparsely fossiliferous grainstones, wackestones, and packstones. Locally these carbonate lithologies compose thin, graded beds. Chert beds, lenses, and nodules, locally spiculitic, are scattered throughout the Mississippian limestone section. Contact between the black shale and the overlying carbonate rocks is sharp and disconformable (fig. 6d), marking an abrupt change in lithology and fauna.

In the No. 1 Federal Elliott, Mississippian limestone rests conformably on the Woodford. Woodford black shale grades upward through 10 ft of interbedded dark-gray lime mudstone, black siltstone, and black glauconitic sandstone into medium to dark-gray fine-grained Mississippian grainstones and lime mudstones (app. B;

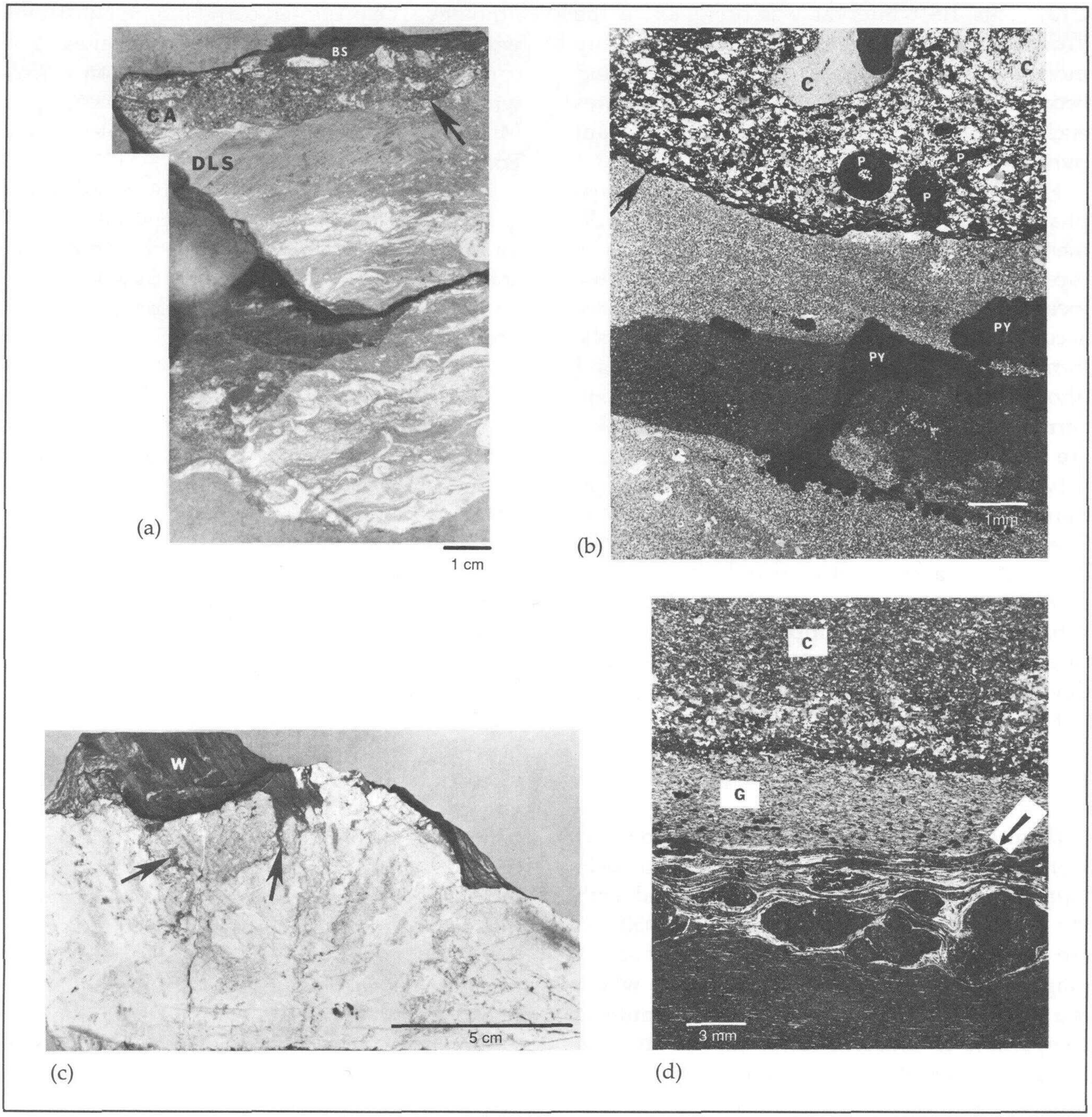


FIGURE 6. Photos of Woodford contacts, (a) Core slab showing lower contact, arrow, in No. 1 Walker at 11,689 ft (app. B; C5, sample C5-14). Silurian-Devonian limestone, DLS, overlain by basal Woodford chert arenite, CA, and black shale, BS, at top of core, (b) Thin-section photomicrograph of area at arrow in (a). Chert, C; pyrite, PY; phosphate, P. Three phosphatic grains from left to right are ooid containing a chert nucleus, aggregate of probable fecal origin, and skeletal fragment. Finer grains are chert (light) and phosphate (black). Below contact is fine-grained grainstone. Crossed nicols. (c) Core chip from 13,850 ft in No. 1 A. E. State (app. B; C3). Woodford black shale, W, in solution cavities in Silurian-Devonian limestone. Contorted laminae in shale and shale penetrating limestone crevices at arrows indicate soft-sediment infiltration of mud into the underlying limestone, (d) Thin-section photomicrograph of Woodford-Mississippian contact, arrow, at 8,459 ft in No. 1 Brennand and Price (app. B; C10, sample C10-1). Upper Woodford consists of brachiopod shells and trilobite carapaces (white ribbonlike material), black shale clasts, and silt-sized grains (white specks) that are mostly dolomite. Fine white streaks in black shale at base are brachiopod and trilobite fragments. Mississippian above contact is fine-grained grainstone, G, and chert bed containing scattered, unreplaced remnants of carbonate, C. Crossed nicols.

C13). This 10-ft interval was assigned to the Woodford Formation because it is markedly more radioactive than the overlying rocks and because it contains diagnostic Woodford features such as varvelike parallel laminae and abundant pyrite.

High concentrations of glauconite and phosphate in sedimentary rocks indicate low sedimentation rates (Odin and Letolle, 1980). The top stratum of the Woodford at these two localities is consequently inferred to have accumulated more slowly than the rest of the formation. Commonly, glauconitic grains and phosphatic ooids and pellets are unbroken, current-induced primary sedimentary structures are absent, and brachiopods possess articulated valves, indicating little or no active sediment transport at the close of Woodford deposition. The abundance of reduced iron, sulfur, and carbon and the absence of oxidized phases document absence of oxidation and imply absence of subaerial exposure. The upper boundary at these two localities thus suggests a submarine hiatus during which sedimentation slowed or ceased but the sea floor did not emerge.

Lithofacies Correlation

Basal siltstone in Woodford cores from the Northwestern Shelf and northern Midland Basin (app. B; C5, C9, C11) is herein correlated with the lower Woodford unit of Ellison (1950) on the basis of lithology, radioactivity, and stratigraphic position (fig. 7). Basal siltstone, which is a hybrid of silt-sized quartz and dolomite, is comparable to Ellison's lower unit in its high carbonate content and low radioactivity. Unfortunately, Ellison's cores were discarded, and direct comparison of lithologies was impossible. In the subsurface, both the lower unit and the basal siltstone immediately overlie the regional unconformity.

Stratigraphic position and lithology also suggest correlation of basal Woodford siltstone with the upper Middle to lower Upper Devonian Onate Formation in southeastern New Mexico. Both units rest on the regional unconformity surface and comprise a stratigraphic succession of interbedded siltstone, carbonate, and shale in which dolomitic siltstone is the dominant lithology. The proposed correlation is consistent with that by Wright (1979), who suggested a correlation of the lower unit of Ellison (1950) with the Ives Breccia Member of the upper Middle Devonian to Lower Mississippian Houy Formation in Central Texas.

Basal siltstone also occupies the same stratigraphic position above the regional unconformity as the Canutillo Formation in West Texas and the Misener and Sylamore Sandstones in Oklahoma and Arkansas. These formally named units are mostly late Middle to early Late Devonian in age and are locally as young as Early Mississippian. Although the units are diachronous across the southern Midcontinent (Amsden and others, 1967; Freeman and Schumacher, 1969; Rosado, 1970; Amsden and Klapper, 1972; Amsden, 1975), they are at least partly correlative.

The black shale lithofacies is correlated with the middle and upper Woodford units of Ellison (1950) also on the basis of lithology, radioactivity, and stratigraphic position (fig. 7). Ellison's middle and upper units are not described as separate lithofacies in this report because striking, lithologic differences between them are absent in cores (app. B; C1, C6). Although both units are pyritic black shale exhibiting parallel laminae, the middle unit is more radioactive (Ellison, 1950); hence, the middle and upper units can be mapped using gamma-ray logs (fig. 7; pls. 3 through 7). Wright (1979) correlated the middle unit with the Doublehorn Shale Member and the upper unit with the unnamed phosphatic member of the Houy Formation in Central Texas, thereby implying that the upper unit is partly Kinderhookian. Wright's correlation seems reasonable because the middle unit in both formations has higher radioactivity and more spores than does the upper unit (Ellison, 1950; Cloud and others, 1957).

Well log correlations (pls. 3 through 7) show that complete Woodford intervals containing all three units of Ellison (1950) are common only in the Midland, Delaware, and Val Verde Basins (pl. 3, A–A´, wells 4, 9; pl. 4, B–B´, well 5; pl. 5, C–C´, wells 2 through 6, 9, 10; pl. 6, D–D´, wells 9 through 12; pls. 7, E–E´, wells 10, 11, 16, 17). Elsewhere Woodford sections are incomplete mostly because of the absence of the lower or

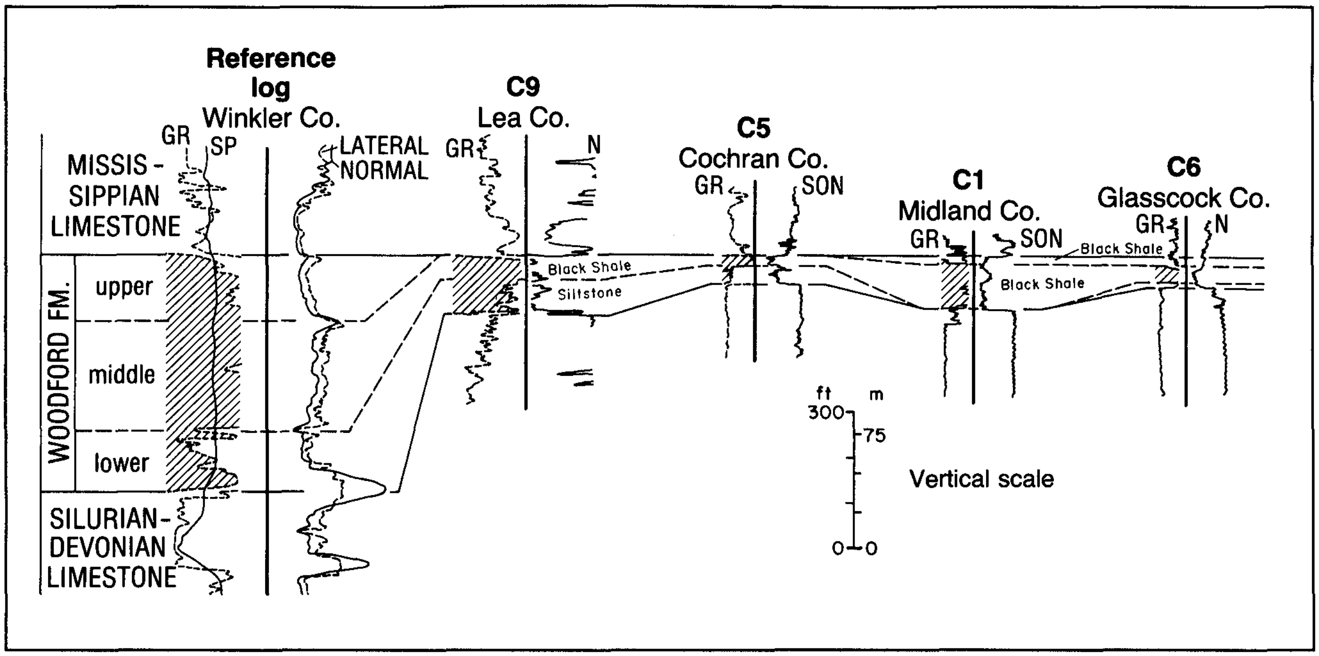


FIGURE 7. Log correlation of Woodford lithofacies. Reference log from Ellison (1950). Datum is top of Woodford. For detailed core descriptions see appendix B (Cl, C5, C6, C9).

upper units. The lower unit gradually pinches out and is overstepped by the middle unit along the basin flanks (pls. 3 through 7), indicating depositional onlap. Lines of section showing onlap include (1) from the Midland Basin toward the Eastern Shelf (pl. 3, A–A´, wells 9 through 13; pl. 4, B–B´, wells 11 through 15; pl. 5, C–C´, wells 9 through 12), (2) from the Midland Basin onto the Pecos Arch (pl. 7, E–E´, wells 11 through 14), (3) westward from the Delaware Basin toward the Diablo Platform (pl. 4, B–B´, wells 1 through 3; pl. 5, C–C´, wells 1, 2), and (4) in the western Midland Basin (pl. 4, B–B´, well 10). Many sections in which the upper unit is absent are overlain by Mississippian limestone, indicating nondeposition or erosional truncation that occurred after Woodford deposition but before Mississippian limestone deposition. Sections showing truncation include (1) along the eastern margin of the Central Basin Platform (pl. 3, A–A´, well 8; pl. 4, B–B´, well 9), (2) in the northern and central Midland Basin (pl. 7, E–E´, wells 7, 8, 11), and (3) on the Northwestern Shelf (app. B; C5, C9). Most of the lines of section that show onlap also show evidence of increased truncation of the Woodford in the direction of onlap, suggesting that these were the last flooded and first exposed areas during the Late Devonian transgression and latest Devonian regression. The patterns of onlap and truncation (pls. 3 through 7) indicate that all of the structural provinces shown in figure 1a had topographic expression in the Late Devonian. Onlap in the western Midland Basin supports the observation of Galley (1958) that a middle Paleozoic precursor of the Central Basin Platform lay slightly to the east of the present-day structure.

Lithofacies Distribution

Correlations shown in the cross sections (pls. 3 through 7) and the Woodford lithofacies distribution shown in a fence diagram (fig. 8) reveal that black shale is nearly ubiquitous and the most widely distributed lithofacies. Siltstone is more common in the northern part of the study area and in basinal depocenters. Silt-sized quartz is more abundant in northern and eastern areas, and silt-sized dolomite is more abundant in the far western outcrop belt and along the Central Basin Platform. Log correlations indicate that basal siltstone is areally restricted to deep parts of the Delaware, Midland, and Val Verde Basins, proximal areas on the Northwestern Shelf, and a few localities on the Central Basin Platform (pl. 3, A–A´, wells 3 through 10; pl. 4, B–B´, wells

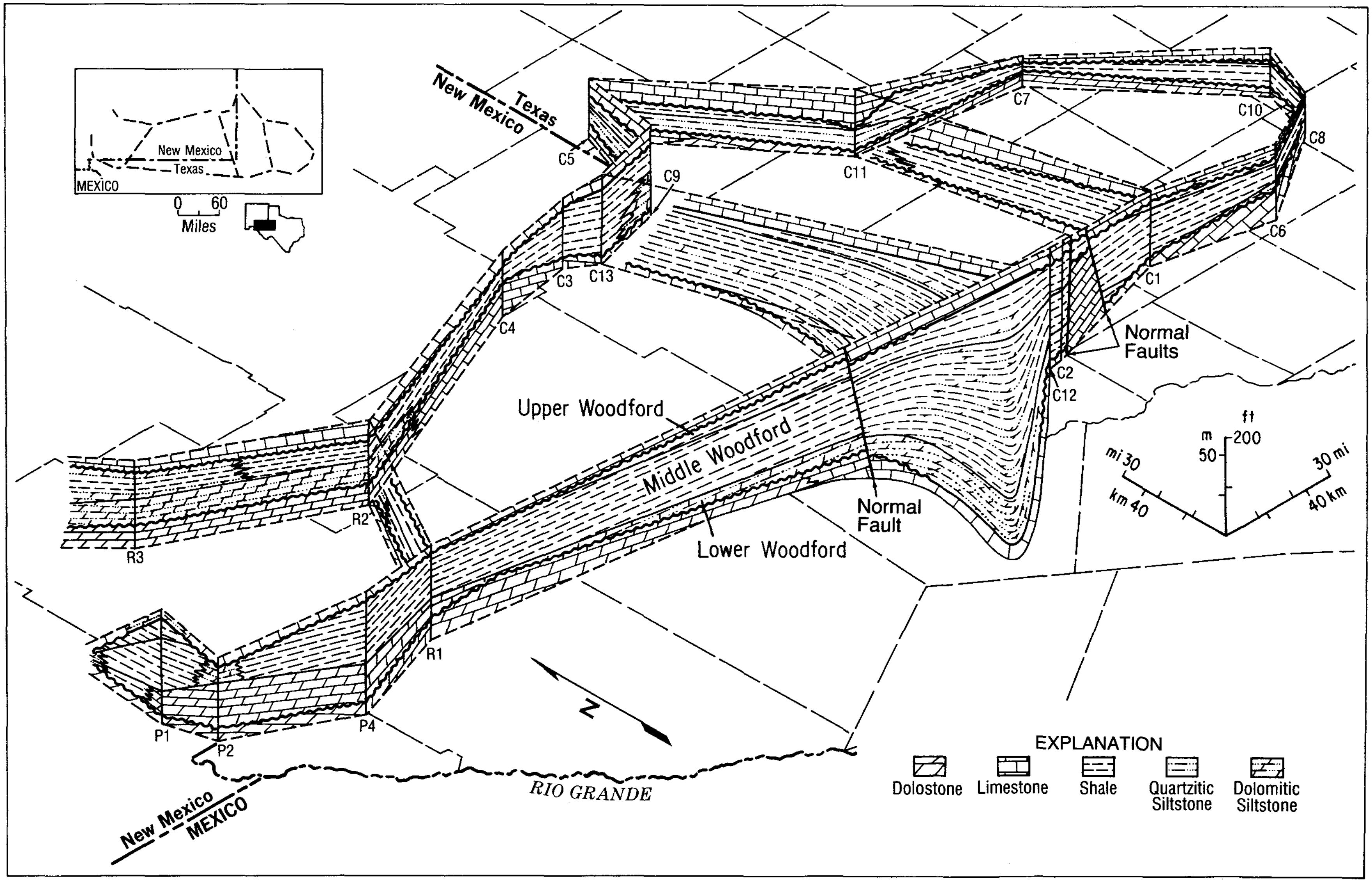


FIGURE 8. Fence diagram of Upper Devonian units. Correlation from outcrop to subsurface from Rosado (1970). Datum is top of Woodford. Locality numbers refer to map symbols in appendix A.

2 through 5, 7, 9, 11, 12; pl. 5, C–C′, wells 2 through 6, 9, 10; pl. 6, D–D′, wells 6 through 12; pl. *7,* E–E′, wells 7, 8, 10, 11, 16, 17).

Facies changes between black shale and siltstone appear in many parts of the study area (fig. 8; pls. 3 through 7). Siltstone beds common throughout the Sly Gap Formation in southeastern New Mexico correlate with black shale in the Percha and Woodford Formations to the south and east (Laudon and Bowsher, 1949; Ellison, 1950; Rosado, 1970). Dolomitic siltstones of the Onate Formation in New Mexico also correlate with dolostone and cherty dolostone beds of the Canutillo Formation in West Texas and with black shales in the Percha and Woodford Formations (King and others, 1945; Rosado, 1970). On the Northwestern Shelf, siltstone is the basal unit of the Woodford at some localities (app. B; C5, C9), but it is higher in the section at others (app. B; C3, C13). In the Delaware and Val Verde Basins, siltstone beds appear to be common throughout the formation, as indicated by the generally reduced radioactivity and the highly erratic nature of the gamma-ray log patterns shown in plates 5 through 7 (pl. 5, C–C′, logs 4, 6; pl. 6, D–D′, logs 9 through 13; pl. 7, E–E′, logs 16, 17).

Depositional Processes

Siltstone

Many of the siltstone strata and siltstone-shale couplets in the Woodford Formation (fig. 5a through f) closely resemble the silt and mud turbidites described by Piper (1978) and Stow and Piper (1984) and the distal storm deposits described by Aigner (1982, 1984). In the Woodford, these strata range from laminae less than 2 mm thick to beds rarely more than 10 to 15 cm thick. They commonly contain graded layers (fig. 5a, d through f), climbing ripple cross-stratification (fig. 5d), horizontal stratification, fading (incipient) ripple forms (fig. 5e), flow-sheared laminae (fig. 5c), and laminae contorted by soft-sediment failure (fig. 5b). Many of these strata are partial or complete Bouma sequences that have scoured bases, normally graded sequences, and a vertical succession of primary sedimentary structures that indicate rapid deposition from a waning current during a single event.

Both fine-grained turbidites and distal storm deposits described in the literature have similar thicknesses and sedimentary structures (Piper, 1978; Aigner, 1982, 1984; Stanley, 1983; Stow and Piper, 1984; Schieber, 1987; Davis and others, 1989). Mud turbidites in the deep ocean consist of the division E mud of Bouma (1962), which Piper (1978) subdivided into laminated, graded, and ungraded units. The vertical pattern and the contained sedimentary structures, such as grading and low-amplitude climbing ripples, are diagnostic of turbidite origin (Stow and Piper, 1984). Silt turbidites are silt-dominated sequences that exhibit the same suite of sedimentary structures and the same divisions (Bouma A through F) as classical sandy turbidites (Stow and Piper, 1984). The siltstone and shale layers in the Woodford Formation (fig. 5a through f) differ from silt and mud turbidites described in the literature (for example, Piper, 1978; Stanley, 1983; Stow and Piper, 1984) only in the scarcity of bioturbation in the shale that is common at the top of the turbidite sequence (Bouma division E mud and division F pelagite). This difference indicates that anoxic bottom conditions toxic to benthic organisms prevailed throughout the basin during deposition of the shale laminae.

Sedimentary processes related to storms, such as wind-forced currents (Morton, 1981), ebb currents produced by storm surge setup (Nelson, 1982), and seaward-flowing currents caused by coastal downwelling (Swift and others, 1983), deposit sediment that has textures and structures virtually identical to those of turbidites. Distal storm deposits characteristically are fine grained, thinly stratified, and normally graded, having scoured bases and Bouma sequences (Aigner, 1982). They differ from proximal equivalents in grain size and layer thickness and in their having no hummocky stratification or oscillatory ripples, both of which, when present, indicate deposition under combined flow conditions above wave base (Aigner, 1982). Whether storms produce turbidity currents is debatable, but it is clear that storms generate bottom currents that transport large quantities of sediment (Hayes, 1967; Morton, 1981, 1988; Nelson, 1982; Walker, 1984, 1985). Storm-generated bottom flows and turbidity currents may represent end members of a single process if, as suggested by

Walker (1984, 1985), distal storm currents passing below wave base become turbidity currents. Such a subtle change in the transport mechanism may explain the present difficulty in distinguishing fine-grained turbidites from storm deposits in the stratigraphic record. Whether the siltstones and siltstone-shale couplets in the Woodford Formation are turbidites or storm deposits is likewise problematic, but the presence of grading and partial or complete Bouma sequences indicates deposition from bottom flows.

Black Shale

Most layers in the black shale lithofacies (fig. 4a through h) do not have grading or Bouma divisions as do beds in the siltstone. Black shale that displays undisturbed parallel laminae typically contains higher concentrations of marine organic matter, less clastic material, and more planktonic microfossils (for example, radiolarians, spores, conodonts) than do the Bouma E and F shales of the siltstone-shale couplets (fig. 5a through f). Shale displaying parallel laminae constitutes the bulk of the Woodford black shale lithofacies and is mostly pelagic in origin.

Origin of the thin varvelike siltstone and shale laminae in pelagic black shale (fig. 4a, b, e) is less certain. These laminae may represent mud turbidites or storm layers too small or far from the source to produce grading and recognizable Bouma divisions, or they may represent episodic fallout from the pycnocline. Pierce (1976), Maldonado and Stanley (1978), and Stanley (1983) described detachment of low-concentration turbidity plumes and entrainment of the muddy water along the isopycnals in strongly density stratified water columns. Episodic fallout of material (for example, terrigenous silt and planktonic tests) occurs as particle concentration builds up and exceeds the density of the pycnocline, producing a relatively clean, well-sorted, structureless lamina of widespread areal extent. Similar laminae are common in muddy marine sediments, such as those found in the eastern Mediterranean Sea near the Nile delta (Maldonado and Stanley, 1978; Stanley, 1983). Sediment deposition by this process seems likely during Woodford accumulation because of the exclusively fine grained texture of the rocks and because of the strong density stratification that existed within the basin. Water-density stratification is an inherent property of the sea and, judging from the scarcity of bioturbation and its implicit link with bottom stagnation and anoxia (Byers, 1977; Arthur and Natland, 1979; Demaison and Moore, 1980; Leggett, 1980; Ettenshon and Barron, 1981; Stanley, 1983; Pratt, 1984; Ettensohn and Elam, 1985; Stein, 1986; Davis and others, 1989) strong density stratification probably occurred during Woodford black shale deposition. (See also Paleoceanography, p. 33.) In this context, the relative abundances of benthic fossils, trace fossils, and undisturbed parallel laminae in the Woodford (figs. 4a through h, 5a through h) indicate that the black shale and siltstone lithofacies represent anaerobic and dysaerobic biofacies, respectively (Rhoads and Morse, 1971; Byers, 1977).

Lithologic Patterns and Origin of Sediments

The Woodford Formation consists of varying proportions of terrigenous, pelagic, and authigenic constituents (app. C), and textural and compositional evidence indicates much resedimentation within the basin. Terrigenous material includes fine-grained quartz, muscovite, microcline feldspar, illite, wood and leaf fragments, vitrinite, and the trace heavy minerals (zircon and tourmaline). The silt-sized silicate minerals are most common in the northern basin. Locally, in rocks from the Northwestern Shelf, coarse-grained mica flakes glitter on fresh bedding surfaces (app. B; C4, C5), and the silt-sized fraction is subarkosic (app. C). The distribution and texture of these minerals indicate that the principal source was the land north of the basin, the Pedernal Massif and northern Concho Arch (fig. 1b).

Siltstone depocenters lie in the northern, central, southern, and westernmost parts of the basin (fig. 9a) in areas coincident with the modern-day Northwestern Shelf, the deepest parts of the Delaware, Val Verde, and Midland Basins, and the Sacramento Mountains. The patchy distribution of these depocenters suggests that sediment

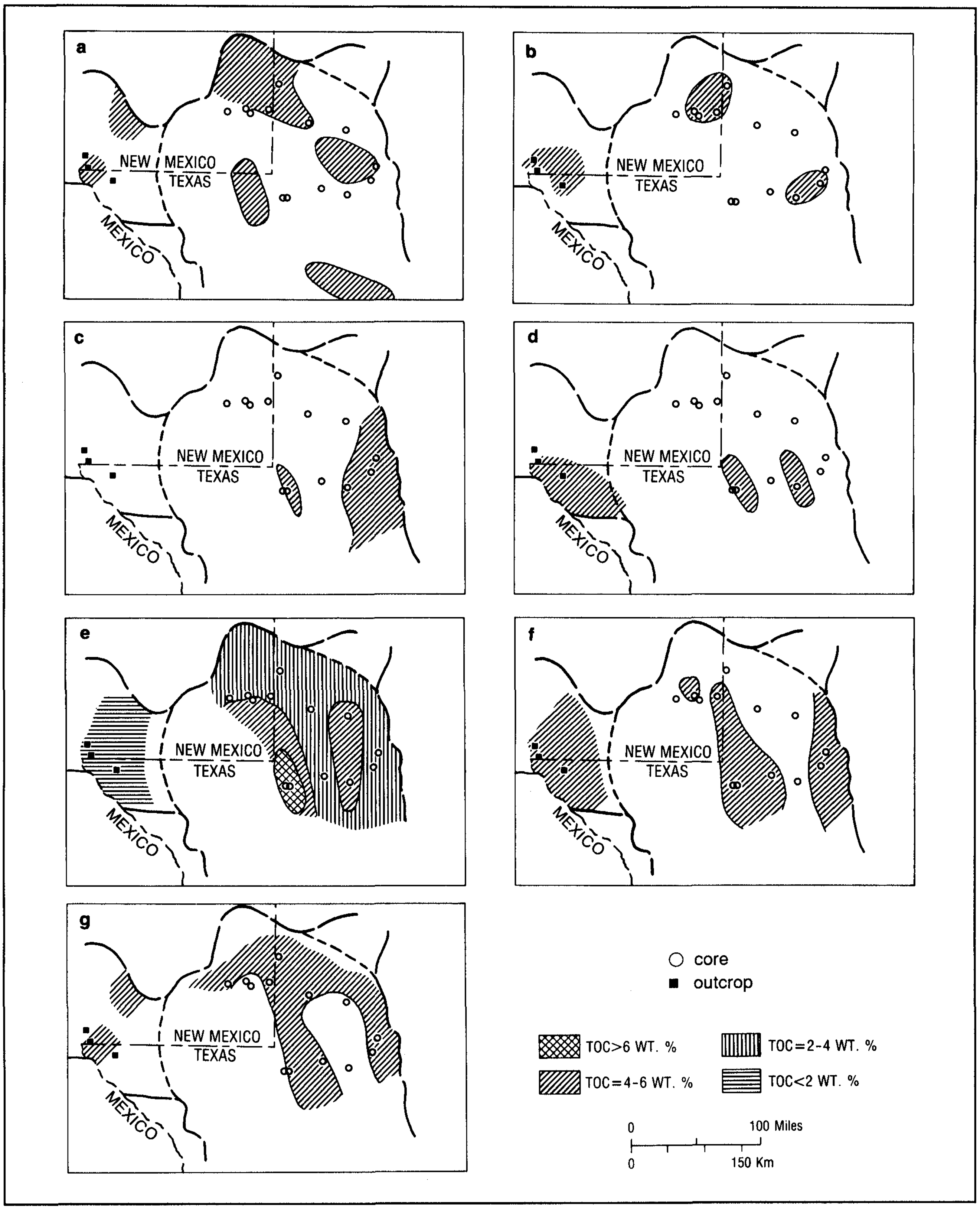


FIGURE 9. Regional lithologic variations in Upper Devonian rocks in West Texas and southeastern New Mexico. Maps show Late Devonian shoreline and limit of Tobosa Basin depocenter (fig. Ib). (a) Siltstone depocenters, (b) Illite depocenters, (c) Recycled vitrinite depocenters, (d) Radiolarian chert depocenters, (e) TOC concentration in black shale, (f) Depocenters of silt-sized dolomite where dolomite/quartz ratio is greater than 1. (g) Depocenters of dysaerobic, shallow-water sedimentary structures.

bypassing was common as silt and mud moved from siliciclastic source areas downslope into the basin. This inference is consistent with the interpretation that most silt was deposited from bottom flows, a mechanism sensitive to bottom irregularities and channelization.

The most abundant terrigenous component in the Woodford is illite (app. C). Detrital illite has an apparent Rb-Sr source age of 540 m.y., an age uncommon in North American basement rocks but common in regionally metamorphosed rocks found in large areas of Africa and South America (Morton, 1985). The source age and the good fit to the isochron for data from widely different localities in West and Central Texas are cited as evidence that illite came from a southern (Gondwana) source or was thoroughly mixed during transport from multiple sources (Morton, 1985). In the present study, the highest concentrations of illite (>60%) were found in northern, southeastern, and westernmost regions (fig. 9b) in the present-day Northwestern and Eastern Shelves, Midland Basin, and western outcrop belt. The wide distribution of illite depocenters and their proximity to northern siltstone depocenters and siliciclastic source areas suggest that illite came from multiple sources on the Pedernal Massif and Concho Arch (fig. 9b). The broad extent of the exposed land implies that it derived from diverse stratigraphic levels. Although contribution from a Gondwana source cannot be ruled out because of the absence of control in the southern part of the basin, a mixed provenance for illite seems most likely.

Trace amounts of vitrinite are ubiquitous, documenting a small contribution of land plant debris to all parts of the basin. Recycled vitrinite was found only in the eastern and central parts of the basin (fig. 9c) in black shale from the Central Basin Platform, southern Midland Basin, and Eastern Shelf (app. D), indicating that these areas were close to emergent land that displayed eroding bedrock. A few wood and leaf impressions were found mostly in northern and eastern parts of the basin in rocks from the Northwestern and Eastern Shelves (app. B; C4, C7, C13). Their distribution implies that land areas on the Pedernal Massif and Concho Arch supported most of the terrestrial plant life in the study area during the Late Devonian. Abundances of vitrinite and land plant remains are low, however, even in the siltstones, indicating that terrestrial source areas were only sparsely vegetated.

Pelagic constituents include radiolarians, amorphous particulate organic matter, algal spores, conodonts, fish fragments, and associated fecal material. Radiolarian chert is most common in the central and eastern parts of the basin (fig. 9d) at localities on the present-day Central Basin Platform and in the southeastern Midland Basin (app. B; C2, C6). Chert is also abundant in the Canutillo Formation in West Texas (King and others, 1945; Rosado, 1970). Anomalously high biogenic silica is perhaps the best indication of nutrient-rich water upwelling in ancient seas (Parrish and Barron, 1986; Hein and Parrish, 1987) and suggests that upwelling occurred in the basin and was most pronounced in central and western areas. Intrabasinal upwelling is a likely consequence of the major oceanic upwelling that occurred adjacent to the study area along the margin of the North American craton during the Late Devonian. This upwelling episode is recorded as extensive Upper Devonian novaculite beds of biogenic origin in the Ouachita allochthon (Park and Croneis, 1969; Lowe, 1975; Parrish, 1982).

Volumetrically, amorphous organic matter (AOM), which accounts for nearly all of the TOC, is the most abundant pelagic constituent in the Woodford (app. C). The highest TOC concentrations (>6 wt %) are found in the center of the basin on the modern-day Central Basin Platform (fig. 9e). Somewhat lower TOC values (4 to 6 wt %) are found to the east and north in areas coincident with parts of the western and eastern Midland Basin, southern Northwestern Shelf, and western margin of the Eastern Shelf (fig. 9e). Localities that have the highest TOC concentrations also have the most radiolarian chert, suggesting that high TOC values record increased biologic productivity at sites of intrabasinal upwelling. The area that has the highest TOC's (fig. 9e) is surrounded by siltstone depocenters (fig. 9a), supporting the inference that it was bypassed by siliciclastic sediment.

Authigenic material includes dolomite, pyrite, secondary silica, glauconite, anhydrite, calcite, and phosphatic ooids. Some cored intervals on the Central Basin Platform and Northwestern Shelf (app. B; C2, C3) contain abundant pristine, euhedral dolomite rhombs floating in organic-rich black shale. The texture and association are similar to those observed in Deep Sea Drilling Project (DSDP) cores and in very young sediments in the Gulf of California (Baker and Kastner, 1981), suggesting that the rhombs are authigenic and formed in situ. Most of the dolomite in the Woodford, however, appears to be resedimented because it contains abraded anhedral and subhedral silt-sized grains and commonly appears randomly mixed with quartz in graded layers and Bouma sequences (fig. 5e, f, h). Derivation from ancient dolomitic rocks is not indicated. The poor durability of dolomite precludes long-distance subaerial transportation. Moreover, dolomite in the Woodford is typically monocrystalline and monotonously uniform in texture, whereas in older Paleozoic rocks, dolomite texture is quite variable. One would expect to see dolomitic rock fragments and a greater variety of textures if Woodford dolomite were terrigenous detritus.

If most of the dolomite in the Woodford is resedimented but not terrigenous in origin, then it must be penecontemporaneous. Early formation of dolomite in marine sediment is promoted by hypersaline brine (Zenger, 1972) and by low concentrations of dissolved sulfate that develop in organic-rich sediments as the result of microbial sulfate reduction (Baker and Kastner, 1981). Given the abundance of organic matter and the presence of anhydrite in the Woodford, both are plausible mechanisms for contemporaneous dolomitization in the Permian Basin during the Late Devonian.

Areas that have a high ratio of dolomite to quartz (fig. 9f) are found in the central, northern, eastern, and westernmost parts of the basin, suggesting that these were the areas of highest carbonate production. The highest dolomite/quartz ratio is in the center of the basin (app. C; C2) where very little detrital quartz is found, and the quartz typically is much finer grained than dolomite. This observation is further evidence that the basin center, which coincides with the modern-day Central Basin Platform, was bypassed by siliciclastic detritus.

Secondary silica is a common cement in primary sedimentary structures, such as burrows and syneresis cracks, where it is associated locally with calcite and anhydrite. Burrows and syneresis cracks are abundant in the northern, central, and eastern basin (fig. 9g) in areas that were onlapped by Woodford sediments (for example, the Northwestern and Eastern Shelves, Central Basin Platform, and western Midland Basin). They are less abundant or absent in cores farther east in the Midland Basin. The distribution and association with anhydrite suggest that these structures are shallow-water indicators formed under dysaerobic conditions above the anoxic zone.

Benthic components are scarce and include trilobite fragments, brachiopods, and biogenic pellets. Some of the pellets in siltstone and others associated with scattered trilobite fragments in shale may be fecal material from a sparse benthos. However, many are found in black shale that has parallel laminae and has no burrows or benthic fossils, suggesting that they originated in the upper water column amid a thriving, normal marine biota. Most benthic fossils are found in the shelf regions, but biogenic pellets are also common in rocks from the Central Basin Platform (app. C; C2, C12).

Depositional Setting

Paleogeography

Late Devonian paleogeography of the study area (fig. 10) was inferred from the patterns of onlap (pls. 3 through 7) and lithology (fig. 9) described earlier. The widespread, blanketlike distribution and nearly uniform lithology of the Woodford indicate that the entire region was one of low relief during the Late Devonian. Major topographic features in the model include (1) the land in the north and northwest representing the Pedernal Massif and Concho Arch, (2) the ancestral Delaware and Val Verde Basins, (3) the shallow Midland Basin, (4) an intrabasinal archipelago representing the ancestral Central Basin Platform and Pecos Arch, (5) shallow shelf regions to the north and east representing the ancestral Northwestern and Eastern Shelves, (6) a western shelf that had irregular channels and shoals representing parts of the Northwestern Shelf and Diablo Platform, and (7) a land mass to the southwest representing the southern part of the Diablo Platform (fig. 10).

The Pedernal Massif and northern Concho Arch represent the southern end of the Transcontinental Arch, which was the dominant topographic high in the western North American craton during the Late Devonian (Poole and others, 1967; Poole, 1974; Heckel and Witzke, 1979). Grain size and composition of Woodford siltstones indicate that this arch supplied most of the terrigenous sediment to the basin and consequently must have had the highest elevations in the study area. The absence of deltas and coarse clastic wedges, however, indicates that elevations were not high enough to create an orographic barrier to winds or to introduce major rainfall, runoff, and clastic influx into the basin.

The Northwestern and Eastern Shelves and the Diablo Platform are onlapped by Woodford

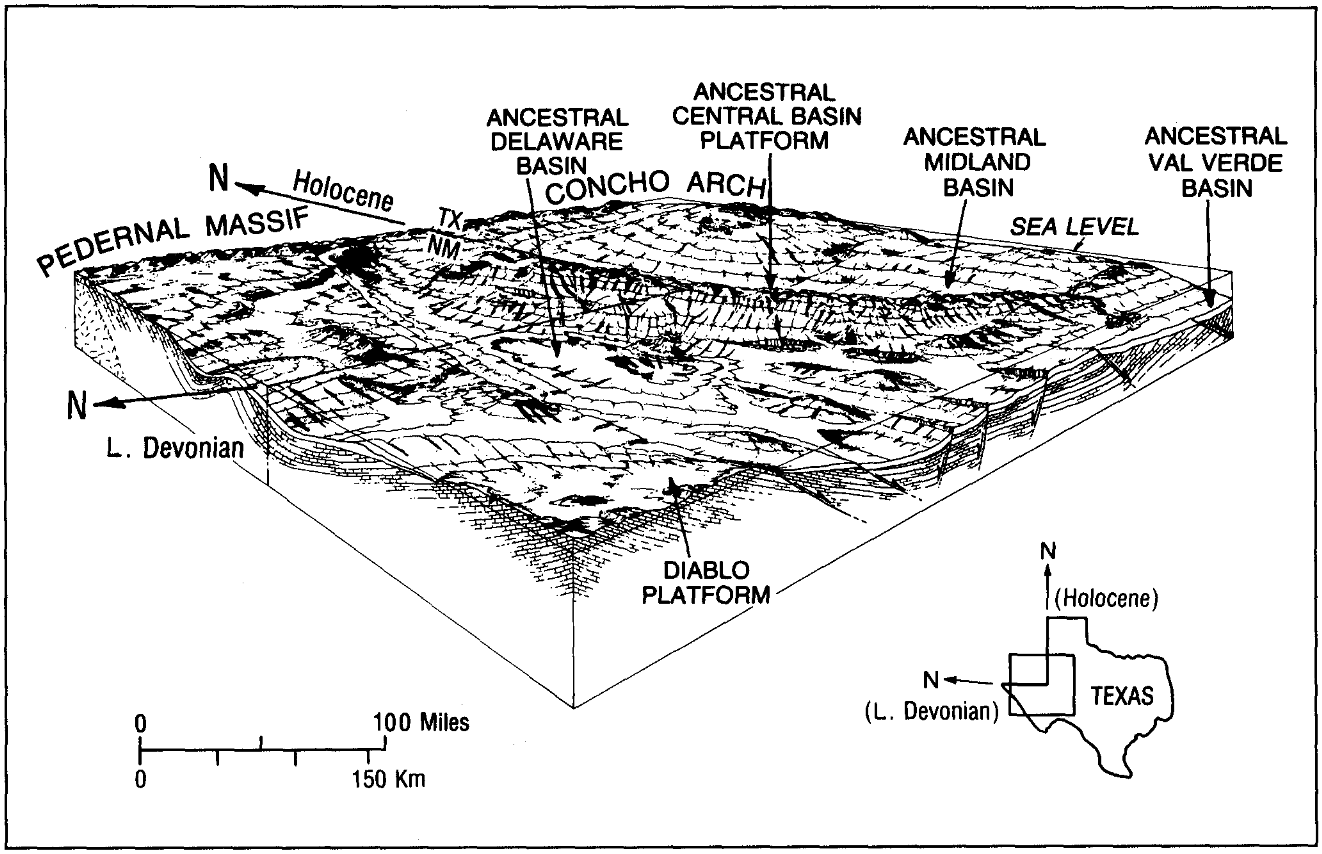


FIGURE 10. Late Devonian paleogeography of West Texas and southeastern New Mexico.

sediment (pls. 3 through *7),* indicating that they were low-relief expanses of intermediate elevation, and that during the Late Devonian transgression they became shallow-water shelf environments that had local channels, scattered islands, and protected shoals. The westernmost outcrop belt is characterized by complex facies changes (Stevenson, 1945; Laudon and Bowsher, 1949; Rosado, 1970), indicating that it comprised an extensive, low-relief cratonic shelf that had prominent shoals and channels (Rosado, 1970). The southern Diablo Platform may have remained emergent, but it was not a major source of terrigenous sediment (Wright, 1979).

The deepest parts of the Late Devonian epeiric sea coincided with the deepest parts of the present-day Delaware and Val Verde Basins (fig. 10), where the thickest and most complete Woodford sections are found (pls. 3 through 7). Gradual changes in well log signatures at formation boundaries in these depocenters suggest that the Woodford may be conformable with the bounding formations (pl. 5, C–C´, wells 4, 6; pl. 6, D–D´, wells 10, 11, 13; pl. 7, E–E´, wells 16, 17). That the Midland Basin was a topographic depression (fig. 10) is supported by the following evidence: (1) the Woodford thickens and contains all three units toward the basin axis and (2) the Woodford generally has no bottom features (such as anhydrite-bearing burrows and syneresis cracks), that would indicate elevations above the anoxic and sulfate-reducing zones.

The ancestral Central Basin Platform and Pecos Arch are shown as a continuous intrabasinal archipelago (fig. 10). Whether the two actually connected is unknown, but the onlap of both structures by the Woodford indicates that both were topographically high during the Late Devonian. Lithologic patterns (fig. 9) indicate that the Central Basin Platform was bypassed by terrigenous sediment, and stratigraphic onlap indicates that bypassing occurred because the platform was elevated above the surrounding provinces. The abundance of dysaerobic primary sedimentary structures on the platform (fig. 9g) suggests a shallow-water setting and supports this conclusion. Folk (1959) inferred the presence of an island chain along the platform during the Early Ordovician on the basis of the abundance of feldspar in the Ellenburger Formation. Similarly, the presence of recycled vitrinite in the black shale lithofacies (fig. 9c) indicates that eroding bedrock existed nearby and that scattered islands lay along the platform during Late Devonian eustatic highstand.

Paleotectonics

Ellison (1950) recognized anomalously thin but complete Woodford intervals on structural highs along the Central Basin Platform and interpreted them as evidence of contemporaneous uplift during Woodford deposition. Pre-Mississippian truncation of the Woodford along the ancestral Central Basin Platform (for example, pl. 4, well 9) and on the Northwestern Shelf (app. B; C5, C9), where the lower unit is well developed and the upper unit is absent, is further evidence of contemporaneous uplift in these areas. Vertical tectonic adjustments in the Late Devonian most likely reflect reactivation of basement structures because truncated sections are found along zones of weakness in the basement and near the major Paleozoic fault systems (pls. 1, 2) that formed along reactivated basement faults (Walper, 1977; Muehlberger, 1980; Hills, 1984). In figure 10, contemporaneous vertical movements are illustrated by the schematic representations of normal faults in the Delaware and Val Verde Basins. These faults represent the dominant Paleozoic faults shown in plates 1 and 2.

Epeirogeny in the southern Midcontinent probably was linked to renewed tectonism along the continental margins. The Acadian orogeny produced highlands (fig. 11) that shed coarse terrigenous elastics toward the craton to form the Catskill delta (Ettensohn and Barron, 1981; Faill, 1985; Ettensohn, 1987). The Antler orogeny also produced a rising highland (fig. 11) that shed coarse elastics into a subsiding foreland basin (Poole and others, 1967; Poole, 1974). Forces transmitted from the Antler erogenic belt have been correlated with minor faulting, uplift, and subsidence in New Mexico (Poole and others, 1967) and are inferred to account for Late Devonian epeirogeny in the study area.

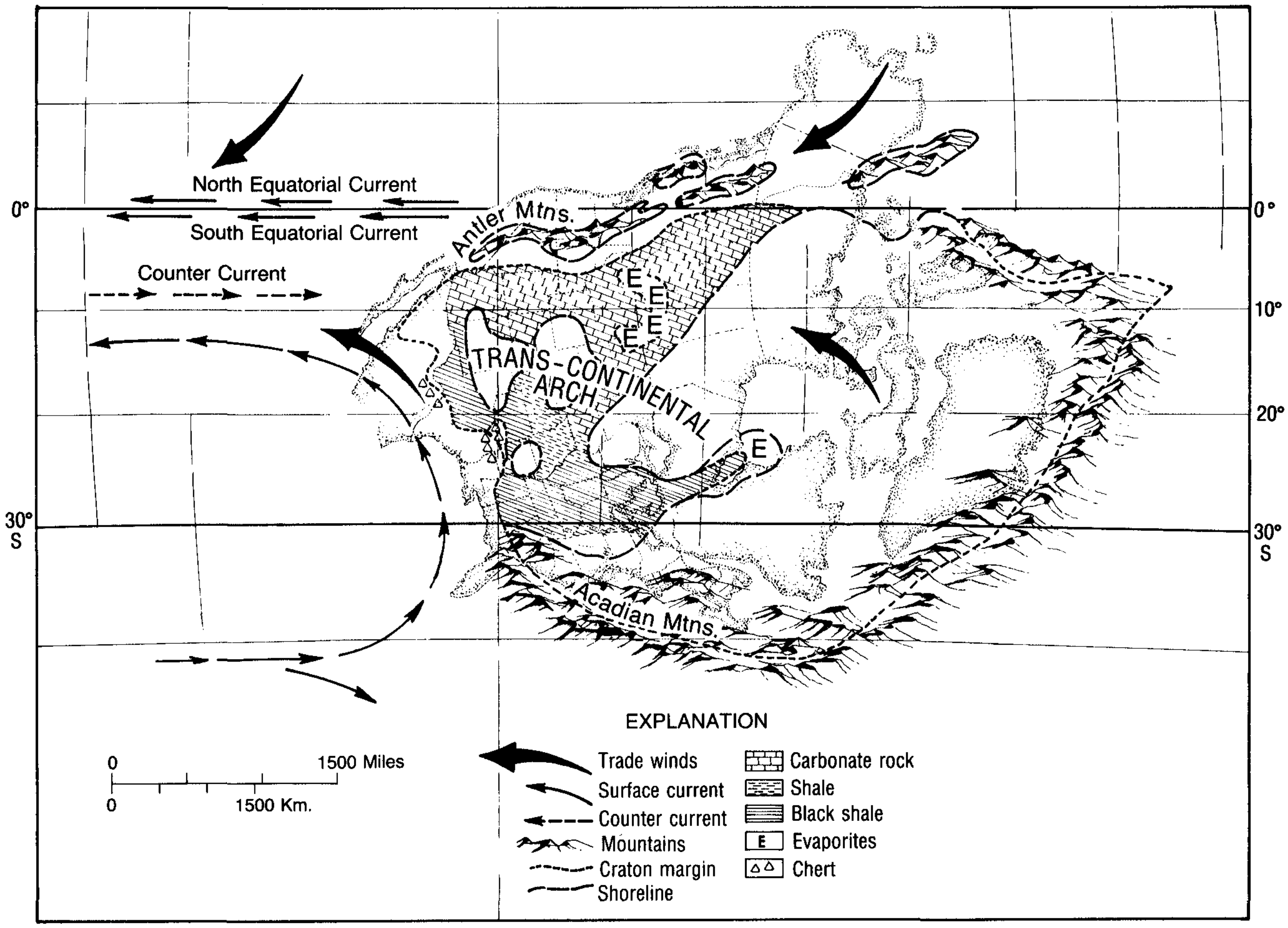


FIGURE 11. Late Devonian paleogeography of North America. After Heckel and Witzke (1979).

Paleoclimate

The paucity of terrestrial organic matter in the Woodford Formation, including the siltstone lithofacies, suggests that land in the region was mostly barren, and the absence of coarse-grained sediments and thick deltaic or fan deposits indicates that the land was low lying and not drained by large rivers. Furthermore, the presence of anhydrite in primary sedimentary structures documents hypersalinity within the basin. Together these observations indicate that the Permian Basin was arid during the Late Devonian. An arid paleoclimate and hypersalinity suggest that some of the dolomite in the Woodford formed in shallow-water evaporitic settings. Episodic resedimentation by bottom flows would account for the hybrid mixture of dolomite and quartz grains composing graded layers and Bouma divisions.

Arid-climate indicators support a Paleogeographic reconstruction in which the study area lies along the western margin of North America at approximately 15 degrees south latitude in the warm, arid southern trade-wind belt between the wet equatorial doldrums and the wet southern temperate zone (Heckel and Witzke, 1979; fig. 11). In this reconstruction the Late Devonian paleoequator lies along the Antler orogenic belt and the Canadian Rockies from California to Alberta. Other plate tectonic reconstructions of the Late Devonian also place the study area at low southern latitudes in the warm tropics or on the paleoequator (Lowe, 1975; Ettensohn and Barron, 1981; Parrish, 1982).

Paleoceanography

Features characteristic of black shale in the Woodford, including high organic content, abundant pyrite, and parallel laminae, indicate that bottom waters were stagnant and anoxic during deposition. The abundance of pelagic marine fossils and marine types of organic matter indicates that surface waters supported a luxuriant, normal marine biota. Coexistence of a putrid bottom and fertile surface waters requires a strongly stratified water column and implies the presence of a pycnocline (Byers, 1977; Arthur and Natland, 1979; Demaison and Moore, 1980; Ettensohn and Barron, 1981; Stanley, 1983; Ettensohn and Elam, 1985; Stein, 1986). The arid climate and hypersaline indicators imply that a pycnocline formed as a result of the strong density contrast between warm, normal-salinity surface water and cold, somewhat hypersaline bottom water. Anaerobic conditions developed below the pycnocline because no vertical mixing was occurring and because oxygen had been depleted owing to the high demand created by decay of the large volume of organic matter.

The abundance of marine organic matter and pelagic fossils indicates that efficient circulation of surface water and continuous resupply of nutrients characterized the upper part of the water column. Upwelling off the west and southwest coasts of North America during the Late Devonian (Lowe, 1975; Heckel and Witzke, 1979; Parrish, 1982) was the most likely source of the nutrients. No record exists of large rivers discharging into the basin (that is, deltas or fans) that would indicate a significant, continuous terrestrial source. Published circulation models suggest that oceanic surface currents flowing along the continental margin were diverted northward and northeastward, carrying upwelled water onto the North American craton (Lowe, 1975; Heckel and Witzke, 1979; Ettensohn and Barron, 1981). The model shown in figure 12 suggests that upwelled water moved eastward into the basin primarily as counter currents. In the southeast trade-wind belt, net flow of surface water would have been directed westward out of the basin by the Coriolis force and the Ekman spiral. The arid climate that produced hypersalinity caused net evaporation of surface water, particularly over shallow-water shelves, platforms, and shoals. The loss of surface water via wind-driven currents and evaporation would have amplified the negative water balance required by eustatic rise, causing inflowing counter currents to be stronger than outflowing surface currents.

The model in figure 12 differs from other published models (Lowe, 1975; Heckel, 1977; Demaison and Moore, 1980; Witzke, 1987) in that the floor of the basin in this model remained stagnant and anoxic, receiving sulfide-rich mud that had parallel laminae, even though net evaporation, local brine production, and negative water balance was occurring. This happened because the circulation pattern developed during a major marine transgression; therefore, much of the increased volume of water flowing onto the craton can be accounted for by the addition of hypersaline brine to stagnant bottom waters. Consequently, dense water gradually filled depressions in the epeiric sea without deep circulation being necessary to maintain water balance.

The existence of only dysaerobic (siltstone) and anaerobic (black shale) biofacies in the Woodford Formation indicates that bottom water became depleted in oxygen soon after the Late Devonian transgression began. Early oxygen depletion most likely was related to the early development of hypersalinity and strong density stratification. Dense water accumulated at the bottom of the water column in topographic lows and probably caused many local pycnoclines to develop during the initial stages of transgression. Later, at transgressive highstand, a single pycnocline (fig. 12) apparently developed, allowing anaerobic mud, represented by the black shales of the middle Woodford unit, to accumulate uniformly across the entire region. Dysaerobic bottom indicators found locally in the black shale on topographic highs (burrows, syneresis cracks, and anhydrite) may record some of the small-scale eustatic regressions documented by Johnson and others (1985) and reflect short-term fall of the pycnocline caused by falling sea level.

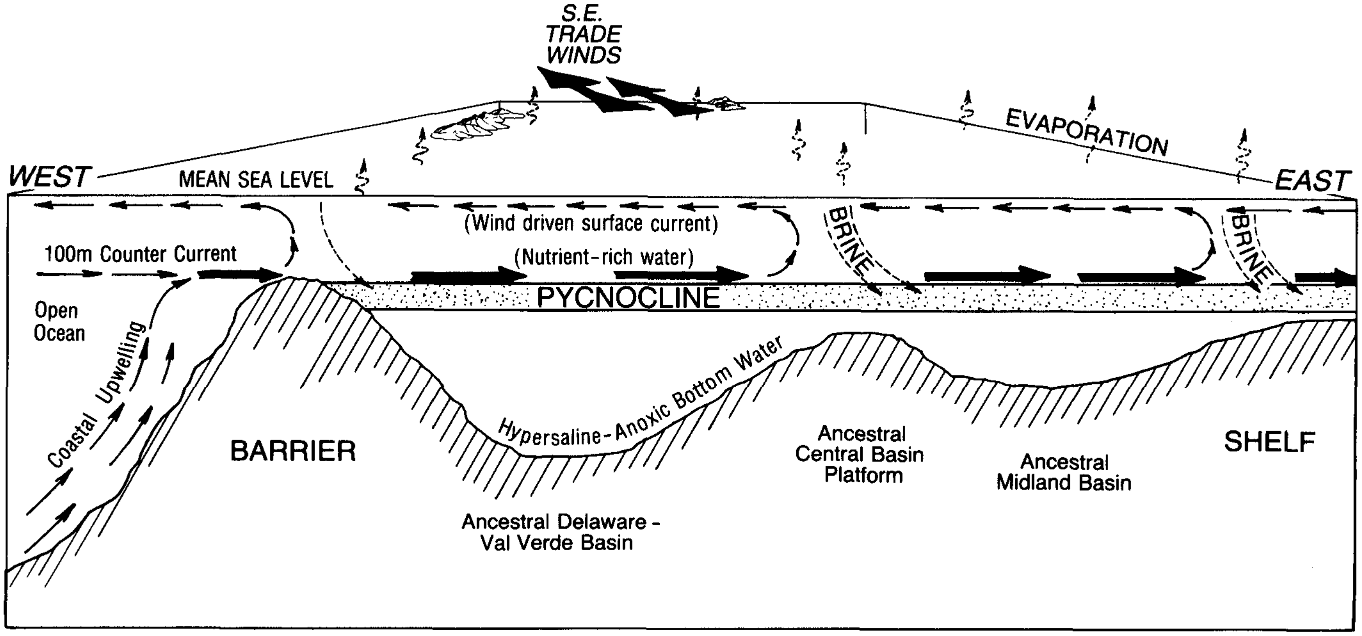


FIGURE 12. Model of Late Devonian circulation during eustatic highstand.

Depositional Mechanisms

Because the study area was once located in the tropics (fig. 11), and particularly because the Late Devonian was an epoch of worldwide transgression and global warming (Johnson and others, 1985), storms were most likely frequent and geologically significant events (Marsaglia and Klein, 1983; Morton, 1988; Barron, 1989). Frequent storms are therefore the most plausible mechanism for explaining the generation of bottom flows. Triggering mechanisms for bottom flows include (1) turbid, dense discharge from deltas, submarine fans, and rivers in flood, (2) spontaneous slumping of rapidly deposited, unconsolidated sediment, (3) slope failure resulting from earthquakes, and (4) sediment liquefaction and autosuspension during storms (Walker, 1984).

The absence of deltas and submarine fans in the Woodford precludes the first two mechanisms. What little turbid flood discharge entered the basin would not have been dense enough to sink beneath marine or hypersaline basin water (Drake, 1976; Pierce, 1976). Most likely, flood discharge was hypopycnal, or it produced detached turbidity layers by processes similar to those that had occurred in modern submarine canyons off southern California (Pierce, 1976) and in the Nile cone and Hellenic trench regions of the Mediterranean Sea (Maldonado and Stanley, 1978; Stanley and Maldonado, 1981). Deposition from turbid, muddy plumes would not produce graded layers or Bouma sequences but could yield the varvelike laminae (Pierce, 1976; Stanley, 1983) characteristic of the black shale lithofacies in the Woodford.

Earthquakes associated with epeirogenic movements probably triggered some bottom flows, but the subtlety of structural displacement during the Late Devonian indicates that these movements probably were weak and infrequent. Furthermore, bottom flows starting in shallow water would be diverted along the pycnocline in strongly stratified seas (Pierce, 1976; Stanley, 1983), unless they entrained brine from restricted hypersaline basins, shelves, or shoals (Arthur and Natland, 1979).

Storms, rather than earthquakes, probably were the most frequent and powerful agents of sediment transport in the warm Late Devonian tropics. They can account for both the indiscriminate mixing of siliciclastic and dolomite grains and the generation of bottom flows that persisted into basinal depocenters. In modern seas, storms can disrupt density stratification

(Mooers, 1976a, b), a condition that could minimize flow detachment and promote sustained bottom flows. It is probable that such a process happened in Late Devonian times as well. Storm winds and surge would flush shallow-water, hypersaline environments and give rise to very dense bottom flows consisting of sediment-laden brine. Briny bottom flows would maintain their integrity below the pycnocline even in strongly stratified basins.

Evidence indicates that bottom flows periodically disturbed anoxia that existed beneath the pycnocline. In black shales, burrows are commonly confined to graded layers and Bouma divisions, indicating that the bottom was briefly inhabited by organisms after sediment deposition. Bottom flows originating in shallow, aerobic or dysaerobic environments apparently entrained enough oxygen to sustain a temporary benthic population. However, oxygen was quickly depleted by the meager fauna, decay of organic matter, and absence of oxygen resupply. And because bottom oxygenation was short-lived, anaerobic conditions quickly returned, killing the few allochthonous organisms. Burrowed layers in the Cretaceous Mowry Shale (Davis and others, 1989) and the Devonian Chattanooga Shale (Potter and others, 1982) have been similarly explained, and entrainment of oxygen and benthic organisms in turbidity currents apparently occurred in modern sediments in the Santa Barbara Basin (Sholkovitz and Soutar, 1975).

Basal siltstones in proximal shelf and basin environments (app. B; C5, C9, C11) consist of vertically stacked siltstone-shale couplets, documenting episodic deposition from bottom flows. The greater numbers and thicknesses of siltstones in the deepest parts of the Delaware, Midland, and Val Verde Basins indicate that these depocenters were locations where bottom flows, initiated in various parts of the basin, finally converged. The high frequency of bottom flows in basinal depocenters implies that basin axes were dysaerobic more often than were distal shelves, slopes, and platforms. Thus, the lower concentrations of organic matter in the basins (fig. 9e) can be attributed to the combined effects of dilution by clastic sediment and destruction by oxidation, aerobic microbes, and the temporary benthos.

Synopsis of Depositional History

Woodford deposition began when the sea drowned marine embayments in what are now the deepest parts of the Delaware and Val Verde Basins and advanced over a subaerially eroded and dissected terrane composed mostly of carbonate rocks of Ordovician to Middle Devonian age. A broad epeiric sea formed that had irregular bottom topography and scattered, low-relief land masses. The basin lay in the arid midtropics surrounded by lands that supported little vegetation and few rivers. Oceanic water from an area of coastal upwelling flowed into the expanding epeiric sea and maintained a thriving, normal marine biota in the upper levels of the water column. Net evaporation locally produced hypersaline brines, and strong density stratification developed that restricted vertical circulation. The basin quickly became dysaerobic and then anaerobic as sea level continued to rise. Once oxygen was eliminated from the bottom, sulfide-rich mud began to accumulate. Rising sea level and persistent oceanographic and climatic patterns allowed anaerobic mud deposition to continue slowly during the rest of the Late Devonian Epoch. Frequent storms and occasional earthquakes triggered bottom flows that supplied silty mud to proximal shelves and deep basin troughs and caused much resedimentation throughout the basin. Tectonic stress arising from the Antler orogeny initiated epeirogenic movements throughout the region and caused contemporaneous movements along reactivated basement faults.

Woodford deposition probably ended because sea level stabilized or dropped and oceanographic patterns changed, thus halting the strong net flow of ocean water onto the craton and forcing deep circulation through most of the basin. Glauconite and calcified benthic epifauna accumulated on the floor of the epeiric sea, marking a change in bottom conditions from anaerobic to dysaerobic and locally aerobic and recording the improved vertical circulation through most of the basin.

Petroleum Potential

The Woodford Formation is currently generating oil in the Midland Basin, Central Basin Platform, and Eastern and Northwestern Shelves and is currently generating gas in the Delaware and Val Verde Basins. Thermal maturity of the Woodford Formation was deduced from the depth and R_o data in appendix D and the depth versus R_o log-normal relationship derived for the Woodford in the Anadarko Basin (Cardott, 1989). Oil generation in the Woodford occurs between R_0 values of 0.5 and 1.3 percent (Cardott, 1989) at depths between 6,000 and 13,000 ft in the Permian Basin. These depths correspond to depths below sea level of approximately 4,000 to 10,000 ft in the region east of the Central Basin Platform and 2,000 to 9,000 ft in the Delaware Basin and regions to the west (fig. la; pl. 1). Condensate and wet-gas generation occurs between R_0 values of 1.3 and 2.0 percent (Cardott, 1989) at depths between 13,000 and 18,000 ft common only in the Delaware and Val Verde Basins. These depths correspond to depths below sea level of approximately 9,000 to 14,000 ft in the region west of the Central Basin Platform and south of the Pecos Arch (fig. la; pl. 1). Dry gas is generated between R_0 values of 2.0 and 5.0 percent at depths between 18,000 and 26,000 ft (Cardott, 1989), or at depths below sea level of 14,000 to 22,000 ft in the Delaware and Val Verde Basins (fig. 1a; pl. 1).

Commercial production of hydrocarbons from the Woodford is possible in areas where the formation is highly fractured. The fractured Upper Devonian shales (Ohio, Chattanooga, Antrim, Bakken, and Woodford) that produce gas in the Appalachian and Michigan Basins and oil in the Williston and Ardmore Basins illustrate the commercial potential and provide appropriate geological models for exploration in the Permian Basin. In West Texas and southeastern New Mexico, optimum drilling targets are the siltstones and radiolarian cherts because they are competent lithologies that are the most likely to maintain open fracture systems. Areas that have the greatest density of major faults are the most prospective: these include the Central Basin Platform, southernmost Midland Basin, and parts of the Northwestern Shelf (fig. la; pls. 1, 2). Production may be possible from the well-developed basal siltstone in the northern part of the Midland Basin and adjacent Northwestern Shelf (for example, app. B; C5, C11 in Cochran and Gaines Counties, Texas). Although faults are uncommon there, commercial production could be established in zones where porosity has been enhanced or permeability can be artificially stimulated. Gas undoubtedly is present in siltstones and fractured shales in the Delaware and Val Verde Basins; however, drilling depths would make costs prohibitive in most places.

Summary

The Woodford Formation is an organic-rich petroleum source rock that has long been recognized as an important marker unit because of its black shales, anomalously high radioactivity, widespread distribution, and stratigraphic position between carbonates. The Woodford is mostly Late Devonian in age and is stratigraphically equivalent to the Devonian black shales (for example, Chattanooga, Ohio, Antrim, New Albany, Bakken, Exshaw, and Percha) that are present in many North American basins. At most localities, the Woodford overlies a major regional unconformity and is diachronous.

In the Permian Basin, the Woodford is thickest (661 ft) in the Delaware Basin depocenter and locally is absent from structural highs on the Central Basin Platform and Pecos Arch. Structural relief in the subsurface is 20,000 ft; it developed primarily during the late Paleozoic as a response to erogenic activity in the Ouachita Fold Belt.

Two lithofacies, black shale and siltstone, compose the Woodford. The black shale exhibits varvelike parallel laminae, abundant pyrite, very high radioactivity, and high concentrations of marine organic matter (mean = 4.5 ± 2.6 wt % TOC). It is the most widely distributed and distinctive rock type in the formation. Siltstone is a hybrid of silt-sized quartz and dolomite grains and exhibits discontinuous or disrupted stratification, graded layers, fine-grained Bouma sequences, and moderately high radioactivity. It is restricted to deep basin and proximal shelf settings and is commonly the basal unit. On the basis of lithology and stratigraphic position, basal siltstone is correlated with the Onate and Canutillo Formations in New Mexico and West Texas, the Misener and Sylamore Sandstones in Oklahoma and Arkansas, and the Ives Breccia Member of the Houy Formation in Central Texas. The black shale lithofacies is correlated with the Sly Gap and Percha Formations in the west and the Doublehorn Shale and phosphatic members of the Houy Formation in Central Texas. Black shale is mostly pelagic and represents an anaerobic biofacies, whereas siltstone was deposited by bottom flows and comprises a dysaerobic biofacies. Upward transition from basal siltstone to black shale locally records the worldwide marine transgression that occurred during the Late Devonian.

The Woodford onlaps Paleozoic structures flanking the Midland, Delaware, and Val Verde Basins, indicating that all of the major structural provinces in the modern-day Permian Basin had topographic expression in the Late Devonian. The blanketlike geometry and nearly uniform lithology, however, indicate that the region was one of low relief. The increased size and abundance of siliciclastic grains (quartz, muscovite, feldspar) and wood fragments in the northern part of the basin show that the Pedernal Massif and northern Concho Arch were the principal source areas of terrigenous sediment. In contrast, most dolomite formed contemporaneously on distal platforms and shelves in highly reduced, low-sulfate mud or restricted marine environments. Resedimentation of dolomite grains and mixing with siliciclastics were accomplished by bottom flows.

Woodford black shale records widespread bottom stagnation and anoxia during deposition and a strongly density-stratified water column. High concentrations of marine organic matter and siliceous pelagic micro-organisms in the shale indicate high biological productivity in surface waters supported mainly by dynamic upwelling. Episodes of hypersalinity, documented by the presence of anhydrite in burrows and syneresis cracks, suggest an arid paleoclimate and indicate that density stratification was caused, at least partly, by accumulation of hypersaline bottom water.

The plate tectonic reconstruction most consistent with an arid paleoclimate and dynamic upwelling places the study area on the western margin of North America in the dry tropics near 15 degrees south latitude. In this setting, southeasterly trade winds and the Ekman spiral would push surface waters westward toward the open ocean and upwelled oceanic water eastward onto the craton as counter currents. The negative water balance required for marine transgression would be amplified by flow into the basin replacing water lost by evaporation.

This circulation model accounts for the large supply of nutrients needed to support high biological productivity in the upper part of the water column of the epeiric sea. Furthermore, the low-latitude paleogeography and Late Devonian global warming imply frequent tropical storms and suggest that the bottom flows that caused the deposition of hybrid quartz/dolomite siltstones were storm generated.

The end of Woodford deposition coincided with the end of the Late Devonian eustatic rise. Bottom oxygenation, recorded as accumulations of glauconite and calcitic benthic fossils, indicates that new oceanographic conditions included deep circulation in most of the basin. The stabilization or fall of sea level would have ended the strong net flow of ocean water containing upwelled nutrients onto the craton and forced deep circulation to maintain water balance.

The Woodford Formation is now in the oil window in the Midland Basin, Central Basin Platform, and Eastern and Northwestern Shelves, and it is in the gas window in the Delaware and Val Verde Basins. Commercial production of hydrocarbons is possible from intervals that are highly fractured, but optimum drilling targets are siltstone and radiolarian chert beds in densely faulted regions, such as the Central Basin Platform, southernmost Midland Basin, and parts of the Northwestern Shelf.

Development of reserves in unusual geological settings such as the Woodford Formation in the Permian Basin undoubtedly will be required to meet future demands for petroleum. These reserves can be discovered through comprehensive studies, similar to the present report, that integrate stratigraphic, petrologic, and geochemical data. Such studies can help predict the location and lithology of unconventional oil and gas reservoirs that are inherently difficult to find.

Acknowledgments

This study, funded by the Bureau of Economic Geology, at The University of Texas at Austin, was begun while the author was a Research Fellow at the Bureau on sabbatical from Tulsa University (TU). Peter K. Krynine, project Research Assistant, helped compile the well log data, describe core, and conduct the field work; his efforts are gratefully acknowledged. David V. LeMone (The University of Texas at El Paso [UTEP]) shared his thoughts on the stratigraphy and origin of the Percha, provided relevant UTEP theses, suggested appropriate outcrops for study, and accompanied the author to Bishop Cap, New Mexico. Paul C. Franks (TU) read parts of the manuscript and offered helpful suggestions. The manuscript benefited greatly from critical reviews by S. C. Ruppel, W. B. Ayers, Jr., E. H. Guevara, W. A. Ambrose, and A. R. Scott, all at the Bureau.

Cores were supplied by Shell Oil Company, Mobil Oil Corporation, and the Exxon Company. Vitrinite reflectance and visual kerogen analyses were performed by Robert Littlejohn, Kerogen Prep, Inc., Tulsa, Oklahoma, and TOC was determined by Geochem Laboratories, Inc., Houston, Texas.

Maps and cross sections (pls. 1 through 7) were drafted at the Bureau of Economic Geology by Margaret D. Koenig and Kerza Prewitt, under the supervision of Richard L. Dillon. The text figures were drafted in Tulsa: the fence diagram by Sharon S. Scott and the lithology logs and Paleogeographic block diagram by Herbert S. Scott. Final modifications were made at the Indiana Geological Survey (IGS) and the Bureau. Drafts of the manuscript were typed by Margaret Andrews (TU) and Marilyn DeWees (IGS). Word processing and typesetting were done at the Bureau by Susan Lloyd under the supervision of Susann Doenges. Technical editing was by Tucker F. Hentz. Margaret L. Evans designed the report. Lana Dieterich was the editor.

References

Aigner, Thomas, 1982, Calcareous tempestites: storm-dominated stratification in Upper Muschelkalk limestones (Middle Trias, SW-Germany), *in* Einsele, Gerhard, and Seilacher, Adolf, eds., Cyclic and event stratification: Berlin, Springer-Verlag, p. 180–198.

———————— 1984, Storm depositional systems, *in* Friedman, G. M., Neugebauer, H. J., and Seilacher, Adolf, eds., Lecture notes in earth sciences, v. 3: New York, Springer-Verlag, 174 p.

Amsden, T. W., 1975, Hunton Group (Late Ordovician, Silurian, and Early Devonian) in the Anadarko Basin of Oklahoma: Oklahoma Geological Survey Bulletin 121, 214 p.

———————— 1980, Hunton Group (Late Ordovician, Silurian, and Early Devonian) in the Arkoma Basin of Oklahoma: Oklahoma Geological Survey Bulletin 129, 136 p.

Amsden, T. W., Caplan, W. M., Hilpman, P. L., McGlasson, E. H., Rowland, T. L., and Wise, O. A., 1967, Devonian of the southern Midcontinent area, United States, *in* Oswald, D. H., ed., International symposium on the Devonian System: Calgary, Canada, Alberta Society of Petroleum Geologists, v.1, p. 913–932.

Amsden, T. W., and Klapper, Gilbert, 1972, Misener sandstone (Middle-Upper Devonian), north-central Oklahoma: American Association of Petroleum Geologists Bulletin, v. 56, no. 12, p. 2323–2334.

Arthur, M. A., and Natland, J. H., 1979, Carbonaceous sediments in the North and South Atlantic: the role of salinity in stable stratification of Early Cretaceous basins, *in* Talwani, Manik, Hay, William, and Ryan, W. B. P., eds., Deep drilling results in the Atlantic Ocean: continental margins and paleoenvironment: American Geophysical Union, Maurice Ewing Series 3, p. 375–401.

Baker, P. A., and Kastner, Miriam, 1981, Constraints on the formation of sedimentary dolomite: Science, v. 213, no. 4504, p. 214–216.

Barron, E. J., 1989, Severe storms during Earth history: Geological Society of America Bulletin, v. 101, no. 5, p. 601–612.

Bolton, Keith, Lane, H. R., and LeMone, D. V., 1982, Symposium on the paleoenvironmental setting and distribution of the Waulsortian facies: El Paso Geological Society and The University of Texas at El Paso, 202 p.

Bouma, A. H., 1962, Sedimentology of some flysch deposits: Amsterdam, Elsevier, 168 p.

Broadhead, R. R, Kepferle, R. C, and Potter, P. E., 1982, Stratigraphic and sedimentologic controls of gas in shale—example from Upper Devonian of northern Ohio: American Association of Petroleum Geologists Bulletin, v. 66, no. 1, p. 10–27.

Burrowes, O. G., and Krause, F. F., 1987, Overview of the Devonian System: subsurface of Western Canada Basin, *in* Krause, F. F., and Burrowes, O. G., eds., Devonian lithofacies and reservoir styles in Alberta, 13th CSPG Core Conference and Display and Second International Symposium on the Devonian System: Calgary, Canada, Canadian Society of Petroleum Geologists, p. 1–20.

Byers, C. W., 1977, Biofacies patterns in euxinic basins: a general model, *in* Cook, H. E., and Enos, Paul, eds., Deep-water carbonate environments: Society of Economic Paleontologists and Mineralogists Special Publication No. 25, p. 5–17.

Cardott, B. J., 1989, Thermal maturation of the Woodford Shale in the Anadarko Basin, *in* Johnson, K. S., ed., Anadarko Basin Symposium, 1988: Oklahoma Geological Survey Circular 90, p. 32–46.

Cloud, P. E., Barnes, V. E., and Hass, W. H., 1957, Devonian-Mississippian transition in central Texas: Geological Society of America Bulletin, v. 68, no. 7, p. 807–816.

Cluff, R. M., 1980, Paleoenvironment of the New Albany Shale Group (Devonian-Mississippian) of Illinois: Journal of Sedimentary Petrology, v. 50, no. 3, p. 767–780.

Cluff, R. M., Reinbold, M. L., and Lineback, J. A., 1981, The New Albany Shale Group of Illinois: Illinois State Geological Survey Circular 518, 83 p.

Comer, J. B., and Hinch, H. H., 1987, Recognizing and quantifying expulsion of oil from the Woodford Formation and age-equivalent rocks in Oklahoma and Arkansas: American Association of Petroleum Geologists Bulletin, v. 71, no. 7, p. 844–858.

Davis, H. R., Byers, C. W., and Pratt, L. M., 1989, Depositional mechanisms and organic matter in Mowry Shale (Cretaceous), Wyoming: American Association of Petroleum Geologists Bulletin, v. 73, no. 9, p. 1103–1116.

Demaison, G. J., and Moore, G. T., 1980, Anoxic environments and oil source bed genesis: American Association of Petroleum Geologists Bulletin, v. 64, no. 8, p. 1179–1209.

Dow, W. G., 1977, Kerogen studies and geological interpretations: Journal of Geochemical Exploration, v. 7, no. 2, p. 77–79.

Drake, D. E., 1976, Suspended sediment transport and mud deposition on continental shelves, *in* Stanley, D. J., and Swift, D. J. P., eds., Marine sediment transport and environmental management: New York, John Wiley, American Geological Institute, p. 127–158.

Duncan, D. C, and Swanson, V. E., 1965, Organic-rich shale of the United States and world land areas: U.S. Geological Survey Circular 523, 30 p.

Dutton, S. P., Goldstein, A. G., and Ruppel, S. C, 1982, Petroleum potential of the Palo Duro Basin, Texas Panhandle: The University of Texas at Austin, Bureau of Economic Geology Report of Investigations No. 123, 87 p.

Ellison, S. P., Jr., 1950, Subsurface Woodford black shale, West Texas and southeast New Mexico: University of Texas, Austin, Bureau of Economic Geology Report of Investigations No. 7, 20 p.

Ettensohn, F. R., 1987, Rates of relative plate motion during the Acadian orogeny based on the spatial distribution of black shales: Journal of Geology, v. 95, no. 4, p. 572–582.

Ettensohn, F. R., and Barron, L. S., 1981, Depositional model for the Devonian-Mississippian black shales of North America: a paleoclimatic-paleogeographic approach, *in* Roberts, T. G., ed., Geological Society of America Cincinnati '81 Field Trip Guidebooks, v. II: Economic Geology, Structure, p. 344–361.

Ettensohn, F. R., and Ham, T. D., 1985, Defining the nature and location of a Late Devonian-Early Mississippian pycnocline in eastern Kentucky: Geological Society of America Bulletin, v. 96, no. 10, p. 1313–1321.

Ettensohn, F. R., Fulton, L. P., and Kepferle, R. C, 1979, Use of scintillometer and gamma-ray logs for correlation and stratigraphy in homogeneous black shales: Geological Society of America Bulletin, v. 90, part I, p. 421–423; part n, p. 828–849.

Ewing, T. E., 1991, Tectonic map of Texas: The University of Texas at Austin, Bureau of Economic Geology, scale 1:750,000.

Faill, R. T., 1985, The Acadian orogeny and the Catskill delta, *in* Woodrow, D. L, and Sevon, W. D., eds., The Catskill delta: Geological Society of America Special Paper 201, p. 15–37.

Folk, R. L., 1959, Thin-section examination of pre-Simpson Paleozoic rocks, *in* Barnes, V. E., ed., Stratigraphy of the pre-Simpson Paleozoic subsurface rocks of Texas and southeast New Mexico, v. 1: Austin, University of Texas Publication No. 5924, p. 95–130.

Folk, R. L., and Pittman, J. S., 1971, Length-slow chalcedony: a new testament for vanished evaporites: Journal of Sedimentary Petrology, v. 41, no. 4, p. 1045–1058.

Francis, B. M., 1988, Petrology and sedimentology of the Devonian Misener Formation, north-central Oklahoma: University of Tulsa, Master's thesis, 176 p.

Freeman, Tom, and Schumacher, Dietmar, 1969, Qualitative pre-Sylamore (Devonian-Mississippian) physiography delineated by onlapping conodont zones, northern Arkansas: Geological Society of America Bulletin, v. 80, no. 11, p.2327–2334.

Frezon, S. E., and Jordan, Louise, 1979, Oklahoma, *in* Craig, L. G, and Connor, C. W., coordinators, Paleotectonic investigations of the Mississippian System in the United States, part I, Introduction and regional analyses of the Mississippian system: U.S. Geological Survey Professional Paper 1010-1, p. 146–159.

Galley, J. E., 1958, Oil and geology in the Permian Basin of Texas and New Mexico, *in* Weeks, L. G., ed., Habitat of oil: Tulsa, Oklahoma, American Association of Petroleum Geologists, p. 395–446.

Click, E. E., 1979, Arkansas, *in* Craig, L. C., and Connor, C. W., coordinators, Paleotectonic investigations of the Mississippian System in the United States, part I, Introduction and regional analyses of the Mississippian System: U.S. Geological Survey Professional Paper 1010-H, p. 125–145.

Graves, R. W., 1952, Devonian conodonts from the Caballos Novaculite: Journal of Paleontology, v. 26, no. 4, p. 610–612.

Ham, W. E., 1969, Regional geology of the Arbuckle Mountains, Oklahoma, *in* Ham, W. E., ed., Geology of the Arbuckle Mountains: Oklahoma Geological Survey Guidebook 17, p. 5–21.

Ham, W. E., and Wilson, J. L., 1967, Paleozoic epeirogeny and orogeny in the central United States: American Journal of Science, v. 265, p. 332–407.

Harlton, B. H., 1956, The Harrisburg Trough, Stephens and Carter Counties, Oklahoma, *in* Hicks, I. C., Westheimer, J. M., Thomlinson, C. W., Putman, D. M., and Selk, E. L., eds., Petroleum geology of southern Oklahoma, a symposium, v. 1; sponsored by the Ardmore Geological Society: Tulsa, American Association of Petroleum Geologists, p. 135–143.

Hass, W. H., 1951, Age of Arkansas Novaculite: American Association of Petroleum Geologists Bulletin, v. 35, no. 12, p. 2526–2541.

Hass, W. H., and Huddle, J. W., 1965, Late Devonian and Early Mississippian age of the Woodford Shale in Oklahoma, as determined from conodonts: U.S. Geological Survey Professional Paper 525-D, p. D125–D132.

Hayes, M. O., 1967, Hurricanes as geological agents, south Texas coast: American Association of Petroleum Geologists Bulletin, v. 51, no. 6, p. 937–942.

Heckel, P. H., 1977, Origin of phosphatic black shale facies in Pennsylvanian cyclothems of Mid-Continent North America: American Association of Petroleum Geologists Bulletin, v. 61, no. 7, p. 1045–1068.

Heckel, P. H., and Witzke, B. J., 1979, Devonian world palaeogeography determined from distribution of carbonates and related lithic palaeoclimatic indicators, *in* House, M. R., Scrutton, C. T., and Bassett, M. G., eds., The Devonian System: Special Papers in Palaeontology No. 23, p. 99–123.

Hein, J. R., and Parrish, J. T., 1987, Distribution of siliceous deposits in space and time, *in* Hein, J. R., ed., Siliceous sedimentary rock-hosted ores and petroleum: New York, Van Nostrand Reinhold, p. 10–57.

Hills, J. M., 1984, Sedimentation, tectonism, and hydrocarbon generation in Delaware Basin, West Texas and southeastern New Mexico: American Association of Petroleum Geologists Bulletin, v. 68, no. 3, p. 250–267.

Hoenig, M. A., 1976, Stratigraphy of the "Upper Silurian" and "Lower Devonian," Permian Basin, West Texas: The University of Texas at El Paso, Master's thesis, 81 p.

Horak, R. L, 1985, Tectonic and hydrocarbon maturation history in the Permian Basin: Oil and Gas Journal, v. 83, no. 21, p. 124–129.

Huffman, G. G., 1958, Geology of the flanks of the Ozark uplift: Oklahoma Geological Survey Bulletin No. 77, 281 p.

Huffman, G. G., and Starke, J. M., 1960, Noel shale in-northeastern Oklahoma: Oklahoma Geology Notes, v. 20, p. 159–163.

Hunt, J. M., 1979, Petroleum geochemistry and geology: San Francisco, Freeman, 617 p.

Johnson, J. G., Klapper, Gilbert, and Sandberg, C. A., 1985, Devonian eustatic fluctuations in Euramerica: Geological Society of America Bulletin, v. 96, no. 5, p. 567–587.

Jones, T. S., and Smith, H. M., 1965, Relationships of oil composition and stratigraphy in the Permian Basin of West Texas and New Mexico, *in* Young, Addison, and Galley, J. E., eds., Fluids in subsurface environments: Tulsa, American Association of Petroleum Geologists, p. 101–224.

Keroher, G. C., and others, 1966, Lexicon of geologic names of the United States for 1936–1960: U.S. Geological Survey Bulletin 1200, part 3, P-Z, p. 4292–4293.

King, P. B., King, R. E., and Knight, J. B., 1945, Geology of the Hueco Mountains, El Paso and Hudspeth Counties, Texas: U.S. Geological Survey, Oil and Gas Investigations Preliminary Map 36.

Kottlowski, F. E., 1963, Paleozoic and Mesozoic strata of southwestern and south-central New Mexico: New Mexico Bureau of Mines and Mineral Resources Bulletin 79, p. 24–32.

Landis, E. R., 1962, Uranium and other trace elements in Devonian and Mississippian black shales in the central Midcontinent area: U.S. Geological Survey Bulletin 1107-E, p. 289–336.

Laudon, L. R., and Bowsher, A. L., 1949, Mississippian formations of southwestern New Mexico: Geological Society of America Bulletin, v. 60, no. 1, p. 1–88.

Leggett, J. K., 1980, British lower Paleozoic black shales and their paleo-oceanographic significance: Geological Society of London Journal, v. 137, pt. 2, p. 139–156.

LeMone, D. V., 1971, General stratigraphy of the Franklin Mountains, *in* Robledo Mountains, New Mexico, Franklin Mountains, Texas, 1971 Field Conference: Society of Economic Paleontologists and Mineralogists Permian Basin Section Publication 71-13, p. ix.

Leventhal, J. S., 1981, Pyrolysis gas chromatography-mass spectrometry to characterize organic matter and its relationship to uranium content of Appalachian Devonian black shales: Geochimica et Cosmochimica Acta, v. 45, no. 6, p. 883–889.

Lindberg, F. A., ed., 1983, Correlation of Stratigraphic Units of North America (COSUNA) Project, Southwest/Southwest Mid-Continent Region: Tulsa, American Association of Petroleum Geologists.

Lloyd, E. R., 1949, Pre-San Andres stratigraphy and oil-producing zones in southeastern New Mexico: New Mexico Bureau of Mines and Mineral Resources Bulletin 29, 87 p.

Lowe, D. R., 1975, Regional controls on silica sedimentation in the Ouachita system: Geological Society of America Bulletin, v. 86, no. 8, p. 1123–1127.

Lucia, F. J., 1971, Lower Paleozoic history of the western Diablo Platform, West Texas and south central New Mexico, *in* Robledo Mountains, New Mexico, Franklin Mountains, Texas, 1971 Field Conference: Society of Economic Paleontologists and Mineralogists Permian Basin Section Guidebook Publication 71-13, p. 174–214.

Maldonado, Andres, and Stanley, D. J., 1978, Nile cone depositional processes and patterns in the Late Quaternary, *in* Stanley, D. J., and Kelling, Gilbert, eds., Sedimentation in submarine canyons, fans, and trenches: Stroudsburg, Pennsylvania, Dowden, Hutchinson and Ross, p. 239–257.

Marsaglia, K. M., and Klein, G. deV., 1983, The paleogeography of Paleozoic and Mesozoic storm depositional systems: Journal of Geology, v. 91, no. 4, p. 117–142.

Mapel, W. J., Johnson, R. B., Bachman, G. O., and Varnes, K. L., 1979, Southern Midcontinent and southern Rocky Mountain region, *in* Paleotectonic investigations of the Mississippian System in the United States, part I, Introduction and regional analyses of the Mississippian System: U.S. Geological Survey Professional Paper 1010-J, p. 160–187.

McGlasson, E. H., 1967, The Siluro-Devonian of West Texas and southeast New Mexico, *in* Oswald, D. H., ed., International symposium on the Devonian System: Calgary, Canada, Alberta Society of Petroleum Geologists, v. 2, p. 935–948.

Meissner, F. F., 1978, Petroleum geology of the Bakken Formation, Williston Basin, North Dakota and Montana: Montana Geological Society 24th Annual Conference, 1978 Williston Basin Symposium, p. 207–227.

Mooers, C. N. K., 1976a, Introduction to the physical oceanography and fluid dynamics of continental margins, *in* Stanley, D. J., and Swift, D. J. P., eds., Marine sediment transport and environmental management: New York, John Wiley, p. 7–21.

———————— 1976b, Wind-driven currents on the continental margin, *in* Stanley, D. J., and Swift, D. J. P., eds., Marine sediment transport and environmental management: New York, John Wiley, p. 29–52.

Morton, J. P., 1985, Rb-Sr dating of diagenesis and source age of clays in Upper Devonian black shales of Texas: Geological Society of America Bulletin, v. 96, no. 8, p. 1043–1049.

Morton, R. A., 1981, Formation of storm deposits by wind-forced currents in the Gulf of Mexico and the North Sea, *in* Nio, S. D., Shattenhelm, R. T. E., and Van Weering, T. C. E., eds., Holocene marine sedimentation in the North Sea Basin: International Association of Sedimentologists Special Publication 5, p. 385–396.

———————— 1988, Nearshore responses to great storms, *in* Clifton, H. E., ed., Sedimentologic consequences of convulsive geologic events: Geological Society of America Special Paper 229, p. 7–22.

Muehlberger, W. R., 1980, Texas lineament revisited: New Mexico Geological Society Guidebook, 31st Field Conference, Trans-Pecos Region, p. 113–121.

Munn, J. K, 1971, Breedlove field, Martin County, Texas: American Association of Petroleum Geologists Bulletin, v. 55, no. 3, p. 403–411.

Nelson, C. H., 1982, Modern shallow-water graded sand layers from storm surges, Bering Shelf: a mimic of Bouma sequences and turbidite systems: Journal of Sedimentary Petrology, v. 52, no. 2, p. 537–545.

Odin, G. S., and Letolle, Rene, 1980, Glauconitization and phosphatization environments: a tentative comparison, *in* Bentor, Y. K., ed., Marine phosphorites—geochemistry, occurrence, genesis: Society of Economic Paleontologists and Mineralogists Special Publication No. 29, p. 227–237.

Park, D. E., and Croneis, Carey, 1969, Origin of Caballos and Arkansas Novaculite formations: American Association of Petroleum Geologists Bulletin, v. 53, no. 1, p. 94–111.

Parrish, J. T., 1982, Upwelling and petroleum source beds, with reference to Paleozoic: American Association of Petroleum Geologists Bulletin, v. 66, no. 6, p. 750–774.

Parrish, J. T., and Barron, E. J., 1986, Paleoclimates and economic geology: Society of Economic Paleontologists and Mineralogists Short Course Notes No. 18, 162 p.

Pashin, J. C., and Ettensohn, F. R., 1987, An epeiric shelf-to-basin transition: Bedford-Berea sequence, northeastern Kentucky and south-central Ohio: American Journal of Science, v. 287, p. 893–926.

Pedersen, T. F., and Calvert, S. E., 1990, Anoxia vs. productivity: what controls the formation of organic-carbon-rich sediments and sedimentary rocks: American Association of Petroleum Geologists Bulletin, v. 74, no. 4, p. 454–466.

Peirce, F. L., 1962, Devonian cavity fillings in subsurface Silurian carbonates of West Texas: American Association of Petroleum Geologists Bulletin, v. 46, no. 1, p. 122–124.

Pierce, J. W., 1976, Suspended sediment transport at the shelf break and over the outer margin, *in* Stanley, D. J., and Swift, D. J. P., eds., Marine sediment transport and environmental management: New York, John Wiley, p. 437–458.

Piper, D. J. W., 1978, Turbidite muds and silts on deep sea fans and abyssal plains, *in* Stanley, D. J., and Kelling, Gilbert, eds., Sedimentation in submarine canyons, fans, and trenches: Stroudsburg, Pennsylvania, Dowden, Hutchinson and Ross, p. 163–176.

Pittenger, H. A., 1981, Provenance, depositional environment and diagenesis of the Sylamore sandstone in northeastern Oklahoma and northern Arkansas: University of Tulsa, Master's thesis, 109 p.

Poole, F. G., 1974, Flysch deposits of Antler foreland basin, western United States, *in* Dickinson, W. R., ed., Tectonics and sedimentation: Society of Economic Paleontologists and Mineralogists Special Publication No. 22, p. 58–82.

Poole, R G., Baars, D. L, Drewes, Harald, Hayes, P. T., Ketner, K. B., McKee, E. D., Teichert, Curt, and Williams, J. S., 1967, Devonian of the southwestern United States, *in* Oswald, D. H., ed., International symposium on the Devonian System, v. 1: Calgary, Canada, Alberta Society of Petroleum Geologists, p. 879–912.

Potter, P. E., Maynard, J. B., and Pryor, W. A., 1982, Appalachian gas bearing Devonian shales: statements and discussions: Oil and Gas Journal, v. 80, no. 4, p. 290–318.

Pratt, L. M., 1984, Influence of paleoenvironmental factors on preservation of organic matter in middle Cretaceous Greenhorn Formation, Pueblo, Colorado: American Association of Petroleum Geologists Bulletin, v. 68, no. 9, p. 1146–1159.

Pray, L. C., 1961, Geology of the Sacramento Mountains escarpment, Otero County, New Mexico: New Mexico Bureau of Mines and Mineral Resources Bulletin 35, 144 p.

Rhoads, D. C., and Morse, J. W., 1971, Evolutionary and ecologic significance of oxygen-deficient marine basins: Lethaia, v. 4, no. 4, p. 413–428.

Roen, J. B., 1984, Geology of the Devonian black shales of the Appalachian basin: Organic Geochemistry, v. 5, no. 4, p. 241–254.

Rosado, R. V., 1970, Devonian stratigraphy of south-central New Mexico and far West Texas: The University of Texas at El Paso, Master's thesis, 108 p.

Ruppel, S. C., 1985, Stratigraphy and petroleum potential of pre-Pennsylvanian rocks, Palo Duro Basin, Texas Panhandle: The University of Texas at Austin, Bureau of Economic Geology Report of Investigations No. 147, 81 p.

Schieber, Jiirgen, 1987, Storm-dominated epicontinental clastic sedimentation in the mid-Proterozoic Newland Formation, Montana, U.S.A.: Neues Jahrbuch fur Geologic und Palaontologie Monatshefte, v. 7, p. 417–439.

Sholkovitz, Edward, and Soutar, Andrew, 1975, Changes in the composition of the bottom water of the Santa Barbara Basin: effect of turbidity currents: Deep-Sea Research, v. 22, no. 1, p. 13–21.

Schopf, T. J. M., 1983, Paleozoic black shales in relation to continental margin upwelling, *in* Thiede, John, and Suess, Erwin, eds., Sedimentary records of ancient coastal upwelling: coastal upwelling, its sediment record, part B: New York, Plenum Press, p. 579–596.

Stanley, D. J., 1983, Parallel laminated deep-sea muds and coupled gravity flow-hemipelagic settling in the Mediterranean: Smithsonian Contributions to the Marine Sciences No. 19, 19 p.

Stanley, D. J., and Maldonado, Andres, 1981, Depositional models for fine-grained sediment in the western Hellenic trench, eastern Mediterranean: Sedimentology, v. 28, no. 2, p. 273–290.

Stein, Ruediger, 1986, Organic carbon and sedimentation rate—further evidence for anoxic deep-water conditions in the Cenomanian/Turonian Atlantic Ocean: Marine Geology, v. 72, no. 3/4, p. 199–209.

Stevenson, F. V., 1945, Devonian of New Mexico: Journal of Geology, v. 53, p. 217–245.

Stow, D. A. V., and Piper, D. J. W., 1984, Deep-water fine-grained sediments: facies models, *in* Stow, D. A. V., and Piper, D. J. W., eds., Fine-grained sediments: deep-water processes and facies: Geological Society of London, Special Publication No. 15, p. 611–646.

Sutherland, P. K., and Manger, W. L., 1979, Comparison of Ozark shelf and Ouachita basin facies for Upper Mississippian and Lower Pennsylvanian series in eastern Oklahoma and western Arkansas, *in* Sutherland, P. K., and Manger, W. L., eds., Ozark and Ouachita shelf-to-basin transition, Oklahoma-Arkansas: Norman, Oklahoma, Oklahoma Geological Survey Guidebook 19, p. 1–13.

Swanson, V. E., 1960, Oil yield and uranium content of black shales: U.S. Geological Survey Professional Paper 356-A, 44 p.

-------- 1961, Geology and geochemistry of uranium in marine black shales—a review: U.S. Geological Survey Professional Paper 356-C, 112 p.

Swift, D. J. P., Figueiredo, A. G., Freeland, G. L., and Oertel, G. P., 1983, Hummocky cross-stratification and megaripples: a geological double standard: Journal of Sedimentary Petrology, v. 53, no. 4, p. 1295–1317.

Taff, J. A., 1902, Geological atlas of the United States: U.S. Geological Survey Atoka Folio No. 79.

Tissot, B. P., Demaison, G. J., Masson, Peter, Delteil, J. R., and Combaz, Andre, 1980, Paleoenvironment and petroleum potential of Middle Cretaceous black shale in Atlantic basins: American Association of Petroleum Geologists Bulletin, v. 64, no. 12, p. 2051–2163.

Tissot, B. P., and Welte, D. H., 1984, Petroleum formation and occurrence, 2d ed.: New York, Springer-Verlag, 699 p.

Walker, R. G., 1984, Turbidites and associated coarse clastic deposits, *in* Walker, R. G., ed., Facies models, 2d ed.: Geoscience Canada, Reprint Series 1, p. 171–188.

__________ 1985, Geological evidence for storm transportation and deposition on ancient shelves, *in* Tillman, R. W., Swift, D. J. P., and Walker, R. G., eds., Shelf sands and sandstone reservoirs: Society of Economic Paleontologists and Mineralogists Short Course Notes 13, p. 243–302.

Walper, J. L., 1977, Paleozoic tectonics of the southern margin of North America: Gulf Coast Association of Geological Societies Transactions, v. 27, p. 230–241.

Witzke, B. J., 1987, Models for circulation patterns in epicontinental seas applied to Paleozoic facies of North America craton: Paleoceanography, v. 2, no. 2, p. 229–248.

Wright, W. F., 1979, Petroleum geology of the Permian Basin: Midland, Texas, West Texas Geological Society, 98 p.

Zenger, D. H., 1972, Dolomitization and uniformitarianism: Journal of Geological Education, v. 20, no. 3, p. 107–124.

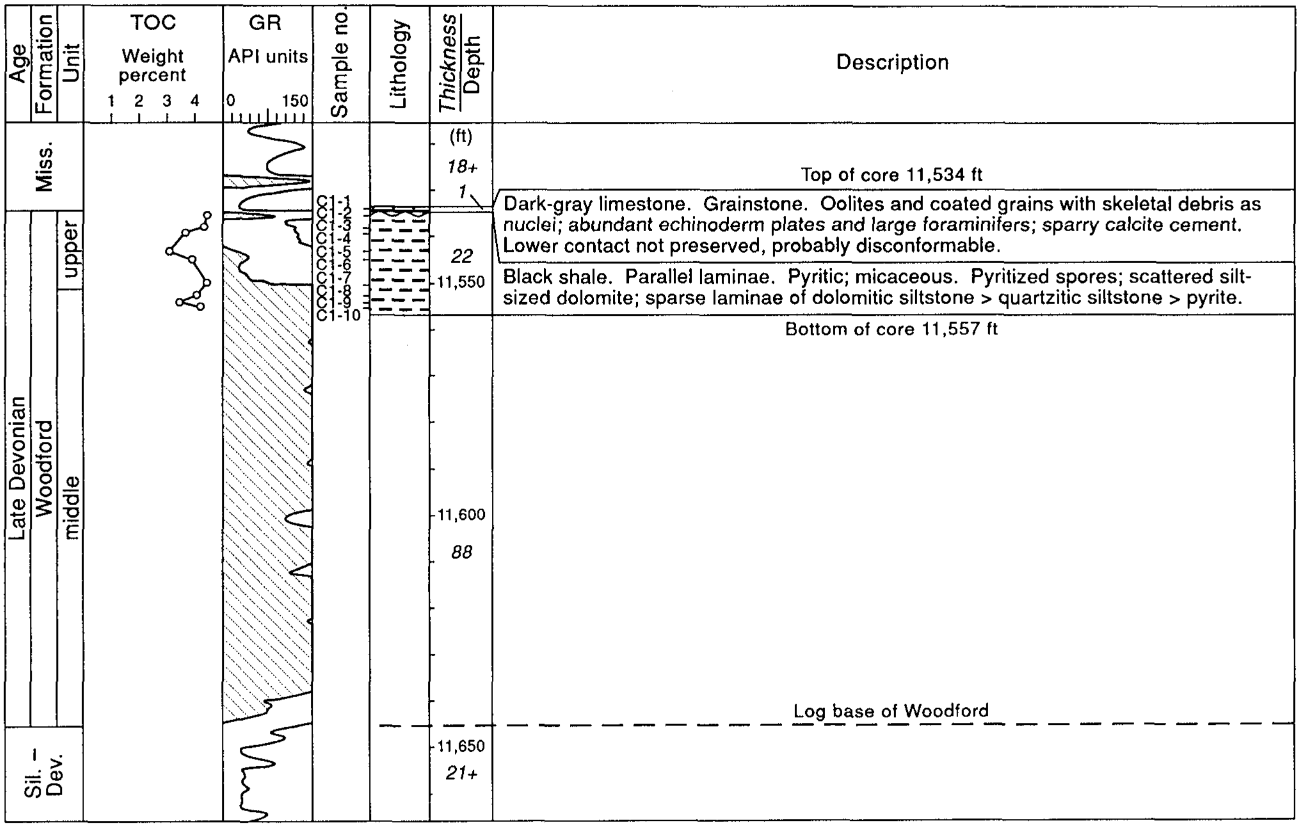
APPENDICES

Appendix A. Location of cores and measured sections.

Map symbol	Operator	Well	County	State	Location
		Cores			
C1	Mobil	#1918 Parks Unit 2	Midland	Texas	Sec. 14, Block 40, C.F. O'Neal Survey
C2	Humble	#43 Yarborough & Allen	Ward	Texas	Sec. 66, E.J. Brady Survey
C3	Humble	#1 A. E. State	Lea	New Mexico	Sec. 16, T.15S., R.33E.
C4	Shell	#1 Champeau Federal	Chaves	New Mexico	Sec. 31, T.15S., R.30E.
C5	Pan American	#1 Walker	Cochran	Texas	Sec. 8, Block Z, PSL Survey
C6	Shell	#1 Chrieseman	Glasscock	Texas	Sec. 12, Block 36, T.5S., T&P Survey
C7	Standard of Texas	#1-28 Canon	Dawson	Texas	Sec. 28, Block 33, T.5N., T&P Survey
C8	Roden & Cosden	#1 Reed	Sterling	Texas	Sec. 9, Block 30, W&NW Survey
C9	Shell	#5 Pacific Royalty	Lea	New Mexico	Sec. 10, T.15S., R.37E.
C10	McGrath & Smith	#1 Brennand & Price	Mitchell	Texas	Sec. 7, Block 17, SPRR Survey
C11	Shell	A#1 Williamson	Gaines	Texas	Sec. 110, Block H, D&WRR Survey
C12	Shell	#1 Sealy Smith	Ward	Texas	Sec. 38, Block A, G&MMB&A Survey
C13	Humble	#1 Federal Elliott	Lea	New Mexico	Sec. 1, T.16S., R.34E.
		Measured Sections			
P1	Bishop Cap		Doña Ana	New Mexico	Sec. 25, T.24S., R.3E.
P2	Anthony Gap, Northern Franklin Mountains		Doña Ana	New Mexico	Sec. 34, T.26S., R.4E.
P4	Martin Canyon, Hueco Mountains		El Paso	Texas	106°00'30" W. Longitude, 31°48'30" N. Latitude
		Sections from Rosado (1970)			
R1	Magnolia	#1 University 39881	Hudspeth	Texas	Sec. 19, Block C, University Lands Survey
R2	Gulf	#1 Munson Federal	Chaves	New Mexico	Sec. 28, T.19S., R.18E.
R3	Alamo Canyon, Sacramento Mountains		Otero	New Mexico	Sec. 2, T.17S., R.10E.

Appendix B. Description of cores and measured sections. For map locations, see figure 2 and plates 1 and 2.

C1
Mobil No. 1918, Parks Unit 2
Midland County, Texas
Section 14, Block 40, C. F. O'Neal Survey
Elevation 2825 ft



Top of core 11,534 ft

Dark-gray limestone. Grainstone. Oolites and coated grains with skeletal debris as nuclei; abundant echinoderm plates and large foraminifers; sparry calcite cement. Lower contact not preserved, probably disconformable.

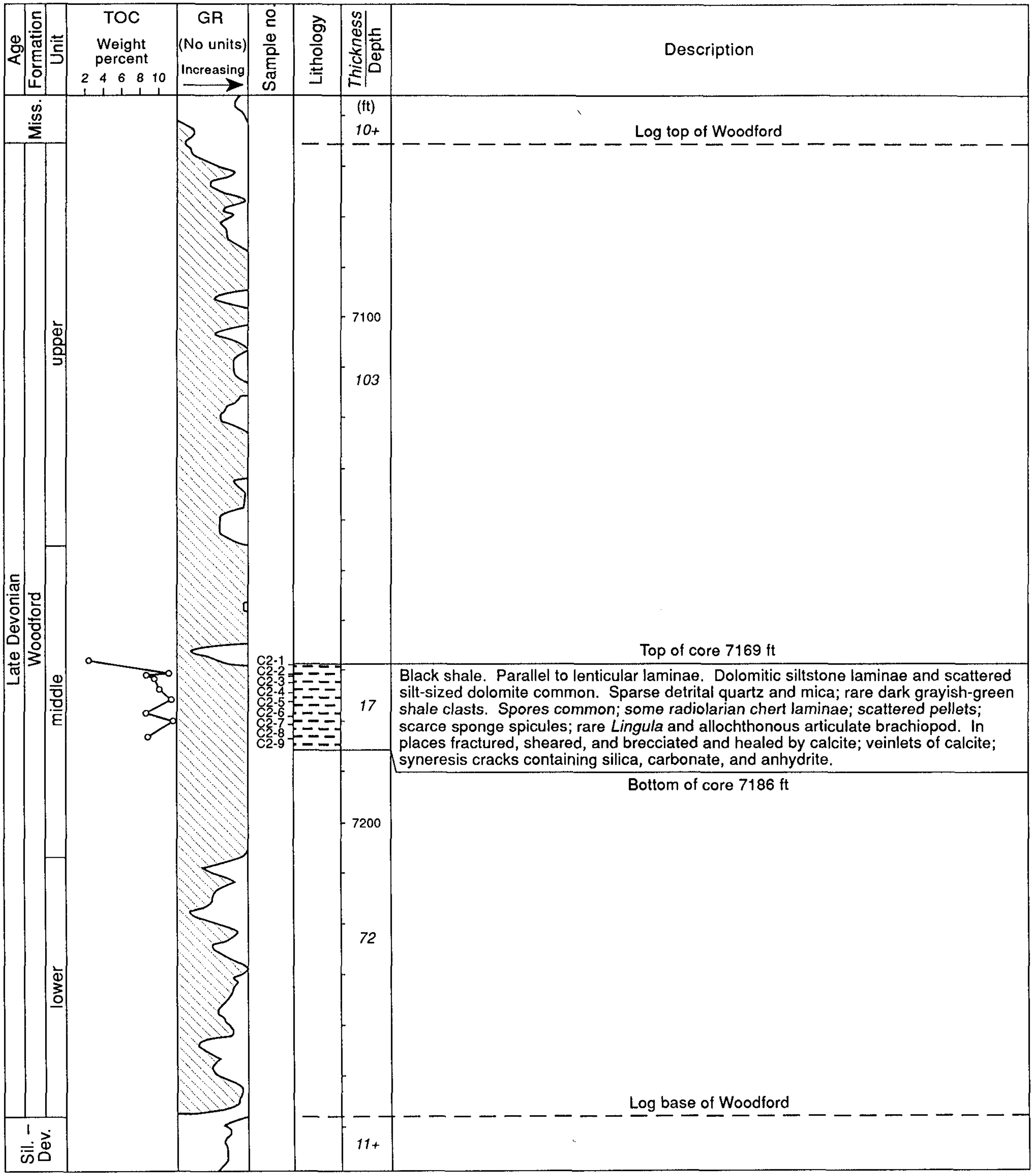
Black shale. Parallel laminae. Pyritic; micaceous. Pyritized spores; scattered silt-sized dolomite; sparse laminae of dolomitic siltstone > quartzitic siltstone > pyrite.

Bottom of core 11,557 ft

Log base of Woodford

QA 14570c

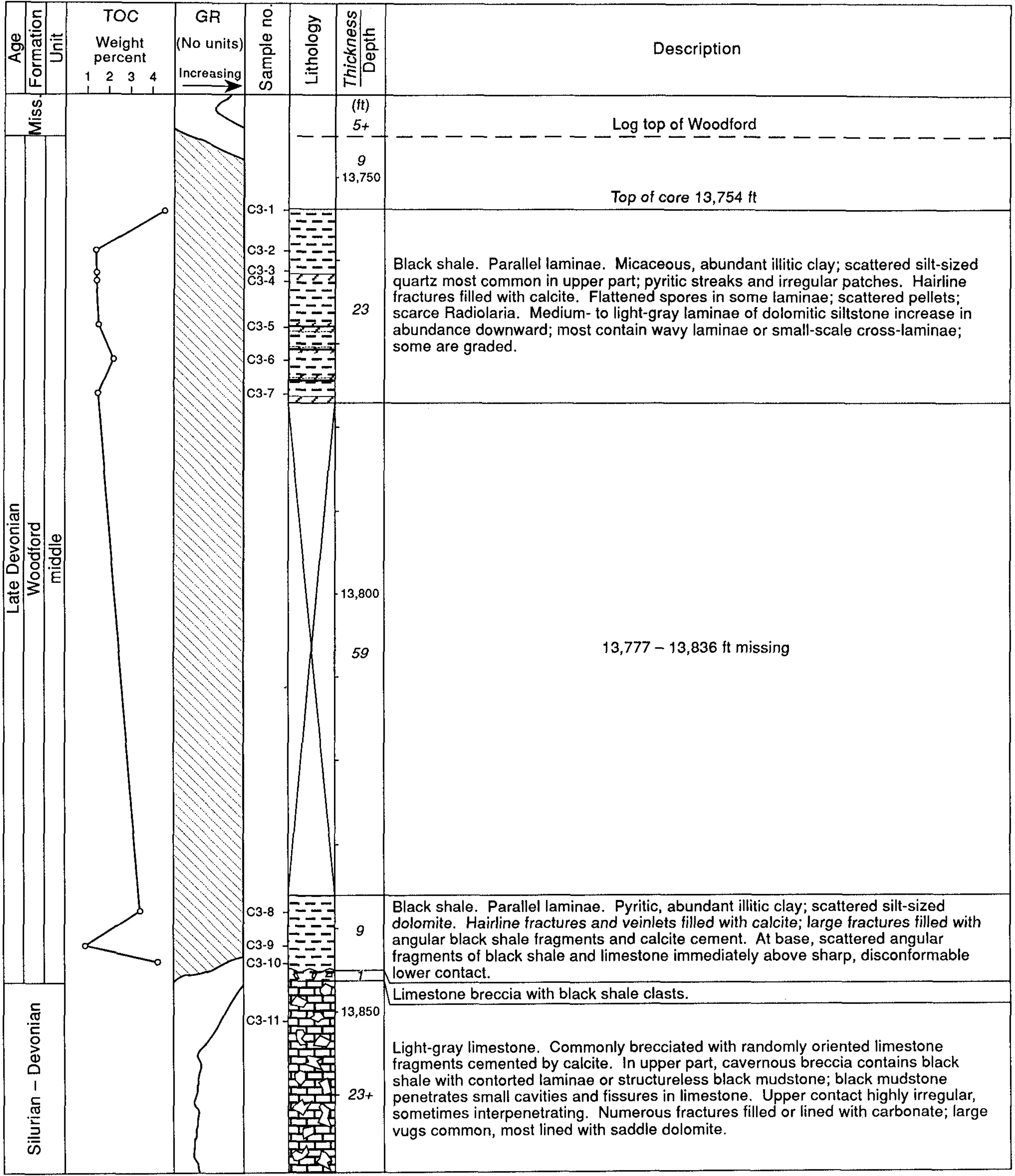
C2
Humble No. 43 Yarborough and Allen
Ward County, Texas
Section 66, E. J. Brady Survey
Elevation 2756 ft



Black shale. Parallel to lenticular laminae. Dolomitic siltstone laminae and scattered silt-sized dolomite common. Sparse detrital quartz and mica; rare dark grayish-green shale clasts. Spores common; some radiolarian chert laminae; scattered pellets; scarce sponge spicules; rare *Lingula* and allochthonous articulate brachiopod. In places fractured, sheared, and brecciated and healed by calcite; veinlets of calcite; syneresis cracks containing silica, carbonate, and anhydrite.

QA 14571c

C3
Humble No. 1 A. E. State
Lea County, New Mexico
Section 16, T 15 S – R 33 E
Elevation 4203 ft



Log top of Woodford

Top of core 13,754 ft

Black shale. Parallel laminae. Micaceous, abundant illitic clay; scattered silt-sized quartz most common in upper part; pyritic streaks and irregular patches. Hairline fractures filled with calcite. Flattened spores in some laminae; scattered pellets; scarce Radiolaria. Medium- to light-gray laminae of dolomitic siltstone increase in abundance downward; most contain wavy laminae or small-scale cross-laminae; some are graded.

13,777 – 13,836 ft missing

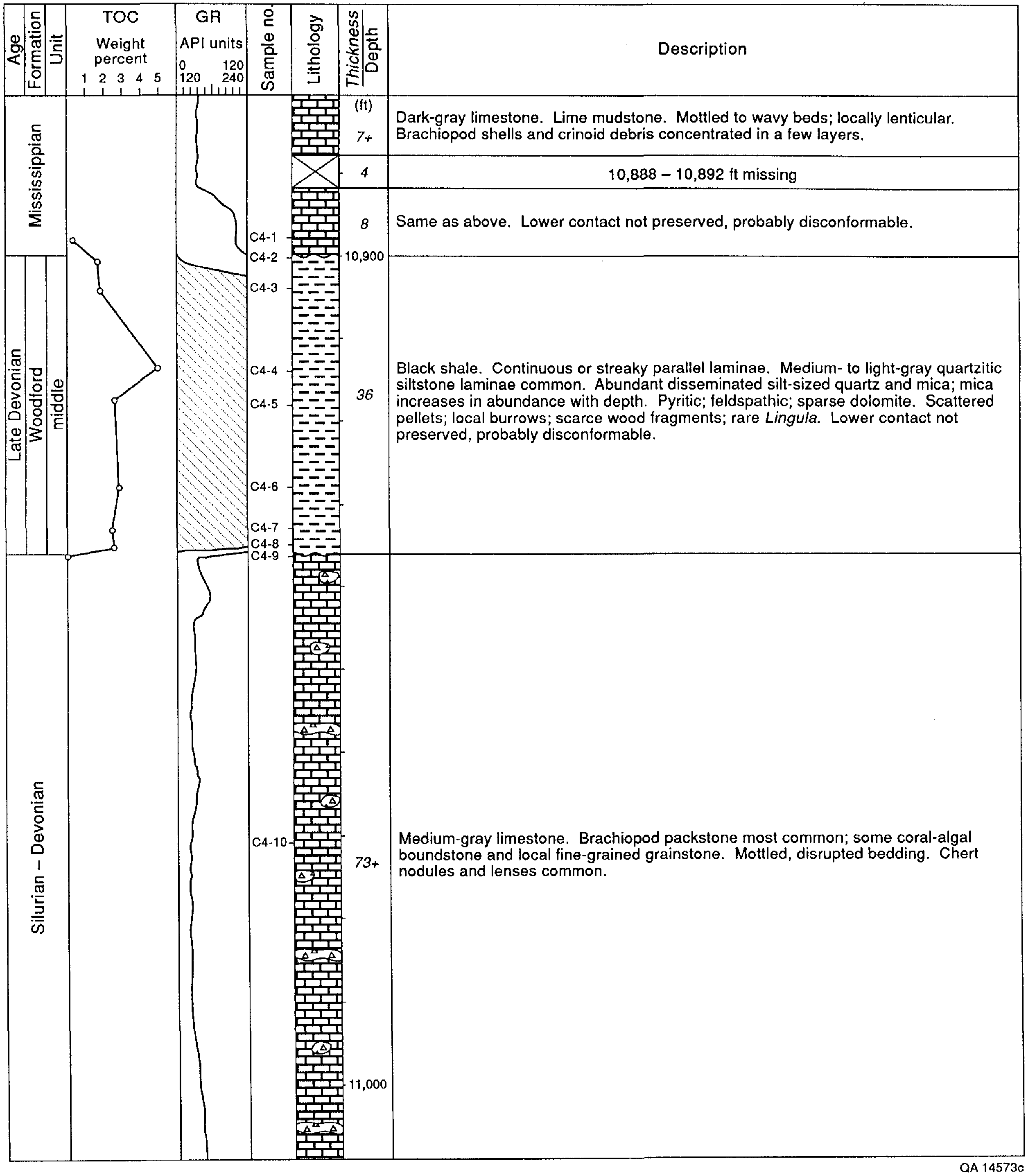
Black shale. Parallel laminae. Pyritic, abundant illitic clay; scattered silt-sized *dolomite. Hairline fractures and veinlets filled with calcite; large fractures filled* with angular black shale fragments and calcite cement. At base, scattered angular fragments of black shale and limestone immediately above sharp, disconformable lower contact.

Limestone breccia with black shale clasts.

Light-gray limestone. Commonly brecciated with randomly oriented limestone fragments cemented by calcite. In upper part, cavernous breccia contains black shale with contorted laminae or structureless black mudstone; black mudstone penetrates small cavities and fissures in limestone. Upper contact highly irregular, sometimes interpenetrating. Numerous fractures filled or lined with carbonate; large vugs common, most lined with saddle dolomite.

QA 14572c

C4
Shell No. 1 Champeau Federal
Chaves County, New Mexico
Section 31, T 15 S – R 30 E
Elevation 3923 ft



Dark-gray limestone. Lime mudstone. Mottled to wavy beds; locally lenticular. Brachiopod shells and crinoid debris concentrated in a few layers.

10,888 – 10,892 ft missing

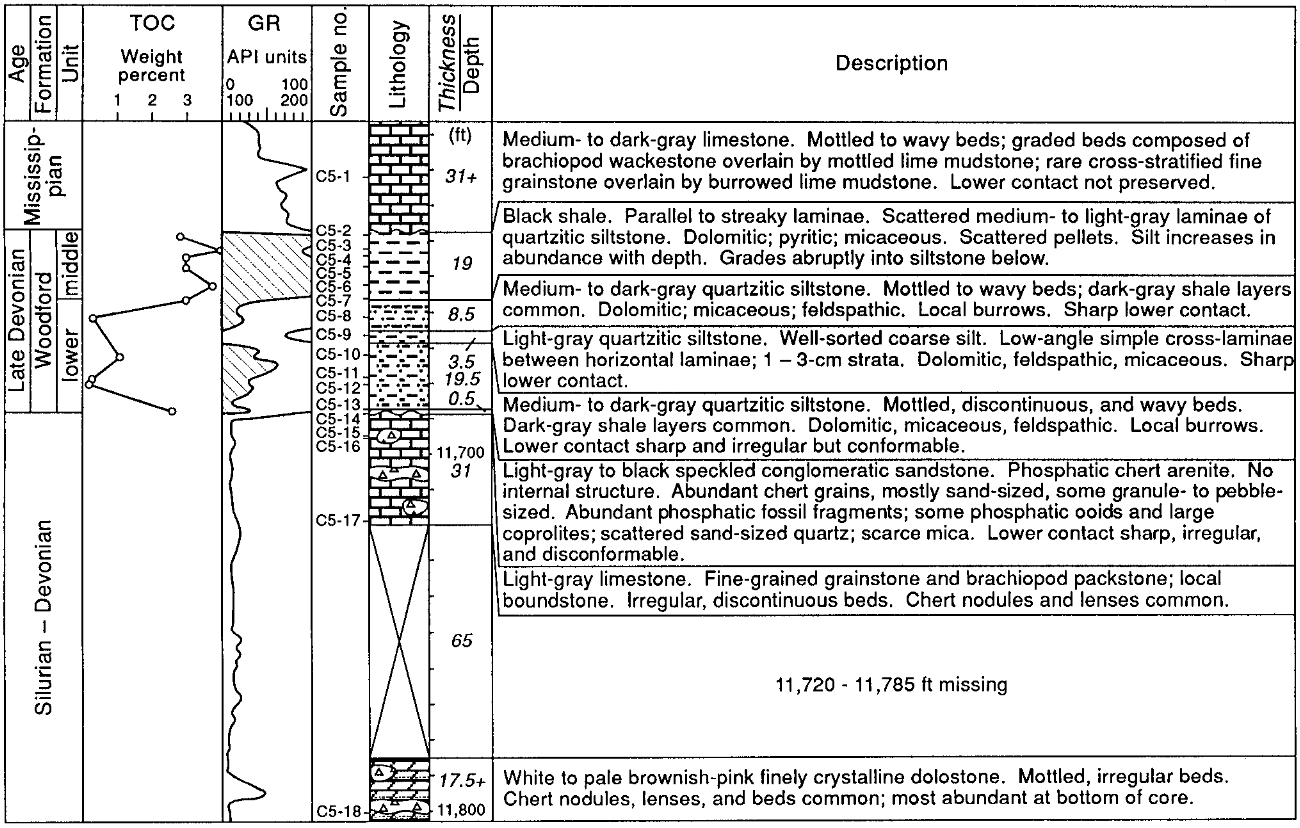
Same as above. Lower contact not preserved, probably disconformable.

Black shale. Continuous or streaky parallel laminae. Medium- to light-gray quartzitic siltstone laminae common. Abundant disseminated silt-sized quartz and mica; mica increases in abundance with depth. Pyritic; feldspathic; sparse dolomite. Scattered pellets; local burrows; scarce wood fragments; rare *Lingula*. Lower contact not preserved, probably disconformable.

Medium-gray limestone. Brachiopod packstone most common; some coral-algal boundstone and local fine-grained grainstone. Mottled, disrupted bedding. Chert nodules and lenses common.

QA 14573c

C5
Pan American No. 1 Walker
Cochran County, Texas
Section 8, Block Z, PSL Survey
Elevation 3883 ft



Medium- to dark-gray limestone. Mottled to wavy beds; graded beds composed of brachiopod wackestone overlain by mottled lime mudstone; rare cross-stratified fine grainstone overlain by burrowed lime mudstone. Lower contact not preserved.

Black shale. Parallel to streaky laminae. Scattered medium- to light-gray laminae of quartzitic siltstone. Dolomitic; pyritic; micaceous. Scattered pellets. Silt increases in abundance with depth. Grades abruptly into siltstone below.

Medium- to dark-gray quartzitic siltstone. Mottled to wavy beds; dark-gray shale layers common. Dolomitic; micaceous; feldspathic. Local burrows. Sharp lower contact.

Light-gray quartzitic siltstone. Well-sorted coarse silt. Low-angle simple cross-laminae between horizontal laminae; 1 – 3-cm strata. Dolomitic, feldspathic, micaceous. Sharp lower contact.

Medium- to dark-gray quartzitic siltstone. Mottled, discontinuous, and wavy beds. Dark-gray shale layers common. Dolomitic, micaceous, feldspathic. Local burrows. Lower contact sharp and irregular but conformable.

Light-gray to black speckled conglomeratic sandstone. Phosphatic chert arenite. No internal structure. Abundant chert grains, mostly sand-sized, some granule- to pebble-sized. Abundant phosphatic fossil fragments; some phosphatic ooids and large coprolites; scattered sand-sized quartz; scarce mica. Lower contact sharp, irregular, and disconformable.

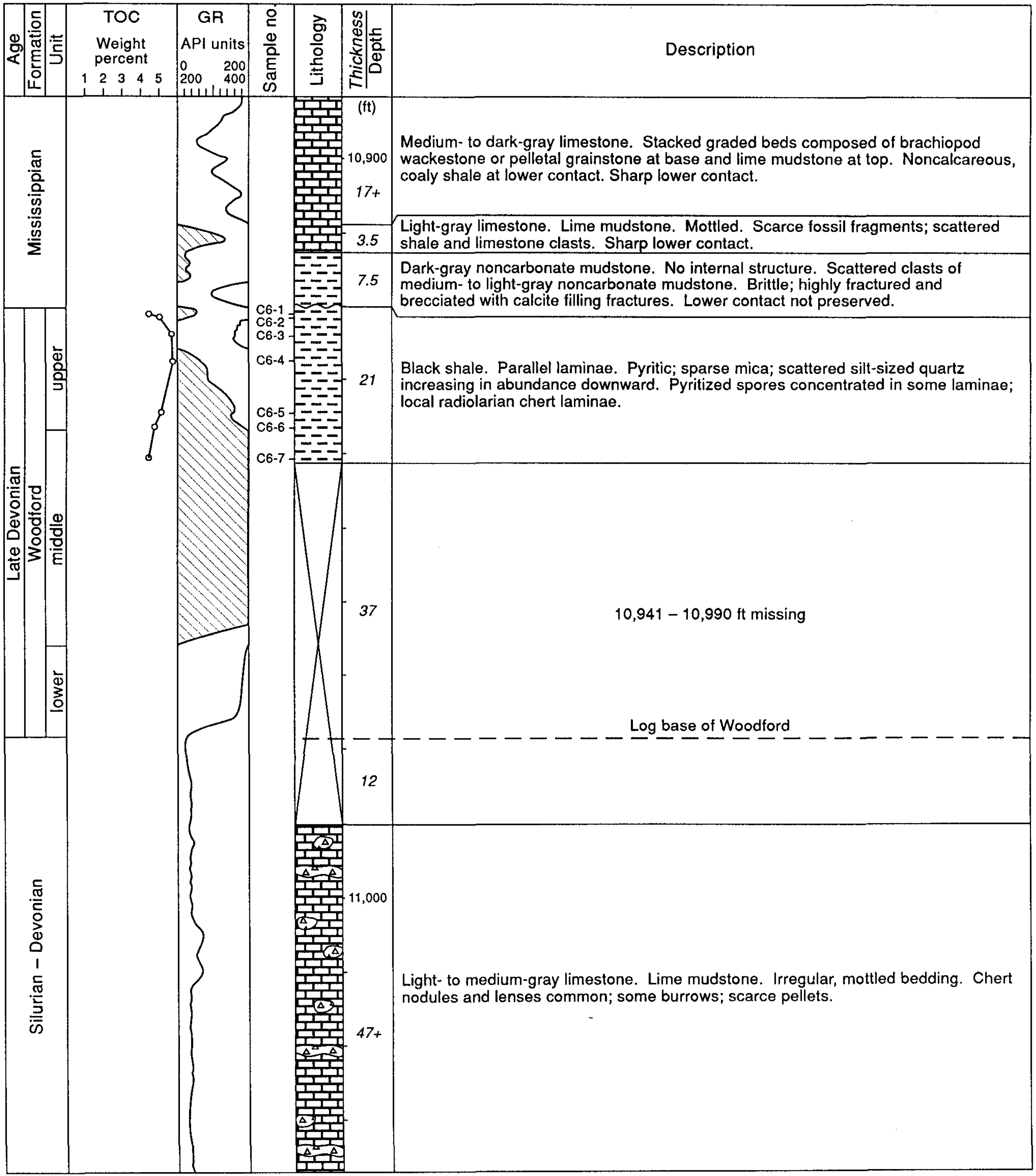
Light-gray limestone. Fine-grained grainstone and brachiopod packstone; local boundstone. Irregular, discontinuous beds. Chert nodules and lenses common.

11,720 - 11,785 ft missing

White to pale brownish-pink finely crystalline dolostone. Mottled, irregular beds. Chert nodules, lenses, and beds common; most abundant at bottom of core.

QA 14574c

C6
Shell No. 1 Chriesman
Glasscock County, Texas
Section 12, Block 36, T 5 S, T and P Survey
Elevation 2697 ft



Medium- to dark-gray limestone. Stacked graded beds composed of brachiopod wackestone or pelletal grainstone at base and lime mudstone at top. Noncalcareous, coaly shale at lower contact. Sharp lower contact.

Light-gray limestone. Lime mudstone. Mottled. Scarce fossil fragments; scattered shale and limestone clasts. Sharp lower contact.

Dark-gray noncarbonate mudstone. No internal structure. Scattered clasts of medium- to light-gray noncarbonate mudstone. Brittle; highly fractured and brecciated with calcite filling fractures. Lower contact not preserved.

Black shale. Parallel laminae. Pyritic; sparse mica; scattered silt-sized quartz increasing in abundance downward. Pyritized spores concentrated in some laminae; local radiolarian chert laminae.

10,941 – 10,990 ft missing

Light- to medium-gray limestone. Lime mudstone. Irregular, mottled bedding. Chert nodules and lenses common; some burrows; scarce pellets.

QA 14575c

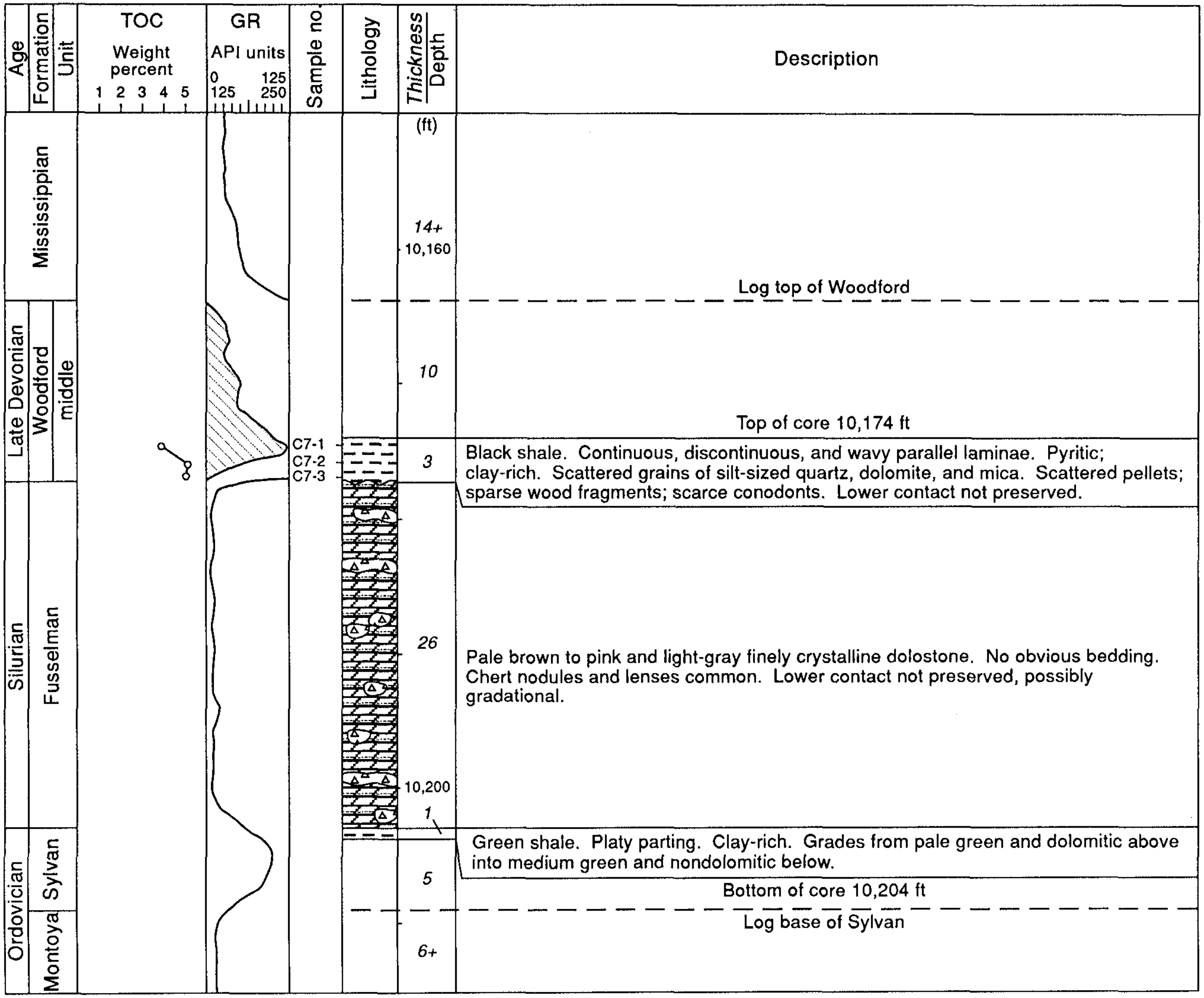
C7

Standard of Texas No. 1-28 Canon

Dawson County, Texas

Section 28, Block 33, T 5 N, T and P Survey

Elevation 2711 ft



Log top of Woodford

Top of core 10,174 ft

Black shale. Continuous, discontinuous, and wavy parallel laminae. Pyritic; clay-rich. Scattered grains of silt-sized quartz, dolomite, and mica. Scattered pellets; sparse wood fragments; scarce conodonts. Lower contact not preserved.

Pale brown to pink and light-gray finely crystalline dolostone. No obvious bedding. Chert nodules and lenses common. Lower contact not preserved, possibly gradational.

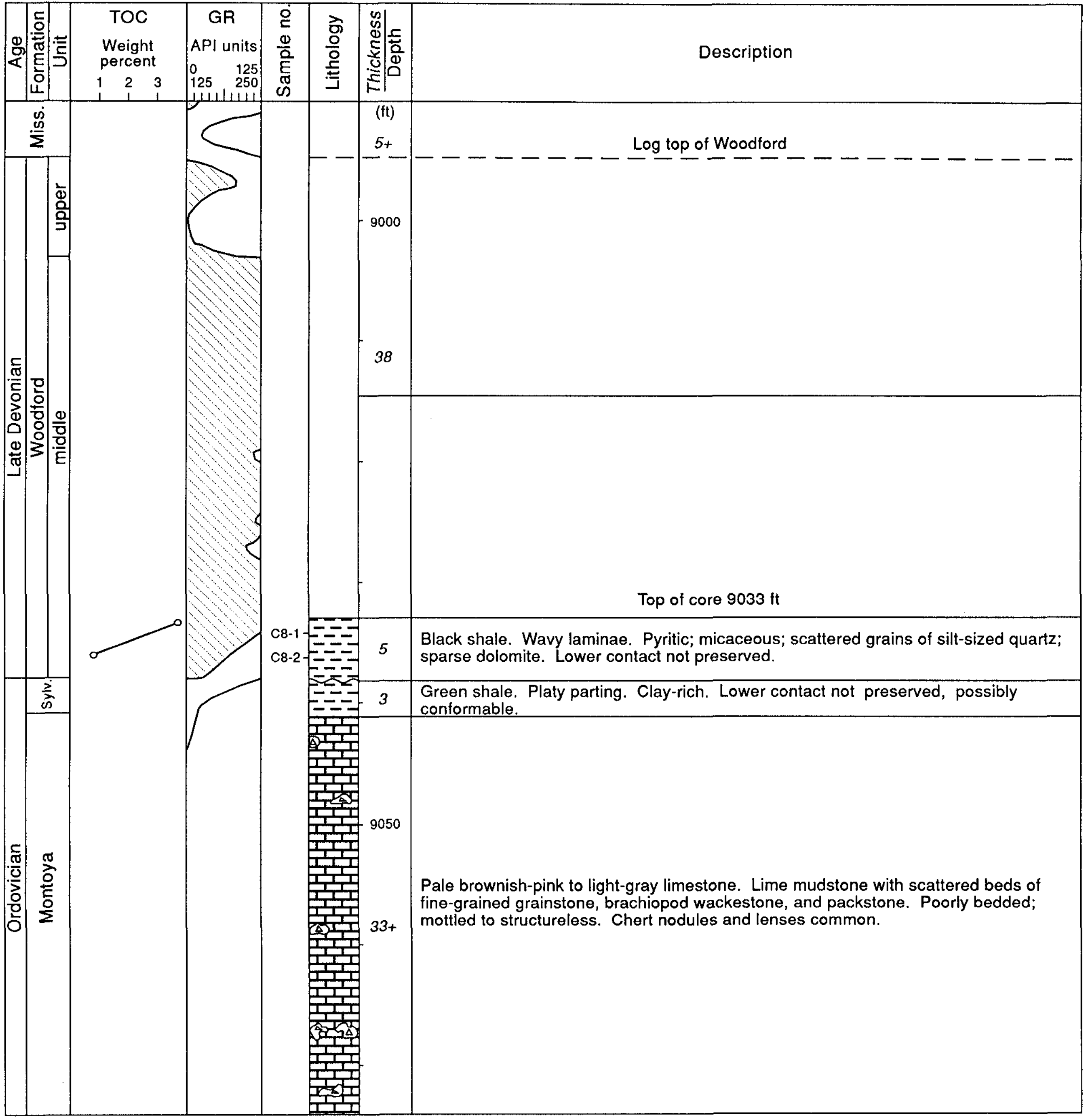
Green shale. Platy parting. Clay-rich. Grades from pale green and dolomitic above into medium green and nondolomitic below.

Bottom of core 10,204 ft

Log base of Sylvan

QA 14576c

C8
Roden and Cosden No. 1 Reed
Sterling County, Texas
Section 9, Block 30, W and NW Survey
Elevation 2569 ft



Log top of Woodford

Top of core 9033 ft

5 — Black shale. Wavy laminae. Pyritic; micaceous; scattered grains of silt-sized quartz; sparse dolomite. Lower contact not preserved.

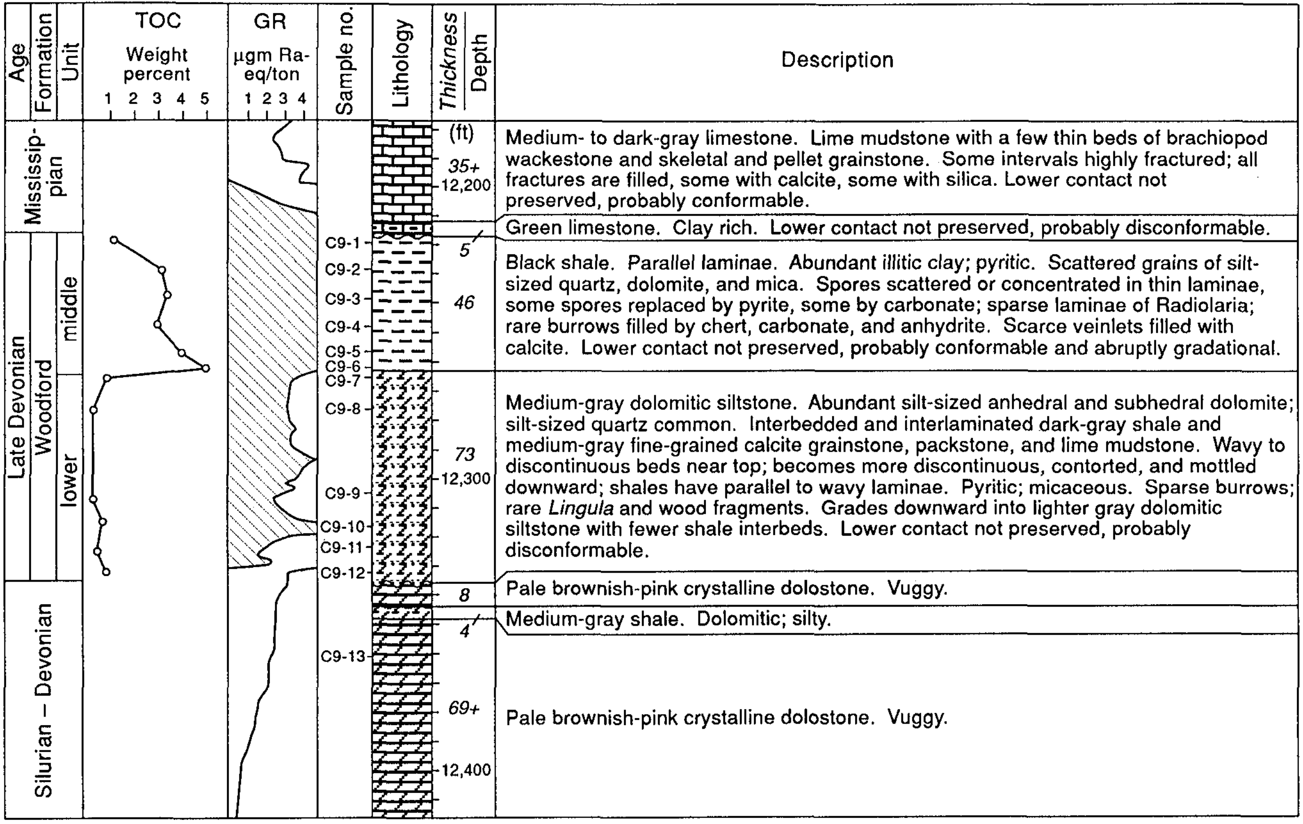
3 — Green shale. Platy parting. Clay-rich. Lower contact not preserved, possibly conformable.

33+ — Pale brownish-pink to light-gray limestone. Lime mudstone with scattered beds of fine-grained grainstone, brachiopod wackestone, and packstone. Poorly bedded; mottled to structureless. Chert nodules and lenses common.

QA 14577c

C9

Shell No. 5 Pacific Royalty
Lea County, New Mexico
Section 10, T 15 S – R 37 E
Elevation 3814 ft



Medium- to dark-gray limestone. Lime mudstone with a few thin beds of brachiopod wackestone and skeletal and pellet grainstone. Some intervals highly fractured; all fractures are filled, some with calcite, some with silica. Lower contact not preserved, probably conformable.

Green limestone. Clay rich. Lower contact not preserved, probably disconformable.

Black shale. Parallel laminae. Abundant illitic clay; pyritic. Scattered grains of silt-sized quartz, dolomite, and mica. Spores scattered or concentrated in thin laminae, some spores replaced by pyrite, some by carbonate; sparse laminae of Radiolaria; rare burrows filled by chert, carbonate, and anhydrite. Scarce veinlets filled with calcite. Lower contact not preserved, probably conformable and abruptly gradational.

Medium-gray dolomitic siltstone. Abundant silt-sized anhedral and subhedral dolomite; silt-sized quartz common. Interbedded and interlaminated dark-gray shale and medium-gray fine-grained calcite grainstone, packstone, and lime mudstone. Wavy to discontinuous beds near top; becomes more discontinuous, contorted, and mottled downward; shales have parallel to wavy laminae. Pyritic; micaceous. Sparse burrows; rare *Lingula* and wood fragments. Grades downward into lighter gray dolomitic siltstone with fewer shale interbeds. Lower contact not preserved, probably disconformable.

Pale brownish-pink crystalline dolostone. Vuggy.

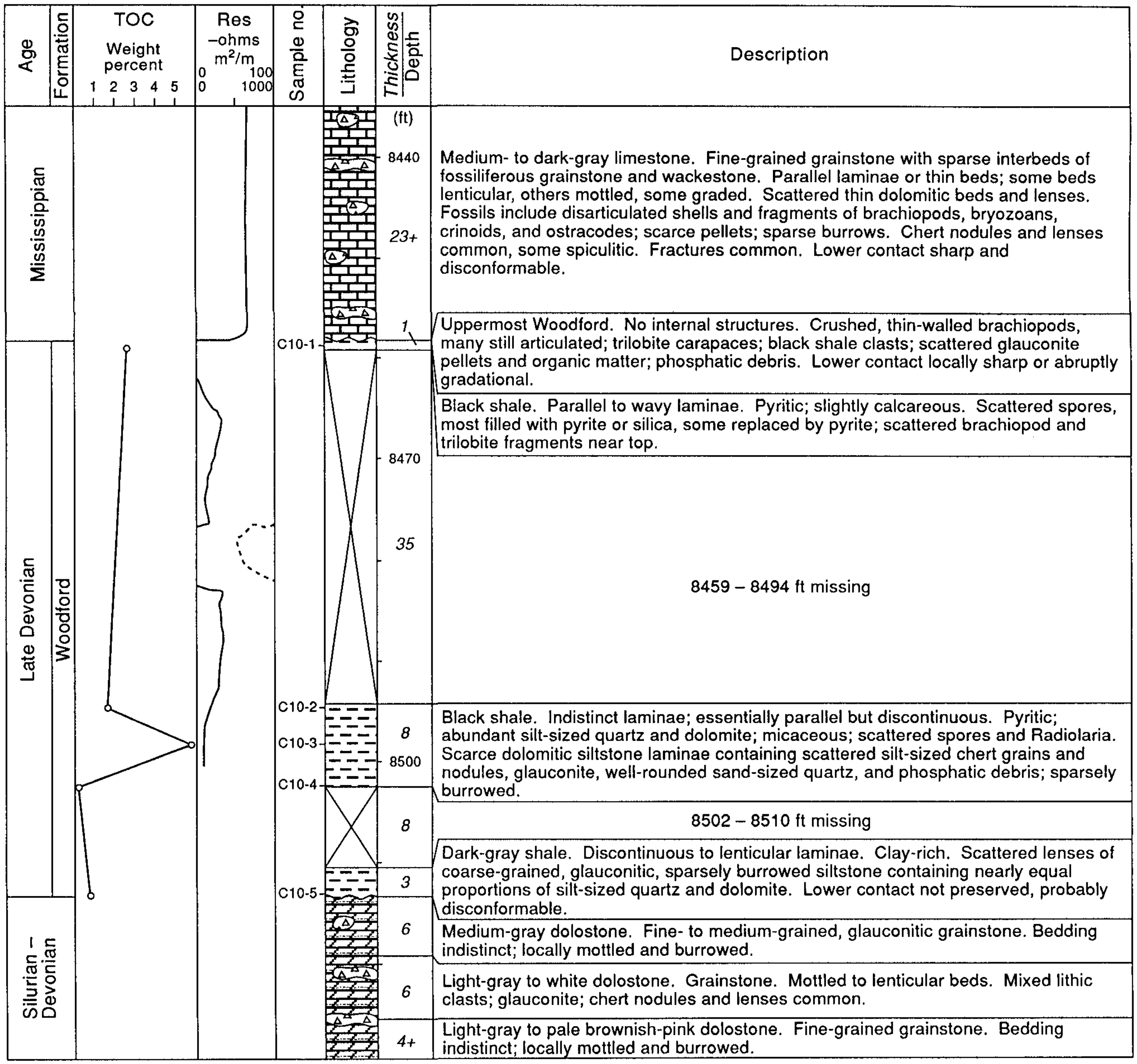
Medium-gray shale. Dolomitic; silty.

Pale brownish-pink crystalline dolostone. Vuggy.

QA 14578c

C10

McGrath and Smith No. 1 Brennand and Price
Mitchell County, Texas
Section 7, Block 17, SPRR Survey
Elevation 2332 ft



Medium- to dark-gray limestone. Fine-grained grainstone with sparse interbeds of fossiliferous grainstone and wackestone. Parallel laminae or thin beds; some beds lenticular, others mottled, some graded. Scattered thin dolomitic beds and lenses. Fossils include disarticulated shells and fragments of brachiopods, bryozoans, crinoids, and ostracodes; scarce pellets; sparse burrows. Chert nodules and lenses common, some spiculitic. Fractures common. Lower contact sharp and disconformable.

Uppermost Woodford. No internal structures. Crushed, thin-walled brachiopods, many still articulated; trilobite carapaces; black shale clasts; scattered glauconite pellets and organic matter; phosphatic debris. Lower contact locally sharp or abruptly gradational.

Black shale. Parallel to wavy laminae. Pyritic; slightly calcareous. Scattered spores, most filled with pyrite or silica, some replaced by pyrite; scattered brachiopod and trilobite fragments near top.

8459 – 8494 ft missing

Black shale. Indistinct laminae; essentially parallel but discontinuous. Pyritic; abundant silt-sized quartz and dolomite; micaceous; scattered spores and Radiolaria. Scarce dolomitic siltstone laminae containing scattered silt-sized chert grains and nodules, glauconite, well-rounded sand-sized quartz, and phosphatic debris; sparsely burrowed.

8502 – 8510 ft missing

Dark-gray shale. Discontinuous to lenticular laminae. Clay-rich. Scattered lenses of coarse-grained, glauconitic, sparsely burrowed siltstone containing nearly equal proportions of silt-sized quartz and dolomite. Lower contact not preserved, probably disconformable.

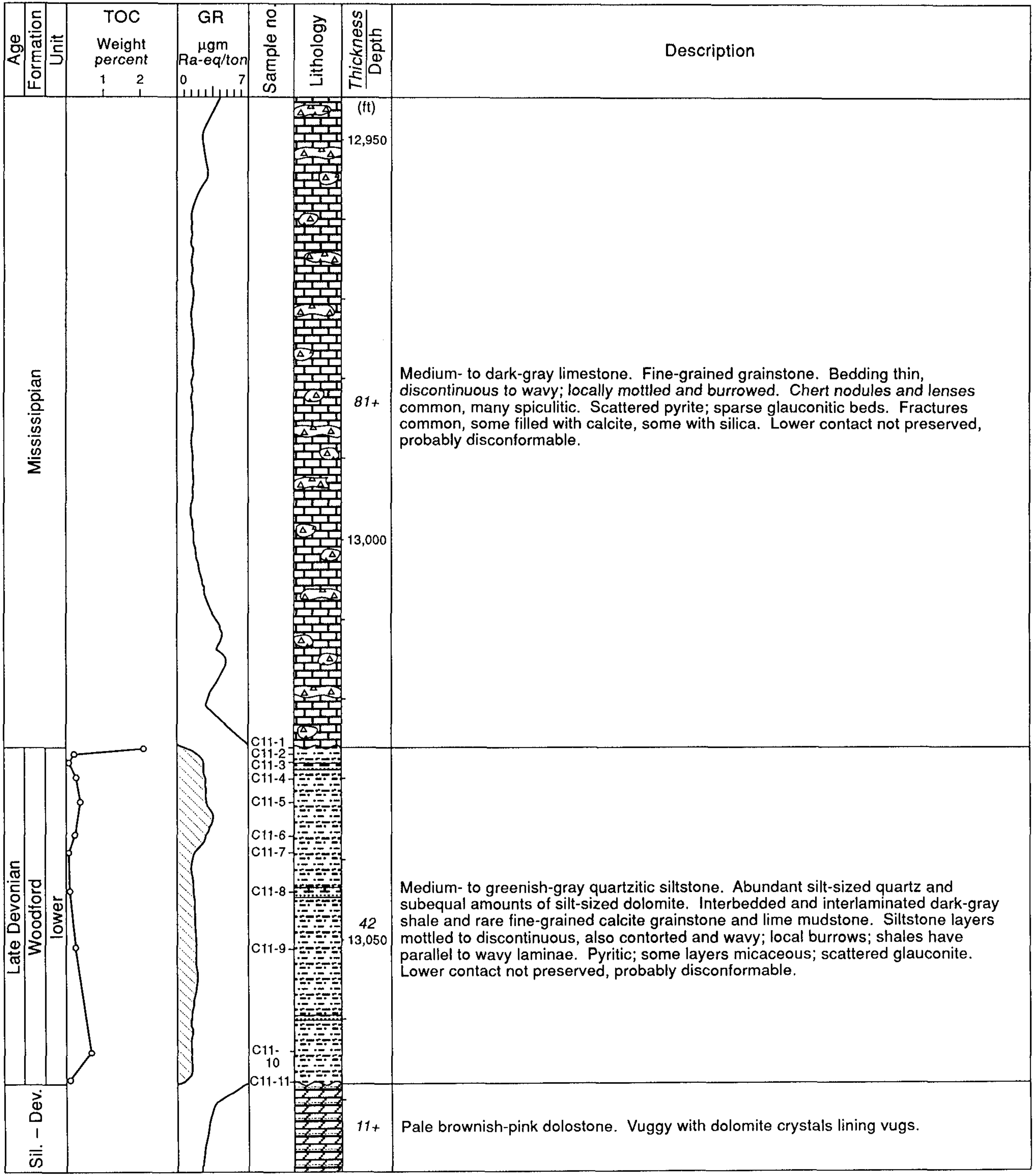
Medium-gray dolostone. Fine- to medium-grained, glauconitic grainstone. Bedding indistinct; locally mottled and burrowed.

Light-gray to white dolostone. Grainstone. Mottled to lenticular beds. Mixed lithic clasts; glauconite; chert nodules and lenses common.

Light-gray to pale brownish-pink dolostone. Fine-grained grainstone. Bedding indistinct; locally mottled and burrowed.

QA 14579c

C11
Shell A No. 1 Williamson
Gaines County, Texas
Section 110, Block H, D and W RR Survey
Elevation 3229 ft



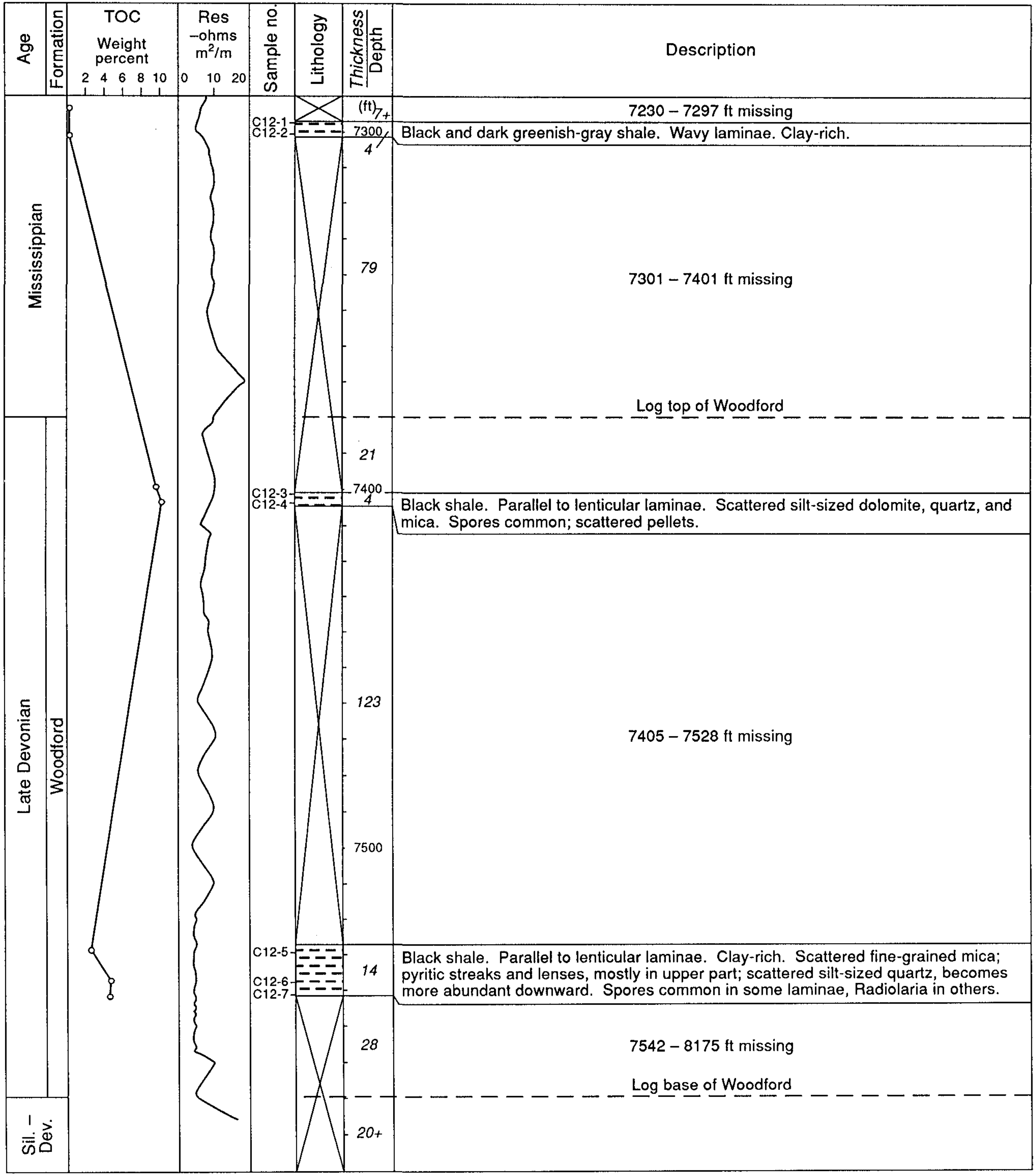
Medium- to dark-gray limestone. Fine-grained grainstone. Bedding thin, discontinuous to wavy; locally mottled and burrowed. Chert nodules and lenses common, many spiculitic. Scattered pyrite; sparse glauconitic beds. Fractures common, some filled with calcite, some with silica. Lower contact not preserved, probably disconformable.

Medium- to greenish-gray quartzitic siltstone. Abundant silt-sized quartz and subequal amounts of silt-sized dolomite. Interbedded and interlaminated dark-gray shale and rare fine-grained calcite grainstone and lime mudstone. Siltstone layers mottled to discontinuous, also contorted and wavy; local burrows; shales have parallel to wavy laminae. Pyritic; some layers micaceous; scattered glauconite. Lower contact not preserved, probably disconformable.

Pale brownish-pink dolostone. Vuggy with dolomite crystals lining vugs.

QA 14580c

C12
Shell No. 1 Sealy Smith
Ward County, Texas
Section 38, Block A, G and MMB and A Survey
Elevation 2736 ft



7230 – 7297 ft missing

Black and dark greenish-gray shale. Wavy laminae. Clay-rich.

7301 – 7401 ft missing

Log top of Woodford

Black shale. Parallel to lenticular laminae. Scattered silt-sized dolomite, quartz, and mica. Spores common; scattered pellets.

7405 – 7528 ft missing

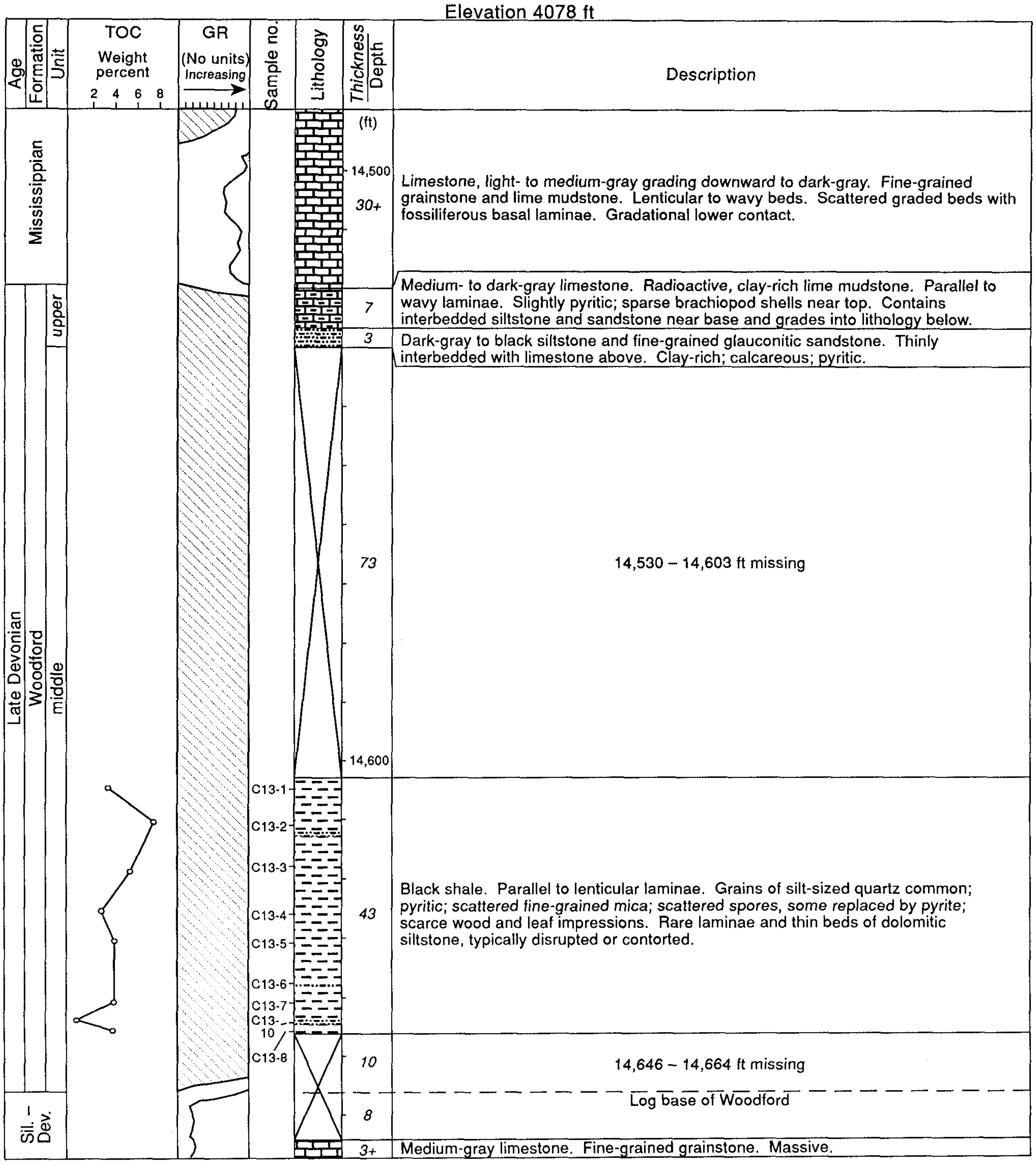
Black shale. Parallel to lenticular laminae. Clay-rich. Scattered fine-grained mica; pyritic streaks and lenses, mostly in upper part; scattered silt-sized quartz, becomes more abundant downward. Spores common in some laminae, Radiolaria in others.

7542 – 8175 ft missing

Log base of Woodford

QA 14581c

C13
Humble No. 1 Federal Elliott
Lea County, New Mexico
Section 1, T 16 S – R 34 E
Elevation 4078 ft



Limestone, light- to medium-gray grading downward to dark-gray. Fine-grained grainstone and lime mudstone. Lenticular to wavy beds. Scattered graded beds with fossiliferous basal laminae. Gradational lower contact.

Medium- to dark-gray limestone. Radioactive, clay-rich lime mudstone. Parallel to wavy laminae. Slightly pyritic; sparse brachiopod shells near top. Contains interbedded siltstone and sandstone near base and grades into lithology below.

Dark-gray to black siltstone and fine-grained glauconitic sandstone. Thinly interbedded with limestone above. Clay-rich; calcareous; pyritic.

14,530 – 14,603 ft missing

Black shale. Parallel to lenticular laminae. Grains of silt-sized quartz common; pyritic; scattered fine-grained mica; scattered spores, some replaced by pyrite; scarce wood and leaf impressions. Rare laminae and thin beds of dolomitic siltstone, typically disrupted or contorted.

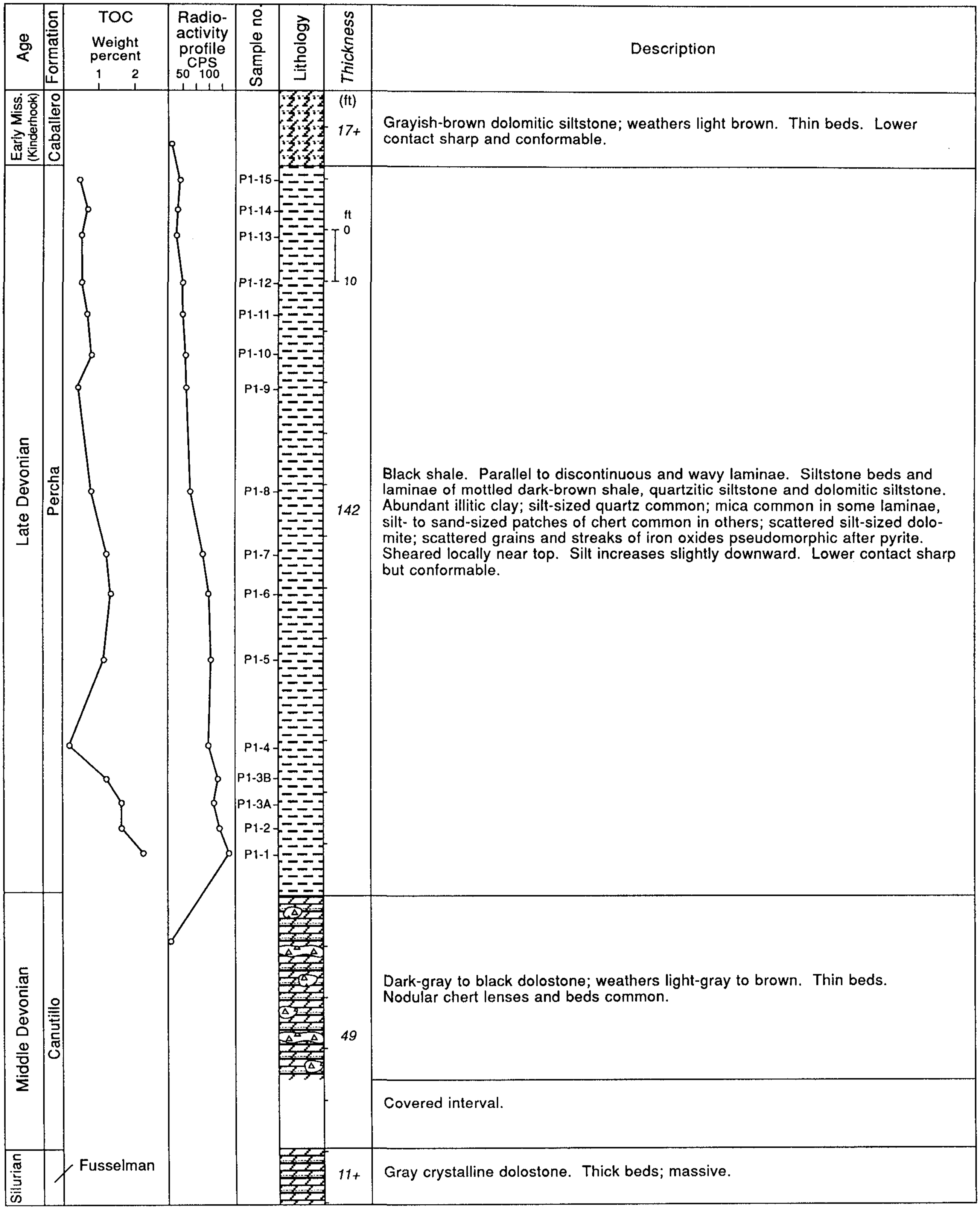
14,646 – 14,664 ft missing

Log base of Woodford

Medium-gray limestone. Fine-grained grainstone. Massive.

QA 14582c

P1
Bishop Cap
Doña Ana County, New Mexico
NE/4 Section 25, T 24 S – R 3 E



Grayish-brown dolomitic siltstone; weathers light brown. Thin beds. Lower contact sharp and conformable.

Black shale. Parallel to discontinuous and wavy laminae. Siltstone beds and laminae of mottled dark-brown shale, quartzitic siltstone and dolomitic siltstone. Abundant illitic clay; silt-sized quartz common; mica common in some laminae, silt- to sand-sized patches of chert common in others; scattered silt-sized dolomite; scattered grains and streaks of iron oxides pseudomorphic after pyrite. Sheared locally near top. Silt increases slightly downward. Lower contact sharp but conformable.

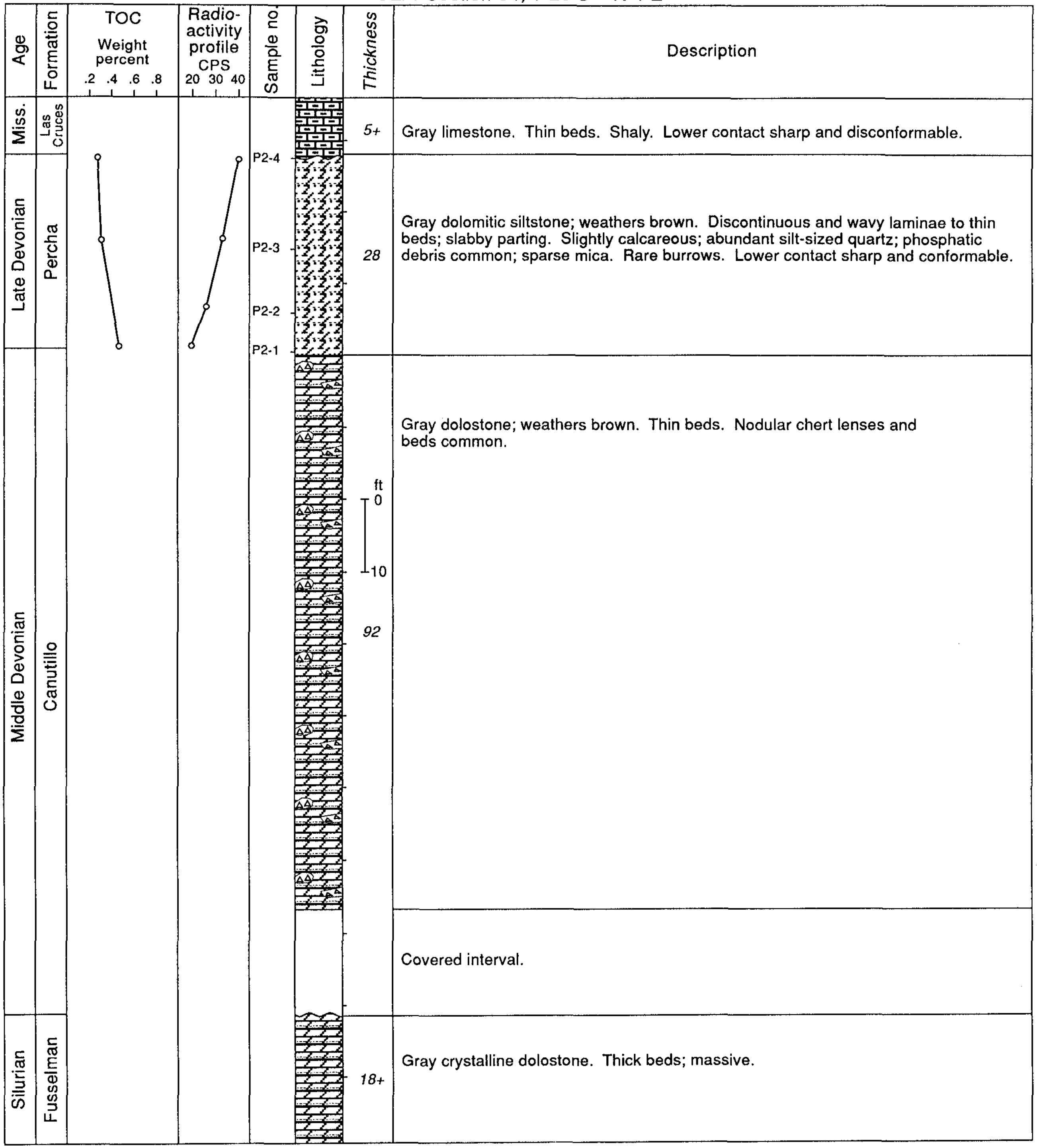
Dark-gray to black dolostone; weathers light-gray to brown. Thin beds. Nodular chert lenses and beds common.

Covered interval.

Gray crystalline dolostone. Thick beds; massive.

QA 14583c

P2
Anthony Gap
North Franklin Mountains
Doña Ana County, New Mexico
SE/4 Section 34, T 26 S – R 4 E



Gray limestone. Thin beds. Shaly. Lower contact sharp and disconformable.

Gray dolomitic siltstone; weathers brown. Discontinuous and wavy laminae to thin beds; slabby parting. Slightly calcareous; abundant silt-sized quartz; phosphatic debris common; sparse mica. Rare burrows. Lower contact sharp and conformable.

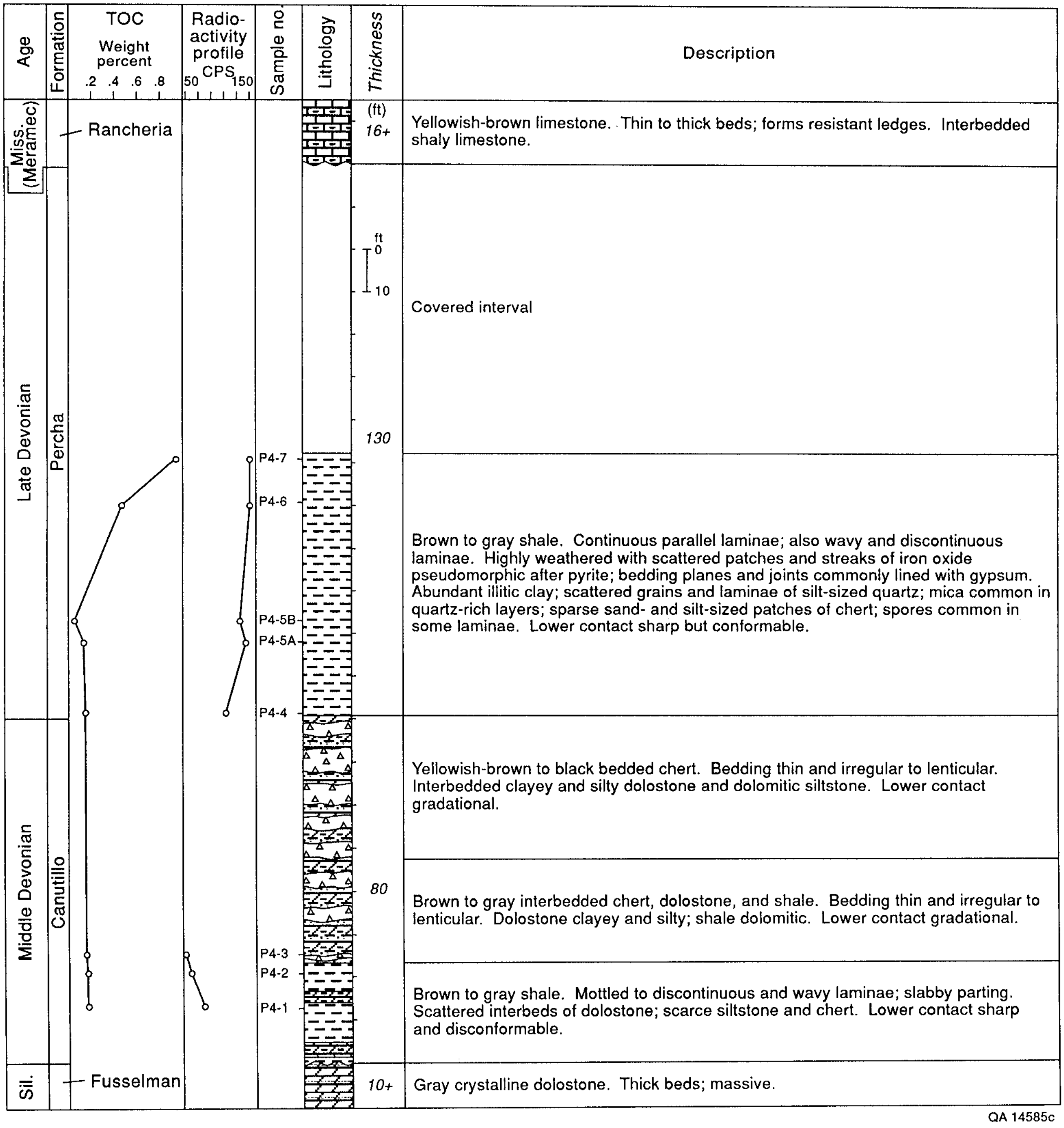
Gray dolostone; weathers brown. Thin beds. Nodular chert lenses and beds common.

Covered interval.

Gray crystalline dolostone. Thick beds; massive.

QA 14584c

P4
Martin Canyon
Hueco Mountains
El Paso County, Texas
106° 00' 30" W. Longitude – 31° 48' 30" N. Latitude



Yellowish-brown limestone. Thin to thick beds; forms resistant ledges. Interbedded shaly limestone.

Covered interval

Brown to gray shale. Continuous parallel laminae; also wavy and discontinuous laminae. Highly weathered with scattered patches and streaks of iron oxide pseudomorphic after pyrite; bedding planes and joints commonly lined with gypsum. Abundant illitic clay; scattered grains and laminae of silt-sized quartz; mica common in quartz-rich layers; sparse sand- and silt-sized patches of chert; spores common in some laminae. Lower contact sharp but conformable.

Yellowish-brown to black bedded chert. Bedding thin and irregular to lenticular. Interbedded clayey and silty dolostone and dolomitic siltstone. Lower contact gradational.

Brown to gray interbedded chert, dolostone, and shale. Bedding thin and irregular to lenticular. Dolostone clayey and silty; shale dolomitic. Lower contact gradational.

Brown to gray shale. Mottled to discontinuous and wavy laminae; slabby parting. Scattered interbeds of dolostone; scarce siltstone and chert. Lower contact sharp and disconformable.

Gray crystalline dolostone. Thick beds; massive.

Appendix C. Point-count data for the Woodford Formation.

Core and sample no.	Depth (ft)	Terrigenous				Pelagic		Authigenic		
		Quartz (%)	Mica (%)	Feldspar (%)	Illite (%)	AOM* (%)	Pellets (%)	Dolomite (%)	Pyrite (%)	Other (%)
					BLACK SHALE					
C1–4	11,540	6	3	— **	68	11	—	1	—	—
C1–9	11,555	14	2	1	45	10	—	22	6	—
C2–3	7,172	3	—	—	43	25	4	23	1	1
C2–8	7,181	—	—	1	34	35	5	19	2	4
C3–1	13,754	1	—	—	76	14	5	1	2	1
C3–10	13,884	2	—	—	53	13	—	20	—	12
C4–2	10,899	15	1	1	52	5	8	3	13	2
C4–7	10,933	17	2	2	56	8	—	6	8	1
C5–2	11,639	5	—	—	67	8	11	—	7	2
C5–5	11,648	6	—	—	64	9	2	15	2	2
C6–3	10,924	2	1	—	77	17	—	1	—	2
C7–2	10,176	16	—	—	53	15	3	7	5	1
C8–1	9,033	2	—	—	79	12	—	5	2	—
C9–2	12,228	9	—	—	69	10	—	2	3	7
C10–4	8,502	9	—	—	57	6	—	25	3	—
C12–4	7,404	3	2	—	50	31	7	4	2	1
C13–4	14,626	10	3	1	61	9	—	9	6	1
					SILTSTONE					
C3–6	13,772	6	—	—	—	—	—	68	24	2
C5–8	11,662	36	4	2	28	—	—	30	—	—
C10–4	8,502	32	—	—	—	—	—	39	—	29 ***
C11–5	13,033	43	—	1	14	—	—	41	—	2

* Volume percent of amorphous organic matter (AOM) = wt % TOC × 3. The conversion factor, 3, represents the density difference between organic matter and minerals, ~2.5, and a generalized value of carbon in kerogen, 80 wt %, or 2.5/0.8 ≈ 3.

** Less than 1.

*** Fossils, calcite cement, and phosphate.

Appendix D. Organic content of the Woodford Formation.

Core no.	Depth (ft)	TOC* (wt %)	Kerogen morphology	Primary (%)	Recycled (%)
BLACK SHALE					
C1	11,536–11,555	3.9	Amorphous**	1.14	ND
C2	7,169–7,184	9.0	Amorphous	0.55	0.87
C3	13,745–13,776	2.3	Amorphous	1.44	ND
C3	13,838–13,844	2.9	Amorphous	1.66	ND
C4	10,898–10,936	2.7	Amorphous	1.05	ND
C5	11,639–11,657	3.2	Amorphous	0.79	ND
C6	10,921–10,941	5.1	Amorphous	1.52	2.21
C7	10,174–10,177	4.6	Amorphous	0.68	ND
C8	9,033–9,036	2.4	Amorphous	0.78	1.15
C9	12,219–12,263	3.3	Amorphous	0.92	ND
C10	8,459–8,513	2.2	Amorphous	0.61	0.99
C12	7,401–7,542	6.3	Amorphous	0.54	ND
C13	14,605–14,644	4.2	Amorphous	1.64	ND
P1	Outcrop	1.1	Amorphous	1.92	ND
P3	Outcrop	0.1	Amorphous	NA	NA
P4	Outcrop	0.4	Amorphous	NA	NA
SILTSTONE					
C5***	11,662–11,688	0.9	Amorphous	0.85	ND
C9****	12,266–12,333	0.7	Amorphous	0.99	ND
C11***	13,026–13,068	0.4	Amorphous	1.32	ND
P2****	Outcrop	0.4	Amorphous	NA	ND

* Data represent mean values of samples in designated depth interval.

** Amorphous kerogen is aquatic, nonterrestrial organic matter that yields oil during thermal maturation (Hunt, 1979; Tissot and Welte, 1984).

*** Quartz-dominated siltstone.

**** Dolomite-dominated siltstone.

ND not detected.

NA not analyzed.

Environmental Science and Pollution Research (2022) 29:43058–43071
https://doi.org/10.1007/s11356-021-18022-z

Exhibit 5

RESEARCH ARTICLE

Occurrence and behavior of uranium and thorium series radionuclides in the Permian shale hydraulic fracturing wastes

Punam Thakur[1] · **Anderson L. Ward**[2] · **Tanner M. Schaub**[3]

Received: 27 July 2021 / Accepted: 6 December 2021 / Published online: 29 January 2022

Abstract

Over the last decade, there has been a rapid growth in the use of hydraulic fracturing (fracking) to recover unconventional oil and gas in the Permian Basin of southeastern New Mexico (NM) and western Texas. Fracking generates enormous quantities of wastes that contain technologically enhanced naturally occurring radioactive materials (TENORM), which poses risks to human health and the environment because of the relatively high doses of radioactivity. However, very little is known about the chemical composition and radioactivity levels of Permian Basin fracking wastes. Here, we report chemical as well as radiochemical compositions of hydraulic fracking wastes from the Permian Basin. Radium, the major TENORM of interest in unconventional drilling wastes, varied from 19.1 ± 1.2 to 35.9 ± 3.2 Bq/L for ^{226}Ra, 10.3 ± 0.5 to 21.5 ± 1.2 Bq/L for ^{228}Ra, and 2.0 ± 0.05 to 3.7 ± 0.07 Bq/L for ^{224}Ra. In addition to elevated concentrations of radium, these wastewaters also contain elevated concentrations of dissolved salts and divalent cations such as Na^+ (31,856–43,000 mg/L), Ca^{2+} (668–4123 mg/L), Mg^{2+} (202–2430 mg/L), K^+ (148–780 mg/L), Sr^{2+} (101–260 mg/L), Cl^- (5160–66,700 mg/L), SO_4^{2-} (291–1980 mg/L), Br^- (315–596 mg/L), SiO_2 (20–32 mg/L), and high total dissolved solid (TDS) of 5000–173,000 mg/L compared to background waters. These elevated levels are of radiological significance and represent a major source of Ra in the environment. The recent discovery of large deposits of recoverable oil and gas in the Permian Basin will lead to more fracking, TENORM generation, and radium releases to the environment. This paper evaluates the potential radiation risks associated with TENORM wastes generated by the oil and gas recovery industry in the Permian Basin.

Keywords Fracking · Oil and gas · Radium · Alpha spectrometry · Gamma spectrometry

Introduction

The Permian Basin, which stretches from southeastern New Mexico into west Texas, is now recognized as the largest and most prolific oil and gas producing region in the USA. The area is approximately 482,803-m long by 402,336-m wide and comprises several basins of which the Midland Basin is the largest, followed by the Delaware Basin, with the Marfa Basin being the smallest (Fig. 1). Although the Permian Basin has been drilled continuously for over 100 years, the innovation of hydraulic fracturing technology in 1947 and its combination with horizontal drilling in the 1990s opened access to deep oil-rich shale deposits. This technology has enabled the recovery of oil and natural gas from tight shale formations that were previously considered uneconomical, resulting in a "shale gas boom." In 2019 alone, the Permian Basin accounted for more than 35% of crude oil and more than 16% of total dry natural gas produced in the USA. According to recent estimates by the U.S. Geological

Responsible Editor: Georg Steinhauser

✉ Punam Thakur
pthakur@cemrc.org

Anderson L. Ward
Anderson.ward@cbfo.doe.gov

Tanner M. Schaub
tschaub@nmsu.edu

[1] Carlsbad Environmental Monitoring & Research Center, 1400 University Drive, Carlsbad, NM 88220, USA

[2] U.S. Department of Energy, Carlsbad Field Office, 4021 National Parks Highway, Carlsbad, NM 88221, USA

[3] CAIL and NMSU Research Cores Program, New Mexico State University, Las Cruces, NM 88003, USA

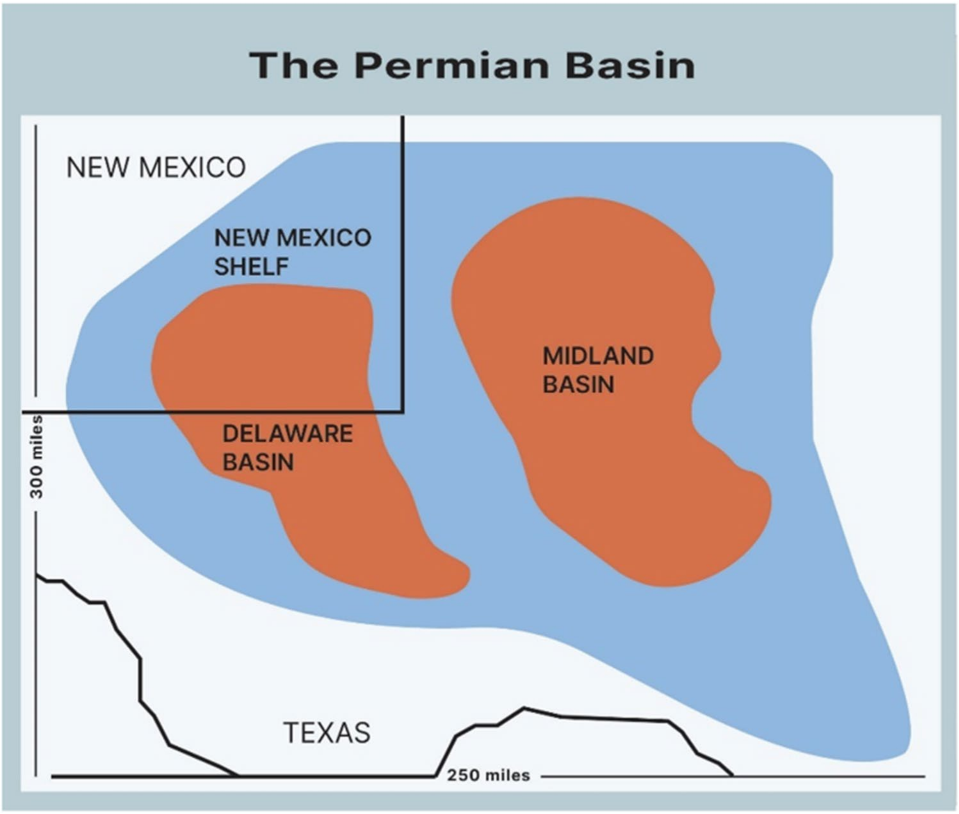


Fig. 1 Map of the Permian Basin

Survey, technically recoverable oil and gas reserves in the Permian Basin are some 7.4×10^{12} L of oil and 80 billion m^3 of natural gas (Gaswirth et al. 2018). Projections suggest that oil and gas production could grow from the current 7.4×10^8 million L per day to nearly 1.9×10^9 L per day by 2030.

Hydraulic fracturing, or fracking, is a well-stimulation technique used to extract oil and natural gas trapped in low-permeability rock-like shale. The process involves drilling down to the sedimentary rocks, sometimes as far as 3000 m, then drilling horizontally for as many as several kilometers. Water is a key ingredient in fracking operations, where each Permian Basin operation requires approximately 4 million L (1.1 million gal) of water (Kondash et al. 2018). This is not much compared to the fracking operations in other basins around the country, which may require as much as 15–22 million L (4–6 million gal). However, the sheer number of wells in the Permian means it produces more wastewater than other basins.

This water is mixed with proppant (crystalline silica sand or engineered ceramics, which holds the cracks in the fractured shale open) and chemical additives before injection into the well under high pressure (7000–12,000 psi) to open existing fractures or initiate new fractures. Fracking generates two major types of wastewater, flowback water, and produced water. Flowback water is the portion of injected water that returns to the surface during the initial period of well completion, whereas produced water is the naturally occurring water that exists in the formation and is generated over the lifetime of the well once the well is in production mode. The typical fracked well generates 1.7 to 14.3 million L (450,000 to 3.8 million gal) of wastewater over the first 5–10 years of production (Kondash 2017). The American Petroleum Institute (API) estimates that oil and gas production generates more than 3×10^{12} L of wastewater each year in the USA (API 2000).

Both flowback and produced waters are usually hypersaline, containing elevated concentrations of anions (Cl^-, Br^-), divalent cations (e.g., Ba^{2+}, Ca^{2+}, Sr^{2+}), metalloids (e.g., Se, As), fracking chemicals, and naturally occurring radioactive material (NORM). These components are transported to the surface with the wastewater and can accumulate in drilling equipment and pipes over time in the form of scale and sludge. With the new wells being drilled at a record pace, increased potential for NORM exposure as well as human health and the environmental impacts must be considered. The generation of NORM by oil and gas production has been documented for decades (Jonkers 1997). The geologic formations that contain oil and gas deposits also contain NORM such as uranium, thorium, and radium (Walter et al. 2012). The anthropogenic enhancement (e.g., mining, milling, processing of uranium ore, and oil and gas exploration) of NORM leads to the generation of TENORM. The level of NORM/TENORM in unconventional oil and gas waste can vary substantially from one facility to another depending on geological formation and the salinity of the produced water. Generally, the concentration of NORM increases with salinity (Rowan et al. 2011). Since salinity often increases with the age of a well, old wells tend to exhibit higher NORM levels than newly drilled ones. For example, black shale, such as the Marcellus, usually contains higher levels of ^{238}U, ^{235}U, ^{40} K, and ^{232}Th than sandstones and limestones that have lower levels of organic matter (Nabhani et al. 2016).

One radionuclide of particular interest in fracking waste is radium, including the isotopes ^{226}Ra (half-life, $t_{1/2} = 1600$ years) and ^{228}Ra ($t_{1/2} = 5.8$ years), both of which are produced by the radioactive decay of uranium (^{238}U decay series) and thorium (^{234}Th decay series) that are present in rocks of the oil-producing formations. Unlike uranium and thorium, radium is a highly water-soluble component of TENORM. Dissolved radium either remains in solution in the flowback and produced waters or coprecipitates with barium, strontium, or calcium to form hard sulfate scales and carbonate sludges (Kraemer and Reid 1984). Radium-bearing scale and sludge can accumulate in oil field equipment, such as pipes and storage tanks, and enter the environment during disposal.

Following the discharge of wastewater, radium tends to associate with suspended sediment particles and accumulate in streambeds. Radium in flowback and produced waters can range from undetectable levels to as high as 1000 Bq/L. Radium concentration in these waters generally shows a positive correlation with total dissolved solids (TDS) and barium content despite variation in reservoir lithology (Rowan et al. 2011). These levels are significantly higher than the maximum contaminant levels for drinking water of 0.56 Bq/L (15 pCi/L) for the gross alpha (excluding uranium and radon) and 0.185 Bq/L (5 pCi/L) for total dissolved radium (USEPA 2000).

Another pathway to dispersal is atmospheric, as both the thorium and uranium decay chains contribute to airborne radionuclides. Radium decays to radon, a radioactive gas, which escapes the ground and subsequently decays as airborne particulate. According to EPA estimates, radon is the number one cause of lung cancer among nonsmokers (USEPA 2000). Radium, together with its daughter product, radon, are the main contributors to environmental radioactivity. Furthermore, radon decay products ^{210}Pb and ^{210}Po can build up in scale on the internal surfaces of oil and gas handling pipes and in sludge in refineries, becoming potential inhalation and ingestion hazards for workers (Thakur and Ward 2020).

In addition to oil and gas exploration, the Permian Basin of southeastern NM is also home to the world's only operational deep geologic transuranic nuclear waste repository, the DOE's Waste Isolation Pilot Plant (WIPP). Plutonium isotopes ($^{239+240}$Pu) and ^{241}Am are expected to account for more than 99% of the total radioactivity scheduled for disposal in the WIPP repository (Thakur and Ward 2019; ATWIR 2020). In this context, accurate measurement of TENORM levels in oil field waste is essential to observe the composition of Permian Basin fracking waste "stream-sand" to identify effective strategies to mitigate radiation exposure from these materials. Despite the meteoric rise of fracking in the Permian Basin, radionuclide concentration data for hydraulic fracking waste remains extremely sparse. Here, we determine radioactivity levels in the Permian Basin shale fracking waste samples and evaluate the radiation risks associated with TENORM generated from the recovery of oil and gas by fracking in this region.

Experimental

Reagents

The extraction chromatography materials employed in this work are TEVA Resin, a quaternary ammonium salt, also known as Aliquat® 336, and TRU Resin, which contains octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide [CMPO] dissolved in tri-n-butyl phosphate [TBP]. Both resins were in the 50–100 µm particle size range and obtained from Eichrom Technologies, Inc., (Lisle, IL, USA). Trace metal grade HCl, HNO_3, $HClO_4$, and HF were obtained from Fisher Scientific Inc. (Hampton, NH, USA) Reagent-grade copper chloride ($CuCl_2 \cdot 2H_2O$), sodium sulfide ($Na_2S \cdot 9H_2O$), ascorbic acid, sulfamic acid, and sodium nitrite ($NaNO_2$) were also purchased from Fisher Scientific and were used as received. All other materials were ACS reagent grade and were used as received. The radioactive isotopes ^{209}Po, ^{229}Th, ^{236}Pu (or ^{242}Pu), ^{243}Am, and ^{232}U, obtained from Eckert & Ziegler Analytics, Inc. (Atlanta, GA, USA) and diluted to the appropriate levels. A ^{232}U tracer was prepared by removing its ^{228}Th daughter using barium sulfate precipitation (Sill 1974).

Sample collection and pretreatment

Seven samples of flowback and produced waters (1–4 L) were collected from a storage tank in August 2019 and January 2020 from the Delaware Basin, near Carlsbad, in southeastern New Mexico. Three samples of waste proppant sand were also collected from the Carlsbad area. Water samples were collected in 1-L Nalgene bottles, whereas the sand samples were collected in Ziploc® bags. Before sample pretreatment, the pH of the water samples was measured, and samples were filtered through a 0.45-µm Whatman filter. Samples of produced water were difficult to filter and therefore were used without filtration. Water samples were acidified to pH ~ 2 with concentrated HNO_3.

TDS of flowback and produced waters were determined gravemetrically by evaporating waters and measuring the mass of residues left in a high precision balance.

Sample preparation

Samples of 50–150 mL were used for TENORM and actinide measurements. The samples were spiked with 0.5 mL of 50 mg/mL $Fe(NO_3)_3{\cdot}9H_2O$ carrier and approximately 0.050–0.062 Bq of ^{209}Po, $^{236}Pu/^{242}Pu$, ^{243}Am, ^{229}Th, and ^{232}U as tracers for yield monitoring. The samples were digested on a hot plate using 10–20 mL of concentrated HNO_3 and 10 mL of 30% H_2O_2 at 90–100 °C for about an hour. Sand samples were spiked with appropriate tracers and digested with $HF+HNO_3$ up to the complete decomposition of silica. The digested sand samples were then treated with concentrated $HClO_4$ and HNO_3 to remove fluoride ions. The inside walls of the beaker are rinsed carefully with HNO_3 to gather residual HF, and evaporation was repeated to ensure the complete removal of HF. The suspended material retained on the filters was air-dried and then digested with HNO_3+HCl and HF, if necessary.

Actinides and TENORMs were concentrated by iron hydroxide coprecipitation with ammonium hydroxide (pH ~ 8 to 9). After decantation and centrifugation, precipitates were dissolved in 10 mL of 3 M HNO_3. The oxidation state of Pu was adjusted to Pu(IV) by adding 0.5 mL of 1.5 M sulfamic acid + 1.0 mL of 1.5 M ascorbic acid. After waiting for 3 min, 3.5 M $NaNO_2$ was added dropwise until the solutions became colorless. The sample solutions were covered with a watch glass and heated to ~ 50–60 °C on a hot plate for about 30–40 min to allow oxidation of Pu to Pu (IV). To ensure that Po is present as Po(IV), 2–3 drops of 30% H_2O_2 were added to each column load solution and mixed well prior to loading.

Separation of actinide and TENORM radionuclides

The TEVA + TRU chromatography columns were used to separate individual radionuclides. Plutonium, thorium, and polonium were separated on the TEVA resin, whereas uranium and americium were separated on the TRU resin column. Valence-adjusted samples in 3 M HNO_3 were loaded onto TEVA columns preconditioned with 10 mL of 3 M HNO_3 followed by the washing of columns with 6 mL of 3 M HNO_3. Americium and uranium pass through the column, and these effluents are kept for americium and uranium analysis using TRU chromatography. After washing, polonium was first stripped from the TEVA column with 20 mL of 8 M HNO_3, and thorium was eluted with 15 mL of 9 M HCl. After thorium elution, the Pu was removed from the TEVA column with 20 mL of freshly prepared 0.1 M HCl + 0.05 M HF + 0.03 M $TiCl_3$. The Am/U fractions from the 3 M HNO_3 eluate of the TEVA column were evaporated to dryness and dissolved in 10 mL of 2 M HNO_3. The sample solutions were then loaded onto the TRU columns, preconditioned with 10 mL of 2 M HNO_3. After washing, the column with 12 mL of 2 M HNO_3, americium was first stripped from the column with 20 mL of 4 M HCl followed by elution of uranium with 20 mL of 0.1 M ammonium bioxalate $(NH_4)_2C_2O_4$.

Alpha-source preparation and counting

Alpha-counting sources for plutonium, americium, thorium, and uranium were prepared by the NdF_3-micro coprecipitation method, whereas alpha source for polonium was prepared by the CuS microprecipitation. The alpha sources for uranium, thorium, and polonium were covered with a thin film to prevent daughter recoil contamination of detectors (Inn et al. 2008).

An alpha spectroscopy system (Mirion Technologies, Inc.), equipped with 72 Passivated Implanted Planar Silicon (PIPS) detectors, connected to an Apex-Alpha software system, was used for the acquisition, analysis, and storage of alpha spectra. The PIPS detectors have an active surface area of 450 mm^2. The distance between the sample and the detector surface is ~ 3 mm, and the nominal counting efficiency is ~ 20%. A set of stainless-steel alpha standards, procured from Canberra, was used to establish calibration and counting efficiencies. Samples were counted for at least 24 h and an overall recovery of ~ 70 to 95% was obtained.

Inorganic cation and anion analyses

The major ions were analyzed by a Metrohm USA 930 Compact Ion Chromatograph (IC) FLEX, while trace metal analysis was conducted using inductively coupled plasma mass spectrometers (PerkinElmer, NexION 2000). The Metrohm 930 Compact IC Flex system used for cation/anion analysis is equipped with one standard pump, one guard column, one chromatographic column, a conductivity detector, one chromatography enclosure, and an autosampler. The system is operated by a dedicated computer, using Metrohm MagIC Net® software. Only one type of analysis can be performed at a time. The "cation" system is used to analyze cations such as calcium, magnesium, potassium, sodium. Prior to performing "anion" analyses, the system was flushed and set up appropriately.

The ICP-MS were calibrated prior to performing analysis using pure standards, matrix-matched standards, or relevant certified reference materials to assure traceability of the reported results. The precision between replicates observed within the linear range of the instrument was typically < 1%. The replicate precision for the method is typically < 5%. Based on analysis of secondary source standards and method performance samples a ± 10% accuracy level can be expected. For samples with more complex matrices like oil field water, an instrument precision of < 5%, a method precision of < 20%, and an accuracy level of ± 20% are expected.

Radium measurement by gamma counting

Radium activities in the samples were measured using gamma spectroscopy with a Broad Energy Germanium detector (BeGe) (Mirion Technologies, Inc.) calibrated with matrix-specific standards obtained from Eckert & Ziegler Analytics, Inc. Each day, before the start of an analysis, background and instrument quality-control checks were performed, reviewed, and validated. Liquid samples were weighed into a new 1.5 L Marinelli and sealed with polyethylene tape. Solid samples were sealed in 300-mL tin-plated steel cans and stored for at least 21 days, to allow radon progeny to reach equilibrium with parent radionuclides, before counting. The ^{226}Ra activities in liquid samples were determined directly by measuring the 186.2 keV gamma photopeak (3.28% abundance) and indirectly by measuring the gamma photopeaks of ^{214}Pb (295 and 351 keV) and ^{214}Bi (609 keV) in solid samples. The ^{228}Ra activities were determined indirectly by measuring their immediate, short-lived daughter ^{228}Ac ($t_{1/2\,=}$ 6.1 h) using 911 and 969 keV gamma photo peaks. The ^{224}Ra was determined by measuring the gamma photopeaks of ^{212}Pb (238 keV) and ^{208}Tl (583 keV). Samples were counted for 48 h to minimize statistical counting error, which was typically in the range of 10–15%.

For liquid samples without U, this approach provides an accurate ^{226}Ra result. However, the presence of ^{235}U in samples such as soil, sediment, drill cuttings, and scale causes interference with direct ^{226}Ra measurement because one of its gamma lines is of similar energy, 185.7 keV (54% abundance). This could lead to an overestimation of ^{226}Ra activity. In such cases, possible contributions from ^{235}U on ^{226}Ra activities were corrected. Excess ^{226}Ra is calculated by converting the ^{235}U value to ^{226}Ra activity by a factor equal to the ratio of the gamma yields, i.e., 50.4/3.28. The gamma peaks of the ^{222}Rn daughters, ^{214}Pb (295.1 keV, 19.2% abundance and 352 keV, 37.1% abundance), and ^{214}Bi (609.3 keV, 46.1% abundance and 1120.3 keV, 15% abundance) gamma lines were also used to infer ^{226}Ra activity when ^{238}U was present in the sample. However, ^{222}Rn being a gas can escape, if the sample container is permeable to radon gas, eventually accumulating in any headspace above the bulk matrix to cause an underestimation of ^{226}Ra activity. The gamma spectra of a produced water sample from the Permian Basin are shown in Fig. 2.

Results and discussion

Inorganic constituents in the flowback and produced waters

The amount of total dissolved solids (TDS) is a measure of all inorganic and organic substances dissolved in water and is an aggregate indicator of water quality. Based on TDS, water is classified as fresh (TDS < 1000 mg/L), brackish (1000 < TDS < 10,000 mg/L), saline (10,000 < TDS < 35,000 mg/L), or hypersaline (TDS > 35,000 mg/L). The TDS of drinking water is typically < 300 mg/L. The quality of Permian Basin flowback water varied from brackish to hypersaline with TDS in

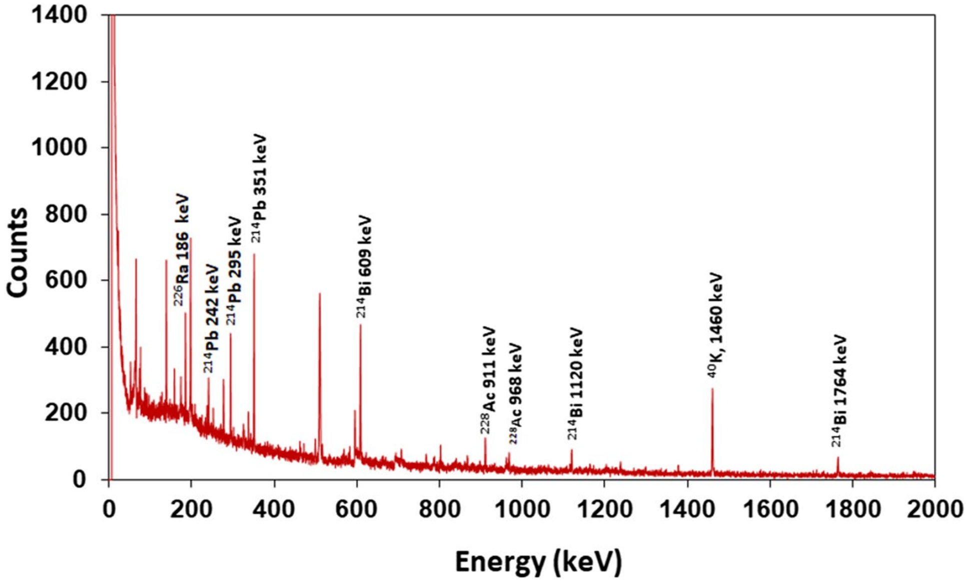


Fig. 2 A typical gamma spectra of produced water, count time = 24 h

the range of 5000 to 118,000 mg/L in this study. All produced water samples were hypersaline with TDS ranging from 40,000 to 173,000 mg/L. These values are similar to those reported for flowback and produced waters from other parts of the USA. The levels of TDS in wastewaters from various shale formations around the USA range from 120,000 in Marcellus Shale, to 13,000 in Fayetteville Shale, 30,00 in Woodford Shale, 80,000 in Barnett Shale, 110, 000 in Haynesville Shale, and 250,000 mg/L in Appalachian Shale (USDOE 2011; Rowan et al. 2011). The level of TDS in Marcellus Shale flowback water, from storage impoundments in southwestern Pennsylvania, ranged from 48,100 to 117, 500 mg/L (Zhang et al. 2015). The level of TDS in Marcellus Shale flowback from northeastern Pennsylvania was significantly higher at 278,000 mg/L (Nelson et al. 2014). Baseline characterization of groundwater in the Culebra aquifer in the vicinity of the WIPP site show TDS ranging from 17,000 to 280,000 mg/L. The pH of these waters varied in the range 7.05–7.3. The major constituents measured in Permian flowback and produced waters are listed in Table 1.

TENORM constituents in the flowback and produced waters

The activity concentrations of TENORM measured in Permian Basin flowback and produced water samples are listed in Table 2. Both ^{226}Ra and ^{228}Ra were detected in all flowback and produced water samples, whereas ^{224}Ra was detected in only one produced water sample. Permian flowback and produced waters contained ^{226}Ra, ^{228}Ra, and ^{224}Ra at activity concentrations in the range from 19.1 ± 1.2 to 35.9 ± 3.2 Bq/L, 10.3 ± 0.5 to 21.5 ± 1.2 Bq/L and 2.0 ± 0.05 to 3.7 ± 0.07 Bq/L, respectively. The range of ^{226}Ra + ^{228}Ra activity concentrations was much lower than that of Marcellus Shale-produced water (< MDC–666 Bq/L) and Gulf Coast shales (0.02–117 Bq/L) but are comparable to the range 29.1–63.7 Bq/L reported in Bakken-produced water in SD, USA (Lauer et al. 2016). However, activity concentrations of ^{226}Ra + ^{228}Ra in the Permian Shale are significantly higher than those of ^{226}Ra (0.04–8.6 Bq/L) and ^{228}Ra (0.05–3.7 Bq/L) measured in produced waters from southern San Joaquin Valley of California (McMahon et al. 2018).

Table 1 Concentration of major ions in the flowback and produced waters from the New Mexico portion of the Permian Basin

Constituents	Flowback water (mg/L)	Produced water (mg/L)
pH	7.05–7.2	7.1–7.3
TDS	5000 ± 200 to 118,000 ± 4500	40,000 ± 1900 to 173,000 ± 8234
Sodium	31,856 ± 1876 to 40,000 ± 2134	32,725 ± 1200 to 43,000 ± 1600
Magnesium	202 ± 18 to 1150 ± 157	451 ± 42 to 2430 ± 150
Calcium	668 ± 38 to 1630 ± 112	3552 ± 225 to 4123 ± 467
Potassium	148 ± 20 to 750 ± 87	165 ± 9 to 780 ± 54
Strontium	101 ± 8 to 195 ± 16	202 ± 14 to 260 ± 21
Chloride	5160 ± 765 to 37,800 ± 2033	59,400 ± 2078 to 66,700 ± 2600
Bromide	315 ± 32 to 520 ± 44	352 ± 22 to 596 ± 63
Silica	20 ± 3 to 26 ± 5	22 ± 3 to 32 ± 8
Sulfate	291 ± 15 to 785 ± 165	856 ± 60 to 1980 ± 200

Table 2 Activity concentration (Bq/L) of TENORM radionuclides measured in flowback and produced water samples from the Permian Basin

Radionuclides	Flowback water unfiltered, Bq/L	Flowback water filtered, Bq/L	Produced water unfiltered, Bq/L
^{210}Po	0.011 ± 0.007–0.014 ± 0.005	Not detected	0.03 ± 0.005–0.20 ± 0.02
^{238}U	0.021 ± 0.01–0.038 ± 0.01	0.005 ± 0.003–0.022 ± 0.009	0.001 ± 0.001–0.012 ± 0.04
^{234}U	0.041 ± 0.01–0.059 ± 0.02	0.029 ± 0.01–0.037 ± 0.02	0.008 ± 0.001–0.028 ± 0.06
^{235}U	Not detected	Not detected	0.001 ± 0.001–0.009 ± 0.001
^{228}Th	0.18 ± 0.02–1.23 ± 0.04	Not detected	0.14 ± 0.02–1.03 ± 0.04
^{232}Th	0.004 ± 0.002–0.020 ± 0.001	Not detected	0.001 ± 0.001–0.003 ± 0.001
^{230}Th	0.002 ± 0.001–0.005 ± 0.001	Not detected	0.003 ± 0.001–0.014 ± 0.005
^{226}Ra	4.6 ± 2.1–8.8 ± 3.2	2.5 ± 1.2–4.3 ± 2.3	19.1 ± 1.2–35.9 ± 3.2
^{228}Ra	2.7 ± 1.2–3.6 ± 1.5	Not detected	10.3 ± 0.5–21.5 ± 1.2
^{224}Ra	Not detected	Not detected	2.0 ± 0.05–3.7 ± 0.07
^{40} K	Not detected	Not detected	4.33 ± 2.2–33.9 ± 4.5

Measurements of ^{224}Ra in oil field waters are rare, but there have been a few reports of ^{224}Ra in produced water samples. For example, McMahon et al. (2018) reported ^{224}Ra in the range of 0.09 to 4.8 Bq/L in produced water samples from southern San Joaquin Valley, California. Levels of ^{224}Ra levels in produced water from Ukraine ranged from 1.57 to 5.51 Bq/L (Plyatsuk et al. 2017). Samples of produced water from Ghana showed ^{224}Ra in the range of 0.7–7.0 Bq/L (Kpeglo et al. 2016). These data suggest that ^{224}Ra could be an important component of the total radium ($Ra_{total} = {}^{226}Ra + {}^{228}Ra + {}^{224}Ra$) inventory in oil field waters.

Several authors have reported the presence of ^{226}Ra and ^{228}Ra in oil field wastewater. The range of radium concentrations measured in various produced and flowback waters are summarized in Table 3. There is evidence that radium activity in subsurface waters depends, to some extent, on salinity, pH, and the redox state of the water (Kraemer and Reid 1984; Vinson et al. 2013). In a critical investigation of radium data for 215 produced water samples from eight different geologic settings, Fisher (1998) reported ^{226}Ra concentrations in the range of 0.048–190.5 Bq/L. Furthermore, there was an excellent correlation ($r^2 = 0.96$, slope = 1.03) between ^{226} and ^{228}Ra concentrations. Low radium concentrations also appear to be much more common than high concentrations, where ~ 75% of produced water samples have shown ^{226}Ra concentrations less than 11.1 Bq/L, whereas only about 11% of the samples had ^{226}Ra concentrations greater than 37 Bq/L (Fisher 1998). Concentrations of ^{226}Ra in produced water vary from 62.9 to 984.2 Bq/L in unfiltered samples and 56.2 to 891.7 Bq/L in filtered samples (Barbot et al. 2013, Frazier et al. 2015). In contrast, ^{228}Ra concentrations varied from 13.5 to 70.3 (unfiltered sample) and 13.8 to 68.8 (filtered sample).

In a compilation of published data, Rowan (2011) observed significantly higher concentrations of radium in produced water from Marcellus Shale than in water from non-Marcellus shale. This database showed that produced waters from Marcellus Shale contain more radium (^{226}Ra + ^{228}Ra < MDC–666 Bq/L) than the non-Marcellus produced water (< MDC–248 Bq/L). Furthermore, radium concentrations increased with TDS. Some studies have shown that radium in produced water increases with salinity (Cl^- concentrations). This increase is attributed to the complexation of radium with Cl^- (or SO_4^{2-} or CO_3^{2-} ions) and competition with Na^+ or other cations for ion-exchange sites. Speciation calculations in pure Ra–Cl or Ra–SO_4 systems show that $RaSO_4$ complexes are more significant than Cl^-, even when the SO_4^{2-} concentrations are as low as 0.5% of Cl^- concentrations. Complexes with Cl^- and SO_4^{2-}, particularly SO_4^{2-}, can significantly

Table 3 Ranges of activity levels of ^{226}Ra and ^{228}Ra in flowback and produced waters from different shale

Location/field	Sample type	^{226}Ra Bq/L	^{228}Ra Bq/L	^{228}Ra/^{226}Ra	Reference
USA	Produced water	22.5–30.8	25.5–30.1	0.97–1.14	Zielinski and Budahn 2007
US Gulf Coast	Produced water	< 0.002–58	0.02–59	0.65–2.25	Kraemer and Reid 1984
Louisiana, USA	Produced water	< MDC–34.4	< MDC–34.3	-	Hamilton et al. 1991
Marcellus Shale, PA, USA	Flowback water	33.9–82.1	19.2–44.0	-	Frazier 2015
Bakken Shale, ND, USA	Produced water			0.42–0.49	Lauer et al. 2016
Norway	Produced water	0.5–16	0.5–21	-	Eriksen et al. 2006
Norway	Produced water	< MDC–10.4	< MDC–10.0	-	Strand et al. 1997
Tunisia	Produced water	0.37–19	-	-	Hrichi et al. 2013
Nigeria, Delta state	Produced water	3.5–10.8	3.4–9.3	0.30–2.93	Avwiri et al. 2013
Marcellus Shale, PA, USA	Flowback water	0.0–92.9	-	-	Zhang et al. 2015
Syria, Al Jafra, Attla, Qahar		9.9–111.2	8.8–67.4	-	Al-Masri 2006
Egypt	Formation water	5–40	1–59	-	Shawky et al. 2001
Egypt	Produced water	5.3–27.9	< MDC–7.7	-	Moater et al. 2010
Algeria	Formation water	5.1–14.8	-	-	
Ghanna, Salpond, Jubliee oil Field	Produced water	6.2–22.3	6.4–33.5	0.99–1.69	Kpeglo et al. 2016
Brazil, Bacia de Campos	Produced water	0.012–6.0	0.05–12.0	-	Vegueria et al. 2002
Ukraine	Produced water	27.4–39.8	3.2–5.57	0.12–0.19	Plyatsuk et al. 2017
Iraq	Produced water	20.3–67.3*	-	-	Ali 2017
Romania	Formation water	0.005–10.2	-	-	Botezatu and Grecea 2004
Indonesia, S. Java Sea	Produced water	0.3–2.1	0.02–0.66	-	Neff and Foster 1997
The Netherlands, Dutch North Sea	Produced water	< 2–302	< 1–20	-	NRPA 2004
Poland, Baltic basin Lublin Trough	Produced water	4–66	4–36	0.42–1.0	Jodłowski et al. 2017

increase radium mobility (Kraemer and Reid 1984, McMahon et al. 2018).

Reported uranium and thorium concentrations in oil field wastewater are very scarce. Typical concentrations of these radionuclides in produced water usually range from 1 to 10 Bq/L. The concentration of natural uranium (^{238}U, ^{235}U, and ^{234}U) and thorium isotopes (^{228}Th, ^{230}Th, and ^{232}Th), measured in Permian Shale flowback and produced waters, were lower than 0.06 Bq/L except for ^{228}Th (Table 2). This observation is consistent with the data from other formations. For example, Nelson et al. (2016) reported uranium and thorium concentrations <0.005 Bq/L in produced waters from Marcellus Shale. The Pennsylvania Department of Environmental Protection (PA DEP) reported concentrations of ^{238}U in Marcellus Shale in the range of 0.0003–0.10 Bq/L, with ^{232}Th ranging from 0.0003 to 0.001 Bq/L (Barbot et al. 2013, Frazier et al. 2015). Other oil-producing regions outside of the USA, such as the Bugruvate oil and gas fields in Ukraine showed concentrations in the range of 0.005–0.007 Bq/L for ^{238}U, 0.01–0.013 Bq/L for ^{234}U, and 0.058–0.19 Bq/L for ^{232}Th (Plyatsuk et al. 2017). Uranium isotopes (^{234}U and ^{238}U) in produced water from Ghana were in the range of 0.001–0.006 Bq/L, whereas thorium isotopes (^{228}Th, ^{230}Th, and ^{232}Th) ranged from 0.001 to 0.012 Bq/L (Kpeglo et al. 2016). Analysis of Permian Basin waters shows a slight enrichment of ^{234}U, relative to ^{238}U (^{234}U/^{238}U$\,=1.4$–2.3), which is common in groundwater and is indicative of daughter recoil (Osmond et al. 1983).

Radioactivity in oil field wastes originates primarily from elements in the ^{232}Th and ^{238}U decay series. The parent isotope in the natural Th decay series, ^{232}Th ($t_{1/2}=1.4\times10^{10}$ years), is insoluble in natural groundwater and brine but is known to be particle-reactive, readily sorbing on hydrous metal oxides and mineral surfaces of geomedia (Melson et al. 2012). Oxidation/reduction reactions in groundwater are also unlikely under natural conditions. As a result, the activity concentration of Th-isotopes in produced waters is expected to be very low (Langmuir and Herman 1980). Consistent with these expectations, the activity concentrations of ^{232}Th and ^{230}Th in unfiltered produced water from the Permian Basin are quite low (<0.05 Bq/L) (Table 2). However, ^{232}Th decays slowly by alpha emission to ^{228}Ra ($t_{1/2}=5.75$ years), which is a divalent alkaline earth element that is highly soluble in low-sulfate brine. ^{228}Ra is therefore likely to have been in secular equilibrium with ^{232}Th for millions of years. Relative to ^{232}Th, produced water is therefore enriched in ^{228}Ra. ^{228}Ra decays by beta emission to the short-lived ^{228}Ac ($t_{1/2}=6.15$ h), which is not only particle-reactive but forms insoluble complexes and decays rapidly to the low-solubility α-emitter ^{228}Th ($t_{1/2}=1.91$ years). Similar to other Th isotopes, ^{228}Th is also insoluble in natural pore waters of shale formations, and consequently, its concentrations in produced waters are low. Ingrowth of ^{228}Th begins at a rate relative to its half-life and the decay product ^{224}Ra ($t_{1/2}=3.63$ days), which is also soluble in the brine, rapidly grows to a steady-state radioactive equilibrium. However, ^{228}Th concentration in produced water is usually higher, relative to other thorium isotopes. This is attributed to ^{228}Ra decay rather than the leaching of thorium (Table 2).

The parent isotope in the natural U decay series, ^{238}U ($t_{1/2}=4.47\times10^{9}$ years), like ^{232}Th, is insoluble and remains immobile in the subsurface. However, unlike ^{232}Th, ^{238}U can be redox-sensitive. The dominant forms of uranium in geologic environments are the uranous (U^{4+}) and uranyl (UO_2^{2+}) ions. In anoxic conditions, such as those found in deep shales, the stable form of uranium is U^{4+}, which is essentially insoluble in groundwater and brine. In oxic environments, uranium exists as the more soluble U(VI), which can form numerous complexes. Compared to the low solubility of ^{238}U decay series actinides in oil field waters, the ^{238}U decay product, ^{226}Ra, is highly soluble. Dissolved radium is likely to remain in secular equilibrium with its parents in brine until it decays. It may also be adsorbed onto clay particles, by ion exchange processes, and may substitute for other divalent cations such as Ba^{2+}, Ca^{2+}, and Sr^{2+} in the divalent-ion-rich brine to form minerals such as barite ($BaSO_4$), anhydrite ($CaSO_4$), and calcite ($CaCO_3$). It may also form precipitates with sulfate with which it comes in contact. Dissolved radium that is in secular equilibrium with its parents (^{238}U, ^{232}Th) at depth in a shale reservoir, may be sequestered from its parents when pumped to the surface (Rowan et al. 2011).

Radium activity ratio

The ^{228}Ra/^{226}Ra activity ratio measured in the Permian Basin produced water ranges from 0.48 to 0.65 with a mean of 0.57 ± 0.04, whereas the ^{224}Ra/^{226}Ra ratio ranges from 0.093 to 0.11 with a mean of 0.10 ± 0.02. This ^{228}Ra/^{226}Ra activity ratio is comparable to the 0.45 ratio (range 0.42–0.49) reported for Bakken produced water (Lauer et al. 2016), but higher than the ratios reported for Marcellus Shale produced water, which is generally less than 0.3 (Rowan et al. 2011) and lower than those ratios reported for produced water from southern San Joaquin Valley, California (0.14–2.3) (McMahon et al. 2018). Because ^{226}Ra is part of the ^{238}U decay series, and ^{224}Ra and ^{228}Ra are part of the ^{232}Th decay series, the ^{228}Ra/^{226}Ra activity ratio in produced water generally reflects the Th/U ratio of the reservoir lithologies, which ranges from 0.1 to 2.0. There is limited information on ^{224}Ra/^{226}Ra activity ratio in oil field waters. McMahon et al. (2018) reported ^{224}Ra/^{226}Ra activity ratios between 0.2 and 5.5 and a mean of 1.5 in produced water from San Joaquin Valley, California. The ratios in Ghanaian produced water varied from 0.11 to 0.31 with a mean of 0.22 (Kpeglo et al.

2016). The ^{224}Ra/^{226}Ra activity ratios in Ukrainian-produced water were in the range of 0.49–0.99 with a mean of 0.74 (Plyatsuk et al. 2017). ^{224}Ra/^{228}Ra ratios > 1 are common in groundwater and primarily reflect the effect of alpha-recoil release of the short-lived ^{224}Ra from solids, and adsorption of radium on solid surfaces (Hancock and Murray 1996; Vengosh et al. 2009). In the ^{232}Th decay series, ^{224}Ra is followed by two alpha decays while ^{228}Ra is followed only by one alpha decay. Therefore, ^{224}Ra shows a higher probability of migration because of the direct transfer of atoms across the solid/liquid phase boundary or by lattice destruction due to the recoil effect (Fleischer 1980). This mechanism is similar to that responsible for uranium isotope disequilibrium and ^{234}U/^{238}U activity ratios that are generally > 1 in groundwater.

Published reports of ^{210}Po in oil and gas wastewater are also limited. In this study, ^{210}Po was slightly above the detection limit in both filtered samples of flowback and produced water (Table 2). No ^{210}Po was measured above the detection limit in the filtered flowback water samples. However, produced water concentrations in the range of 0.032 ± 0.005 to 0.20 ± 0.06 Bq/L are consistent with the range 0.022 to 0.085 Bq/L reported in produced water samples from the US Gulf Coast (Lagera et al. 1999) and the 0.022 to 0.14 Bq/L reported for produced water from two offshore oil fields in Ghana (Kpeglo et al. 2016). Although ^{226}Ra is highly soluble in oil field waters, the decay product radionuclides (^{210}Pb, ^{210}Bi, and ^{210}Po) are relatively insoluble and remain mostly adsorbed to mineral phases in the subsurface environment. This is consistent with the observation of the higher concentrations of ^{210}Po found in filter residues. Residue concentrations ranged from 28.2 ± 6.5 to 78.3 ± 15.5 Bq/g, with a mean of 53.3 ± 12.6 Bq/g. This suggests that most of the ^{210}Po remain associated with the suspended particles with only a small dissolved fraction. However, it is important to keep in mind that radioactivity would continue to increase for decades as longer-lived isotopes (^{210}Pb, $t_{1/2} = 22$ years; ^{210}Po, $t_{1/2} = 138$ days) approach radioactive equilibrium with ^{226}Ra. Both ^{210}Pb and ^{210}Po are important from the perspective of risk assessment because of their bioavailability and ability to accumulate in higher organisms (Thakur and Ward 2019).

Transuranic constituents in the flowback and produced waters

None of the transuranic radionuclides ($^{239+240}$Pu, ^{238}Pu, ^{237}Np, and ^{241}Am) were detected in any of the oil field water samples. This observation is of particular significance to operations at WIPP, which is intended to serve as a permanent repository for transuranic waste. Baseline concentrations of anthropogenic radionuclides in the Carlsbad area are listed in Table 4. Air emission is recognized as the major pathway for radionuclides to the accessible environment during facility operations. After the facility is permanently closed, there is no credible, probable mechanism for radionuclide release to the surrounding environment unless the site is breached by humans. Under such a scenario, any releases would be through groundwater that is predominantly non-potable water and classified as brine (National Research Council 1996). The ability to measure TENORM and their ratios, as well as actinides, in environmental samples allows accurate identification of the source of contaminants, i.e., oil field wastes versus WIPP, should issues of regulatory compliance ever arise.

Radioactivity in proppant

The levels of radionuclides measured in samples of proppant sand used in fracking are listed in Table 5. Proppant sand contained nominal concentrations of elements from the U and Th decay series. Measured concentrations of radionuclides were in the range of 0.02 to 2.16 for ^{40}K, 0.003 to 0.017 for ^{238}U, 0.0006 to 0.01 Bq/g for ^{232}Th, < MDC to 0.061 Bq/g for ^{226}Ra, and 0.002 to 0.01 Bq/g for ^{228}Ra. Jodłowski et al. (2017) reported concentrations ranging from 0.12 to 0.27 for ^{40}K, 0.014 to 0.39 Bq/g for ^{238}U, 0.015 to 0.41 Bq/g for ^{226}Ra, and 0.008 to 0.52 Bq/g for ^{228}Ra in flowback proppant sand. Analysis of proppant sand in Pennsylvania, sampled from sand hoppers before being mixed with fluids, showed concentrations in the range of 0.001 to 0.27 Bq/L for ^{40}K, 0.0004 to 0.012 Bq/g for ^{238}U, 0.0003 to 0.004 Bq/g for ^{232}Th, 0.006–0.013 for ^{226}Ra, and 0.0005 to 0.005 for ^{228}Ra. These studies indicate that radioactivity levels in proppant sand are less than or comparable to the

Table 4 Background concentrations of anthropogenic radionuclides in the Carlsbad area. Values were taken from the CEMRC annual report (www.cemrc.org/annualreport)

Environmental media	Ground water (Bq/L)	Surface water (Bq/L)	Sediment (Bq/g)	Surface soil (Bq/g)
^{238}Pu	Not detected	Not detected	Not detected	Not detected
$^{239+240}$Pu	Not detected	Not detected	2.1×10^{-4}–2.9×10^{-4}	3.7×10^{-5}–3.1×10^{-4}
^{241}Am	Not detected	Not detected	6.9×10^{-5}–1.0×10^{-4}	1.1×10^{-5}–1.3×10^{-4}
^{137}Cs	0.3 ± 0.06–1.46 ± 0.5	Not detected	0.002 ± 0.001–0.029 ± 0.001	0.0014 ± 0.006–0.008 ± 0.003

Table 5 Activity concentration (Bq/g) of TENORM radionuclides measured in filter particulate and proppant sand samples

Radionuclides	Flowback water Filter particulate Bq/g	Proppant sand Bq/g
^{210}Po	0.028 ± 0.01–0.078 ± 0.02	Not detected
^{238}U	0.011 ± 0.006–0.03 ± 0.009	0.003 ± 0.0008–0.017 ± 0.004
^{234}U	0.026 ±0.01 - 0.046±0.02	0.002 ± 0.0004–0.02 ± 0.002
^{235}U	Not detected	< MDC (0.0001)–0.001 ± 0.0003
^{228}Th	0.12 ± 0.03–0.16 ± 0.05	0.0005 ± 0.0002–0.01 ± 0.002
^{232}Th	0.017 ± 0.003–0.034 ± 0.01	0.0006 ± 0.0001–0.01 ± 0.001
^{230}Th	0.034 ± 0.01–0.095 ± 0.03	0.001 ± 0.0004–0.018 ± 0.003
^{226}Ra	ND	< MDC (0.0084)–0.061 ± 0.008
^{228}Ra	ND	0.002 ± 0.0004–0.01 ± 0.0006
^{224}Ra	ND	Not detected
^{40} K	ND	0.024 ± 0.005–2.16 ± 0.05

ND, not determined

natural background levels of radioactivity typically found in surface soil. Thus, there is little potential for radiological exposure to workers and members of the public from proppant sand. It is worth noting that some proppant sands incorporate radioactive tracers with different half-lives to allow downhole mapping of the injection profile and fracture propagation during fracking (Scott 1995;1997). The radionuclides used as tracers are regulated by the Nuclear Regulatory Commission (USNRC 2018) and typically have different half-lives that may range from 40.2 h (^{140}La) to 28.90 years (^{90}Sr) depending on the stage of fracking in which they are used (Gadeken 1989). Tracer concentrations are regulated to ensure that air emissions of radioactive material to the environment, excluding ^{222}Rn and its daughters, will not result in exposures to individual members of the public above 0.1 mSv in a year from those emissions (USNRC 2018).

Flux of radium in the Permain-produced water

As discussed in the preceding section, the dominant radionuclide in oil and gas wastewater is radium. Therefore, the annual flux of radium in the produced water was calculated by taking into account the average concentrations of ^{226}Ra measured in the produced waters and the volume of produced water generated each year since 2011. The data for the annual generation of produced water was taken from the Center for Western Priorities. Figure 3 shows the volume of produced water generated and the estimated concentrations of ^{226}Ra in tetra becquerel (TBq = 1 × 10^{12} Bq) that could be expected in produced water.

Baseline concentrations of NORM/TENORM in the Carlsbad region of the Permian Basin

Although the ability to measure TENORM and actinides in the same sample is essential for accurate source identification, perhaps more important is knowledge of the radiological baseline. A comprehensive radiological baseline study, completed before WIPP disposal operations began, provides the basis for comparison of operations and post-closure compliance monitoring (DOE/WIPP 1992). Herczeg et al. (1988) also quantified naturally occurring isotopes of uranium and radium in freshwater, springs, and saline groundwater in the Delaware Basin of southeastern New Mexico, a subprovince of the greater Permian Basin. These data are invaluable for interpreting any fluctuations in radionuclide concentrations in environmental samples in the Permian Basin.

High concentrations of radium, similar to those found in produced water, have been reported in groundwater samples collected from saline springs (Herczeg et al. 1988). Historical data from the monitoring of groundwater in the Culebra aquifer at WIPP (WIPP Site Report 1995) show ^{226}Ra concentrations in the range of 1.23 to 9.1 Bq/L and ^{228}Ra in the range of 0.2 to 1.41 Bq/L (Table 6). Concentrations of ^{234}U and ^{238}U in the groundwater vary from 0.3 to 1.46 Bq/L and

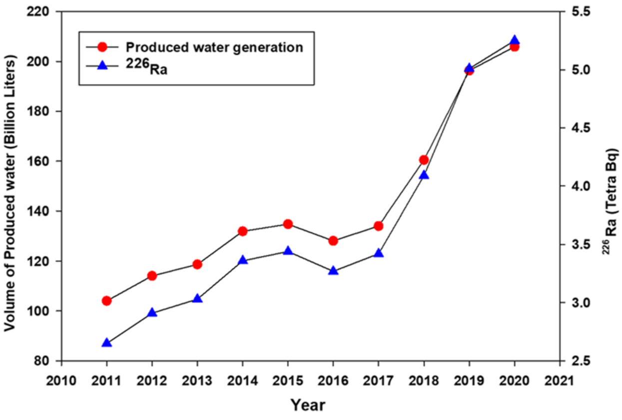


Fig. 3 Uranium concentrations in natural and oil field waters in the Permian Basin. Data for drinking and surface waters were taken from the CEMRC report 1998 and that of groundwater were from the WIPP site report 1995

0.056–0.25 Bq/L, respectively. All of the groundwater samples show a radioactive disequilibrium between ^{234} and ^{238}U isotopes with a ^{234}U/^{238}U activity ratio in the range of 4.9 to 8.1. This disequilibrium is attributed mostly to the higher solubility of ^{234}U, relative to ^{238}U, and preferential leaching. Other contributing factors include ^{234}U recoil and crystal damage. In groundwater from the Culebra aquifer, ^{226}Ra activity varied from < MDC to 10.4 Bq/L, whereas ^{238}U concentrations were in the range of 0.1 to 7.4 Bq/L (Chapman 1988). Marked disequilibrium also exists between ^{238} and ^{234}U activities in Culebra groundwater with ^{234}U/^{238}U activity ratios ranging from 1.5 to 18 and TDS ranging from 17,000 to 280,000 mg/L (Chapman 1988).

The NORM concentrations in surface waters, sediments, and soils in the vicinity of WIPP were also evaluated, as they are more directly linked to human exposure and environmental contaminations. The ^{226}Ra and ^{228}Ra concentrations in surface water were all < 0.1 Bq/L, whereas concentrations of uranium and thorium isotopes were < 2 Bq/L (Table 6). The ^{234}U/^{238}U activity ratios in surface water samples are in the range of 0.87 to 3.66 and are very similar among the different reservoirs (CEMRC report 1998). All of the reservoirs appeared to be slightly enriched in ^{234}U compared to ^{238}U (CEMRC report 1998).

Baseline soil concentrations of NORM in this area are also listed in Table 6. Levels of ^{234}U were in the range 0.005–0.14 Bq/g compared to a range of 0.005–0.093 Bq/g for ^{238}U. Isotopes of thorium were in the range of 0.008–0.02 Bq/g for ^{230}Th and 0.006–0.021 Bq/g for ^{232}Th, whereas ^{40} K ranged from 0.13 to 0.28 Bq/g. Natural background concentrations of these radionuclides in the US soil are in the range of 0.004 to 0.14 Bq/g, with a mean of 0.035 Bq/g for ^{238}U; 0.004 to 0.13 Bq/g, with a mean of 0.035 Bq/g for ^{232}Th; 0.008 to 0.16 Bq/g, with a mean of 0.041 Bq/g for ^{226}Ra; and 0.1 to 0.7 Bq/g, with a mean of 0.37 Bq/g for ^{40} K (UNSCEAR 2000). A typical concentration of uranium isotopes in various natural and oil field waters is shown in Fig. 4. Concentrations in oil field waters are consistent with natural background levels found in surface soils. However, radium concentrations are elevated above background levels for soil and groundwater.

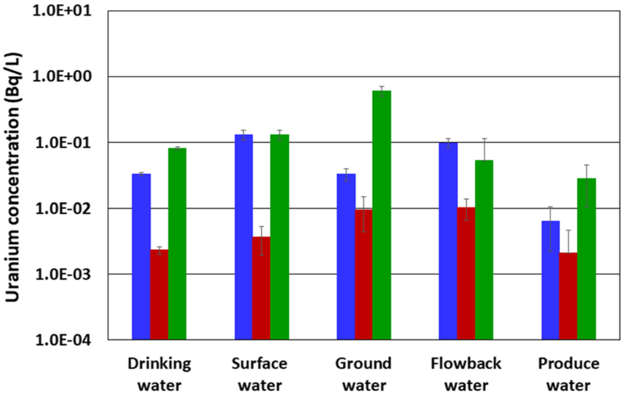


Fig. 4 Produced water volume and estimated concentrations of ^{226}Ra in these waters. Data for the volume of produced water generation were from ref. Center for Western Priorities. ^{226}Ra content was calculated using the average ^{226}Ra concentration measured in this study

Radiological dose assessment to the workers and the public

More than 80% of the radiation dose received by humans comes from natural radiation sources (NRC-BEIR-IV 2006; USNRC 2010), which are comprised primarily of primordial radionuclides such as ^{40} K and the progenies of ^{238}U and ^{232}Th decay series. Human exposure to radionuclide releases from transuranic waste disposed at WIPP is likely to be low compared to the USA and international standards (National Research Council 1996). However, handling, transportation, and storage of oil field waste that include TENORM can expose workers to high levels of radiation. Similarly, disposal of oil field wastes by burial, land spreading, injection

Table 6 Background concentrations of NORM in the Carlsbad area. Values were taken from the CEMRC annual report 1999–2018 (www.cemrc.org/annualreport)

Radionuclides	Ground water (Bq/L)	Surface water (Bq/L)	Sediment (Bq/g)	Surface soil (Bq/g)
^{226}Ra	1.23–9.07	0.004–0.05	0.017–0.048	0.003–0.043
^{228}Ra	0.2–1.41	< MDC–0.03	0.013–0.039	0.007–0.02
^{238}U	0.056–0.25	0.001–0.20	0.013–0.062	0.005–0.093
^{234}U	0.3–1.46	0.002–0.57	0.013–0.091	0.005–0.14
^{235}U	0.003–0.082	0.00015–0.006	0.0011–0.0081	0.0002–0.0009
^{228}Th	0.03–0.214	0.002–0.008	0.013–0.042	0.15–0.17
^{232}Th	Not detected	Not detected	0.014–0.048	0.006–0.021
^{230}Th	0.016–0.040	0.02–0.10	0.004–0.07	0.008–0.020
^{210}Po	0.009–0.10	< MDC	0.007–0.036	0.016–0.032
^{40} K	8.1–63.1	0.81–2.72	0.31–0.51	0.13–0.28

Values have an uncertainty of about 10–20%

into deep wells, or dumping into shallow trenches or the sea can increase the likelihood of human exposure to high levels of radioactivity and toxic metals.

The radiation dose from radionuclides in the oil field wastes can be inferred from three different dose indices, which include (1) the radium equivalent radioactivity (Ra_{eq}), (2) the gamma dose rate (D (nGy/h)), and (3) the effective annual dose rate (D_{eff}). These three indices are representative of reference doses in the outdoor air at a height of 1 m above the ground surface and can be calculated using the activity-to-dose conversion model adopted by the UNSCEAR (2000) and modified by Tufail (2012). Because 98.5% of the radiological effects from uranium-series elements are produced by radium and its daughter products, the contribution from ^{238}U and other ^{226}Ra precursors are normally ignored. Rather than calculate the dose of every radionuclide in the produced water, a single annual effective dose (mSv/year) is calculated from the activity concentrations of ^{226}Ra, ^{232}Th, and ^{40} K, according to Tufail (2012) as

$$D_{eff} = \left(0.463A_{\mathrm{Ra}} + 0.604A_{\mathrm{Th}} + 0.0417A_{\mathrm{K}}\right) \times 6.136 \times 10^{-3} \tag{1}$$

In Eq. (1), A_{Ra}, A_{Th}, and A_{K} are the activity concentrations in Bq/L of ^{226}Ra (can be assumed to be the concentration of ^{238}U), ^{232}Th, and ^{40} K, respectively. The annual effective doses calculated by Eq. (1) from the activity concentrations in oil field waters (Table 2) and groundwater near the WIPP site (Table 6) would be 0.1–0.2 mSv/year from the oil field waters and 0.01–0.05 mSv/year from the groundwater. Zhang et al. (2015) evaluated health risks associated with NORM generated from Marcellus Shale gas exploration and concluded that total effective dose equivalent (TEDE) would be well below the NRC limit for the general public of 1 mSv/year even under the worst-case scenario assumptions. Workers in the centralized waste treatment facilities might receive excessive TEDE; however, appropriate measures such as a safety distance of 5 m can reduce TEDE to an acceptable level.

This and previous studies showed that there is little or limited potential for radiation exposure to the public and workers from the oil and gas development. However, there are potential radiological environmental impacts from oil field wastes if spilled. Therefore, these waste materials must be handled, stored, and disposed of in compliance with regulations that ensure the safety of workers and the public. There should also be site-specific circumstances and situations where the use of personal protective equipment by workers or other controls should be evaluated. According to the Nuclear Regulatory Commission (USNRC 2010), an average American receives a radiation dose of about 6.2 mSv per year from all sources of radiation (3.1 mSv) from naturally occurring sources and about 3.1 mSv from man-made sources and applications. The radiation dose from the oil and gas development is much lowered than the natural background level of radiation.

Conclusion

The objectives of this study were to quantify background levels of radium in the Permian Basin and quantify the concentration range and dose associated with oil field wastes. The quality of oil field water varied from brackish to hypersaline with TDS > 5000 mg/L. Radium, the major TENORM of interest in hydraulic fracturing wastes were in the range of 19.1 ± 1.2 to 35.9 ± 3.2 Bq/L for ^{226}Ra, 10.3 ± 0.5 to 21.5 ± 1.2 Bq/L for ^{228}Ra, and 2.0 ± 0.05–3.7 ± 0.07 Bq/L for ^{224}Ra. In addition to elevated concentrations of radium, these wastewaters also contain elevated concentrations of dissolved salts (Na, Cl, Br), divalent cations (Ca, Mg, Sr) compared to background waters. The ^{228}Ra/^{226}Ra activity ratios (0.48–0.65) in Permian-produced water were consistent with the ratios measured in other US Shale-produced waters such as Bakken and Marcellus shales.

These elevated levels are of radiological significance and represent a major source of Ra in the environment. However, the risk assessment study indicates that there is little or limited potential for radiation exposure to the public and workers from the oil and gas development. The resulting dose from the activity concentrations in oil field waters and groundwater near the WIPP site was around 0.1–0.2 mSv/year from the oil field waters and 0.01–0.05 mSv/year from the groundwater, which are well below the natural background radiation dose of 3.1 mSv and the NRC limit effective dose limit of 1 mSv/year for the general public.

Acknowledgements This research is supported by a grant from the US Department of Energy, Carlsbad Field Office of DOE through Grant No. DE-EM 0005159. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the sponsors.

Author contribution All authors contributed to the study's conception and design. Punam Thakur: investigation, method development, writing, and data curation; Anderson L Ward: writing, article review, and graphics; Tanner M. Schaub: sample collection and article review.

Funding The project is funded by the US Department of Energy (USDOE) through a grant.

US-DOE, Grant No. DE-EM 0005159

Availability of data and materials Not applicable.

Declarations

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

References

Al-Masri MS (2006) Spatial and monthly variations of radiumisotopes in produced water during oil production monthlyvariations of radium isotopes in produced water duringoil production. Appl Radiat Isot 64:615–623

Ali K (2017) Radiological hazard Assessment Due to NaturalOccurring Radioactive Materials (NORM) in Oil and GasProduction Industry East Baghdad Oil Field. Iraqi J Sci 58:115–126

API (2000) Overview of exploration and production waste volumes and waste management practices in the United States, prepared by ICF Consulting for the American Petroleum Institute. DC, May, Washington

ASER (2016) Waste isolation pilot plant annual site environmental report for 2016. DOE/WIPP-17–3591. www.wipp.energy.gov/library/aser/DOE. Accessed May 2021

ATWIR - Annual Transuranic Waste Inventory Report (2020) DOE/TRU-20–3425 Revision 0 November 2020. U.S. Department of Energy Carlsbad Field Office

Avwiri GO, Esi E, Agbalagba EO (2013) Gamma spectroscopy analysis of produced water from selected flow stations in Delta State, Nigeria. Int J Environ Monit Anal 1:167–174

Barbot E, Vidic NS, Gregory KB, Vidic RD (2013) Spatial and temporal correlation of water quality parameters of produced waters from Devonian-Age shale following hydraulic Fracturing. Environ Sci Technol 47:2562–2569

Botezatu E, Grecea C (2004) Radiological impact assessment on behalf of oil/gas industry. J Prev Med 12:16–21

CEMRC- Carlsbad Environmental Monitoring and Research Center 1998 Report Carlsbad, NM. Accessed April 2021

CEMRC- Carlsbad Environmental Monitoring and Research Center Annual Report 1999–2018. http://www.cemrc.org/annualreport. Accessed June 2021

Center for Wearwern Priorities New Mexico Oil and gas Spill tracker. http://westernpriorities.org. Accessed October 2021

Chapman JB (1988). Chemical and radiochemical characteristics of groundwater in the culebra dolomite, Southeastern New Mexico. Environmental Evaluation Group, EEG Report 39. DOE/AL/10752–39.

DOE/WIPP-92-037 (1992) Statistical summary of the radiological baseline for the waste isolation pilot plant. Waste Isolation Pilot Plant, Carlsbad NM

Eriksen DO, Sidhu R, Stralberg E (2006) Radionuclides in produced water from Norwegian oil and gas installations-concentrations and bioavailability. Czechoslovak J Phys 56:D43–D48

Fisher RS (1998) Geologic and geochemical controls on naturally occurring radioactive materials (NORM) in produced water from oil, gas, and geothermal operations. Environ Geosci 5:139–150

Fleischer RL (1980) Isotopic disequilibrium of uranium: ALPHA-recoil damage and preferential solution effects. Science 207:979–981

Frazier JR (2015) Characterization of naturally occurring radioactive materials and radiological conditions in the oil and gas field. Marcellus Shale Coalition Pittsburgh, Pennsylvania 15241. from geochemical and isotopic tracers. Appl Geochem 38:161–175

Gadeken LL (1989) Radioactive well logging method, Patent EP 89304075-A

Gaswirth SB, French KL, Pitman JK, Marra KR, Mercier TJ, Leathers-Miller HM, Schenk CJ, Tennyson ME, Woodall CA, Brownfield ME, Finn TM, Le PA (2018) Assessment of undiscovered continuous oil and gas resources in the Wolfcamp Shale and Bone Spring Formation of the Delaware Basin, Permian Basin Province, New Mexico and Texas, 2018: U.S. Geological Survey Fact Sheet 2018–3073, 4 p., https://doi.org/10.3133/fs20183073.

Guerin (2014). Permian Basin: America's newest fracking boom where there's not much water. High Country News.

Hajer H-E- B, Baccouche S (2013) Evaluation of radiological impacts of TENORM in the Tunisian petroleum industry. J Environ Radioact 115:107–113

Hamilton LD, Meinhold AF, Nagy J (1991) Produced water radionuclide hazard/risk assessment -phase I Report, prepared for the American Petroleum Institute, Washington, D.C. Brookhaven National Laboratory, BNL 47403

Hancock GJ, Murray AS (1996) Source and distribution of dissolved radium in the Bega River estuary, southeastern Australia. Earth Planet Sci Lett 138:45–155

Herczeg AL, Simpson JH, Anderson RF, Trier RM, Gathieu GG, Deck BL (1988) Uranium and radium mobility in groundwaters and brines within the delaware basin, Southeastern New Mexico, USA. Chem Geol 72:181–196

Hrichi H, Baccouche S, Belgaied (2013) Evaluation of radiological impacts of TENORM in the Tunisian petroleum industry. 115:107–113

Inn K, Hall E, Woodward J, Stewart B, Pollanen R, Selvig L, Turner S, Outola I, Nour S, Kurosaki H, Larosa J, Schultz M, Lin Z, Yu Z, McMahon C (2008) Use of thin collodion films to prevent recoil-ion contamination of alpha-spectrometry detectors. J. Radioanal. Nucl. Chem. 276:385–390

Jodłowski CNDP, Macuda J, Nowak J (2017) Radioactivity in wastes generated from shale gas exploration and production North Eastern Poland. J Environ Radioact 175(176):34–38

Jonkers G, Hartog FA, Knaepen WAI, Lancée PFJ (1997) Characterization of NORM in oil & gas production (E&P) industry. In: International Symposium on Radiological Problems with Natural Radioactivity in the Non-nuclear Industry, Amsterdam, The Netherlands, September.

Kondash AJ, Albright E, Vengosh A (2017) Quantity of flowback and produced waters from unconventional oil and gas exploration. Sci Tot Environ 574:314–321

Kondash AJ, Lauer NE, Vengosh A (2018) The intensification of the water footprint of hydraulic fracturing. Sci Adv 4:5982

Kpeglo DO, Mantero J, Darko EO, Emi-Reynolds G, Faanu A, Manjon G, Vioque I, Akaho EHK, Garcia-Tenorio R (2016) Radiochemical characterization of produced water from twoproduction offshore oilfield In Ghana. J Environ Radioact 152:35–45

Kraemer TF, Reid DF (1984) The occurrence and behaviour of radium in saline formation water of the U.S. Gulf Coast Region. Isot Geosci 2:153–174

Lagera L, Hart A, Graham B (1999) Radionuclides in oil and gas operational discharges and environmental samples associated with offshore oil and gas production facilities. I: Continental Shelf Associates, Inc. Radionuclides, metals, and hydrocarbons in oil and gas operational discharges and environmental samples associated with offshore production facilities on the Texas/Louisiana continental shelf with an environmental assessment of metals and hydrocarbons. Prepared for U.S. Department of Energy. (DOE/MT/92001–23). Tulsa, OK (US): National Petroleum Technology Office, chapter 6.

Langmuir D, Herman JS (1980) The mobility of thorium in natural waters at low temperatures. Geochim Cosmochim Acta 44:1753–1766

Lauer NE, Harkness JS, JS, Vengosh A, (2016) Brine spills associated with unconventional oil development in North Dakota. Environ, Sci Technol 50:5389–5397

Luisa Torres L, Yadav OP, Khan E (2018) Risk assessment of human exposure to Ra-226 in oil produced water from the Bakken Shale. Sci Total Environ 626:867–874

McMahon PB, Kulongoski JT, Vengosh A, Cozzarelli IM, Matthew K, Landon MK, Kharaka YK, Gillespie JM, Davis TA (2018) Regional patterns in the geochemistry of oil-field water, southern San Joaquin Valley, California, USA. Appl Geochem. 98:127–140

Melson NH, Haliena BP, Kaplan DI, Barnett MO (2012) Adsorption of tetravalent thorium by geomedia. Radiochim Acta 100:827–832

Moater F, Shadizadeh SR, Karbassi AR, Ardalani E, Akbari Derakhshi R, Asadi M (2010) Determination of naturally occurring radioactive materials (NORM) in formation water during oil exploration. J Radioanal Nucl Chem 283:3–7

Nabhani Khalid AL, Khan F, Yang M (2016) Technologically enhanced naturally occurring radioactive materials in oil and gas production: a silent killer. Process Saf Environ 99:237–247

National Research Council (1996) The Waste Isolation Pilot Plant: A Potential Solution for the Disposal of Transuranic Waste. The National Academies Press, Washington, DC. https://doi.org/10.17226/5269

National Research Council (2006) Health Risks from Exposure to Low Levels of Ionizing Radiation: BEIR VII Phase 2. The National Academies Press, Washington, DC. https://doi.org/10.17226/11340

Neff JM, Foster K (1997) Composition, Fates, and effects of Produced Water Discharges toOffshore Waters of the Java Sea, Indonesia. Report to Pertimena/Maxus, Jakarta, Indonesia

Nelson AW, May D, Knight AW, Eitrheim ES, Mehrhoff M, Shannon R, Litman R, Schultz MK (2014) Matrix complications in the determination of radium levels in hydraulic fracturing flowback water from Marcellus Shale. Environ Sci Technol Lett 1:204–208

Nelson AW, Eitrheim ES, Knight AW, May D, Mehrhoff MA, Shannon R, Litman R, Burnett WC, Forbes TZ, Schultz MK (2016) Understanding the radioactive ingrowth and decay of naturally occurring radioactive materials in the environment: an analysis of produced fluids from the Marcellus Shale Environ. Health Perspectives 123:689–696

NRPA (Norwegian Radiation Protection Authority) (2004) Natural radioactivity in produced water from the Norwegian oil and gas industry in 2003. Strålalevern Rapport 2005:2

Osmond JK, Cowart JB, Ivanovich M (1983) Uranium isotopic dis-equilibrium in ground water as an indicator of anomalies. Int J Appl Radiat Isot 34:283–308

Plyatsuk LD, Burla OA, Yu AI, Hurets LL, Roy IO (2017) Investigation of produced waters radioactivity of oil and gas deposits in the Dnieper-Donets province. J Eng Sci 4:G17–G21

Rowan EL, Engle MA, Kirby CS, Kraemer TF (2011). Radium content of oil- and gas-field produced waters in the Northern Appalachian Basin (USA): summary and discussion of data. Scientific Investigations Report 2011–5135. Available: http://pubs.usgs.gov/sir/2011/5135/pdf/sir2011–5135.pdf

Schmidt HW, Kurz K (1906) Natural radioactive substances in thermal brines. Phys Z 7:213–224

Scott III GL (1995) US Patent No. US5441110: System and method for monitoring fracture growth during hydraulic fracture treatment. US Patent Publications

Scott III GL (1997) US Patent No. 5635712: Method for monitoring the hydraulic fracturing of a subterranean formation. US Patent Publications

Shawky S, Amer H, Nada AA, El-Maksoud TMA, Ibrahiem NM (2001) Characteristics of NORM in the oil industry from eastern and western deserts of Egypt. Appl Radiat Isot 55:135–139

Sill C (1974) Purification of radioactive tracers for use in high sensitivity alpha spectrometry. Anal Chem 46:1426–1431

Strand T, Lysebo I, Kristensen D, Birovljev A (1997) Deposits of naturally occuring radioactivity in production of oil and natural gas. NRPA report 1997:1. Østerås, Norwegian Radiation Protection Authority, 1997

Thakur P, Ward AL (2019) Sources and distribution of 241Am in the vicinity of a deep geologic repository. Environ Sci Pollut Res 26:2328–2344

Thakur P, Ward AL (2020) 210Po in the environment: insight into the naturally occurring polonium isotope. J Radioanal Nucl Chem 323:27–49

Tufail M (2012) Radium equivalent activity in the light of UNSCEAR report. Environ Monit Assess 184:5663–5667

UNSCEAR (2000) Sources and effects of ionizing radiation. United Nations Scientific Committee on the Effects of Atomic Radiation. Report to the General Assembly, with scientific annexes. New York: United Nations.

USDOE-U. S. Department of Energy (2011) Available online: http://www.statista.com/statistics/250408/flowback-water-salinity-from-different-us-shales-by-tds-concentration/

USNRC (2010) U.S. nuclear regulatory commission. "CFR – code of federal regulations title 4249 10 part 20 standards for protection against radiation." https://www.nrc.gov/reading-rm/doc-collections/cfr/. Accessed 27 April 2021. (U.S. Government Printing Office, 4251 Washington, DC)

USNRC (2018) Consolidated guidance about materials licenses: program-specific guidance about well logging, tracer, and field flood study licenses (NUREG-1556, Volume 14, Revision 1). Office of Nuclear Material Safety and Safeguards U.S. Nuclear Regulatory Commission Washington, DC 20555–0001

US Environmental Protection Agency (2000) National Water Quality Inventory Report to Congress, Washington DC 20460

Vegueria JSF, Godoy JM, Miekeley N (2002) Environmental impact studies of barium and radium discharges by produced waters from the "Bacia de Campos" oil field offshore platforms, Brazil. J Environ Radioact 62:23–38

Vengosh A, Hirschfeld D, Vinson D, Dwyer G, Raanan H, Rimawi O, Al-Zoubi A, Akkawi E, Marie A, Haquin G, Zaarur S, Ganor J (2009) High naturally occurring radioactivity in fossil groundwater from the Middle East. Environ Sci Technol 43:1769–1775

Vinson DS, Tagma T, Bouchaou L, Dwyer GS, Warner NR, Vengosh A (2013) Occurrence and mobilization of radium in fresh to saline coastal groundwater inferred radioactive material at US Geological Survey research site B. Appl Geochem 22:2125–2137

Walter GR, Benke RR, Pickett DA (2012) Effect of biogas generation on radon emissions from landfills receiving radium-bearing waste from shale gas development. J Air Waste Manage Assoc 62:1040–1049

Waste Isolation Pilot Plant (WIPP)- Site Enviromental Report for the calender year 1995. DOE/WIPP 96–2182

Zhang T, Bain D, Hammack R, Vidic RD (2015) Analysis of radium-226 in high salinity wastewater from unconventional gas extraction by inductively coupled plasma-mass spectrometry. Environ Sci Technol 49:2969–2976

Zhang T (2015) Origin and fate of radium in flowback and produced water from Marcellus shale gas exploration. PhD thesis , University of Pittsburgh.

Zielinski RA, Budahn JR (2007) Mode of occurrence and environmental mobility of oil-field radioactive material at US Geological Survey research site B. Appl Geochem 22:2125–2137

Exhibit 6

United States
Environmental Protection
Agency

A Regulators' Guide to the Management of Radioactive Residuals from Drinking Water Treatment Technologies

Office of Water (4606M)
EPA 816-R-05-004
July 2005
www.epa.gov/safewater

Printed on Recycled Paper

Acknowledgments

The Guide was prepared for the U.S. Environmental Protection Agency, Office of Water, Office of Ground Water and Drinking Water, Drinking Water Protection Division by the Cadmus Group, Inc. under contract No. 68-C-02-069. Special acknowledgment goes to those who helped develop and review the document including: Loren Setlow and Daniel Schultheisz (U.S. EPA's Office of Radiation and Indoor Air); Suzanne Kelly (U.S. EPA's Office of Ground Water and Drinking Water, Underground Injection Control Program); Robert Bastian and Jan Pickrel (U.S. EPA's Office of Wastewater); Stuart Walker (U.S. EPA's Office of Solid Waste and Emergency Response, Office of Site Remediation and Technology Innovation); Fred Ferate (U.S. Department of Transportation, Radioactive Materials Branch); and Catherine Mattsen, Gary Comfort, Andy Imboden, and Charlotte Abrams (Nuclear Regulatory Commission, Office of Nuclear Material Safety and Safeguards, Division of Industrial and Medical Nuclear Safety, Rulemaking and Guidance Branch). Sincere thanks also go to those who participated in the review process and provided their insights, opinions, and comments.

Please note that the U.S. EPA statutes and regulations described in this document contain legally binding requirements. This guidance document replaces all earlier U.S. EPA draft guidance documents on radionuclides residual disposal for drinking water treatment. The recommendations in this document are not substitutes for those statutes or regulations, nor is this document a regulation. This guide is strictly voluntary and does not impose legally-binding requirements on U.S. EPA, states, local or tribal governments, or members of the public, and may not apply to a particular situation based upon the circumstances. Although U.S. EPA recommends the approaches outlined in this document, state and local decisionmakers are free to adopt approaches that differ from those presented in this guide. Interested parties are free to raise questions about the appropriateness of the application of this guide. Any U.S. EPA decisions regarding a particular water system or wastestream will be made based on the applicable statutes and regulations. U.S. EPA will continue to review and update this guide as appropriate.

Executive Summary

The revised Radionuclides Rule came into effect on December 8, 2003. U.S. EPA's revisions to the Rule provide standards that, if met, ensure that all customers served by community water systems (CWSs) receive water that meets the Maximum Contaminant Levels (MCLs) for radionuclides in drinking water. Regulated radionuclides include radium-226, radium-228, gross alpha particle activity, uranium, and beta particle and photon radioactivity.

In accordance with the Rule, all CWSs must complete initial compliance monitoring by December 8, 2007. While most systems will be in compliance with the revised Rule, systems in areas of the country with elevated levels of naturally occurring radionuclides, and the few systems located near facilities that could potentially contaminate source waters with radioactive substances, might have to install new or upgrade existing treatment to meet these revised standards. These treatment processes will produce residuals containing regulated radionuclides.

This guide is intended for state regulators, technical assistance providers, and field staff. It is designed to help states address radionuclide residual disposal by outlining options available to help systems address elevated radionuclide levels. It provides an overview of the types of treatment listed as Best Available Technologies (BATs) and Small System Compliance Technologies (SSCTs) by U.S. EPA, the wastes produced by these technologies, waste disposal options and considerations, and the federal statutes and regulations governing waste disposal. This guide, however, is not intended to identify concentrations of radionuclides that are appropriate for each disposal option. As part of U.S. EPA's Advance Notice of Proposed Rulemaking (ANPR) effort on low-activity waste (68 FR 65120, November 18, 2003), the Agency is evaluating the conditions under which various disposal options would be appropriate for radioactive material (with a focus on hazardous waste landfills); that guidance is still applicable.

Some states have been grappling with the issue of radioactive residual disposal for some time, while others are just beginning to address these waste disposal issues. Relevant state agencies and programs (e.g., drinking water, radiation control, solid waste) will benefit from coordinating with each other to determine appropriate disposal options. The challenge for states is to find a balance between appropriate treatment technologies, safe waste disposal practices, worker safety, and cost, yet ensure compliance with the Radionuclides Rule and other drinking water regulations. Note that this guide presents a generalized overview of residual management. Due to the variability in state regulations, waste concentration and characteristics, and removal efficiencies associated with treatment technologies, systems' residual management responsibilities may be more extensive or complex than presented.

The federal statutes and regulations discussed in the guide set the minimum standards by which systems must operate. States, however, have the authority to set more stringent standards. State treatment and waste disposal regulations may, as a result, be stricter and significantly more complex than those presented in this guide. Systems should always be reminded to check with their state before proceeding with treatment installation or modification and waste disposal to ensure they are meeting all relevant federal, state, and local requirements.

Contents

List of Tables

List of Figures

Acronyms

AA	Activated Alumina
AEA	Atomic Energy Act
ALARA	As Low as Reasonably Achievable
AX	Anion Exchange
BAT	Best Available Technology
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CESQG	Conditionally Exempt Small Quantity Generator
CWA	Clean Water Act
CWS	Community Water System
CX	Cation Exchange
DOT	Department of Transportation
U.S. EPA	United States Environmental Protection Agency
FBRR	Filter Backwash Recycling Rule
HMO	Hydrous Manganese Oxide
ICRP	International Commission on Radiological Protection
ISCORS	Interagency Steering Committee on Radiation Standards
IX	Ion Exchange
LLRW	Low-Level Radioactive Waste
MARLAP	Multi-Agency Radiological Laboratory Analytical Protocols Manual
MARSSIM	Multi-Agency Radiation Survey and Site Investigation Manual
MCL	Maximum Contaminant Level
MPRSA	Marine Protection, Research, and Sanctuaries Act
MSWLF	Municipal Solid Waste Landfill
NCP	National Oil and Hazardous Substances Pollution Contingency Plan
NCRP	National Council on Radiation Protection and Measurements
NPDES	National Pollutant Discharge Elimination System
NRC	Nuclear Regulatory Commission
OGWDW	Office of Ground Water and Drinking Water
OSHA	Occupational Safety and Health Administration
PFLT	Paint Filter Liquids Test
POTW	Publicly Owned Treatment Works
POU	Point of Use
PPE	Personal Protection Equipment
RCRA	Resource Conservation and Recovery Act
RO	Reverse Osmosis
SDWA	Safe Drinking Water Act
SPARRC	Spreadsheet Program to Ascertain Radionuclides Residuals Concentration
SSCT	Small System Compliance Technology
TBLL	Technically Based Local Limit
TCLP	Toxicity Characteristic Leaching Procedure
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
TENORM	Technologically Enhanced Naturally Occurring Radioactive Materials
UIC	Underground Injection Control
USDW	Underground Source of Drinking Water

Introduction

The Radionuclides Rule

Community water systems (CWSs) were required to begin complying with the revised Radionuclides Rule on December 8, 2003. The Rule retained the maximum contaminant levels (MCLs) for combined radium-226/228, gross alpha particle activity, and beta particle and photon radioactivity. The Rule also revised and added to existing requirements, set a new MCL for uranium[1] and separate monitoring requirements for radium-228, and required CWSs to monitor at each entry point to the distribution system. For more information on the Rule's requirements, see: http://www.epa.gov/safewater/radionuc.html.

Table 1: Radionuclides MCLs

Combined radium-226 and 228	5 pCi/L
Gross alpha particle activity (excluding radon and uranium)	15 pCi/L
Beta particle and photon radioactivity	4 mrem/year
Uranium	30 µg/L

Public Health Risks of Exposure to Radionuclides in Drinking Water

Radiation exposure is regulated on the assumption that any exposure carries some risk of a health effect. Radiation-induced health effects can be *deterministic*, in which biological damage is readily observed and proportional to the level of exposure, or *stochastic*, in which the probability of a health effect is related to the level of exposure, but the severity is not. Deterministic effects have only been observed at relatively high exposures delivered over a short time. Doses associated with exposures to natural background radiation or typical radioactive materials in water treatment plants are generally many times lower than the high doses that are needed to cause such effects. Stochastic effects are more typical of low radiation doses, often delivered over a period of time (e.g., chronic exposures). The principal concern associated with low dose radiation exposure is the possible occurrence of cancer years after the exposure occurs. In addition, uranium can be chemically toxic to the kidneys.

Measuring Radiation

Quantities of radioactive material are measured as radioactivity or activity in curies, i.e., disintegrations (decays) per second. The potential for health hazards increases as activity increases. Radioactive material found in water treatment plant residuals or source water is usually measured in microcuries or picocuries (pCi).

The body's exposure to ionizing radiation is typically expressed in millirem (mrem). Dose standards are typically expressed as a rate of exposure, in millirems per unit of time (e.g., hours or years).

Fundamentals of Radiation

Human beings are constantly exposed to radiation from natural and manmade sources. The average radiation dose to an individual in the United States is about 360 mrem/yr (see Table 2 on the following page). On average, 80 percent of that exposure comes from natural sources including cosmic radiation from outer space; terrestrial radiation from natural radioactive materials in rocks, soil, and minerals; and radiation inhaled or ingested from food and water.[2] Additional exposure comes from manmade sources of radiation including medical X-rays and industrial use of radioactive material. Table 2 on the following page summarizes average annual exposures to radiation within the United States. Note that radiation exposure can vary greatly according to factors such as an individual's location, lifestyle, and daily activities.

Radiation is characterized as "ionizing" and "non-ionizing." Uranium and radium occur naturally in rocks and soil as the result of radioactive decay, or the release or transfer of excess energy, of uranium-238 and thorium-232. This excess energy is ionizing radiation. Ionizing radiation is of sufficient energy to break chemical bonds and remove electrons, potentially causing biological damage. Non-ionizing radiation, such as visible light and infrared, is lower

---

[1] "Uranium" refers to all isotopes that make up naturally occurring uranium: U-238, U-235, and U-234.

[2] U.S. Department of Energy and U.S. EPA Interagency Steering Committee on Radiation Standards (ISCORS), 2003-04.

energy (e.g., microwaves or radiowaves) and "bounces off or passes through matter without displacing electrons."[3] Its effect on human health is undetermined.

The four most common types of ionizing radiation are:

- Alpha radiation (emitted by radon, thorium, and uranium), which can occur naturally or as the result of manmade activities. It cannot penetrate the skin but can be a significant internal hazard if alpha-emitting radionuclides are ingested or inhaled.
- Beta radiation emitted by radium-228 and manmade contaminants from industrial uses of radioactive materials or facilities disposing of radioactive material. It can penetrate outer layers of skin, but beta-emitting radionuclides are more of a concern as an internal hazard if ingested or inhaled.
- Gamma radiation, also referred to as "photon" emissions (radium-226 emits both alpha and gamma radiation). Gamma radiation originates from processes inside the nucleus. Radioactive materials that emit gamma radiation are of concern because the gamma rays pose an external radiation exposure hazard and can penetrate the body.
- X-Ray radiation, which is also photon radiation, although x-rays originate from outside the nucleus. X-rays are slightly lower in energy than gamma radiation and are the single largest source of manmade radiation exposure.

Table 2: Average Annual Exposure to Radiation

Radiation Source	Average Exposure[1]	Typical Range of Variability[2]
	(mrem/year)	
Natural Sources		
Terrestrial	30	10-80
Radon	200	30-820
Cosmic	30	20-100
Internal	40	
Man-made Sources		
Medical	50	
Consumer products	10	
Other	1	
Total	**361**	**90-1080**

[1] National Council on Radiation Protection, 1987
[2] Huffert, A.M., et al, 1994; Fisher, Eugene.

Guide Overview

This guide is intended for regulators, technical assistance providers, and field staff helping drinking water systems protect the public from exposure to excessive levels of regulated radionuclides in drinking water through the use of treatment technology, and their staffs from exposure to radioactive wastes generated by treatment. It focuses primarily on treatment for radium and uranium, the most common naturally-occurring regulated radionuclides. This guide provides:

1. Information on how systems can determine whether installing additional or new treatment technologies is the best option for addressing radionuclides in source water, taking into account the residuals produced, disposal options, and required operator skill level.
2. Descriptions of the different treatment options listed by the U.S. Environmental Protection Agency (U.S. EPA) as Best Available Technologies (BATs) and Small System Compliance Technologies (SSCTs).[4]

---

[3] Oak Ridge Reservation, 2000. p. G-5

[4] BATs are the best technologies, treatment techniques, or other means that the U.S. EPA administrator determines to be available, after examination for efficacy under field conditions and not solely under laboratory conditions (taking cost into consideration). SSCTs are technologies that have been federally approved for systems serving fewer than 10,000 persons to use in complying with

3. Details on the residual streams produced by these treatment technologies.

4. General options for disposal of the residuals produced by these treatment technologies.

5. Information on key issues related to the disposal of drinking water treatment residuals containing regulated radionuclides, including co-occurrence, applicable federal regulations, and worker safety concerns.

This guide has two main sections:

- **Section I** provides an **overview** of the removal of radionuclides from drinking water and a discussion of worker safety. It is an introduction to non-treatment options, treatment technologies, residuals, disposal options, and measures that systems can take to protect their staffs from radiation exposure.

- **Section II** provides a more **in-depth review of treatment technologies**, the residuals they produce, the disposal options for these residuals, and intermediate processing.

In addition, the appendices include a glossary, a list of references and contacts for more information, and a catalogue of resources that provide more information on the Radionuclides Rule and on the treatment, handling, and disposal of radionuclides.

MCLs.

Section I: Overview of the Removal of Radionuclides from Drinking Water

I-A Determining Whether Additional Treatment is Appropriate: Compliance Options Overview

Installing a new treatment technology requires an investment of both time and money. There are several alternative compliance options that may be more appropriate for some systems. Each option has its own considerations that should be weighed against a system's particular circumstances.

Option	Considerations
Developing a New Source	‣ Are there other sources available that will produce water that complies with all regulations? ‣ Will the new source meet demand? ‣ Is the new source close enough to the system to economically justify using it?
Blending Source Waters	‣ Are there other sources available with radionuclide levels below the MCLs that can be blended with existing sources? ‣ Is it economically feasible to blend sources? ‣ Is it possible to blend the sources so that the MCLs are met at every entry point to the distribution system and all required plant flow rates are maintained? ‣ If the system uses more than one problematic source, would abandoning any one source reduce the radionuclide concentrations?
Connecting With a Nearby System	‣ Is there a nearby system meeting the requirements of the Radionuclides Rule that is willing to interconnect? ‣ Is it economically feasible to connect to the nearby system? ‣ Can the nearby system handle the increased demand of additional customers?
Optimizing Existing Treatment	‣ Has the system attempted to optimize existing treatment? ‣ Is the system currently using a technology approved as a BAT or SSCT for radionuclide removal? ‣ Is it possible to treat the source water to precipitate competing ions for increased radionuclide removal?

If a system determines that the above options are not feasible, installing new or additional treatment may be the most suitable and cost-effective means of complying with the Radionuclides Rule.

I-B Choosing the Right Technology: An Overview of Listed Best Available Technologies and Small System Compliance Technologies

In promulgating the Radionuclides Rule, U.S. EPA listed BATs and SSCTs for removal of radionuclides from drinking water. Although a system can use any means available (if allowed by the state[5]) to achieve compliance, this guide focuses on the BATs and SSCTs that were listed by U.S. EPA on the basis of their efficacy and affordability in the removal of radionuclides from drinking water. If a system chooses to install new or additional treatment, several key factors should be considered.

Option	Considerations
Installing New or Additional Treatment	‣ Will the treatment technology be effective in removing radionuclides given the source water characteristics? Refer to the detailed treatment technology descriptions in Section II beginning on page 27 of this guide for more information. ‣ Will the technology be efficient at removing co-occurring contaminants, helping the system comply with other drinking water standards? ‣ Is the treatment type suitable for the system's size? ‣ Is the operator appropriately trained to operate and maintain the chosen technology? ‣ Can pilot testing be performed to ensure the suitability of the technology? ‣ Does the system have or can it raise or borrow the funds needed to cover the capital and operation and maintenance costs involved in installing and maintaining the treatment, including disposal costs? ‣ What residuals will be produced and can the system properly dispose of the residuals? ‣ Are there additional costs associated with the disposal of wastes generated by the technology selected? ‣ Will the treatment process or residuals generated pose a radiation hazard to workers or result in the need for the state radiation control agency to license the system?

In choosing a treatment technology, systems should also keep in mind that the characteristics of, and contaminant concentrations in the residuals will help to define a system's disposal options. The characteristics and contaminant concentrations will vary according to:

- The concentration of radionuclides in the source water.
- How efficient the treatment is at removing radionuclides.
- Frequency of regeneration (for ion exchange [IX] and activated alumina [AA]).
- Frequency of filter backwash (for treatment methods using granular media filters).
- Frequency of IX resin, AA media, granular filter media, or membrane replacement.
- Loading to the treatment unit.

If possible, systems should conduct pilot tests of the treatment technologies to determine, for example, the regeneration schedule that is most appropriate when using IX, or the frequency with which filters should be backwashed. Pilot tests are a good way to determine whether system operators will have the time and skill to handle the technology or whether a less complex option is more appropriate.

Table 3 on the following page outlines the treatment capabilities and applicability of the BATs and SSCTs listed in the Radionuclides Rule. It also lists the level of operator skill required to operate and maintain the technology. For additional information on each technology including removal efficiencies, see Section II and Appendix E of this guide.

---

[5] Note that "state" refers to the Drinking Water Primacy Agency and/or the Underground Injection Control (UIC) Primacy Agency.

Table 3: Applicability of Best Available Technologies and Small System Compliance Technologies[6]

Treatment Technology	Designation	Customers Served (SSCTs only)	Treatment Capabilities				Source Water Considerations	Operator Skill Required
	BAT and/or SSCT?		*Radium (Ra)*	*Uranium (U)*	*Gross Alpha (G)*	*Beta/photon (B)*		
IX	BAT & SSCT	25-10,000	✓	✓		✓	All ground waters	Intermediate
Point of Use (POU) IX	SSCT	25-10,000	✓	✓		✓	All ground waters	Basic
Reverse Osmosis (RO)	BAT & SSCT	25-10,000 (Ra, G, B) 501-10,000 (U)	✓	✓	✓	✓	Surface waters usually requiring pre-filtration	Advanced
POU RO	SSCT	25-10,000	✓	✓	✓	✓	Surface waters usually requiring pre-filtration	Basic
Lime Softening	BAT & SSCT	25-10,000 (Ra) 501-10,000 (U)	✓	✓			All waters	Advanced
Green Sand Filtration	SSCT	25-10,000	✓				Typically ground waters	Basic
Co-precipitation with Barium Sulfate	SSCT	25-10,000	✓				Ground waters with suitable water quality	Intermediate to Advanced
Electrodialysis/ Electrodialysis Reversal	SSCT	25-10,000	✓				All ground waters	Basic to Intermediate
Pre-formed Hydrous Manganese Oxide Filtration	SSCT	25-10,000	✓				All ground waters	Intermediate
AA	SSCT	25-10,000		✓			All ground waters	Advanced
Coagulation/ Filtration	BAT & SSCT	25-10,000		✓			Wide range of water qualities	Advanced

---

[6] U.S. EPA, December 2000.

I-C Treatment Residuals: An Overview

Each treatment technology listed in Table 3 produces solid residuals (including spent resins, spent filter media, spent membranes, and sludges) and liquid residuals (including brines, backwash water, rinse water, acid neutralization streams, and concentrates).

Because disposal options may be limited, systems need to be aware of the types of residuals that will be generated by each treatment process in order to determine whether the treatment will be practical and affordable. Table 4 outlines the residuals produced by the BATs and SSCTs listed by U.S. EPA for radionuclide removal. For additional information on each technology, see Section II and Appendix E of this guide.

Table 4: Residual Type by Treatment Technology

Treatment	**Types of Residuals**							
	Solid			**Liquid**				
	Spent Resins/ Media	Spent Membranes	Sludge	Brine	Backwash Water	Rinse Water	Acid Neutralization Water	Concentrate
IX	✓			✓	✓	✓		
RO		✓						✓
Lime Softening	✓		✓		✓			
Green Sand Filtration	✓		✓		✓			
Co-precipitation with Barium Sulfate	✓		✓		✓			
Electrodialysis/ Electrodialysis Reversal		✓						✓
Pre-formed Hydrous Manganese Oxide Filtration	✓		✓		✓			
AA	✓			✓	✓	✓	✓	
Coagulation/Filtration	✓		✓		✓			

I-C.1 Residual Estimation: U.S. EPA Spreadsheet Program to Ascertain Radionuclides Residuals Concentration Model

U.S. EPA has developed a Spreadsheet Program to Ascertain Radionuclides Residuals Concentration (SPARRC) model that indicates potential concentrations of radioactivity in residuals and filters at the system. U.S. EPA began developing the model in 1998. This initial version focused on developing the contaminant mass balances in the sludge and other residuals using a complete set of input from the user. While the early version of SPARRC is useful in estimating the volume and concentrations of residuals, it lacked capabilities to estimate the removal efficiencies.

The current version of SPAARC[7] incorporates predictive algorithms to estimate radionuclides and co-contaminant removals, and focuses on a sound estimate of residual radionuclides concentrations and co-occurring pollutants rather than sizing and designing drinking water treatment technologies. It is a flexible and highly interactive tool requiring minimum learning time and was developed as a stand-alone desktop application using state of the art software development tools. The program allows the operator to select the type of treatment process, as well as input and output parameters such as water flows, doses of coagulant and polymer, and filter capacities.

The current SPARRC model covers six technologies and associated co-contaminants including:

Technology	Radionuclides	Co-Contaminant
Coagulation Filtration	Uranium	Arsenic
Lime Softening	Radium and Uranium	None
IX	Radium, Barium, and Uranium	None
RO	Radium and Uranium	None
AA	Uranium	Arsenic
Green Sand Filtration	Radium and Barium	None

The current version of SPARRC is available at http://www.npdespermits.com/sparrc. For questions concerning the model, contact Rajiv Khera at U.S. EPA's Office of Ground Water and Drinking Water at 202-564-4881 or khera.rajiv@epa.gov.

The concentration of radionuclides in the waste stream, the type of waste produced, and federal and state regulations are among the factors that dictate which disposal options are available to a system. Treated water pH, total dissolved solids (TDS), total suspended solids (TSS), and heavy metals concentrations in the waste stream can also limit disposal options. Section I-D provides an overview of applicable federal regulations and the disposal options that may be available to systems removing radionuclides from their source water.

---

[7] Version 1, July 2003. Note that this model is a draft version for which U.S. EPA is still seeking comment and has not gone through a peer review process.

I-D Disposal of Residuals: An Overview of Applicable Statutes, Regulations, and Disposal Options

Treating water for naturally occurring radionuclides will result in residual streams that are classified as "technologically enhanced naturally occurring radioactive materials," or TENORM.[8] TENORM is defined here as naturally occurring materials, such as rocks, minerals, soils, and water whose radionuclide concentrations or potential for exposure to humans or the environment is enhanced as a result of human activities (e.g., water treatment).[9] Pilot tests of treatment technologies are a good way for systems to determine how much waste will be produced, and whether the system will be capable of disposing of the amount, concentration, and type of waste.

Numerous regulations govern the disposal of waste streams containing radionuclides (although there are no federal waste disposal regulations specifically for TENORM wastes), and their interaction is complex. States and disposal facilities can place additional restrictions on systems' disposal options.

I-D.1 Applicable Federal Statutes and Federal Regulations

The following federal statutes and regulations could potentially apply to the disposal of water treatment residuals:

- The Resource Conservation and Recovery Act (RCRA; 40 CFR 239 to 282) establishes programs for regulating nonhazardous solid waste (Subtitle D), hazardous waste (Subtitle C), and Underground Storage Tanks (Subtitle I). RCRA governs the identification, classification, and management of solid[10] and hazardous wastes.[11] The RCRA regulations that apply to different types of disposal units depends on the types of wastes that are accepted.

    - Municipal solid waste landfills (MSWLF) are Subtitle D landfills that accept household and other municipal waste. A MSWLF may receive other types of RCRA Subtitle D wastes, such as commercial and industrial wastes. The Municipal Solid Waste Landfill (MSWLF) requirements (40 CFR 258), establish minimum national criteria for MSWLFs covering landfill location, operation, and design; ground water monitoring; corrective action; closure and post-closure, and financial assurance.

    - Subtitle D landfills that accept nonhazardous waste, but do not accept municipal waste ("industrial landfills"), are also subject to federal regulations (40 CFR Part 257, Subparts A and B). However, state regulations typically have additional requirements that apply to these industrial landfills.

    - Land disposal units that accept hazardous waste are regulated under Subtitle C, and include landfills, surface impoundments, waste piles, land treatment units, and underground injection wells. These disposal units are subject to stringent design and operating standards (40 Parts 264 and 265).

---

[8] See http://www.epa.gov/radiation/tenorm/ for more information.

[9] This definition is in accordance with the concepts presented in National Academy of Sciences. 1999. *Evaluation of Guidelines for Exposures to Technologically Enhanced Naturally Occurring Radioactive Materials*. Washington, D.C.: National Academies Press; and IAEA (2004).

[10] Any garbage, refuse, sludge from a wastewater treatment plant, water supply treatment plant, or air pollution control facility, and other discarded material, including solid, liquid, semisolid, or contained gaseous material, resulting from industrial, commercial, mining, and agricultural operations and from community activities. (U.S. EPA, *Mixed Waste Glossary*) For the purposes of hazardous waste regulation, a solid waste is a material that is discarded by being either abandoned, inherently waste-like, a certain waste military munition, or recycled. (U.S. EPA, 2003)

[11] Hazardous waste is defined under 40 CFR 261.3. Waste is considered hazardous if it is a solid waste (as defined under 40 CFR 261.2) that is not excluded from regulation as hazardous waste under 40 261.4(b) and when it meets the criteria listed under 40 CFR 261.3(a)(2) and (b).

- The Clean Water Act (CWA; 33 USC 1251 to 1387), under which U.S. EPA establishes requirements for direct discharges of liquid waste or the discharge of a liquid waste to publicly owned treatment works (POTW).

- The Safe Drinking Water Act (SDWA; 42 USC 300f et seq.), which requires that U.S. EPA develop minimum federal requirements for underground injection control (UIC) programs (state or primacy) to ensure that underground injection does not endanger current and future underground sources of drinking water (USDWs) (40 CFR 144-148).

- The Atomic Energy Act of 1954, as amended (AEA; 42 USC 2011 et seq.), which requires the Nuclear Regulatory Commission (NRC) to regulate the civilian commercial, industrial, academic, and medical use of nuclear materials. The Act enables the NRC to relinquish some of its regulatory authority over source materials to states through the signing of an agreement between the state's Governor and the NRC Chairperson. Currently, 33 states have entered such agreements and are referred to as "Agreement States." Agreement States must establish radiation protection programs compatible with the NRC's and the NRC remains involved with state licensing, inspection, and rule changes, among other things. For more information and a list of Agreement States, see http://www.hsrd.ornl.gov/nrc.

- Department of Transportation (DOT) regulations (49 CFR 171 to 180), which govern the shipping, labeling, and transport of hazardous (including radioactive) materials.[12]

- The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, 42 USC 9605 et seq.) National Oil and Hazardous Substances Pollution Contingency Plan (NCP, 40 CFR 300) applies to the release or threat of release of hazardous substances (including radionuclides) that many endanger human health and the environment. If disposal of radionuclide-contaminated residuals results in a release or threat of release that endangers human health or the environment, CERCLA may require cleanup of the hazardous substance.

---

[12] In 49 CFR 173.436, DOT provides levels for individual radionuclides (both in terms of concentration and a total consignment activity) that are exempt from the DOT requirements which would normally apply for transporting radioactive material. (See "Hazardous Materials Regulations; Compatibility With the Regulations of the International Atomic Energy Agency; Final Rule." 69 FR 3632, January 26, 2004, at http://www.tgainc.com/pdf/69fr-3631.pdf). In the preamble to the Rule, DOT explains that the exemptions apply to "other natural materials or ores...when those materials or ores are to be used because of some other physical or chemical characteristics...[or] when these have been subjected to physical or chemical processing, when the processing was not for the purpose of extracting radionuclides...provided that their radionuclide concentration does not exceed 10 times the activity concentration in the table in [section] 173.436."

To determine whether a system falls under the DOT radioactive material transport regulations, the system must determine the radionuclide activity concentrations and activities and calculate the effective exemption values (assuming that you have more than one radionuclide). Systems can use "process knowledge" to aid in making these determinations. See Appendix C for additional information.

State TENORM Regulations

States address TENORM in various ways. Although thirteen states currently have regulations addressing TENORM, some only regulate TENORM from specific industries (e.g., oil and gas or phosphate production), while others address all sources of TENORM. For example:

- In Maine, non-exempt facilities abiding by the state's standards for TENORM radiation protection, worker safety, disposal and transfer of waste, dilution of wastes, and unrestricted use and conditional release, may receive a license to transfer or dispose of TENORM wastes without quantity restrictions (10-144A CMR 220, Subpart N).
- Louisiana issues similar licenses to non-exempt facilities and requires that a manifest be obtained from the Department of Environmental Quality prior to shipping TENORM waste to a disposal facility (LAC 33:XV.1408 and 1418).
- Texas also issues general licenses to non-exempt facilities. Systems transferring waste for disposal must choose a facility licensed to accept TENORM wastes (25 TAC 289.25(f) and (h)).

Most states do not have specific TENORM regulations and regulate it the same way as all other sources of radiation. For more information on state regulations, see http://www.tenorm.com/regs2.htm#States.

The remainder of this section and Appendix C contain additional information on these and other applicable federal statutes and regulations as they apply to the disposal of water treatment plant residuals containing radionuclides. States may have additional requirements or restrictions on the disposal of water treatment residuals containing radionuclides. State radiation, hazardous waste, and drinking water programs should coordinate to provide systems with comprehensive information on all relevant requirements (see Appendix D for state contact information).

I-D.2 Applicable Federal Definitions for Waste

Systems should be aware that key definitions vary among regulations. For example, the UIC progam's regulations do not automatically assume the same exemptions as the NRC regulations (e.g., source material is of an "unimportant quantity" (10 CFR 40.13) and is *exempt* from NRC regulation if the uranium or thorium makes up less than 0.05 percent by weight of the material. For natural uranium, this is approximately 335 pCi/g, though this figure is an estimate and actual values may be obtained for different uranium and thorium isotopes). Making systems aware of these distinctions is important in ensuring that they adhere to all applicable federal statutes and regulations. In addition, systems should be made aware of any state licensing requirements related to the generation of non-exempt radioactive materials.

I-D.2.1 Hazardous Waste

Hazardous waste is defined under 40 CFR 261.3. Waste is considered hazardous if it is a solid waste (as defined under 40 CFR 261.2) that is not excluded from regulation as hazardous waste under 40 CFR 261.4(b) and when it meets the criteria listed under 40 CFR 261.3(a)(2) and (b). The RCRA regulations establish two ways of identifying wastes as hazardous under RCRA. A waste may be considered hazardous if it exhibits certain hazardous properties ("characteristics") or if it is included on a specific list of wastes EPA has determined are hazardous ("listing" a waste as hazardous in 40 CFR 261.31 to 261.33). RCRA defines four hazardous waste characteristic properties: ignitability, corrosivity, reactivity, or toxicity (see 40 CFR 261.21-261.24). The hazardous waste characteristics are most applicable to TENORM waste; the toxicity characteristic (40 CFR 261.24) is likely to be the most concern for generators of TENORM wastes.

The presence of radionuclides does not make waste hazardous; hazardous waste generation will most likely be the result of the removal of co-occurring contaminants, such as arsenic, in the waste. Some treatment technologies that are effective in removing radionuclides (e.g., IX) will also be effective in removing other contaminants (e.g., arsenic) that, in high enough concentrations, could make the resulting residuals hazardous or, in some cases, mixed waste. For more information, see *Regulations on the Disposal of Arsenic Residuals from Drinking Water Treatment Plants* (EPA/600/R-

00/025), *Treatment of Arsenic Residuals from Drinking Water Removal Processes* (EPA/600/R-01/033), and U.S. EPA's Arsenic Web page, at http://www.epa.gov/safewater/arsenic.html.

Water systems are required to determine whether the waste they generate is hazardous. This may be done using knowledge of the waste generation process, analytical testing, or a combination of both. Analytical testing may involve leachate tests such as the Toxicity Characteristic Leaching Procedure (TCLP) (Method 1311, as described in U.S. EPA publication SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods"), which applies to 40 substances, including metals, pesticides, and other organic compounds. If the waste is hazardous, it must be managed under RCRA Subtitle C requirements.

Hazardous waste generators are classified as Large Quantity Generators, Small Quantity Generators, or Conditionally Exempt Small Quantity Generators,[13] depending on the amount of hazardous waste produced monthly and the amount of hazardous waste stored on site at any given time. RCRA requirements vary for each generator class. For more information on these requirements, see Section III, Chapter 3, of the *RCRA Orientation Manual* (EPA 530-R-02-016) at http://www.epa.gov/epaoswer/general/orientat/rom33.pdf.

A hazardous waste generator is always liable for the waste. In the event of future problems at the disposal site or with inappropriate handling, the generator remains partially liable.

I-D.2.2 Low-Level Radioactive Waste

The Low-Level Radioactive Waste Policy Act (42 USC 2021b(9)) defines low-level radioactive waste (LLRW) as "radioactive material that (A) is not high level radioactive waste, spent nuclear fuel, or byproduct material (as defined in section 2014(e)(2)...); and (B) the Nuclear Regulatory Commission...classifies as low-level radioactive waste." Generally, LLRW can be thought of as byproduct material as defined in 42 USC 2014(e)(1) (i.e., yielded in or made radioactive by the production or use of special nuclear material) that does not fall into any other category. In addition, LLRW can contain source or special nuclear material. Note that water treatment residuals would *not* meet the definition of byproduct material as defined under 42 USC 2014(e)(2) (waste from processing uranium or thorium ore).

Radium is not considered source material and would not be considered byproduct material when present in water treatment residuals. Uranium and thorium are considered "source material" (42 USC 2014(z)) and are subject to NRC or Agreement State licensing and regulation. However, source material is of an "unimportant quantity" (10 CFR 40.13) and is *exempt* from NRC or Agreement State regulation if the uranium or thorium makes up less than 0.05 percent by weight (or approximately 335 pCi/g for natural uranium) of the material. These limits apply to both liquid and solid residuals. For perspective, in a system with filter media weighing 30,000 pounds, 0.05 percent by weight would be equal to 15 pounds of uranium.

If a system has source material that contains more than 0.05 percent uranium or thorium by weight, and has a total of no more than 15 pounds in its possession at any time, it is considered to have a "small quantity" of source material and is subject to the general license requirements of 10 CFR 40.22 or equivalent Agreement State regulations. (Note that the 0.05 percent level is not health-based.) Under this general license, systems may not possess more than 150 pounds of source material in any one calendar year. Source material held under this general license normally requires disposal at facilities authorized to accept LLRW. In addition, although not licensable by itself, radium that co-occurs with licensable source material would be subject to the requirements of that license.

Systems that exceed the unimportant quantity and small quantity thresholds must apply for specific licenses from the NRC or Agreement State.

---

[13] While these generators are not subject to many RCRA requirements, they are subject to limited generator waste management standards (40 CFR 261.5). Conditionally Exempt Small Quantity Generators must identify their hazardous waste, comply with storage limit requirements, and ensure waste treatment or disposal in a landfill that is permitted under Subtitle C, a state MSWLF, or a state permitted or licensed solid waste landfill.

I-D.2.3 Mixed Waste

Mixed waste is regulated under RCRA and the Atomic Energy Act (AEA) of 1954. Mixed waste "contains both hazardous waste and source...or byproduct material subject to the Atomic Energy Act of 1954" (42 USC 6903.41). Therefore, although highly unlikely, systems generating waste containing uranium or thorium (source material) as well as hazardous waste could potentially have a mixed waste. If wastes contain licensable amounts of source material (any concentration exceeding the "unimportant quantity" in 10 CFR 40.13 (a)) and hazardous waste, these wastes must be disposed of at a facility authorized to accept mixed waste. Because there are limited disposal pathways, generation of a mixed waste should be avoided if at all possible. For more information on licensing requirements and Agreement States, see the discussion of the AEA in Appendix C.

If either portion of the waste is exempted or excluded under RCRA or the AEA (and the regulations promulgated under these Acts), it is not mixed waste. A system generating hazardous waste does not have mixed waste if the amount of source material generated is an "unimportant quantity" (uranium or thorium makes up less than 0.05 percent by weight of the material), or if the waste contains only radium (since radium is not considered source or byproduct material when present in water treatment residuals).

Hazardous waste that contains beta/photon emitters could be considered mixed waste if a licensed source of the contamination can be identified. A few beta/photon emitters occur naturally and can be present in source water; others remain as a legacy of fallout from nuclear weapons testing or originate from discharge from nuclear or medical facilities. Check with the state Radiation Program to see if beta/photon emitters are considered byproduct material. Note that because radium is not considered source or byproduct material, waste containing only radium would not legally be defined as a mixed waste under federal regulations.

I-D.3 Possible Disposal Options if Elevated TENORM is Present

The majority of water treatment systems should not have problems with radiation. The following discussion is intended as guidance for states on disposal options for systems that do have elevated levels of TENORM in their treatment residuals. Table 5 summarizes disposal options for TENORM residuals. Each option is discussed in more detail below.

Table 5: Disposal Options by Type of Residual Produced

Residual Waste	**Disposal Options**				
	Direct Discharge	**Discharge to POTW**	**Recycle**[14]	**Underground Injection**	**Landfill**
Liquid Wastes					
Acid Neutralization Water	✓	✓	✓	✓	
Backwash Water	✓	✓	✓	✓	
Brine	✓	✓	✓	✓	
Concentrate	✓	✓	✓	✓	
Rinse Water	✓	✓	✓	✓	
Solid Wastes					
Sludge		✓		✓	✓
Spent Media					✓
Spent Membranes					✓

I-D.3.1 Options for Disposal of Solid Residuals

Depending on the characteristics of the waste, state and landfill-specific disposal restrictions, cost, and system location, solid waste may be disposed of in a solid waste (RCRA Subtitle D), LLRW, or hazardous waste (RCRA Subtitle C) landfill. See Decision Tree 1 on page 17 of this guide for an overview of the decision making process for systems that generate solid residuals. Systems should also be aware that landfill owners can refuse to accept any waste and have the discretion to return any waste to the generator.[15]

U.S. EPA is aware that some states allow land spreading or soil mixing as an alternative to landfill disposal for water treatment residuals (for example, as a soil amendment on farm fields). One central concern with land spreading is the potential for build-up or movement of radionuclides to create contaminated sites that would require remediation and/or use of institutional and engineering controls. Other factors to take into account include the physical and chemical attributes of the material, the amount of radiation introduced into the soil over time, the mobility of radionuclides and their decay products along multiple pathways of exposure, and the consideration of future controls and future land use. Programs would need to be designed to provide adequate risk protection to human health and the environment.

Other options such as incineration, evaporation ponds, surface impoundments, and sludge dewatering are merely intermediate processing methods; each creates its own residual stream. Additional information appears in Section II-B of this guide, "Intermediate Processing." States should consult their relevant waste disposal programs to determine an appropriate disposal option for systems generating solid residuals containing radionuclides. See Appendix D for contact information.

---

[14] The return of the liquid waste stream into the water system's treatment process.

[15] Please note that if a load is rejected and the material is not identified, DOT exemption paperwork needs to be filled out by a state radiation protection or radiation control employee prior to the load going back on the road. More information about this can be found at the CRCPD Web site at: http://www.crcpd.org/Transportation_related_docs.asp

I-D.3.1.1 Testing for Free Liquids

Systems must perform the Paint Filter Liquids Test (or PFLT; EPA SW 846 Method 9095) to determine if the waste contains any "free liquids" because solid waste landfills cannot accept waste that contains free liquids. If free liquids are present, the system will need to employ an intermediate processing method and determine an appropriate method of disposal for the liquid residuals generated by dewatering. (See Section II-B of this guide, "Intermediate Processing," for more information.)

I-D.3.1.2 Testing for Radionuclides

There is no federal requirement to test waste residuals specifically for radionuclides, and no specific federal regulation governing landfill disposal of water treatment plant solids or sludges containing TENORM. However, systems must comply with more general requirements applicable to the disposal of solid waste.

It is the responsibility of the individual states to determine the most appropriate analytical method for testing water treatment plant waste containing TENORM (and possibly source material) and any requirements or guidelines for disposal. If allowed by the state, systems can use the NRC/U.S. EPA "Guidance on the Definition and Identification of Commercial Mixed Low-Level Radioactive and Hazardous Waste" (available at http://www.epa.gov/radiation/mixed-waste/guidance-identification-llmw.html). If licensable concentrations of source material are found at systems in non-Agreement States, the appropriate NRC regional office should be consulted (see Appendix D).

U.S. EPA and other federal agencies have also developed the Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP), which addresses the need for a consistent national approach to producing radioanalytical laboratory data that meet a project's or program's data requirements. The manual provides guidance for the planning, implementation, and assessment phases of projects that require the laboratory analysis of radionuclides and is available on U.S. EPA's Web site at http://www.epa.gov/radiation/marlap.

States should consult with radiation program staff for more information (see Appendix D), and can also refer to U.S. EPA's list of approved analytical methods at http://www.epa.gov/safewater/methods/methods.html.

I-D.3.1.3 Choosing an Appropriate Landfill

There are several types of landfills that may provide protective disposal for residuals containing radionuclides. The appropriate landfill can depend on the amount, concentration, and physical and chemical attributes of the radiologically-contaminated material, the mobility of radionuclides and their decay products, the consideration of future controls and future land use, and state and local regulations.

I-D.3.1.3.1 Solid waste landfills

Municipal solid waste landfills may have restrictions on the amount of radioactivity they accept. Their ability to accept specific wastes should therefore be verified. These landfills may accept non-hazardous, solid, and TENORM wastes from all water systems, and hazardous waste from Conditionally Exempt Small Quantity Generators (see the MSWLF requirements at 40 CFR 258 and the information on hazardous waste on page 11 of this guide). Industrial solid waste landfills may also accept non-hazardous solid TENORM waste, and may be better equipped to handle such waste as it is more like the waste that industrial landfills typically handle (e.g., sludges and ash).

As they become more aware of issues surrounding disposal of radioactive materials, more landfills are now using monitors to scan incoming trucks for radiation. In some cases, wastes that had previously been accepted were found to contain elevated levels of TENORM. If the monitors are triggered, the source must be identified and evaluated. A list of municipal solid waste landfills (for non-hazardous waste) can be found at http://www.epa.gov/epaoswer/non-hw/muncpl/landfill/section3.pdf.

I-D.3.1.3.2 Hazardous waste landfills

Systems using treatment technologies that remove contaminants such as arsenic, in addition to radionuclides, could potentially generate hazardous waste. Hazardous waste from Large and Small Quantity Generators must meet RCRA Land Disposal Restriction treatment standards (40 CFR 268.40) prior to disposal in a hazardous waste landfill. Facilities permitted under Subtitle C may accept hazardous waste (though not mixed waste) from all generator classes, and vary in their ability to accept TENORM wastes. If hazardous residuals contain source material above 0.05% in weight or other AEA materials they must be disposed of at a facility authorized to accept mixed waste.

Hazardous waste landfills accept hazardous waste from all generator classes, and vary in their ability to accept TENORM wastes. Hazardous waste from Large and Small Quantity Generators must meet RCRA Land Disposal Restriction requirements (40 CFR 268.40). Some hazardous waste landfills have explicit permit conditions while others may have to request state approval before accepting TENORM wastes. Systems should check with the disposal facility to determine whether their TENORM waste is eligible for disposal at a particular hazardous waste landfill.

I-D.3.1.3.3 Low-level radioactive waste landfills

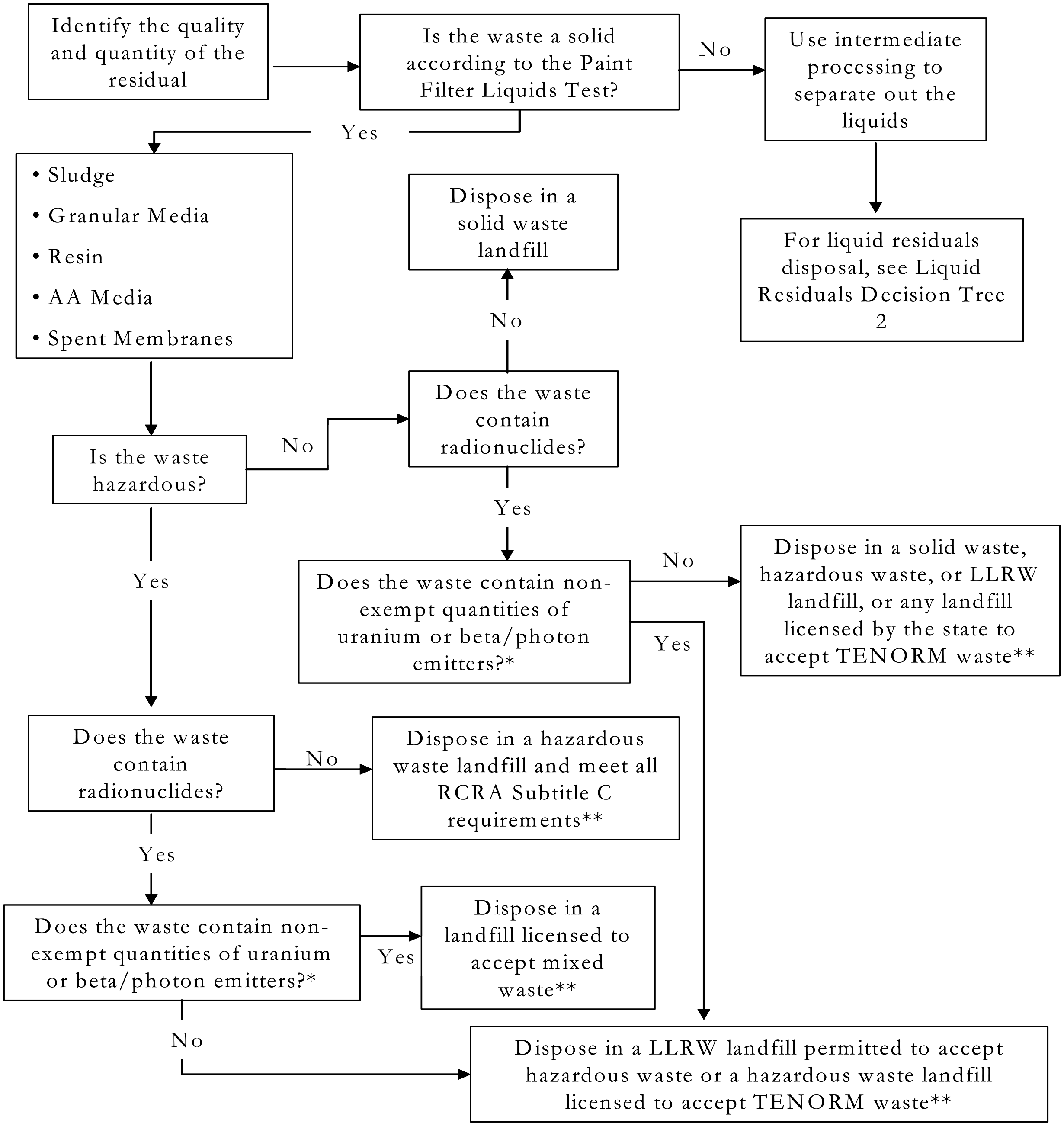
LLRW landfills may be an option for systems generating wastes with radionuclide concentrations deemed to be unacceptable for disposal at a solid or hazardous waste landfill. LLRW landfills are licensed by NRC or by a state under agreement with NRC, and guidelines for disposing of radioactive sludges and solids are more stringent than in a standard landfill. These facilities are licensed based on projected performance and have packaging and burial requirements that are progressively stricter as the radionuclide concentrations increase.

There are three LLRW disposal facilities currently in operation:

Barnwell - South Carolina	Will, after June 30, 2008, accept LLRW only from organizations in South Carolina, Connecticut, and New Jersey. For more information, including waste transport, disposal rates, and site availability, see http://www.state.sc.us/energy/RadWaste/rwdp_index.htm.
Richland - Washington	Accepts certain types of TENORM (although not hazardous or mixed) wastes from all states. Accepts licensed source material only from the 11 states in the Northwest and Rocky Mountain Compacts. State regulators anticipate including activity limits for uranium-238 and radium-226 in the facility's renewed license. For more information, including waste transport, disposal rates, and site availability, see http://www.ecy.wa.gov/programs/nwp/llrw/llrw.htm.
Envirocare - Utah	Has dedicated TENORM disposal and is the only LLRW landfill authorized to accept certain kinds of mixed waste. Does not accept LLRW from Northwest Interstate or Rocky Mountain Compact states. For more information, see http://www.envirocareutah.com.

The Low-Level Radioactive Waste Policy Act gave states the authority to form regional compacts to manage their commercial LLRW. Compact authority generally extends to the import and export of waste to and from states in the compact. If water treatment plants are licensed by the NRC or Agreement State, their disposal options may be limited. Systems should be made aware that compacts may have requirements beyond those of the NRC or Agreement State. For more information on interstate compacts and Agreement States, see http://www.nrc.gov/about-nrc/state-tribal/agreement-states.html.

Decision Tree 1: Solid Residuals Disposal



* Check with the state Radiation Program to see if beta/photon emitters are considered byproduct material and advise system to contact the NRC Regional office or relevant Agreement State agency to discuss potential licensing requirements.

** LDR treatment standards also apply. Check with the state Radiation Program to determine the proper disposal methods for waste containing radionuclides and hazardous waste.

I-D.3.2 Options for Disposal of Liquid Residuals

The options discussed below *may* be used for the disposal of liquid residuals including brines, concentrates, rinse waters, backwash waters, acid neutralization waters, spent filter backwash water, filter-to-waste waters, supernatants, and liquids from dewatering. A system's options will depend on state regulations, the characteristics of the waste, and cost-effectiveness. System location can also affect options; rural systems not located near a receiving body or POTW may have to bulk transport liquid wastes for disposal (which may present additional problems, as systems transporting over 270 pCi/g of uranium or 2,700 pCi/g of radium may be subject to DOT's radioactive material transport regulations). States should consult with the appropriate program contacts to discuss which of these options (or any alternative options) are available. See Appendix D for contact information, Decision Trees 2 and 3 for an overview of the decision making process for systems that generate liquid residuals, and Section II-B for information on intermediate processing methods for residuals.

I-D.3.2.1 Direct Discharge

Direct discharge may be an option for disposal of liquid wastes if a system has an accessible and appropriate receiving body. The CWA requires that anybody discharging pollutants into U.S. waters through a point source must obtain a National Pollutant Discharge Elimination System (NPDES) permit from the authorized state or U.S. EPA Region (CWA, Title IV, Section 402). These permits set limits on the amount of certain pollutants that can be discharged. They also set monitoring and reporting requirements and may include other provisions that protect water quality and public health.

Federal water quality criteria and standards regulations do not set specific limits on radionuclides in discharges. States have the authority to set criteria, standards and derived NPDES limits, and enforce them through permits. In addition, state anti-degradation policies are also designed to protect the quality of certain water bodies and source water protection efforts might restrict the levels of radionuclides in discharged waste. NRC regulations also restrict licensees from releasing effluents containing radionuclides to the general environment (10 CFR 20.1301 to 1302). The BATs and SSCTs listed in the Radionuclides Rule also remove co-occurring contaminants for which NPDES regulations set limits; this could potentially further restrict a system's options.

I-D.3.2.2 Discharge to Publicly Owned Treatment Works

Drinking water systems may be able to discharge liquid wastes to a POTW indirectly through sanitary sewers or force mains or by transporting the waste directly to the POTW. In most cases, such systems are not required to obtain a NPDES permit, but must ensure that their wastes meet the general and specific prohibitions of the Pretreatment Program and any Technically Based Local Limits (TBLLs) that may be established by the state or by the POTW itself. TBLLs should ensure that the POTW systems meet federal (40 CFR 403), state, and local pretreatment regulations, and prevent the discharge of any waste that would interfere with or pass through the POTW treatment process and cause a violation of the POTW's NPDES permit, or inhibit recycling or reuse of the POTW's biosolids. Municipalities (POTW owners) can refuse to accept waste that might trigger these events, and they generally have the legal authority to refuse any wastewater that may pose other disposal problems for the POTW. Refer to Interagency Steering Committee on Radiation Standards (ISCORS') *Assessment on Radioactivity in Sewage Sludge: Recommendations on Management of Radioactive Materials in Sewage Sludge and Ash at Publicly Owned Treatment Works* for more information on POTW legal and regulatory authority, and for guidance on identifying circumstances where discharge of liquid residuals to a POTW may interfere with sewage sludge management practices or may pose a potential worker or general public exposure concern.

Arrangements between POTWs and systems may be enforced and conditioned by a local permit issued to the system or through a contract, depending on federal, state, and local regulations. U.S. EPA regulations on the use and disposal of the sewage sludge produced by POTWs (40 CFR 257 and 503) currently do not cover radioactive material. States should encourage systems to contact the state NPDES program and potential receiving POTW, prior to choosing discharge to a POTW as a disposal option to determine whether the system is capable of meeting the applicable local limits, and to ensure that the wastes will be accepted.

Note that liquid wastes that are mixed with domestic sewage and discharged to a POTW are not regulated under RCRA, because they are subject to the Clean Water Act. This exclusion from RCRA is commonly known as the domestic sewage exclusion (§261.4(a)(1)).[16] A hazardous waste that is accumulated, managed, or transported (e.g., by truck) prior to introduction into the sewer system, however, would still be subject to regulation as a hazardous waste. Encourage systems that believe their wastes to be hazardous to contact the appropriate state agency and local POTW to ensure that wastes are properly managed.

Systems that exceed both the 'unimportant quantity' and 'small quantity' thresholds for uranium will normally be specifically licensed by NRC or Agreement State; there are strict limits set by 10 CFR 20.2003 for disposal into any sanitary sewer systems. Under these conditions: the material must be readily soluble (or readily dispersed biological material) in water; the quantity of licensed or other radioactive material that is released into the sewer in one month, divided by the average monthly volume of water released into the sewer, cannot exceed the concentration listed in Table 3 of Appendix B in 10 CFR 20; and the total quantity of licensed and other radioactive material that the licensee releases into the sanitary sewer in a year cannot exceed 5 curies (185 GBq) of hydrogen-3, 1 curie (37 GBq) of carbon-14, and 1 curie (37 GBq) of all other radioactive materials combined. Additional requirements apply if more than one radionuclide is released. If the state has adopted naturally occurring radioactive material (NORM) or TENORM regulations which apply to water treatment facilities, those regulations should be consulted to determine if there are radionuclide discharge requirements to POTWs.

I-D.3.2.3 Underground Injection

U.S. EPA developed federal regulations under SDWA that address underground injection and protect underground sources of drinking water. To determine which federal UIC regulations apply, systems will need to determine if their waste is radioactive, hazardous, or nonhazardous. Under the UIC regulations, "radioactive" refers to any waste containing radioactive concentrations that exceed those listed in 10 CFR 20, Appendix B, Table 2, Column 2. These concentrations are 60 pCi/L for radium-226, 60 pCi/L for radium-228, and 300 pCi/L for uranium.

Note that the "unity rule" applies if there is more than one radionuclide involved. The "unity rule" sets the concentration limit of each radionuclide such that the sum of the fractions contributed by each radionuclide does not exceed 1. For example, in a material with 30 pCi/L of radium-226, 30 pCi/L of radium-228, and 150 pCi/L of uranium, the fraction contributed by radium-226 is 30/60 pCi/L, or 0.5; the fraction contributed by radium-228 is 30/60 pCi/L, or 0.5; and the fraction contributed by uranium is 150/300 pCi/L, or 0.5.

The sum of these fractions is 1.5, which exceeds 1; underground injection of the material would therefore be prohibited. If, however, the concentrations of radium-226, radium-228, and uranium were 15 pCi/L, 15 pCi/L, and 150 pCi/L, respectively, the fractions would be 15/60 pCi/L, or 0.25 for radium-226, 15/60 pCi/L, or 0.25 for radium-228, and 150/300 pCi/L, or 0.5 for uranium. The sum of these fractions (0.25 + 0.25 + 0.5) is 1. Underground injection of this material would therefore be allowed.

The UIC Program does not regulate single-family residential waste disposal systems such as single-family septic systems. However, SDWA (Section 1431) gives U.S. EPA the authority to take action on a residential waste disposal system if the system introduces contaminants into an underground source of drinking water whose presence or likely presence causes an imminent and substantial endangerment to public health (Section 1431 SDWA).

Table 6 describes the five classes of wells regulated by the UIC Program, the wastes these wells can accept, and the issues systems should consider before pursuing underground injection as a disposal option. Contact the appropriate

---

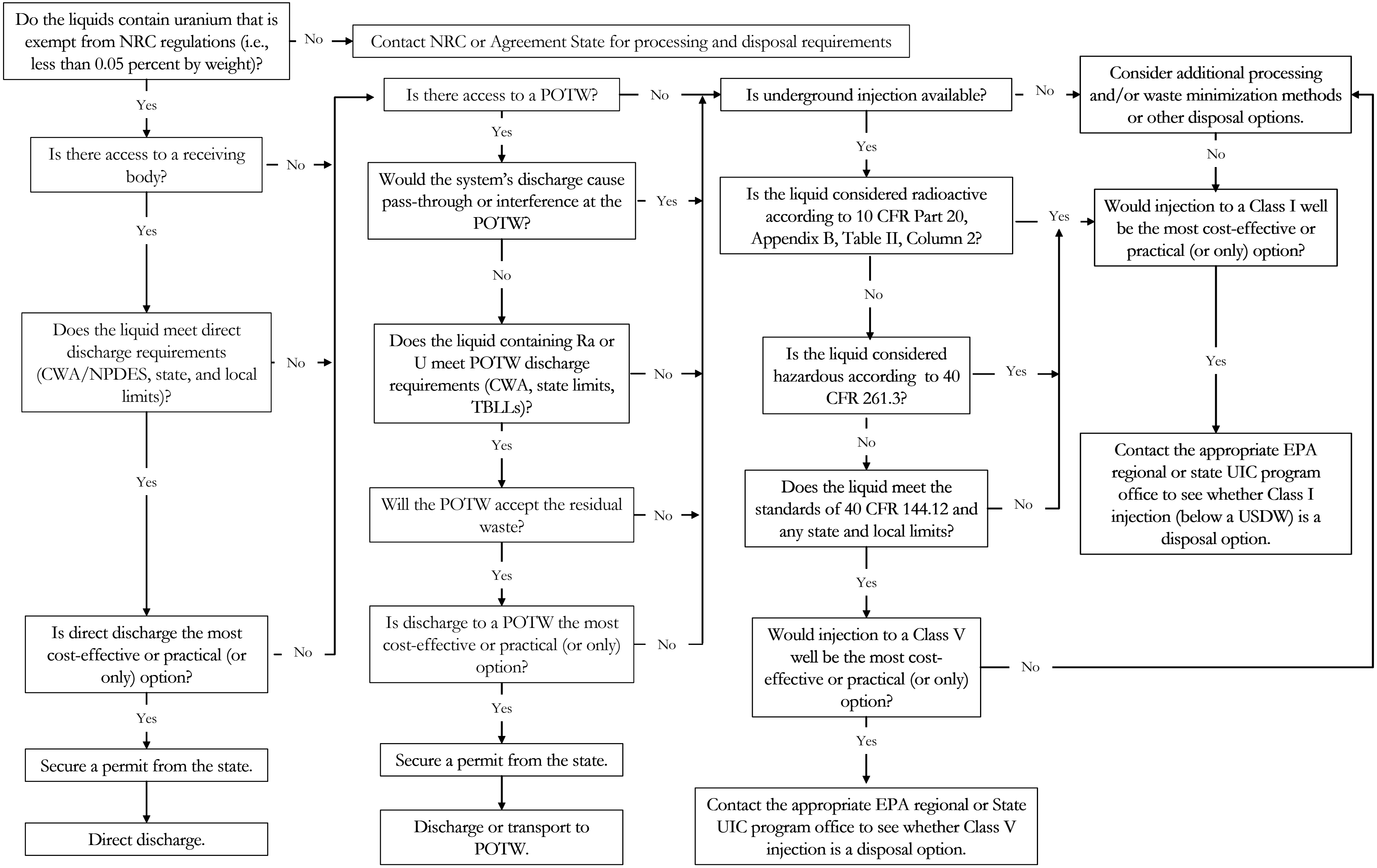
[16] Under this exclusion, these wastes are not considered to be RCRA "solid waste" and therefore cannot be classified as a hazardous waste.

U.S. EPA regional or state UIC program office for any additional state-specific UIC requirements. For additional information, systems should be referred to the appropriate U.S. EPA regional, state, or tribal UIC program listed in Appendix D.

Table 6: Underground Injection of Liquid TENORM Residuals

Class	Use	Considerations
I	Used to place radioactive, hazardous, or non-hazardous fluids (industrial and municipal wastes) into deep isolated formations beneath the lowermost USDW. There are 272 Class I injection facilities nationwide. For more information see: http://www.epa.gov/safewater/uic/classi.html	‣ Class I wells have stringent protective requirements to ensure safe injection ‣ Very few Class I facilities are commercial (able to accept hazardous or mixed waste generated off-site for injection) ‣ Disposal of slurries and solids is allowed in only limited circumstances because of the potential to fracture the receiving formation ‣ Class I wells can be expensive to construct because they are technically complex
II	Used to place produced water and other fluids in connection with oil and gas production.	Not an option
III	Used for mineral extraction.	Not an option
IV	Shallow wells used to inject hazardous or radioactive waste into or above a USDW.	‣ Class IV wells were banned in 1984. ‣ Not an option
V	Includes injection activities not described in Classes I-IV. These are generally shallow wells (e.g., large capacity septic systems and dry wells) used to place a variety of non-radioactive, non-hazardous fluids into or above USDWs.	‣ Not an option for hazardous or radioactive waste disposal ‣ Use of class V wells is prohibited if it will endanger a USDW per CFR 144.12 (cause an exceedance of any primary drinking water standard or otherwise adversely affect public health) ‣ Class V wells must also comply with state specific UIC requirements, which may be more stringent

Decision Tree 2: Liquid Residuals Disposal



I-E Worker Exposure and Safety

Because radiation is invisible, tasteless, and odorless, it is commonly overlooked as a potential hazard at water systems. Exposure to elevated levels of radiation at water treatment facilities may cause serious health effects. Systems need to determine whether a radiation problem exists and, if it does, take appropriate safety precautions to prevent or limit water system staff members' exposure to radiation. For example, if a system tested its treated water 2 years ago and found levels of 3pCi/L for radium-226 and 228, a radiation survey of the facility would be prudent.

Water system staff can be exposed to radiation during normal treatment processes for radionuclides, through handling the residual streams generated by treatment, and during media replacement or transportation. Relatively undetectable levels of radionuclides in source waters can accumulate in measurable or hazardous quantities in piping, pumps, holding tank scale or sludge, IX and granular filters, backwash, and other residual sludge. Radon gas can accumulate in closed or poorly ventilated buildings when thorium, uranium, or radium-bearing materials (including water) are present. Naturally occurring radon gas can enter through openings in the building's concrete or foundation walls. Underground connections to manholes, piping conduits, and utility tunnels provide additional pathways for radon entry. For example, elevated gamma ray levels have been found around IX columns and associated piping at some facilities. This could result in an exceedance of public dose limits.

I-E.1 Radiation Surveys

A system should contact a professional radiation protection specialist or a health physicist for assistance in conducting a radiation survey if: (1) the system has had an analytical result within the past 5 years that has approached or has exceeded an MCL for a regulated radionuclide; or, (2) if calculations derived from use of the U.S. EPA SPARRC model indicates potential concentrations of radioactivity in residuals and filters at the system.[17]

A radiation survey can be conducted by:

1. Using a radiation survey meter to identify any points at which contamination exists.
2. Using an integrating radiation measuring device to determine whether exposure could occur over time.
3. Sampling filter media, wastes, and water through further laboratory analyses. These analyses should focus on finding the principal NORM/TENORM isotopes found in surface and groundwater supplies: radium, uranium, thorium, and potassium as well as their radioactive daughter decay products.[18]

Some states require radiation protection specialists or health physicists who conduct radiation surveys (including radon surveys) to be certified or licensed. State Radiation Control contact information appears in Appendix D.

As a result of the survey, the system may need to establish a monitoring program, change existing management practices, alter methods for managing radioactively contaminated equipment and wastes, or establish worker radiation safety and education programs. The survey may also recommend methods for decontaminating buildings or facilities, if needed.

---

[17] A working draft of SPARRC is available for estimating the volume and concentration of radionuclides in waste produced by water systems. The program allows the operator to select the type of treatment process, as well as input and output parameters such as water flows, doses of coagulant and polymer, and filter capacities. To view the spreadsheet, see http://www.npdespermits.com/sparrc.

[18] Decay products such as isotopes of radon, lead, polonium, and bismuth may need to be analyzed in order to calculate the concentrations of the original parent radionuclide such as radium or uranium. Characterizing the types and amounts of radionuclides present will be beneficial in identifying sources in the drinking water, understanding how, where, and why they are collecting in the treatment plant, correcting a contamination problem in the plant through selection of treatment technologies and management techniques, and aiding management in deciding where hazardous waste products should be disposed or where they might be accepted.

Although designed for post-cleanup surveys of radioactively contaminated sites, U.S. EPA's *Multi-Agency Radiation Survey and Site Investigation Manual* (MARSSIM) (EPA 402-R-97-016 Rev. 1) provides useful information on planning and conducting a survey of potentially contaminated surface soils and building surfaces. The manual and other information on radiation surveys can be obtained from U.S. EPA's Radiation Protection Division Web site at http://www.epa.gov/radiation/marssim.

Seven federal and two state agencies contributed to the development of MARLAP. MARLAP provides guidance for the planning, implementation, and assessment phases of projects that require laboratory analysis of radionuclides. This guidance is intended for project planners, managers, and laboratory personnel and provides extensive detail on the radiological sampling and analytical process, including laboratory procedures. A copy of the manual can be found at: http://www.epa.gov/radiation/marlap/manual.html.

U.S. EPA also recommends that the system check for the presence of radon in buildings encasing system equipment. States should consult with radiation program staff to determine whether radon measurements have been taken in the county, whether a map or survey of indoor radon measurements has been developed for the county, where the system is located, and to determine the appropriate means and methods for conducting radon surveys. The state or private radon proficiency programs may be able to provide a list of licensed or certified radon contractors who could conduct the survey. Additional information on how to find qualified professionals can be found at http://www.epa.gov/iaq/radon/proficiency.html.

For U.S. EPA guidance documents on approaches to risk assessments of soil and water, see the Superfund Radiation Web sites at http://www.epa.gov/superfund/resources/radiation and http://www.epa.gov/superfund/resources/radiation/whatsnew.htm.

I-E.2 Radiation Exposure Due to Water Treatment Operations

The following discussion applies only to systems where there is the potential for accumulation of radioactivity.

Water system workers are most likely to be exposed to elevated levels of radioactive materials when coming into contact with residuals, filter backwash, and sludge; during maintenance of contaminated pumps or piping; or while moving or transporting wastes and filters for disposal. Possible sources of radiation include pumps and piping where mineral scales accumulate; lagoons, and flocculation and sedimentation tanks where residual sludges accumulate; filters, pumping stations, and storage tanks where scales and sludges accumulate; and facilities where filter backwash, brines, or other contaminated water accumulates. Facilities that are enclosed present the potential for enhanced radiation inhalation exposure, particularly from radon. Exposure to radiation can also occur at residuals processing or handling areas at the system and off-site locations such as landfills where residuals are shoveled, transported, or disposed of.

The table below shows the three primary paths of radiation exposure at a system: inhalation, ingestion, and direct exposure.

Pathway	Concern
Inhalation	Inhalation of alpha- or beta-emitting radioactive materials is a concern because radioactive material taken into the body results in radiation doses to internal organs and tissues (e.g., lining of the lungs). Workers could inhale radioactively contaminated dust or water droplets while dealing with residuals or during normal filter operations. Cleaning methods such as air scour, high pressure water sprays, and backwash operations can increase suspension of radioactively contaminated water, dusts, and particulates in respirable air, thus increasing the potential hazard of inhalation or ingestion. Workers can inhale radon and its progeny in both wet and dry conditions. Simple dust masks may not provide adequate protection from exposures via this pathway, and systems may need to implement Occupational Safety and Health Administration (OSHA) requirements for respirators.

Pathway	Concern
Ingestion	Ingestion, or the swallowing of alpha, beta, or gamma-emitting radioactive materials, is a concern for the same reasons as inhalation exposure. Workers can ingest radioactive materials if they fail to observe good sanitary practices including washing their hands before eating; failing to cover their noses and mouths by wearing approved respiratory protection and swallowing contaminated dusts and water droplets; or eating and drinking in areas (including land disposal sites), where dusts or water droplets could settle on food or drink. Simple dust masks may not provide adequate protection from exposures via this pathway.
Direct Exposure	Radioactive materials that emit gamma radiation are of concern because the gamma rays pose an external radiation exposure hazard. Because gamma rays can pass through common construction materials and most protective clothing, the distance between the radioactive material and the person, as well as the time spent in proximity to the material are factors in the amount of exposure the person receives. As gamma radiation travels through air, exposure can occur near a source of radiation as well as through direct contact. Workers most likely to be directly exposed are those who handle or work in the vicinity of resin tanks, residuals, filter backwash, and contaminated brines or waters, or participate in the maintenance of the treatment system or the replacement and transportation of filter media.

The International Commission on Radiological Protection (ICRP) and National Council on Radiation Protection and Measurements (NCRP) have recommended that facilities strive to make the levels of radiation to which the public and the environment are exposed as low as reasonably achievable (ALARA) (i.e., below regulatory limits) taking into account social and economic considerations. Steps that facilities can take include limiting the time that workers spend handling radioactive material, increasing the distance between workers and the material, and providing shielding from the radioactive material.

In addition, OSHA has developed occupational radiation standards (see 29 CFR 1910.1096) that might apply whenever an operator becomes aware of the presence of radiation at the facility. Although these standards may not apply to municipal water treatment plant workers, these workers may be covered by their state OSHA program, requiring that all controls, monitoring, record keeping, and training outlined in the OSHA standards be met.

Additional OSHA standards that may be applicable to water systems include:

- Requirements that personal protection equipment (or PPE, for the eyes, face, head, and extremities) such as protective clothing, respiratory devices, and protective shields and barriers be provided, used, and maintained whenever processes or radiological hazards capable of causing injury through absorption, inhalation, or physical contact necessitate such equipment. There are numerous other requirements related to the possession and use of PPE, including training for employees who would use the equipment. For more information, see 29 CFR 1910.132-136.

- Requirements for practices and procedures to protect employees in general industry from the hazards of entry into permit-required confined spaces. For more information, see 29 CFR 1910.146.

- Lockout/tagout requirements that require employers to establish a program and follow procedures for affixing appropriate lockout or tagout devices to energy isolating devices and disable machines or equipment. This avoids injury to employees by preventing unexpected energization, start-up, or release of stored energy. For more information, see 29 CFR 1910.147.

- Hazardous communication requirements that ensure the potential hazards of chemicals produced during or imported for treatment are evaluated and the information from this evaluation is communicated to employees through measures such as container labeling, material data safety sheets, and employee training, among others. These requirements do not apply to RCRA-defined hazardous waste or ionizing or non-ionizing radiation. For more information, see 29 CFR 1910.1200.

In circumstances where a facility may in the future be licensed by the NRC or Agreement State, worker safety precautions and radiation protection controls would take precedence (e.g., 10 CFR 20.1900, which lists radiation exposure posting requirements).

In addition to the OSHA requirements, systems should be encouraged to follow the safety practices listed below. These measures can reduce workers' risk of exposure to radioactivity and radioactive particulates:

Safety Measures

✓ Use an OSHA-approved respirator to avoid inhalation of biological pathogens and chemically toxic materials in residuals. Simple dust masks may not provide adequate protection.

✓ Limit time spent at land disposal sites to reduce inhalation of contaminated dust.

✓ Ventilate all buildings, especially where waste with high concentrations of radium is stored.

✓ Take standard OSHA measures to limit the potential ingestion of heavy metals and biological pathogens present in filters, residual sludges, and at land disposal sites to help reduce possible ingestion exposure to radioactive materials.

✓ Use protective gloves and frequently wash hands (particularly before eating and drinking) to reduce the potential for ingestion. Similarly, avoid eating and drinking in the vicinity of facilities or land disposal sites where air suspension of contaminated particulates or water droplets could occur.

✓ Avoid direct contact with any solid TENORM waste and use shovels or other remote-handling tools during extraction, transfer, and packaging.

✓ Locate treatment units and waste storage areas as far away from common areas (e.g., offices) as possible.

✓ Shower after exposure to potentially radioactive materials and launder work clothing at the system if possible. If laundering equipment is not available, workers should keep and wash work clothing separately and avoid wearing contaminated clothing into the home. Work boots or shoes should be wiped and cleaned after potential contamination. They should stay at the system or not be worn into the home.

✓ Use gamma survey instruments or equivalent monitors at least once annually to monitor the system's ambient radiation levels in areas where radionuclides are removed.

✓ Monitor levels of radiation to which staff are exposed. Systems should contact, or be referred to, state or other radiation experts for more information on how to monitor radiation levels.

Treatment plants that are licensed by the NRC or Agreement State should be referred to CFR Parts 19 and 20 for licensee reporting, notification, inspection, and safety requirements. Licensed facilities are required to post the regulations listed under Parts 19 and 20, along with numerous other documents related to the license and the activities conducted under the license. Employees likely to receive occupational doses greater than 100 mrem/year must be kept informed and instructed on various issues related to health protection, relevant regulations, and the facility's storage and transport of radioactive materials, among other things. Licensees must also keep individual employees informed of the annual radiation dose that they receive. Current and former employees can also request reports on their exposure to radiation or radioactive material.

10 CFR Part 20 outlines requirements for licensees to develop radiation protection programs (10 CFR 20.1101), sets dose limits and occupational limits for exposure to radiation (10 CFR 20.1201 to 1302), instructs licensees on how to

control access to areas where radiation levels are high or very high (10 CFR 20.1601 and 1602), and sets restrictions on the use of individual respiratory equipment (10 CFR 20.1703 and 1704), among other things.

Part 20 also sets requirements related to storage and control of licensed material, including posting, signage, and labeling requirements (10 CFR 20 Subparts I and J). These regulations stipulate that licensees' radiation protection programs be designed around the ALARA principle and require licensees to limit air emission of radioactive material (excluding radon-222 and its daughters) so that the highest total effective dose equivalent received by any member of the public is no greater than 10 mrem/year. Part 20 also sets notification requirements in the case of an incident at the licensed facility or for cases in which the facility is required to report exposures, radiation levels, or concentrations of radioactive materials exceeding constraints or limits (10 CFR 20.2201 to 2203). Consult with your NRC regional office or relevant state agency to ensure that any licensed facilities in your state are aware of these additional worker safety requirements.

I-E.3 Additional Safety Considerations

Radon is a natural decay product of radium and other radionuclides. It can vary in concentration by time of day or seasonally. It is appropriate for systems to consider radon protection measures when handling wastes containing radium. U.S. EPA recommends that action be taken to reduce radon levels in homes and schools where testing shows average concentrations of 4 pCi/L or greater. Although exposure to radon in homes or schools is evaluated differently than occupational exposure, many nations and the ICRP recommend that intervention levels for exposure to radon in homes also be used in workplaces.[19] U.S. EPA recommends that the action level used for homes and schools be used for water systems.

If radionuclides or radiation have been found in drinking water or at a system, having operators who are trained in treating for radionuclides, and handling, disposing of, and transporting TENORM waste, is highly recommended. In addition, determine whether your state requires someone specifically licensed by the state or NRC to handle these types of residuals. Operators should also be trained in how to measure radioactivity levels. Encourage systems to check with the relevant state office regarding licensing requirements and training opportunities.

Assistance and advice are available from the appropriate State Radiation Control Program (see Appendix D), the Conference of Radiation Control Program Directors at http://www.crcpd.org, and the U.S. EPA Regional Radiation Programs. For additional references on this and other topics discussed in this guide, see Appendix G.

---

[19] ICRP, 1993.

Section II: Treatment Technologies Overview

II-A Treatment Methods, Residuals, and Disposal Considerations

Tables 8 through 16 provide brief overviews of the uses, efficiencies, disposal considerations, and limitations of the BATs and SSCTs listed for radionuclide removal, all of which should be considered when choosing an appropriate treatment technology. In addition, the cost of installing, operating, and disposing of the residuals produced by these technologies, will be significant factors for systems choosing a new technology. As systems begin initial monitoring and treatment for, and disposal of these radionuclides, more information on costs will become available.

Note that many of the considerations for solid and liquid residual disposal are identical, regardless of the chosen treatment technology. These disposal options and considerations, introduced in the previous section, are summarized below in Table 7. Several of the technologies in Tables 8 through 16 do not have special considerations or limitations. Note that for systems licensed by the NRC or Agreement State, disposal of residuals may be further restricted.

Table 7: Common Disposal Considerations for Residuals Produced by BATs and SSCTs

Direct discharge	‣ System must have a NPDES permit ‣ Flow equalization may be required to avoid contaminant spikes ‣ Appropriate receiving bodies must be available ‣ Systems must meet state radionuclides limits
Discharge to a POTW	‣ Pretreatment may be required (e.g., flow equalization, pH adjustment, thickening, or chemical precipitation) prior to discharge to avoid interference with the POTW ‣ Systems must meet the TBLLs established by the state and/or the POTW, abide by the terms of the arrangement with the POTW, and meet state permitting requirements
Underground injection	‣ Systems must determine whether their waste is radioactive or hazardous ‣ Class I hazardous injection wells may be a disposal option for radioactive or hazardous wastes under stringent protective measures, and depending on associated constituents and the volume of waste generated ‣ Class V wells may be a disposal option for non-hazardous, non-radioactive fluids if the system can demonstrate compliance with CFR 40 part 144.12 (i.e., would not cause a violation of any primary drinking water regulation, adversely affect public health, or otherwise endanger a USDW) ‣ Single-family septic systems are exempt from federal UIC regulations ‣ Systems should check with their state to determine whether the state has more stringent UIC requirements ‣ U.S. EPA has the authority to take action on any residential waste disposal system if the system introduces contaminants into a USDW whose presence or likely presence causes an imminent and substantial endangerment to public health (SDWA Section 1431).
Landfill disposal	‣ Systems must determine whether the waste is hazardous or non-hazardous (e.g., using the TCLP) and perform the PFLT to determine whether the waste contains free liquids ‣ Systems must check with their states to determine whether landfilling is an acceptable means of disposal for hazardous and non-hazardous solid waste containing radionuclides ‣ The system must choose the appropriate type of landfill, based on the type, volume, and concentration of solid waste generated ‣ The waste must meet all other requirements for landfilling set forth under RCRA, and by the state and the disposal facility ‣ Resins require dewatering prior to disposal; the residual stream generated from dewatering may be disposed of through direct discharge, discharge to a POTW, or underground injection ‣ Regenerating the media prior to disposal may reduce its radionuclide concentration (regenerant streams will need to be disposed of through direct discharge, discharge to a POTW, or underground injection)

Table 8: IX and POU IX Overview

Use	*BAT*	IX is listed as a BAT for radium, uranium, and beta particle and photon activity removal. Anion exchange (AX) resins remove uranium; cation exchange (CX) resins remove radium and soften water. Mixed bed IX is suitable for beta particle and photon activity removal.
	SSCT	IX and POU IX are listed as SSCTs for systems serving 25-10,000 customers for radium, uranium, and beta particle and photon activity removal. POU IX units treat water from a specific tap and must be owned, controlled, and maintained by the water system or a system contractor.
Efficiency	▸ AX removes up to 95% of uranium;[20] CX removes up to 97% of radium.[21] ▸ See also Appendix E, Tables E-1, E-2, and E-3	
Residuals	*Liquid*	Backwash water, brine (volume varies according to raw water quality, unit size, regenerant concentration and media capacity), and rinse water
	Solid	Spent resins
Additional Disposal Issues*	*Direct discharge*	▸ Normally not an option due to high TDS levels and high contaminant concentrations ▸ Blending brine with backwash and rinse can significantly reduce radionuclide concentrations and TDS but usually not to levels that would allow for direct discharge
Limitations	▸ Regeneration of CX resins may not remove all radium from the resin, complicating disposal ▸ Using potassium chloride as a regenerant can increase the efficiency of CX resin regeneration ▸ Systems should conduct pilot tests of IX treatment to determine a regeneration schedule ▸ Some states do not allow systems to run IX resins to exhaustion for uranium removal ▸ Radionuclides may become so concentrated in the brine and resin that they may require special handling and disposal procedures	

*All of the common disposal considerations in Table 7 must also be taken into account.

---

[20] Lassovszky, P. and Hathaway, S., 1983; Hanson, S., et al, 1987; U.S. EPA, 1992.

[21] Schliekelman, R., 1976; U.S. EPA, 1992a; U.S. EPA, 1977; Brink, W.L., et al, 1978; Lassovszky, P. and Hathaway, S., 1983; U.S. EPA, 1992.

Table 9: RO and POU RO Overview

Use	*BAT*	RO is listed as a BAT for radium, uranium, gross alpha particle activity, and beta particle and photon activity and is also effective at removing other inorganic contaminants, such as heavy metals
	SSCT	RO is listed as a SSCT for radium, gross alpha, and beta particle and photon activity for systems serving 25-10,000 customers, and for uranium for systems serving 501-10,000 customers. POU RO is a SSCT for radium, uranium, gross alpha particle activity, and beta particle and photon activity for systems serving 25-10,000 customers. POU RO units treat water from a specific tap, and must be owned, controlled, and maintained by the water system or a system contractor.
Efficiency	▸ RO can remove at least 90% of these radionuclides from drinking water ▸ See also Appendix E, Tables E-1 and E-4	
Residuals	*Liquid*	Concentrated liquid waste stream
	Solid	Spent membrane
Limitations	▸ Using RO necessitates having a highly skilled operator ▸ Residuals produced can have very high concentrations of the contaminants removed from the water, including radionuclides, which may limit disposal options. The concentration depends on the efficiency of the RO unit: highly efficient units will produce low volumes of residual streams with high concentrations of contaminants while lower efficiency units will produce higher volumes of residual streams with lower concentrations of contaminants.	

Table 10: Lime Softening Overview

Use	*BAT*	Listed BAT for the removal of radium and uranium from drinking water
	SSCT	Listed SSCT for the removal of radium for systems serving 25-10,000 customers and for the removal of uranium for systems serving 501-10,000 customers
Efficiency		‣ Removal efficiency depends on the pH of the influent water ‣ Seventy-five to 90% of radium can be removed from water with pH levels above 10;[22] the pH range for radium removal is 9.5 to 11.0 ‣ Uranium removal can be as low as 16% and as high as 97%;[23] the pH should be at least 10.6 ‣ Adding magnesium carbonate during treatment can increase the efficiency of uranium removal to 99%; ferric chloride may also increase efficiency, depending on raw water uranium concentrations and pH ‣ See also Appendix E, Table E-1
Residuals	*Liquid*	Spent filter backwash water (contains radium, uranium, particulates, and co-occurring contaminants)
	Solid	Spent filter media and lime sludge (contains high concentrations of radium, uranium, and co-occurring contaminants)
Additional Disposal Issues*	*Landfill disposal*	Because of high concentrations of radionuclides and co-occurring contaminants, sludge may require special disposal (i.e., in a LLRW or hazardous waste landfill)
Limitations		‣ Using lime softening technology necessitates having a highly skilled system operator ‣ There are many source water quality concerns that should be addressed to ensure the efficiency of radionuclide removal and the process involves complex water chemistry. This technology may be too complicated, expensive, and time-consuming for small systems to use.

*All of the common disposal considerations in Table 7 must also be taken into account.

Table 11: Green Sand Filtration Overview

Use	*SSCT*	Listed as a SSCT for radium removal for systems serving 25-10,000 customers
Efficiency		‣ Green sand has shown removal efficiencies ranging from 19% to 63% for radium-226 removal and 23% to 82% for radium-228 removal[24] ‣ High concentrations of manganese in an oxidized state increase the efficiency of radium adsorption; high concentrations of manganese in an unoxidized state or iron in the ferric state limit the efficiency of adsorption ‣ See also Appendix E, Tables E-1, E-6, and E-7
Residuals	*Liquid*	Spent filter backwash water (contains radium, particulates, and co-occurring contaminants)
	Solid	Spent filter media and sludge
Limitations		‣ Source water quality can greatly affect the efficiency of green sand filtration in removing radium from drinking water ‣ If the pH of the water is below 6.8, green sand may remove an inadequate level of iron and manganese; running the water through a calcite filter or adding lime or sodium hydroxide can raise the pH above 7.0

---

[22] Brink, W.L., et al, 1978; U.S. EPA, 1977; U.S. EPA, 1992.

[23] Sorg, T., 1990.

[24] Peterson, K., 2000.

Table 12: Co-precipitation with Barium Sulfate Overview

Use	*SSCT*	Listed as a SSCT for radium removal for systems serving 25-10,000 customers
Efficiency	Co-precipitation with barium sulfate (using a soluble barium salt such as barium chloride) has been shown to remove over 95% of radium from mine wastewaters, and between 40% and 90% of radium from drinking water[25]	
Residuals	*Liquid*	Spent filter backwash water (contains radium, particulates, and any co-occurring contaminants)
	Solid	Spent filter media (contains moderate concentrations of radium and any co-occurring contaminants) and high volumes of barium sulfate sludge (may contain high concentrations of radium and any co-occurring contaminants)
Limitations	‣ This technology necessitates having a highly skilled operator ‣ This technology is not widely used. It is more commonly used to remove radium from waste effluents than from drinking water and is only effective for source waters with high sulfate levels. ‣ This technology involves static mixing, detention basins, and filtration. It may not be practical for small systems that do not already have in place suitable filtration to treat high sulfate levels.	

Table 13: Electrodialysis/Electrodialysis Reversal Overview

Use	*SSCT*	Listed as a SSCT for radium removal for systems serving 25-10,000 customers; also effective at removing uranium
Efficiency	See Appendix E, Table E-1	
Residuals	*Liquid*	Concentrated waste stream
	Solid	Spent membranes
Limitations	Systems may have difficulty removing radionuclide build-up from the membrane, which could complicate disposal	

---

[25] Clifford, D.A., et al, 1988.

Table 14: Pre-formed Hydrous Manganese Oxide (HMO) Filtration Overview

Use	*SSCT*	Listed as a SSCT for radium removal for systems serving 25-10,000 customers
Efficiency	Radium removal efficiency depends on the levels of HMO added during the treatment process; removal efficiencies of up to 90% may be achieved[26]	
Residuals	*Liquid*	Spent filter backwash water (contains radium, particulates, and any co-occurring contaminants)
	Solid	Spent filter media (contains moderate concentrations of radium and any co-occurring contaminants) and sludge
Limitations	▸ Operators should determine the appropriate dosage of HMO, taking source water characteristics into consideration ▸ If source water iron levels are high, oxidation can enhance iron removal through filtration; if iron coatings form on the filter, radium can be desorbed ▸ HMO treatment installation may be prohibitively expensive for systems that do not already have a filtration system	

Table 15: AA Overview

Use	*SSCT*	Listed as a SSCT for uranium removal for systems serving 25-10,000 customers
Efficiency	AA may remove up to 99% of uranium in drinking water[27]	
Residuals	*Liquid*	Spent brine (volume varies according to raw water quality, unit size, regenerant concentration and media capacity), rinse water, backwash, and acid neutralization
	Solid	Spent media
Additional Disposal Issues*	*Direct discharge*	▸ Normally not an option due to high TDS levels and high contaminant concentrations ▸ Blending brine with backwash, rinse, and acid neutralization waters can significantly reduce radionuclide concentrations and TDS ▸ Additional pretreatment may be required in addition to flow equalization
Limitations	▸ AA has a higher affinity for other contaminants, such as arsenate, fluoride, and sulfate[28] ▸ The technology is very pH sensitive and the handling of chemicals required for pH adjustment (to increase uranium removal) and regeneration necessitates having a highly skilled system operator ▸ Successful operation may require monitoring effluent pH to establish accurate breakthrough curves ▸ Special disposal procedures may be required for media that can no longer be regenerated, particularly if the media has not been regenerated before removal	

*All of the common disposal considerations in Table 7 must also be taken into account.

---

[26] Tonka Equipment Company, date unknown.

[27] Sorg, T., 1988.

[28] AWWA, 1999.

Table 16: Coagulation/Filtration Overview

Use	*BAT*	Listed as a BAT for uranium removal
	SSCT	Listed as a SSCT for uranium removal for systems serving 25-10,000 customers
Efficiency	‣ The efficiency of uranium removal depends on water pH, the prevailing charge on the floc, and the types and amount of uranium present in the water ‣ Uranium removal efficiencies of 85% to 95% have been observed at pH levels of 6.0 and 10.0[29] ‣ See also Appendix E, Table E-1	
Residuals	*Liquid*	Spent filter backwash water and filter-to-waste (if practiced)
	Solid	Sludge and spent filter media
Additional Disposal Issues*	*Direct discharge*	Blending brine with backwash water can significantly reduce radionuclide concentrations and TDS
Limitations	‣ The use of this technology for uranium removal is only practical if the system has coagulation/filtration in place and can modify the existing processes to optimize uranium removal ‣ Choosing the most suitable coagulant for a system requires an understanding of source water characteristics, especially pH. The choice of coagulants will affect the characteristics of the residuals produced during treatment. ‣ Using this technology necessitates having a highly skilled system operator	

*All of the common disposal considerations in Table 7 must also be taken into account.

---

[29] U.S. EPA, 1992.

II-B Intermediate Processing

For some systems, processing residuals prior to disposal may be cost-effective. The available intermediate processing options vary in complexity and may help determine the final disposal method. Residual processing may be as simple as collecting residuals for direct disposal or as difficult as incorporating complex treatment technologies that generate additional residual streams which must also be addressed. Intermediate processing can make residual streams eligible for disposal via the sometimes otherwise limited methods available to a system and, in some cases, can reduce the volume of waste produced.

Table 17 outlines intermediate processing options, according to the type of residual produced.

Table 17: Intermediate Processing Options

	Intermediate Treatment				
Residual Stream	Flow Equalization	Chemical Precipitation/ pH Adjustment[1]	Thickening[1]	Dewatering[2]	Recycle
Brine, Backwash, Rinse, and Acid Neutralization	✓	✓	✓	✓	✓
Concentrate (i.e., membrane reject stream)		✓	✓	✓	✓
Spent Filter Backwash and Filter-to-Waste	✓	✓	✓	✓	✓
Sludge			✓	✓	✓

[1] Sludge and supernatant produced.

[2] Dewatering is preceded by thickening. Sludge of increased solids concentration and liquid from dewatering produced.

- **Flow equalization** is necessary when residual streams do not have a consistent flow and vary significantly in their physical and chemical characteristics. These may include liquid wastes from IX and AA processes, spent filter backwash, and filter-to-waste. Systems may need to collect the regeneration waste stream in a holding tank to ensure constant flow and radionuclide concentrations. If the tank is mixed, then a sludge will not be produced. If the tank is not mixed, a supernatant and sludge will be generated, and the system must decide how to dispose of these wastes.

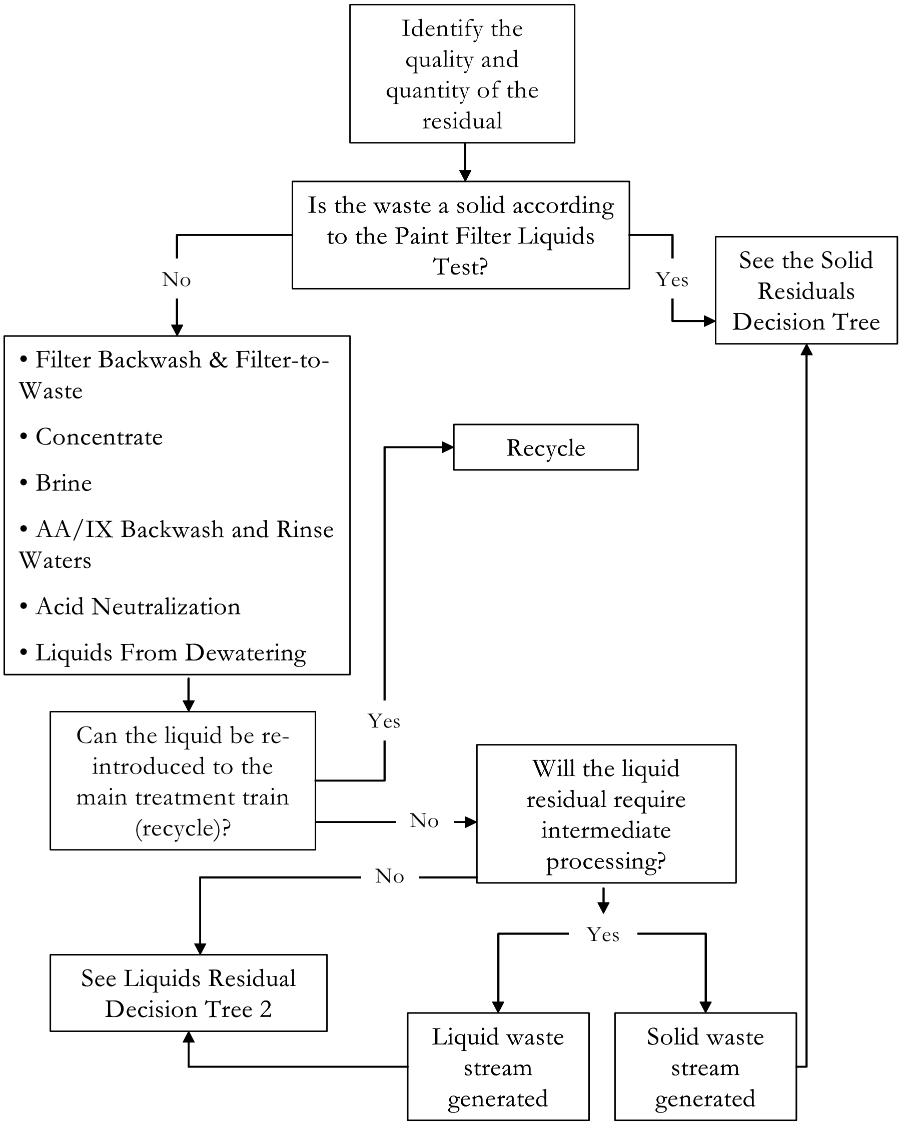
- **Chemical precipitation** involves precipitation of ions into an insoluble form in a reactor vessel followed by separation in a clarifier. (Flocculation can be used to enhance removal of suspended solids.) This procedure generates two waste streams that must be disposed of: a supernatant and the precipitated waste slurry or sludge. Systems may be able to recycle the supernatant. In addition, pH adjustment may be necessary for disposal of residuals. Compliance with specific disposal options may require that acidic or basic liquid residuals be neutralized.

- **Thickening** of liquid residuals, such as spent filter backwash, or sludge will allow the liquid and solids to separate. This produces a sludge and supernatant that may require further processing. Depending on the treatment technology used, both the sludge and the supernatant could contain radionuclides.

- **Dewatering** increases the solids concentration for final disposal, producing a sludge of increased solid concentration and a liquid. This can be done mechanically (e.g., through a centrifuge, belt filter press, or vacuum filter), or non-mechanically (e.g., through sand drying beds, freeze-thaw beds, solar drying beds, or dewatering lagoons). These non-mechanical processes may not be cost-effective; they are very land-intensive and can be climate dependent. Systems should check with their states for design guidelines, regulations, and permitting restrictions for these processes.

- **Recycle** of residuals, such as membrane concentrate and spent filter backwash, is also an option for systems. During treatment with lime softening, a portion of the sludge is recycled. Systems should avoid recycle practices that will concentrate radionuclides to levels that make disposal prohibitively expensive. In addition, the Filter Backwash Recycling Rule (FBRR) applies to those systems using surface water or groundwater under the influence of surface water, who recycle spent filter backwash, thickener supernatant, and liquids from dewatering processes from conventional or direct filtration systems.

Decision Tree 3: Liquid Residuals Disposal: Intermediate Processing



Appendix A: Glossary

Agreement State - A state under a signed agreement with the NRC (in which the NRC relinquishes authority to the Agreement state), that regulates source material, byproduct material, and small quantities of special nuclear material within the state's boundaries.

ALARA (As Low As Reasonably Achievable) - Target radiation exposure level, endorsed by the radiation protection community.[30] This requires making every reasonable effort to maintain exposures to radiation as far below the dose limits in [10 CFR 20.1003] as is practical consistent with the purpose for which the licensed activity is undertaken, taking into account the state of technology, the economics of improvements in relation to state of technology, the economics of improvements in relation to benefits to public health and safety, and other societal and socioeconomic considerations, and in relation to utilization of nuclear energy and licensed materials in the public interest. (10 CFR 20.1003)

Alpha radiation - Positively charged, heavy (equivalent to a helium nucleus, two protons, and two neutrons) particles that are emitted from naturally-occurring and man-made radioactive material (e.g., from nuclear power or radiation used in medicine). Examples of alpha emitting radionuclides include radon, thorium, radium, and uranium.

Beta radiation - Beta particles are negatively charged subatomic particles ejected from the nucleus of some radioactive atoms. They are typically more penetrating but have less energy than alpha particles. They are equivalent to electrons, though beta particles originate in the nucleus and electrons originate outside the nucleus. Examples of beta emitting radionuclides include uranium decay products such as lead-214 and bismuth-214 and thorium decay products such as actinium-228 and lead-212.[31]

Byproduct material - Any radioactive material (except special nuclear material) yielded in or made radioactive by exposure to the radiation incident to the process of producing or utilizing special nuclear material (42 USC 2014 (e)(1)), and the tailings or wastes produced by the extraction or concentration of uranium or thorium from any ore processed primarily for its source material content (42 USC 2014 (e)(2)).

Community Water System - A public water system that serves at least 15 service connections used by year-round residents or regularly serves at least 25 year-round residents.[32]

Conditionally Exempt Small Quantity Generators - Facilities that produce less than 100 kg of hazardous waste, or less than 1 kg of acutely hazardous waste, per calendar month, which accumulate less than 1,000 kg of hazardous waste, 1 kg of acutely hazardous waste, or 100 kg of spill residue from acutely hazardous waste at any one time.[33]

Curie/picocurie - A measure of radioactivity. One Curie of radioactivity is equivalent to 3.7×10^{10} or 37,000,000,000 nuclear disintegrations per second.[34] Concentrations of radioactivity in solid materials in the environment are usually expressed as picocuries per gram (pCi/g) while radioactivity in air or liquids is expressed as picocuries per liter (pCi/L). One picocure is one trillionth of a curie.

---

[30] U.S. DOE, 1997.

[31] http://www.epa.gov/radiation/understand/beta.htm

[32] U.S. EPA, 1997.

[33] U.S. EPA, January 2003.

[34] U.S. EPA, 1994a.

Direct discharge - Discharges from point sources into surface water pursuant to a CWA NPDES permit facility.[35]

Free liquids - Liquids that readily separate from the solid portion of a waste under ambient temperature and pressure (40 CFR 261.10).

Gamma (or X-ray) radiation - Also known as photon radiation, the high-energy portion of the electromagnetic spectrum. The most penetrating type of radiation, capable of passing through the human body and common construction materials. Gamma radiation is emitted during the decay of thorium and uranium.

Gross alpha particle activity - The total radioactivity due to alpha particle emission as inferred from measurements on a dry sample.[36] (Net alpha is this same measurement minus uranium activity.)

Hazardous waste - Hazardous waste is defined under 40 CFR 261.3. Waste is considered hazardous if it is a solid waste (as defined under 40 CFR 261.2) that is not excluded from regulation as hazardous waste under 40 CFR 261.4(b) and when it meets the criteria listed under 40 CFR 261.3(a)(2) and (b). The regulations most likely to be applicable to TENORM waste are the hazardous waste characteristics, especially the toxicity characteristic (40 CFR 261.24).

Industrial waste - Unwanted materials from an industrial operation in the form of liquid, sludge, solid, or hazardous waste.[37]

Ionizing radiation - Radiation that has sufficient energy to strip electrons from an atom.

Land disposal restrictions - Rules that require hazardous wastes to be treated before disposal on land to destroy or immobilize hazardous constituents that might migrate into soil and ground water.[38]

Landfill - An area of land or an excavation in which wastes are placed for permanent disposal, and that is not a land application unit, surface impoundment, or waste pile (40 CFR 257.2).

Large capacity septic systems - Septic systems that have the capacity to serve twenty or more persons per day.

Large Quantity Generators - Facilities that generate more than 1,000 kg of hazardous waste per calendar month, or more than 1 kg of acutely hazardous waste per calendar month.[39]

Low-level radioactive waste - Radioactive waste not classified as high-level radioactive waste, transuranic waste, spent nuclear fuel, or byproduct material as defined in the Atomic Energy Act section 11e.(2) (uranium or thorium mill tailings and waste).

Maximum Contaminant Level - The maximum permissible level of a contaminant in water which is delivered to any regulated user of a public water system (40 CFR 141.2).

---

[35] U.S. EPA, January 2003.

[36] U.S. EPA, 1994a.

[37] U.S. EPA, 1997.

[38] U.S. EPA, 1997.

[39] U.S. EPA, January 2003.

Maximum Contaminant Level Goal - The maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health of persons would occur, and which allows an adequate margin of safety. Maximum contaminant level goals are non-enforceable health goals.[40]

Mixed waste - Radioactive waste that is also a hazardous waste under RCRA. These wastes are jointly regulated by RCRA and the AEA.[41]

Municipal solid waste landfill - A discrete area of land or excavation that receives municipal solid waste.[42]

Non-ionizing radiation - Radiation that "bounces off or passes through matter without displacing electrons."[43] Its effect on human health is undetermined. Sources of non-ionizing radiation include radios, microwaves, and infrared light.

Paint Filter Liquids Test - Test to determine the presence of free liquids in a representative sample of waste, used to determine compliance with 40 CFR 264.314, 265.314, and 258.28. A predetermined amount of material is placed in a paint filter. If any portion of the material passes through and drops from the filter within the 5 minute test period, the material is deemed to contain free liquids.[44]

Publicly Owned Treatment Works - A treatment works as defined by section 212 of the CWA, which is owned by a state or municipality (as defined by section 502(4) of the CWA). Included are any devices and systems used in the storage, treatment, recycling and reclamation of municipal sewage or liquid industrial wastes. It also includes sewers, pipes and other conveyances only if they convey wastewater to a POTW. This definition also includes the municipality as defined in CWA section 502(4) that has jurisdiction over the indirect discharges to and the discharges from the POTW. (40 CFR 403.3(o))

Radiation - The emitting of energy through matter or space in the form of waves (rays or particles).[45]

Radioactive decay - The spontaneous radioactive transformation of one nuclide (or isotope) into a different nuclide or into a lower energy state of the same nuclide.[46] Radionuclides decay principally by emission of alpha particles, beta particles, and gamma rays.[47]

Radionuclide - Any man-made or natural element that emits ionizing radiation.

---

[40] U.S. EPA, 1994a.

[41] U.S. EPA, January 2003.

[42] U.S. EPA, January 2003.

[43] Oak Ridge Reservation, 2000. p. G-5

[44] http://www.epa.gov/epaoswer/hazwaste/test/pdfs/9095a.pdf

[45] U.S. DOE, 1994.

[46] U.S. DOE, 1994.

[47] U.S. EPA, 1991.

Radium - A naturally occurring radioactive metal that exists as one of several isotopes (radium-223, radium-224, radium-226, and radium-228), formed when uranium and thorium decay in the environment. Radium is found at low levels in the natural environment in soil, water, rocks, coal, plants, and food.[48]

Radon - A colorless naturally occurring, radioactive, inert gas formed by radioactive decay of radium atoms in soil, rocks, or water.[49] Radon occurs as the radionuclides radon-220 and radon-222.

Small Quantity Generators - Facilities that generate between 100 kg and 1,000 kg of hazardous waste per calendar month.[50]

Solid waste - Any garbage, refuse, or sludge from a wastewater treatment plant, water supply treatment plant, or air pollution control facility, and other discarded material, including solid, liquid, semisolid, or contained gaseous material, resulting from industrial, commercial, mining, and agricultural operations and from community activities. For the purposes of hazardous waste regulation, a solid waste is a material that is discarded by being either abandoned, inherently waste-like, a certain waste military munition, or recycled.[51]

Source material - Uranium or thorium, or any combination thereof, in any physical or chemical form or ores that contain 0.05 percent or more of uranium, thorium, or any combination of the two. This does not include special nuclear material (10 CFR 40.4).

Technologically Enhanced Naturally Occurring Radioactive Material - Naturally occurring materials, such as rocks, minerals, soils, and water whose radionuclide concentrations or potential for exposure to humans or the environment is enhanced as a result of human activities (e.g., water treatment).[52]

Toxicity Characteristic Leaching Procedure - A laboratory procedure that simulates landfill conditions. It is designed to predict whether a particular waste is likely to leach dangerous levels of chemicals into groundwater and is used to determine whether a waste is considered hazardous under 40 CFR 261.10.[53]

Unimportant quantity - Source material that is exempt from the licensing requirements of NRC and the Agreement States. One exemption is for any: chemical mixture, compound, solution, or alloy in which the source material is by weight less than 0.05 percent of the mixture, compound, solution or alloy. This exemption does not include byproduct material as defined in 10 CFR Part 40 (10 CFR 40.13(a)).

Universal treatment standards - The constituent-specific treatment standards found in 40 CFR 268.48. The standards must be met before hazardous waste can be land disposed.[54]

Uranium - A naturally occurring radioactive element with an atomic number of 92. The principal isotopes by weight are, in the uranium decay series, uranium-234 and uranium-238 (comprising 99.3 percent of natural uranium by mass) and, in the actinium decay series, fissionable uranium-235 (comprising 0.7 percent of natural uranium by mass).

---

[48] U.S. EPA, July 2002.

[49] U.S. EPA, 1997.

[50] U.S. EPA, January 2003.

[51] U.S. EPA, January 2003.

[52] In accordance with concepts presented in NAS (1999) and IAEA (2004).

[53] U.S. EPA, January 2003.

[54] U.S. EPA, *Land Disposal Restrictions Glossary*, Date unknown.

Well - Any bored, drilled or driven shaft or dug hole whose depth is greater than the largest surface dimension; or an improved sinkhole; or a subsurface fluid distribution system used to discharge fluids underground.

Well injection - The subsurface emplacement of fluids through a well.

Appendix B: References

AWWA. 1999. Water Quality and Treatment. New York, NY: McGraw Hill, Inc.

Bennett, D.L. 1978. "The Efficiency of Water Treatment Processes in Radium Removal." Journal AWWA 70(12): 698-701.

Brink, W.L., R.J. Schliekelman, D.L. Bennett, C.R. Bell, and I.M. Markwood. 1978. "Radium Removal Efficiencies in Water Treatment Processes." Journal AWWA 70(1): 31-35.

Clifford, D.A., W. Vijjesworapu, and S. Subramonian. 1988. "Evaluating Various Adsorbents and Membranes for Removing Radium From Groundwater." Journal AWWA 80(7):94.

Final Report: ISCORS Assessment of Radioactivity in Sewage Sludge: Modeling to Assess Radiation Doses. ISCORS 2005-03, NRC NUREG-1783, EPA 832-E-002A, DOE/EH -0670.

FinalReport: ISCORS Assessment of Radioactivity in Sewage Sludge: Recommendations on Management of Radioactive Materials in Sewage Sludge and Ash at Publicly Owned Treatment Works. ISCORS 2004-04, EPA 832-R-03-002B, DOE/EH-0668.

Fisher, Eugene, U.S. EPA Office of Radiation and Indoor Air, Personal Communication with authors of ISCORS Draft Report.

Hanson, S., D. Wilson, and N. Gunaji. 1987. "Removal of Uranium from Drinking Water by Ion Exchange and Chemical Clarification." EPA/600/S2-87/076.

Huffert, A.M., R.A. Meck, and K.M. Miller. 1994. *Background as a Residual Radioactivity Criterion for Decomissioning.* Rep. NUREG-1501. U.S. Nuclear Regulatory Commission.

International Atomic Energy Agency (IAEA). 9 January 2004. Technical Report Series. Report 419. "Extent of Environmental Contamination from Naturally Occurring Radioactive Material (NORM) and Technological Options for Mitigation." Vienna, Austria.

International Commission on Radiological Protection (ICRP). "Protection Against Radon-222 at Home and at Work." ICRP Publication 65. Annals of the ICRP 23(2). Oxford, UK: Pergamon Press.

Lassovszky, P. and Hathaway, S. May 24-28, 1983. "Treatment Technologies to Remove Radionuclides from Drinking Water." Pre-conference Report for the National Workshop on Radioactivity in Drinking Water. Easton, MD.

National Academy of Sciences (NAS). 1999. *Evaluation of Guidelines for Exposures to Technologically Enhanced Naturally Occurring Radioactive Materials.* Washington, D.C.: National Academies Press.

National Council on Radiation Protection. 1987. *Ionizing Radiation Exposure of the Population of the United States*. NCRP Report No. 93. Bethesda, MD.

Nuclear Regulatory Commission and U.S. EPA. 1987. "Guidance on the Definition and Identification of Commercial Mixed Low-Level Radioactive and Hazardous Waste."

Oak Ridge Reservation. 2000. *Annual Site Environmental Report.*

Peterson, K. 1999. "Radionuclides Removal with Optimized Iron/Manganese Filtration." Minnesota Department of Health.

Peterson, K. June 11-15, 2000. “Radionuclides Removal with Optimized Iron/Manganese Filtration.” Presented at AWWA Conference. Denver, CO.

Reid, G.W. et al. May 1985. “Treatment, Waste Management and Cost of Radioactivity Removal from Drinking Water.” *Health Physics Journal*, Vol. 48.

Schliekelman, R. June 1976. “Determination of Radium Removal Efficiencies in Illinois Water Supply Treatment Processes.” U.S. EPA Technical Note. ORP/TAD-76-2.

Snoeyink, V., et al. 1984. “Characteristics and Handling of Wastes from Groundwater Treatment Systems.” Seminar on Experiences with Groundwater Contamination. AWWA National Conference.

Sorg, T. April 1980. “Removal of Radium-226 from Drinking Water by Reverse Osmosis in Sarasota County, Florida.” Journal AWWA.

Sorg, T. 1988. “Methods for Removing Uranium from Drinking Water.” Journal AWWA 80(7).

Sorg, T. 1990. “Removal of Uranium from Drinking Water by Conventional Treatment Methods,” in *Radon, Radium, and Uranium in Drinking Water*. C. Richard Cothern with Paul A. Rebers. Chelsea, MI: Lewis Publishers.

Tonka Equipment Company. *Radium Removal from Potable Water*. Tonka Technical Bulletin. http://www.tonkawater.com/pdf/RadiumRemovalTech_Bulletin.pdf

U.S. Department of Energy. 1994. “Appendix C - Glossary.” In: *Committed to Results: DOE's Environmental Management Program, An Introduction (EM Primer)*. DOE/EM-0152P.

U.S. Department of Energy. 1997. “Applying the ALARA Process for Radiation Protection of the Public and Compliance with 10 CFR Part 834 and DOE 5400.5 ALARA Program Requirements,” Volume 1, Draft.

U.S. Department of Energy and U.S. EPA Interagency Steering Committee on Radiation Standards (ISCORS). 2003. *Assessment on Radioactivity in Sewage Sludge: Recommendations for Management of Radioactive Materials in Sewage Sludge and Ash at Publicly Owned Treatment Works*. Draft Report. DOE-EH-0668, EPA 832-R-03-002B.

U.S. EPA. Date unknown. *Land Disposal Restrictions Glossary*. http://www.epa.gov/epaoswer/hazwaste/ldr/glossary.htm

U.S. EPA. Date unknown. Radiation *Glossary*. http://www.epa.gov/radiation/glossary/index.html

U.S. EPA. Date unknown. SW-846 Manual. “Test Methods for Evaluating Solid Waste, Physical/Chemical Methods.”

U.S. EPA. 1977. “Manual of Treatment Techniques for Meeting the Interim Primary Drinking Water Regulations.” EPA 600/8-77-005.

U.S. EPA. 1981. *Radioactivity in Drinking Water*. Health Effects Branch, Criteria and Standards Division, Office of Drinking Water. EPA 570/9-81-002.

U.S. EPA. 1982. “Disposal of Radium-Barium Sulfate Sludge From a Water Treatment Plant in Midland, South Dakota.” Technical Assistance Program Report prepared by Fred C. Hart Associates, Inc. for U.S. EPA Region 8.

U.S. EPA. 1986. “Technology and Costs for Treatment and Disposal of Waste Byproducts by Water Treatment for Removal of Inorganic and Radioactive Contaminants.”

U.S. EPA. July 18, 1991. “National Primary Drinking Water Regulations; Radionuclides; Proposed Rule.” Federal Register. Vol. 56, No. 138.

U.S. EPA. 1992. “Evaluation of Demonstration Technologies: Quail Creek Water Supply System.” EPA 812-R-93-001.

U.S. EPA. 1994a. *Drinking Water Glossary: A Dictionary of Technical and Legal Terms Related to Drinking Water*. EPA 810-B-94-006.

U.S. EPA. 1994b. “Suggested Guidelines for the Disposal of Naturally Occurring Radionuclides Generated by Drinking Water Plants, Waste Disposal Work Group.” Office of Drinking Water.

U.S. EPA. 1995. “Management of Water Treatment Plant Residuals.” EPA/625/R-95-008.

U.S. EPA. 1997. *Terms of Environment*. Revised Edition. EPA 175-B-97-001.

U.S. EPA. May 2000. *Regulations on the Disposal of Arsenic Residuals from Drinking Water Treatment Plants*. EPA/600/R-00/025.

U.S. EPA. August 2000. *Multi-Agency Radiation Survey and Site Investigation Manual* (MARSSIM). EPA 402-R-97-016. Rev. 1.

U.S. EPA. December 7, 2000. “National Primary Drinking Water Regulations; Radionuclides, Final Rule.” Federal Register. Vol. 65, No. 236.

U.S. EPA. June 2002. *Treatment of Arsenic Residuals from Drinking Water Removal Processes*. EPA/600/R-01/03.

U.S. EPA. July 2002. *EPA Facts About Radium*.

U.S. EPA. January 2003. *RCRA Orientation Manual*. Office of Solid Waste and Emergency Response. EPA 530-R-02-016.

U.S. EPA. November 2003. Advance Notice of Proposed Rulemaking. “Approaches to an Integrated Framework for Management and Disposal of Low-Activity Radioactive Waste: Request for Comment; Proposed Rule.” Federal Register. Vol. 82, No. 222.

U.S. EPA. May 2004. “A Citizen’s Guide to Radon.” Office of Air and Radiation. EPA 402-K02-006.

Wade Miller Associates. July 1991. “Regulatory Impact Analysis of Proposed National Drinking Water Regulations for Radionuclides." Prepared under contract 68-C0-0069 for the U.S. EPA.

Appendix C: Applicable Federal Statutes and Regulations

Atomic Energy Act (AEA)

The 1954 AEA regulates the development and use of nuclear facilities, and the creation, generation, and disposal of source, special nuclear, and byproduct material (all designated as radioactive material under the jurisdiction of the AEA). The Act enables the NRC to establish relationships with states that allow these "Agreement States" to develop and implement regulations governing the use and possession of source, special nuclear, and byproduct materials. Agreement States must establish radiation protection programs compatible with the NRC's; for a list of Agreement States, see http://www.hsrd.ornl.gov/nrc.

NRC has exempted source material from regulation under the AEA if the uranium or thorium makes up less than 0.05 percent by weight (i.e., an "unimportant quantity"). Equivalent exemptions appear in the Agreement States' regulations. For natural uranium, this is equivalent to approximately 335 pCi/g, and therefore, the uranium residuals produced by water treatment plants may, in some cases, be an "unimportant quantity of source material" and exempt from NRC's and the Agreement States' regulations. Source material may be held under a general license if it is greater than 0.05 percent by weight, but the total amount in a treatment plant's possession at any time is less than 15 pounds. This is referred to as a "small quantity" of source material. The general license to use and transfer small quantities of source material is granted under 10 CFR 40.22 and equivalent regulations of the Agreement States. Under this general license, systems may not process more than 150 pounds of source material in a calendar year. Systems that exceed the small quantity thresholds must apply for a specific license from the NRC or Agreement State.

The NRC's "Standards for Protection Against Radiation" (10 CFR Part 20), contains the basic radiation protection standards for persons licensed to receive, possess, use, transfer, and dispose of source, special nuclear, and byproduct materials as defined in the AEA. These regulations set dose limits for radiation workers and the public, and specify requirements for the monitoring and labeling of radioactive materials, the posting of radiation areas, and the reporting of theft or loss of radioactive material. Regulations for licensing of source material are contained in 10 CFR Part 40. Additional requirements for persons licensed by the NRC are contained in 10 CFR Part 19; this includes requirements for instructions and notifications to employees. The NRC's Regulations can be found at http://www.nrc.gov/reading-rm/doc-collections/cfr/.

Because the NRC's transportation duties overlap with the statutory authority of the DOT, the NRC and DOT signed a Memorandum of Understanding in 1979 covering the regulation of the transport of radioactive materials.

For more information, see http://www.nrc.gov/reading-rm/doc-collections/nuregs/staff/sr0980/ml022200075-vol1.pdf#pagemode=bookmarks&page=14 and http://www.nrc.gov/about-nrc.html.

Clean Water Act (CWA)

Wastes generated by water treatment plants and discharged to a receiving body of water (direct discharge) or to a POTW are regulated under the CWA. The Act requires dischargers to have a NPDES permit in order to discharge any pollutants into waters of the United States.

When applying for a NPDES permit, systems must provide information on water temperature, pH, flow rate, and on pollutant levels in the discharge. For copies of NPDES application forms, see http://cfpub.epa.gov/npdes/doctype.cfm?sort=name&program_id=45&document_type_id=8.

See http://cfpub.epa.gov/npdes/statestats.cfm for a list of states that are authorized to administer the NPDES program.

The CWA can also require systems to pretreat waste prior to discharge to a POTW. POTWs are required to establish and enforce pretreatment programs identifying significant dischargers who are subject to pretreatment standards (40 CFR 403). If a system wants to discharge its waste to a POTW, both the system and the POTW are responsible for preventing the introduction of any pollutants that may interfere with the POTW treatment process or contaminate POTW sewage sludge. This allows POTWs to implement Technically Based Local Limits (TBLLs). TBLLs vary among states and POTWs. Systems must check with their state and local POTW before choosing discharge to a POTW as a disposal option.

In addition, if systems located near ocean or saline waters wish to discharge their wastes directly to these waters, they may be affected by the **Marine Protection, Research, and Sanctuaries Act (MPRSA)**. Permits are required for ocean disposal activities although having a NPDES permit may satisfy the requirements set forth under MPRSA.

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

CERCLA is more commonly known as Superfund. It provides broad federal authority to respond to releases or threatened releases of hazardous substances that may endanger public health or the environment. Systems must consider CERCLA when selecting disposal options because they may be liable for incidents that result from disposing of wastes at a mismanaged landfill. For example, if a system disposed of sludge containing radionuclides at an improperly managed landfill and any release or threat of release occurred, the system could be partially or entirely liable for the cleanup.

Department of Transportation (DOT) Regulations

Under the Department of Transportation Act of 1966, DOT has regulatory responsibility for safety in the transportation of all hazardous materials (see 49 CFR 100-185), including radioactive material. DOT regulations govern container design, chemical compatibility, packaging, labeling, permitting, and transportation route requirements. This includes shipments by all modes of transport in interstate, intrastate, or foreign commerce (rail, highway, air, water), and by all means (truck, bus, auto, vessel, airplane, rail-car) except for postal shipments, which are under the jurisdiction of the U.S. Postal Service.

In a Final Rule (69 FR 3631) published on January 26, 2004, DOT adopted radionuclide-specific thresholds to determine when a material containing radionuclides is subject to the DOT requirements for transporting radioactive material. The exemption values consist both of activity concentrations and total consignment activities; a material containing a single radionuclide would have to be above both exemption values for that nuclide in order to be subject to those DOT requirements. If either the activity concentration or the total consignment activity is below the corresponding exemption value, that material is exempt from the DOT requirements for transporting radioactive material. The exemption values are listed in 49 CFR 173.436, and are referred to in the definition of Radioactive Material in 49 CFR 173.403. If more than one radionuclide is present, the appropriate exemption values are to be determined using a mixture rule described in 49 CFR 173.433.

In addition, in paragraph 49 CFR 173.401(b)(4), DOT exempts "natural material and ores containing naturally occurring radionuclides which are not intended to be processed for use of these radionuclides" so long as their activity concentrations and consignment activities do not exceed 10 times the levels listed in 49 CFR 173.436 or calculated using 49 CFR 173.433. For example, because the exempt activity concentration for uranium is listed in 49 CFR 173.436 as 27 pCi/g, and those for radium-226 and radium-228 are 270 pCi/g, systems transporting more than 270 pCi/g of uranium or 2,700 pCi/g of radium must comply with DOT's requirements for transporting radioactive materials (unless the consignment activities are below the consignment activity exemption values - 27 nanocuries and 270 nanocuries, respectively - in which case the material would still be exempt from those requirements). For more information, see http://hazmat.dot.gov.

Treatment plants classified as Large or Small Quantity Generators under RCRA must ensure that any waste to be transported for disposal is handled by a U.S. EPA-approved transporter.

Low-Level Radioactive Waste Policy Act (1980) and Amendments (1985)

This Act made states responsible for disposing of LLRW generated within their borders. States are permitted to form compacts with other states to develop LLRW disposal facilities serving more than one state. These facilities are regulated by the NRC, or Agreement States (see "Nuclear Regulatory Commission (NRC) Regulations" on the previous page, and 10 CFR 61 and 62 for more detail).

Resource Conservation and Recovery Act (RCRA)

The disposal of solid wastes[55] (including sludge) is regulated under RCRA (unless it is disposed of via direct discharge or underground injection). Under RCRA, an entity or person generating a solid waste must determine whether the waste is hazardous using the method described in 40 CFR 262.11.

Solid waste exhibiting toxicity, corrosivity, reactivity, or ignitability characteristics is hazardous. Hazardous waste requires special handling and disposal, and it is subject to RCRA Subtitle C requirements.

If the system wishes to dispose non-hazardous waste in a landfill, RCRA Subtitle D requirements apply. It is recommended that water treatment plants operate in a way that will avoid any generation of hazardous waste.

Municipal Solid Waste Landfill (MSWLF) Requirements

U.S. EPA, through the MSWLF Requirements (40 CFR 258, under RCRA Subtitle D), ensures the protection of human health and the environment by setting minimum national criteria for MSWLFs. A municipal solid waste landfill is a discrete area of land or excavation that receives household waste. A MSWLF may also receive other types of RCRA Subtitle D wastes, such as commercial solid waste, nonhazardous sludge, Conditionally Exempt Small Quantity Generator (CESQG) waste, and industrial nonhazardous solid waste.

These federal requirements cover landfill location, operation, and design; ground water monitoring; corrective action; closure and post-closure, and financial assurance. States and MSWLFs may have additional requirements. For more information on municipal solid waste management, see http://www.epa.gov/msw.

Safe Drinking Water Act (SDWA) - Underground Injection Control (UIC) Program

U.S. EPA is directed by the SDWA to establish minimum federal requirements for state and UIC programs to protect underground sources of drinking water (USDWs) from contamination caused by underground injection activities. Protection includes the oversight of construction, operation, and closure of injection wells. A treatment residual generator interested in UIC as a disposal option should contact the appropriate U.S. EPA regional or state UIC program office to determine the statutory requirements in their state.

---

[55] Any garbage, refuse, sludge from a wastewater treatment plant, water supply treatment plant, or air pollution control facility, and other discarded material, including solid, liquid, semisolid, or contained gaseous material, resulting from industrial, commercial, mining, and agricultural operations and from community activities. For the purposes of hazardous waste regulation, a solid waste is a material that is discarded by being either abandoned, inherently waste-like, a certain waste military munition, or recycled.

Appendix D: State, Regional, Federal, and Tribal Contacts

Table D-1: Regional and State Drinking Water, UIC, and Radiation Control Contacts

U.S. EPA REGION 1				
Drinking Water		Drinking Water Program	www.epa.gov/region1/eco/drinkwater	(617) 918-1111
UIC		Underground Injection Control Program	www.epa.gov/region1/eco/drinkwater/pc_groundwater_discharges.html	(617) 918-1111
Radiation		Pesticides, Toxics, and Radiation Unit	www.epa.gov/region1/topics/pollutants/radioactivity.html	(617) 918-1111
State	**Area**	**Contact**	**Web/Street Address**	**Phone**
CT	Drinking Water	Department of Public Health: Drinking Water Division	www.dph.state.ct.us/BRS/water/dwd.htm	(860) 509-7333
	UIC	Connecticut Department of Environmental Protection	dep.state.ct.us/wtr	(860) 424-3018
	Radiation	Division of Radiation, Department of Environmental Protection	79 Elm Street Hartford, CT 06106-5127 dep.state.ct.us/air2/prgacti.htm#Radiation	(860) 424-3029
ME	Drinking Water	Maine Department of Human Services: Division of Health Engineering	www.state.me.us/dhs/eng/water	(207) 287-2070
	UIC	Maine Department of Environmental Protection	www.state.me.us/dep/blwq/docstand/uic/uichome.htm	(207) 287-7814
	Radiation	Radiation Control Program, Division of Health Engineering	11 State House Station Augusta, ME 04333 www.state.me.us/dhs/eng/rad	(207) 287-5677
MA	Drinking Water	Department of Environmental Protection: Drinking Water Program	www.state.ma.us/dep/brp/dws/dwshome.htm	(617) 292-5770
	UIC	Department of Environmental Protection	www.state.ma.us/dep/brp/dws/uic.htm	(617) 348-4014
	Radiation	Radiation Control Program, Department of Public Health	90 Washington Street Dorchester, MA 02121 www.state.ma.us/dph/rcp/radia.htm	(617) 427-2944
NH	Drinking Water	Department of Environmental Services: Water Supply Engineering Bureau	www.des.state.nh.us/wseb	(603) 271-2513

	UIC	Department of Environmental Services	www.des.state.nh.us/dwspp	(603) 271-2858
	Radiation	Radioactive Material Section, Bureau of Radiological Health, Department of Health and Human Services	Health and Welfare Building 6 Hazen Drive Concord, NH 03301-6527 www.dhhs.state.nh.us/DHHS/RADHEALTH/default.htm	(603) 271-4585
RI	Drinking Water	Department of Health: Office of Drinking Water Quality	www.health.ri.gov/environment/dwq/index.php	(401) 222-6867
	UIC	Rhode Island Department of Environmental Management	www.state.ri.us/dem/programs/benviron/water	(401) 222-3961
	Radiation	Division of Occupational & Radiological Health, Department of Health	3 Capitol Hill, Room 206 Providence, RI 02908-5097 www.health.ri.gov/environment/occupational/index.php	(401) 222-7755
VT	Drinking Water	Department of Environmental Conservation: Water Supply Division	www.vermontdrinkingwater.org	(802) 241-3400
	UIC	Department of Environmental Conservation	www.anr.state.vt.us/dec/ww/uic.htm	(802) 241-4455
	Radiation	Radiological Health, Department of Health	108 Cherry Street P.O. Box 70 Burlington, VT 05402 www.healthyvermonters.info/hp/hp.shtml#Anchor--Radiologic-1387	(802) 865-7743

U.S. EPA REGION 2				
Drinking Water		Division of Environmental Planning and Protection, Drinking Water Section	www.epa.gov/region02/water/drinkingwater	(212) 637-5000
UIC		Water Compliance Branch	www.epa.gov/region02/capp	(212) 637-3766
Radiation		Division of Environmental Planning and Protection, Radiation and Indoor Air Branch	www.epa.gov/region02/org/depp.htm	(212) 637-4010
NJ	Drinking Water	Department of Environmental Protection: Bureau of Safe Drinking Water	www.state.nj.us/dep/watersupply/safedrnk.htm	(609) 292-5550

	UIC	Department of Environmental Protection, Department of Water Quality	www.state.nj.us/dep/dwq/nonpoint.htm	(609) 633-7021
	Radiation	Radiation Protection Programs, Division of Environmental Safety, Health & Analytical Programs, Department of Environmental Protection	P.O. Box 415 Trenton, NJ 08625-0415 www.state.nj.us/dep/rpp	(609) 984-5636
NY	Drinking Water	Department of Health: Bureau of Public Water Supply Protection	www.health.state.ny.us/nysdoh/water/main.htm	(518) 402-7650
	UIC	U.S. EPA Region 2	www.epa.gov/Region2/water/grndtop.htm	(212) 637-4226
	Radiation	Radiological Health Unit, Division of Safety and Health, New York State Dept. of Labor	NYS Office Campus, Building 12, Room 169 Albany, NY 12240	(518)457-1202
		Radioactive Waste Policy and Nuclear Coordination, New York State Energy Research & Development Authority	17 Columbia Circle Albany, NY 12203-6399	(518) 862-1090
		Radiation Section, Division of Hazardous Waste and Radiation Management, New York State Department of Environmental Conservation	625 Broadway, 8th Floor Albany, NY 12233-7255 www.dec.state.ny.us/website/dshm/hazrad/rad.htm	(518) 402-8579
		Bureau of Radiological Health, New York City Department of Health	Two Lafayette Street, 11th Floor New York, NY 10007	(212) 676-1556
		Bureau of Environmental Radiation Protection, New York State Department of Health	547 River Street Troy, NY 12180-2216	(518) 402-7550
PR	Drinking Water	Department of Health: Public Water Supply Supervision Program	www.epa.gov/region02/cepd/prlink.htm	(787) 977-5870
	UIC	Puerto Rico Environmental Quality Board	www.sso.org/ecos/states/delegations/pr.htm	(787) 767-8073
	Radiation	Radiological Health Division, Department of Health	P.O. Box 70184 San Juan, PR 00936-8184	(787) 274-7815
VI	Drinking Water	Department of Planning & Natural Resources: Division of Environmental Protection	www.dpnr.gov.vi/dep/home.htm	(340) 773-1082
	UIC	U.S. EPA Region 2	www.epa.gov/Region2/water/grndtop.htm	(212) 637-4232

	Radiation	N/A		
U.S. EPA REGION 3				
Drinking Water		Water Protection Division	www.epa.gov/reg3wapd	(215) 814-2300
UIC		Water Protection Division	www.epa.gov/reg3wapd/drinkingwater/uic	(215) 814-2300
Radiation		Radiation Program	www.epa.gov/reg3artd/radiation/radiation.htm	(215) 814-2089
DE	Drinking Water	Delaware Health & Social Services: Division of Public Health, Office of Drinking Water	www.state.de.us/dhss/dph	(302) 741-8630
	UIC	Department of Natural Resources and Environmental Control	www.dnrec.state.de.us/water2000/Sections/GroundWat/DWRGrndWat.htm	(302) 739-4762
	Radiation	Office of Radiation Control, Division of Public Health	P.O. Box 637 Dover, DE 19903 www.state.de.us/dhss/dph	(302) 744-4546
DC	Drinking Water	U.S. EPA Region 3	www.epa.gov/reg3wapd/drinkingwater	(202) 535-2190
	UIC	U.S. EPA Region 3	www.epa.gov/reg3wapd/drinkingwater/uic	(215) 814-5445
	Radiation	Department of Health, Environmental Health Administration, Bureau of Food, Drug, and Radiation Protection	51 N Street NE, Room 6025 Washington, DC 20002	(202) 535-2188
MD	Drinking Water	Department of the Environment: Public Water Supply Program	www.mde.state.md.us/Programs/WaterPrograms/Water_Supply/index.asp	(410) 537-3000
	UIC	Department of the Environment	www.mde.state.md.us/Water	(410) 631-3323
	Radiation	Radiological Health Program, Air and Radiation Management Administration, Maryland Department of the Environment	1800 Washington Blvd Suite 750 Baltimore, MD 21230-1724 www.mde.state.md.us/Programs/AirPrograms/Radiological_Health	(410) 537-3300
PA	Drinking Water	Department of Environmental Protection: Bureau of Water Supply Management	www.dep.state.pa.us/dep/deputate/watermgt/wsm/wsm.htm	(717) 787-5017

	UIC	U.S. EPA Region 3	www.epa.gov/reg3wapd/drinkingwater/uic	(215) 814-5445
	Radiation	Bureau of Radiation Protection, Department of Environmental Protection	P.O. Box 8469 Harrisburg, PA 17105-8469 www.dep.state.pa.us/dep/deputate/airwaste/rp/rp.htm	(717) 787-2480
VA	Drinking Water	Department of Health: Division of Water Supply Engineering, Office of Drinking Water	www.vdh.state.va.us/dw	(804) 864-7500
	UIC	U.S. EPA Region 3	www.epa.gov/reg3wapd/drinkingwater/uic	(215) 814-5445
	Radiation	Radiological Health Program, Division of Health Hazards Control, Department of Health	Main Street Station 1500 East Main, Room 240 Richmond, VA 23219 www.vdh.state.va.us/rad	(804) 786-5932
WV	Drinking Water	Bureau for Public Health: Environmental Engineering Division	www.wvdhhr.org/oehs/eed	(304) 558-2981
	UIC	Division of Environmental Protection	www.wvdep.org/item.cfm?ssid=11&ss1id=165	(304) 558-6075
	Radiation	Radiation, Toxics, & Indoor Air Division, Department of Health and Human Resources	815 Quarrier Street - Suite 418 Charleston, WV 25301 www.wvdhhr.org/rtia/	(304) 558-6772

U.S. EPA REGION 4				
Drinking Water		Water Management Division	www.epa.gov/region4/water	(404) 562-9345
UIC		Water Management Division	www.epa.gov/region4/water/uic	(404) 562-9345
Radiation		Air, Pesticides, and Toxic Management Division	www.epa.gov/region4/air/radon	(404) 562-9135
AL	Drinking Water	Department of Environmental Management: Water Supply Branch	www.adem.state.al.us/WaterDivision/WaterDivisionPP.htm	(334) 271-7773
	UIC	Department of Environmental Management	www.adem.state.al.us/WaterDivision/Ground/UIC%20GW/GWUICInfo.htm	(334) 271-7844

	Radiation	Office of Radiation Control, Alabama Department of Public Health	201 Monroe Street, P.O. Box 303017 Montgomery, AL 36130-3017 www.adph.org/radiation	(334) 206-5391
FL	Drinking Water	Department of Environmental Protection: Drinking Water Section	www.dep.state.fl.us/water/drinkingwater	(850) 245-8624
	UIC	Department of Environmental Protection	www.dep.state.fl.us/water/uic/index.htm	(850) 921-9417
	Radiation	Bureau of Radiation Control, Florida Department of Health	4052 Bald Cypress Way, SE, Bin C21 Tallahassee, FL 32399-1741 www.doh.state.fl.us/environment/radiation	(850) 245-4266
GA	Drinking Water	Department of Natural Resources: Drinking Water Program	www.dnr.state.ga.us/dnr/environ	(404) 656-4087
	UIC	Environmental Protection Division	www.dnr.state.ga.us/dnr/environ	(404) 656-3229
	Radiation	Radioactive Materials Program, Environmental Protection Division, Department of Natural Resources	4244 International Parkway, Suite 114 Atlanta, GA 30354 www.ganet.org/dnr/environ/aboutepd_files/branches_files/rmprogram/default.htm	(404) 362-2675
KY	Drinking Water	Department for Environmental Protection: Drinking Water Branch	www.water.ky.gov/dw	(502) 564-3410
	UIC	U.S. EPA Region 4	www.epa.gov/region4/water/uic	(404) 562-9452
	Radiation	Radiation Health & Toxic Agents Branch, Cabinet for Health Services, Department of Public Health	275 East Main Street Mail Stop HS 2E-D Frankfort, KY 40621-0001 chs.ky.gov/publichealth/radiation.htm	(502) 564-7818
MS	Drinking Water	Department of Health: Division of Water Supply	www.msdh.state.ms.us/msdhsite	(601) 576-7518
	UIC	Department of Environmental Quality	www.deq.state.ms.us/MDEQ.nsf/page/Main_Home?OpenDocument	(601) 961-5640
	Radiation	Division of Radiological Health, State Department of Health	3150 Lawson Street, P.O. Box 1700 Jackson, MS 39215-1700 www.msdh.state.ms.us/radiological	(601) 987-6893

NC	Drinking Water	Department of Environment and Natural Resources: Public Water Supply Section	www.deh.enr.state.nc.us/pws	(919) 733-2321
	UIC	Department of Environment and Natural Resources	gw.ehnr.state.nc.us/uic.htm	(919) 715-6165
	Radiation	Division of Radiation Protection, Division of Environmental Health, Department of Environment & Natural Resources	3825 Barrett Drive Raleigh, NC 27609-7221 www.drp.enr.state.nc.us	(919) 571-4141
SC	Drinking Water	Department of Health & Environmental Control: Bureau of Water	www.scdhec.net/water/html/dwater.html	(803) 898-4300
	UIC	Department of Health and Environmental Control	www.scdhec.net/eqc/water/html/uic.html	(803) 898-3549
	Radiation	Bureau of Radiological Health, Department of Health & Environmental Control	2600 Bull Street Columbia, SC 29201	(803)545-4403
		Division of Waste Management, Bureau of Land and Waste Management, Department of Health & Environmental Control	2600 Bull Street Columbia, SC 29201 www.scdhec.net/lwm/html/radio.html	(803) 896-4245
TN	Drinking Water	Department of Environment & Conservation: Division of Water Supply	www.state.tn.us/environment/dws	(615) 532-0191
	UIC	U.S. EPA Region 4	www.epa.gov/region4/water/uic	(404) 562-9452
	Radiation	Division of Radiological Health, Tennessee Department of Environment and Conservation	L&C Annex, Third Floor 401 Church Street Nashville, TN 37243-1532 www.state.tn.us/environment/rad	(615) 532-0364

U.S. EPA REGION 5				
Drinking Water		Water Division, Ground Water and Drinking Water Branch	www.epa.gov/region5/water	(312) 886-6107
UIC		Water Division, UIC Branch	www.epa.gov/region5/water/uic/uic.htm	(312) 886-1492
Radiation		Air and Radiation Division	www.epa.gov/region5/air	(312) 353-2212
IL	Drinking Water	Illinois Environmental Protection Agency: Division of Public Water Supplies	www.epa.state.il.us/water/index-pws.html	(217) 785-8653

	UIC	Illinois Environmental Protection Agency	www.epa.state.il.us/land/regulatory-programs/underground-injection-control.html	(217) 782-6070
	Radiation	Division of Nuclear Safety, Illinois Emergency Management Agency	1035 Outer Park Drive Springfield, IL 62704 www.state.il.us/idns	(217) 785-9868
IN	Drinking Water	Department of Environmental Management: Drinking Water Branch	www.ai.org/idem/owm/dwb	(317) 232-8603
	UIC	U.S. EPA Region 5	www.epa.gov/region5/water/uic/uic.htm	(312) 353-4543
	Radiation	Indoor & Radiologic Health Division, State Department of Health	2 N. Meridian Street, 5F Indianapolis, IN 46204-3003 www.state.in.us/isdh/regsvcs/radhealth/welcome.htm	(317) 233-7146
MI	Drinking Water	Department of Environmental Quality: Drinking Water & Radiological Protection Division	www.michigan.gov/deq	(517) 335-4716
	UIC	U.S. EPA Region 5	www.epa.gov/region5/water/uic/uic.htm	(312) 353-4543
	Radiation	Hazardous Waste and Radiological Protection Section, Waste and Hazardous Materials Division, Michigan Department of Environmental Quality	525 West Allegan Street PO Box 30241 Lansing, MI 48909-7741 www.michigan.gov/deq/0,1607,7-135-3312_4120_4244---,00.html	(517) 373-0530
MN	Drinking Water	Department of Health: Drinking Water Protection Section	www.health.state.mn.us/divs/eh/water	(651) 215-0770
	UIC	U.S. EPA Region 5	www.epa.gov/region5/water/uic/uic.htm	(312) 353-4543
	Radiation	Section of Asbestos, Indoor Air, Lead and Radiation, Division of Environmental Health, Department of Health	121 E. Seventh Place, Suite 220 P.O. Box 64975 St. Paul, MN 55164-0975 www.health.state.mn.us/divs/eh/radiation	(651) 215-0945
OH	Drinking Water	Ohio Environmental Protection Agency: Division of Drinking & Ground Water	www.epa.state.oh.us/ddagw	(614) 644-2752
	UIC	Ohio Environmental Protection Agency	www.epa.state.oh.us/ddagw/uic.html	(614) 644-2771

	Radiation	Bureau of Radiation Protection, Ohio Department of Health	P.O. Box 118 Columbus, OH 43266-0118	(614) 644-7860
WI	Drinking Water	Department of Natural Resources: Bureau of Water Supply	www.dnr.state.wi.us/org/water/dwg	(608) 266-0821
	UIC	Department of Natural Resources	dnr.wi.gov/org/water/dwg/Uiw/index.htm	(608) 266-2438
	Radiation	Radiation Protection Section, Division of Public Health, Department of Health and Family Services	P.O. Box 2659 Madison, WI 53701-2659 www.dhfs.state.wi.us/dph_beh/RadiatioP/	(608) 267-4792

U.S. EPA REGION 6				
Drinking Water		Water Quality Protection Division, Drinking Water Section	www.epa.gov/earth1r6/6wq/swp/drinkingwater/aboutq&a.htm	(214) 665-7155
UIC		Water Quality Protection Division, Source Water Protection	www.epa.gov/earth1r6/6wq/swp/uic	(214) 665-7165
Radiation		Multimedia Planning and Permitting Division	www.epa.gov/earth1r6/6pd/6pd.htm	(214) 665-8124
AR	Drinking Water	Department of Health: Division of Engineering	www.healthyarkansas.com/eng	(501) 661-2623
	UIC	Department of Environmental Quality	www.adeq.state.ar.us/water/branch_permits/default.htm	(501) 682-0646
	Radiation	Division of Radiation Control & Emergency Management, Radioactive Materials Program, Department of Health	4815 West Markham Street, Slot #30 Little Rock, AR 72205-3867	(501) 661-2173
LA	Drinking Water	Office of Public Health: Division of Environmental & Health Services	www.oph.dhh.state.la.us/engineerservice/safewater	(225) 765-5038
	UIC	Department of Natural Resources	www.dnr.state.la.us	(225) 342-5561
	Radiation	Permit Division, Office of Environmental Services	P.O. Box 4313 Baton Rouge, LA 70821-4313 www.deq.state.la.us/permits	(225) 219-3005
NM	Drinking Water	Environment Department: Drinking Water Bureau	www.nmenv.state.nm.us/dwb/dwbtop.html	(505) 827-7545

	UIC	Environment Department	www.nmenv.state.nm.us/gwb/New%20Pages/UIC.htm	(505) 827-2936
	Radiation	Radiation Control Bureau, Environment Department	1190 St. Francis Drive, Rm S2100 P.O. Box 26110 Santa Fe, NM 87502-0110 www.nmenv.state.nm.us/nmrcb/home.html	(505) 476-3236
OK	Drinking Water	Department of Environmental Quality: Water Quality Division	www.deq.state.ok.us/WQDnew	(405) 702-8100
	UIC	Department of Environmental Quality	www.deq.state.ok.us/LPDnew/uicindex.html	(405) 702-5142
	Radiation	Radiation Management Section, Oklahoma Department of Environmental Quality	P.O. Box 1677 Oklahoma City, OK 73101-1677	(405) 702-5155
TX	Drinking Water	Texas Commission on Environmental Quality: Water Supply Division	www.tnrcc.state.tx.us/permitting/waterperm/pdw/pdw000.html	(512) 239-4671
	UIC	Texas Commission on Environmental Quality	www.tceq.state.tx.us	(512) 239-6633
	Radiation	Bureau of Radiation Control, Texas Department of Health	1100 West 49th Street Austin, TX 78756-3189 www.tdh.state.tx.us/radiation/default.htm	(512) 834-6679
		Office of Permitting, Remediation & Registration, Texas Commission on Environmental Quality	P.O. Box 13087, MC 122 Austin, TX 78711-3087 www.tceq.state.tx.us/AC/about/organization/oprr.html	(512) 239-6731

U.S. EPA REGION 7				
Drinking Water		Water Division	www.epa.gov/region07/water/dwgw.htm	(913) 551-7003
UIC		Water Division	www.epa.gov/region07/water	(913) 551-7003
Radiation		Radiation, Asbestos, Lead, and Indoor Programs Branch	www.epa.gov/region7/topics.htm	(913) 551-7003
IA	Drinking Water	Department of Natural Resources: Water Supply Section	www.state.ia.us/epd/wtrsuply/wtrsup.htm	(515) 725-0275
	UIC	U.S. EPA Region 7	www.epa.gov/Region7/water/contact.htm	(913) 551-7413

	Radiation	Bureau of Radiological Health, Iowa Department of Public Health	401 SW 7th Street, Suite D Des Moines, IA 50309 www.idph.state.ia.us/eh/radiological_health.asp	(515) 281-3478
KS	Drinking Water	Department of Health and Environment: Public Water Supply Section	www.kdhe.state.ks.us/pws	(785) 296-5514
	UIC	Department of Health and Environment	www.kdhe.state.ks.us/uic	(785) 296-5509
	Radiation	Radiation and Asbestos Control, Kansas Department of Health & Environment	1000 SW Jackson, Suite 320 Topeka, KS 66612-1366 www.kdhe.state.ks.us/radiation	(785) 296-1565
MO	Drinking Water	Department of Natural Resources: Public Drinking Water Program	www.dnr.state.mo.us/wpscd/wpcp	(573) 751-5331
	UIC	Department of Natural Resources	www.dnr.state.mo.us/homednr.htm	(573) 368-2170
	Radiation	Division of Environmental Health, Department of Health and Senior Services	930 Wildwood Drive, P.O. Box 570 Jefferson City, MO 65102-0570 www.dhss.state.mo.us/RadProtection/	(573) 751-6112
NE	Drinking Water	Department of HHS Regulation & Licensure	www.hhs.state.ne.us/enh/pwsindex.htm	(402) 471-2541
	UIC	Department of Environmental Quality	www.deq.state.ne.us	(402) 471-2186
	Radiation	Radiation Control Programs	P.O. Box 95007 Lincoln, NE 68509-5007 www.hhs.state.ne.us/rad/radindex.htm	(402) 471-2079

U.S. EPA REGION 8			
Drinking Water	Drinking Water Program	www.epa.gov/region08/water/dwhome/dwhome.html	(303) 312-6812
UIC	UIC Program	www.epa.gov/region08/water/uic	(303) 312-6312
Radiation	Radiation Protection Program	www.epa.gov/Region8/search/alpha.html#R	(303) 312-6312

CO	Drinking Water	Department of Public Health & Environment: Drinking Water Program	www.cdphe.state.co.us/wq/wqhom.asp	(303) 692-3500
	UIC	U.S. EPA Region 8	www.epa.gov/Region8/water/uic	(303) 312-6125
	Radiation	Radiation Management Program, HMWMD-B2, Hazardous Materials & Waste Management Division, Department of Public Health & Environment	4300 Cherry Creek Drive South Denver, CO 80246-1530 www.cdphe.state.co.us/hm/rad/radiationservices.asp	(303) 692-3428
MT	Drinking Water	Department of Environmental Quality: Public Water Supply Section	www.deq.state.mt.us/wqinfo	(406) 444-3080
	UIC	U.S. EPA Region 8	www.epa.gov/Region8/water/uic	(303) 312-6125
	Radiation	Radiological Health Program, Department of Public Health & Human Services, Licensure Bureau	2401 Colonial Drive P.O. Box 202953 Helena, MT 59620-2953	(406) 444-1510
ND	Drinking Water	Department of Health: Division of Municipal Facilities	www.ehs.health.state.nd.us/ndhd/environ/mf	(701) 328-5211
	UIC	Department of Health	www.health.state.nd.us/wq/gw/uic.htm	(701) 328-5233
	Radiation	Division of Air Quality, North Dakota Department of Health	1200 Missouri Avenue, Rm 304 P.O. Box 5520 Bismarck, ND 58506-5520 www.health.state.nd.us/ndhd/environ/ee/rad/rad.htm	(701) 328-5188
SD	Drinking Water	Department of Environment & Natural Resources: Drinking Water Program	www.state.sd.us/denr/des/drinking/dwprg.htm	(605) 773-3754
	UIC	U.S. EPA Region 8	www.epa.gov/Region8/water/uic	(303) 312-6125
	Radiation	Office of Health Care Facilities, Licensure & Certification, Systems Development and Regulations	615 East 4th Street Pierre, SD 57501-1700	(605) 773-3356
UT	Drinking Water	Department of Environmental Quality: Division of Drinking Water	www.drinkingwater.utah.gov	(801) 536-4200
	UIC	Department of Environmental Quality	waterquality.utah.gov	(801) 538-6023

	Radiation	Division of Radiation Control, Department of Environmental Quality	168 North 1950 West P.O. Box 144850 Salt Lake City, UT 84114-4850 www.eq.state.ut.us/EQRAD/drc_hmpg.htm	(801) 536-4250
WY	Drinking Water	U.S. EPA Region 8: Wyoming Drinking Water Program	www.epa.gov/region08/water/dwhome/wycon/wycon.html	(307) 777-7781
	UIC	Department of Environmental Quality	deq.state.wy.us/wqd/index.asp?pageid=56	(307) 777-7095
	Radiation	Solid & Hazardous Waste Division, Department of Environmental Quality	Herschler Building, 4E Cheyenne, WY 82002 deq.state.wy.us/shwd	(307) 777-7753

U.S. EPA REGION 9				
Drinking Water		Water Division	www.epa.gov/region09/water	(415) 947-8707
UIC		Water Division	www.epa.gov/region09/water	(415) 947-8707
Radiation		Radiation Protection Program	www.epa.gov/region09/air/radiation	(415) 947-4197
AS	Drinking Water	Environmental Protection Agency: American Samoa	www.epa.gov/Region9/cross_pr/islands/samoa.html	(415) 972-3767
	UIC	U.S. EPA Region 9	www.epa.gov/region09/water/groundwater/uic.html	(415) 972-3767
	Radiation	N/A		
AZ	Drinking Water	Department of Environmental Quality: Drinking Water Monitoring & Assessment Section	www.adeq.state.az.us/environ/water/dw	(602) 771-2303
	UIC	U.S. EPA Region 9	www.epa.gov/region09/water/groundwater/uic.html	(415) 972-3767
	Radiation	Arizona Radiation Regulatory Agency	4814 South 40th Street Phoenix, AZ 85040 www.arra.state.az.us	(602) 255-4845
CA	Drinking Water	Department of Health Services: Division of Drinking Water & Environmental Management	www.dhs.ca.gov	(916) 449-5577

	UIC	U.S. EPA Region 9	www.epa.gov/region09/water/groundwater/uic.html	(415) 972-3767
	Radiation	Radiologic Health Branch, Division of Food, Drugs, and Radiation Safety, California Department of Health Services	15 Capitol P.O. Box 997414, MS 7610 Sacramento, CA 95899-7414 www.dhs.ca.gov/RHB/default.htm	(916) 440-7899
GU	Drinking Water	Guam Environmental Protection Agency	www.epa.gov/region09/cross_pr/islands/guam.html	(671) 972-3770
	UIC	U.S. EPA Region 9	www.epa.gov/region09/water/groundwater/uic.html	(415) 972-3767
	Radiation	N/A		
HI	Drinking Water	Department of Health: Environmental Management Division	www.hawaii.gov/health/eh/sdwb	(808) 586-4258
	UIC	U.S. EPA Region 9	www.epa.gov/region09/water/groundwater/uic.html	(415) 972-3767
	Radiation	Noise, Radiation & IAQ Branch, Department of Health	591 Ala Moana Boulevard Honolulu, HI 96813-4921 www.hawaii.gov/health/environmental/noise/index.html	(808) 586-4700
NV	Drinking Water	Department of Human Resources: Bureau of Health Protection Services	health2k.state.nv.us/bhps/phe/sdwp.htm	(775) 687-6615
	UIC	Department of Environmental Protection	ndep.state.nv.us/bwpc/uic01.htm	(775) 687-4670
	Radiation	Radiological Health Program, Bureau of Health Protection Services, Nevada State Health Division	1179 Fairview Drive, Suite 102 Carson City, NV 89701-5405 health2k.state.nv.us/BHPS/rhs	(775) 687-5394

U.S. EPA REGION 10			
Drinking Water	Drinking Water Unit	yosemite.epa.gov/R10/WATER.NSF/Drinking+Water/About+DWU	(206) 553-8515
UIC	Underground Injection Control Program	yosemite.epa.gov/R10/WATER.NSF/UIC/UIC+Program	(206) 553-1673
Radiation	Radiation Program	yosemite.epa.gov/R10/Airpage.nsf/webpage/Radiation	(206) 553-7660

AK	Drinking Water	Department of Environmental Conservation: Drinking Water & Wastewater Program	www.state.ak.us/dec/eh/dw	(907) 269-7647
	UIC	U.S. EPA Region 10 Ground Water Protection Unit	www.epa.gov/region10	(206) 553-1900
	Radiation	Radiological Health Program, Section of Laboratories, State of Alaska/DH&SS	4500 Boniface Parkway Anchorage, AK 99507-1270 www.hss.state.ak.us/dph/labs/radiological/radiological_health.htm	(907) 334-2107
ID	Drinking Water	Department of Environmental Quality: Water Quality Division	www.deq.state.id.us/water/prog_issues.cfm	(208) 373-0502
	UIC	Department of Water Resources	www.idwr.state.id.us	(208) 327-7956
	Radiation	Department of Environmental Quality	900 N. Skyline, Suite C Idaho Falls, ID 83402 www.deq.state.id.us	(208) 528-2617
OR	Drinking Water	Department of Human Resources: Drinking Water Program	www.ohd.hr.state.or.us/dwp	(503) 731-4317
	UIC	Department of Environmental Quality	www.deq.state.or.us/wq/groundwa/uichome.htm	(503) 229-5945
	Radiation	Radiation Protection Services, Oregon Health Services, Department of Human Services	800 NE Oregon Street, Suite 260 Portland, OR 97232-2162 www.ohd.hr.state.or.us/rps	(503) 731-4014
WA	Drinking Water	Department of Health: Drinking Water Division	www.doh.wa.gov/ehp/dw	(360) 236-3100
	UIC	Department of Ecology	www.ecy.wa.gov/programs/wq/grndwtr/uic	(360) 407-6143
	Radiation	Office of Radiation Protection, Division of Environmental Health, Department of Health	7171 Cleanwater Lane, Bldg #5 P.O. Box 47827 Olympia, WA 98504-7827 www.doh.wa.gov/ehp/rp	(360) 236-3210

Table D-2: Tribal Drinking Water Contacts

U.S. EPA Headquarters		
American Indian Environmental Office	www.epa.gov/indian	(202) 564-0303

U.S. EPA Regional Tribal Capacity Development Coordinators		
U.S. EPA Region 1	www.epa.gov/region01/topics/government/tribal.html	(888) 372-7341
U.S. EPA Region 2	www.epa.gov/region02/nations	(212) 637-3600
U.S. EPA Region 4	www.epa.gov/region04/ead/indian	(404) 562-6939
U.S. EPA Region 5	www.epa.gov/region5/water/stpb	(312) 353-2123
U.S. EPA Region 6	www.epa.gov/region06/6xa/tribal.htm	(800) 887-6063
U.S. EPA Region 7	www.epa.gov/region07/government_tribal	(913) 551-7030
U.S. EPA Region 8	www.epa.gov/region08/tribes	(303) 312-6116
U.S. EPA Region 9	www.epa.gov/region09/cross_pr/indian	(415) 744-1500
U.S. EPA Region 10	yosemite.epa.gov/r10/tribal.NSF	(206) 553-4011

Other Contacts		
Administration for Native Americans	www.acf.dhhs.gov/programs/ana	(877) 922-9262
Bureau of Indian Affairs	www.doi.gov/bureau-indian-affairs.html	(202) 208-3710
Indian Health Service	www.ihs.gov	(301) 443-3024
Native American Water Association	www.nawainc.org	(775) 782-6636

Table D-3: Tribal UIC Contacts

Office	Web site	Phone
Tribal Contacts		
Arizona - Class V Wells (U.S. EPA Region 9)	http://www.epa.gov/region09/water/underground/notes	(415) 972-3544
California (U.S. EPA Region 9)	http://www.epa.gov/region09/water/underground/notes	(415) 972-3544
Michigan, Mille Lacs, Department of Natural Resources and Environment	http://www.millelacsojibwe.org	(320) 532-7721
Navajo (U.S. EPA Region 9)	http://www.epa.gov/region09/water/underground/notes	(505) 599-6317
Osage (U.S. EPA Region 6)	http://www.epa.gov/region6/water/swp/uic	(918) 287-4041

Table D-4: Regional NRC Contacts for Non-Agreement States

Region	Address	Web site	Phone
NRC Region I			
Connecticut, Delaware, New Jersey, Pennsylvania, Vermont, Washington, D.C.	475 Allentown Road King of Prussia, PA 19406-1415	www.nrc.gov/who-we-are/organization/rifuncdesc.html	(610) 337-5000; 1-800-432-1156
NRC Region II			
Virginia, West Virginia, Puerto Rico, Virgin Islands	Sam Nunn Atlanta Federal Center 61 Forsyth Street, Suite 23T85 Atlanta, GA 30303-8931	www.nrc.gov/who-we-are/organization/riifuncdesc.html	(404)-562-4400; 1-800-577-8510
NRC Region III			
Indiana, Michigan, Minnesota, Missouri	2443 Warrenville Road, Suite 210 Lisle, IL 60532-4352	www.nrc.gov/who-we-are/organization/riiifuncdesc.html#funcdesc	(630) 829-9500; 1-800-522-3025
NRC Region IV			
Alaska, Guam, Hawaii, Montana, Idaho, South Dakota, Wyoming	611 Ryan Plaza Drive, Suite 400 Arlington, TX 76011-4005	www.nrc.gov/who-we-are/organization/rivfuncdesc.html	(817) 860-8100; 1-800-952-9677

Appendix E: Radionuclide Levels at Selected Water Treatment Plants

A variety of studies between 1982 and 1995 found that commonly used filtering methods and media for radionuclides at water treatment plants may concentrate uranium and radium at highly different levels of radioactivity. Depending on the radiation level of the water to be treated, as well as the treatment process, residuals and filters can accumulate radionuclides in the range of less than 10 pCi/g or per liter, to thousands of pCi/g or per liter. The method chosen for filtering water may have a significant impact on the radiation protection program that may need to be instituted at the treatment facility and available waste disposal options. Table E-1 summarizes the ranges of radium and uranium concentrations found nationwide in different filter media and backwash. Additional findings from water treatment plants follow in Tables E-2 to E-7.

Table E-1: Summary of Treatment Technologies for Removal of Naturally Occurring Radionuclides in Water[56]

Treatment Technology	Contaminant Removed	Removal Efficiency	Wastes Produced	Waste Concentrations
Cation exchange	Radium	85-97%	Rinse & backwash water Regenerant brine	8 to 94 pCi/L-Ra[1] 50 to 3,500 pCi/L-Ra[1] 22 to 94 pCi/L[2]
Anion exchange	Uranium	95%	Rinse & backwash water Brine regenerant solution	2 to 6e+06 pCi/L[1]-U 35 to 4.5e+06 pCi/L[1]-U 1.3 to 11 pCi/L
Lime softening	Radium Uranium	90% 85-90%[3]	Sludge (at clarifier Sludge (dry) Filter backwash	76 to 4,577 pCi/L-Ra 1 to 21.6 pCi/g-Ra 1 to 10 pCi/g-U 6.3 to 21.9 pCi/L-Ra
Reverse osmosis	Radium Uranium	90+% ---	Reject water	7 to 43 pCi/L-Ra 200 to 750 pCi/L-U
Electrodialysis	Radium Uranium	90% ---	Reject water	No data
Iron removal -Oxidation -Greensand	Radium	0 to 70%[4]	Solids & supernatant from filtration backwash Green sand Media	12 to 1,980 pCi/L-Ra 28 to 250 pCi/g-Ra
Selective sorbents	Radium Uranium	90+%	Selective sorbents (radium selective and activated alumina)	up to 3.6 pCi/g-Ra
Coagulation/ Filtration	Uranium	50 to 85%	Sludge	10,000 to 30,000 pCi/L-U

[1] Peak values

[2] Average for given waste forms

[3] May be increased to 99% by the presence or addition of magnesium carbonate to the water

[4] May be increased to 90% by passing the water through a detention tank after the addition of potassium permanganate prior to filtration

---

[56] Data extracted from U.S. EPA 1982, 1986, 1994b, 1995; Wade Miller Associates 1991; and Reid 1985.

Table E-2: Radium-226 Concentrations in Ion Exchange Treatment Plant Wastes[57]

Location (Ra-226 in raw water)	Average Ra-226 Concentration (pCi/L)			Peak Ra-226 Concentration in Wastes (pCi/L)
	Brine + Rinse	*Brine + Rinse + Backwash*	*Peak 1/4-1/3 of Regeneration Cycle*	
Eldon, IA (46 pCi/L)	530	420	2,000	3,500
Estherville, IA (5 pCi/L)	N/A	52	114	320
Grinnell, IA (6 pCi/L)	110	N/A	260	320
Holstein, IA (13 pCi/L)	175	N/A	576	1,100
Quail Creek, TX (7.3 pCi/L)	NA	93	190	200

Table E-3: Uranium Removal with Anion Exchange[58]

Location	Concentration of Uranium (μg/L)		Gallons Treated	Bed Capacity (lbs U/ft^3)
	Raw Water	*Treated Water*[1]		
Cove, AZ	64	63	31,400	0.017
Fort Lupton, CO	35	35	22,310	0.007
Brighton, CO	23	23	45,460	0.009
Marshdale, CO	28	<0.1	40,610	[2]
Church Rock, NM	52	0.1	20,360	[2]

[1] Uranium concentration of treated water measured after indicated number of gallons treated

[2] Bed capacity not exhausted

---

[57] Schliekelman, R., 1976; U.S. EPA, 1992.

[58] Lassovszky, P. and Hathaway, S., 1983.

Table E-4: Radium Removal with Reverse Osmosis – Sarasota, FL[59]

System (capacity – Kgpd)	Raw Water TDS (mg/L)	Ra-226 (pCi/L)			Ra-226 Removal Efficiency	Percent Recovery
		Raw Water	***Treated Water***	***Reject Water***		
Bay Lakes Estates MHP (40)	2,532	3.2	0.1	--	97%	--
Venice (1,000)	2,412	3.4	0.3	7.8	91%	64%
Sorrento Shores (200)	3,373	4.6	0.2	7.9	96%	39%
Spanish Lakes MHP (70)	1,327	10.4	1.2	20.5	88%	31%
Nokomis School (0.8)	1,442	11.1	0.5	11.9	95%	--
Bayfront TP (1.6)	895	12.1	0.6	19.4	95%	28%
Kings Gate TP (30)	1,620	15.7	2.0	--	87%	--
Sarasota Bay MHP (5)	2,430	20.5	0.3	37.9	98%	50%
AVERAGE					*93%*	

Table E-5: Radium Concentrations in Lime Softening Sludges and Backwash Waters[60]

Location and Type of Sludge (Ra in raw water)	Percent Solids	Wet Basis (pCi/L)		Dry Basis (pCi/g)	
		Ra-226	***Ra-228***	***Ra-226***	***Ra-228***
West Des Moines, IA (9.3 pCi/L)					
Lagoon Sludge	37.6%	5,159	596	10.8	1.3
Clarifier Sludge	1.6%	< 20	< 40	< 0.02	< 0.04
Lagoon Sludge	N/A	2,300	N/A	N/A	N/A
Backwash Water	N/A	6.3	N/A	N/A	N/A
Bushnell, IL					
Clarifier Sludge	19%	4,577	< 45	21.6	< 0.21

---

[59] Sorg, T., 1980.

[60] Snoeyink, V., et al, 1984.

Table E-5, Continued

Location and Type of Sludge (Ra in raw water)	Percent Solids	Wet Basis (pCi/L)		Dry Basis (pCi/g)	
		Ra-226	***Ra-228***	***Ra-226***	***Ra-228***
Clarifier Sludge	12.6%	2,038	236	15.0	1.7
Backwash Water	0.23%	< 20	< 39	N/A	N/A
Webster City, IA (6.1 pCi/L)					
Sludge	N/A	980	N/A	N/A	N/A
Backwash	N/A	50	N/A	N/A	N/A
Peru, IL (5.8 pCi/L)					
Backwash Water	N/A	36.9	N/A	N/A	N/A
Elgin, IL (5.6 pCi/L)					
Lagoon Sludge	57.3%	9,642	9,939	11.3	11.7
Clarifier Sludge	10.3%	948	873	8.6	8.0
Backwash Water	0.05%	< 20	< 40	< 0.02	< 0.04
Sludge	NA	18.3	N/A	N/A	N/A

Table E-6: Concentration of Radionuclides in the Spent Filter Backwash from Green Sand Filtration and Other Iron/Manganese Filtration Processes[61]

Plant	Raw Water			Spent Filter Backwash Water		
	Ra-226 (pCi/L)	Ra-228 (pCi/L)	Uranium (pCi/L)	Ra-226 (pCi/L)	Ra-228 (pCi/L)	Uranium (pCi/L)
Sandstone [1]	9.2	5.2	0.13	40.6	27.4	1.1
Hinckley [2]	7.6	4.5	0.14	270	304	2.3
Madelia [3]	2.1	3.9	< 0.14	108	170	< 0.20
Inver Grove Heights [1]	5.3	1.1	0.62	145	5.9	0.31
Savage [2]	7.5	8.1	0.4	69.9	54.4	0.98

[1] Treatment scheme consists of chlorination, potassium permanganate, and anthracite/sand filter

[2] Treatment scheme consists of aeration, chlorination, potassium permanganate, and anthracite/green sand filter

[3] Treatment scheme consists of aeration, chlorination, detention, potassium permanganate, and anthracite/sand filter

---

[61] Peterson, K. 1999.

Table E-7: Concentration of Radionuclides on Water Treatment Process Media and Materials[62]

Location	Treatment Process	Process Media/Material	Radionuclide Concentration (pCi/g)	
			Ra-226	**Ra-228**
Herscher, IL	Iron removal	Filter media	111.6	38.9
Dwight Correctional Institute, IL	Natural green sand	Green sand	29-46	
Peru, IL	Lime softening	Filter media	4.6	3.6
Elgin, IL	Lime softening	Filter media	16.0	8.3
Elkhorn, WI	Iron removal	Filter media (sand)	1.47	0.48

---

[62] Bennett, D.L., 1978; Brink, W.L., et al, 1978.

Appendix F: Thorium and Uranium Decay Series

Figure F-1: Thorium Decay Series

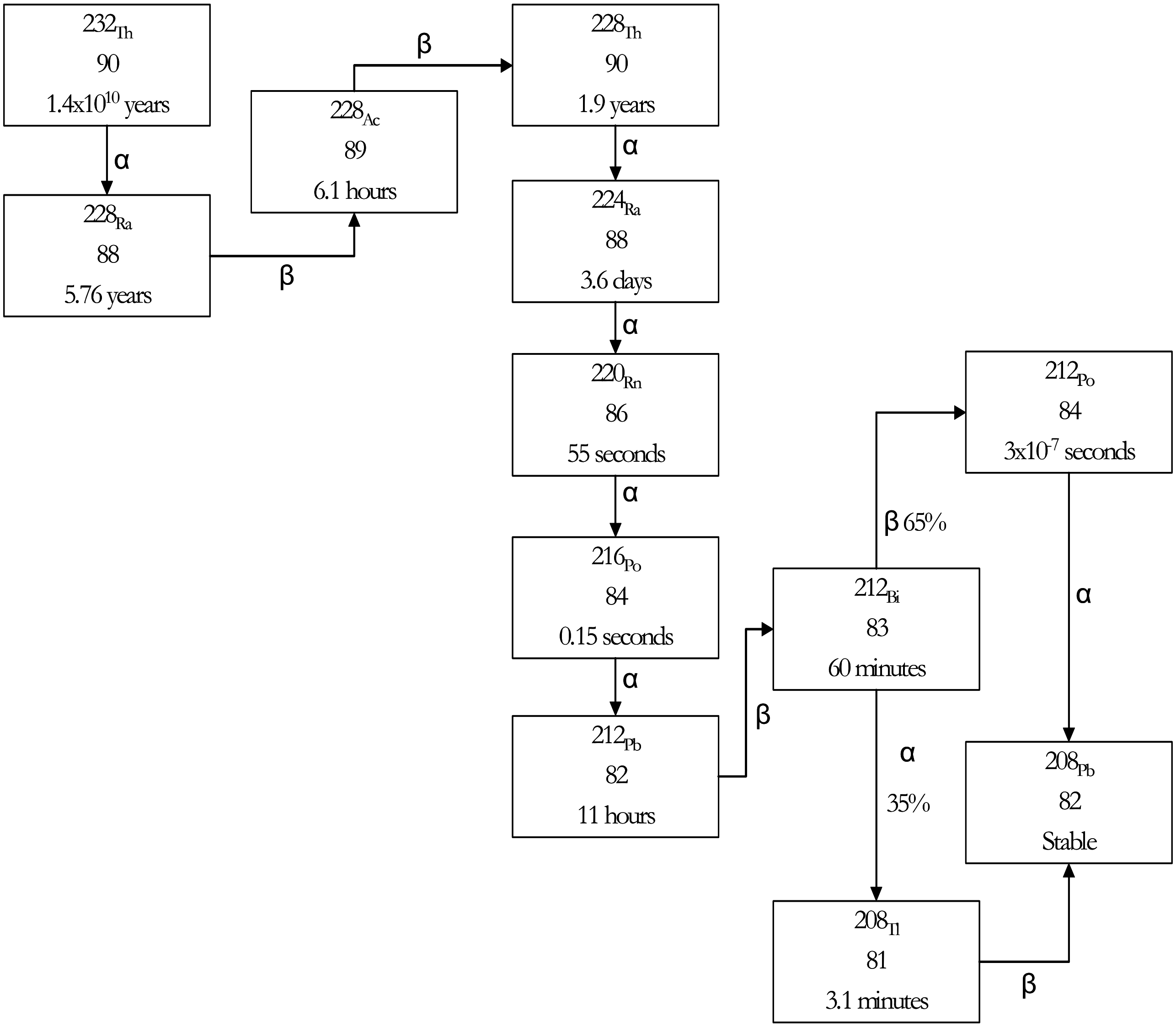
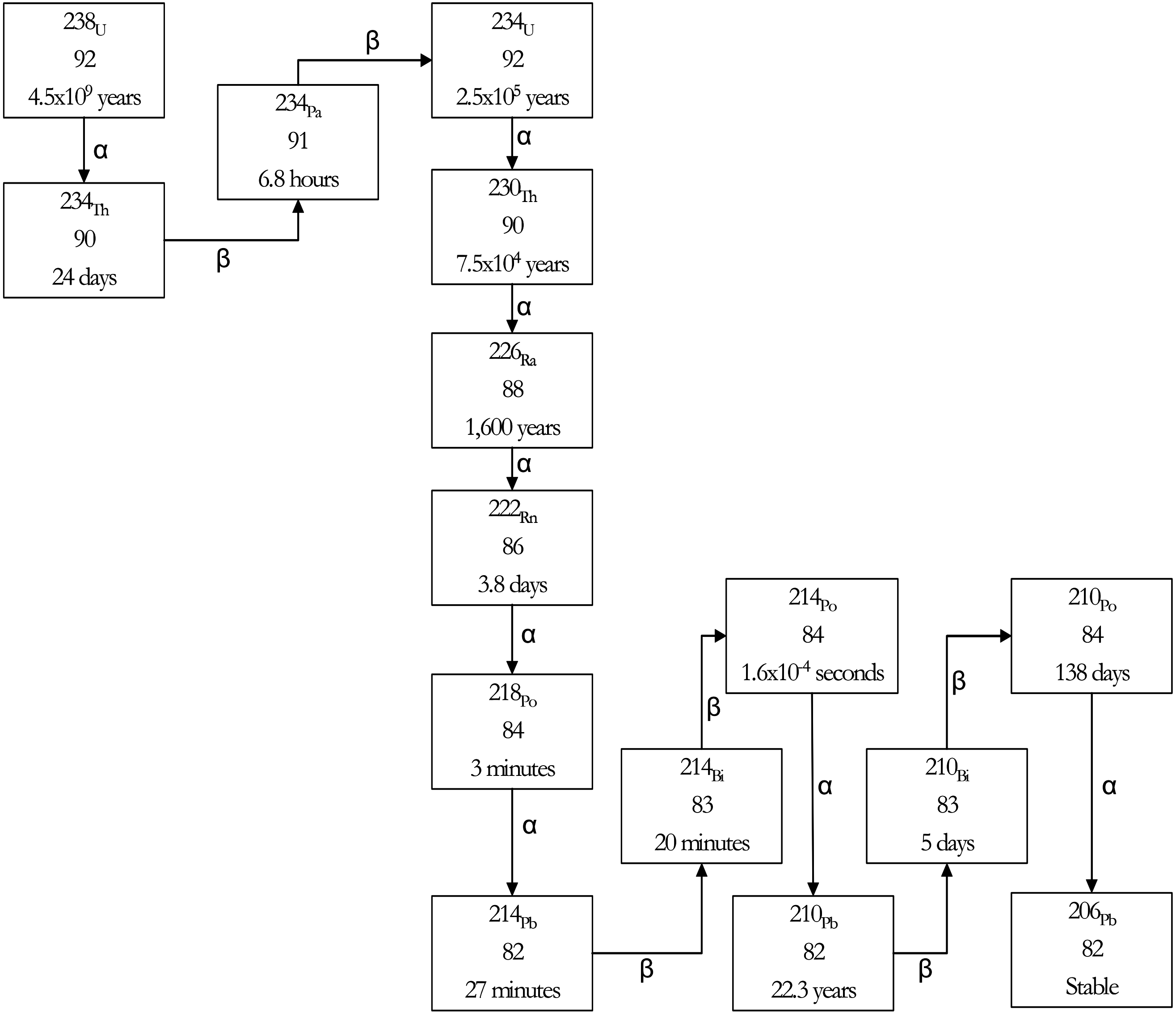


Figure F-2: Uranium Decay Series



Appendix G: Additional Reference Materials

The following resources provide more information on the Radionuclides Rule, and the treatment, handling, and disposal of radionuclides:

Documents

Evaluation of EPA's Guidelines for Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM), Report to Congress, EPA 402-R-00-01, June 2000
(http://www.epa.gov/radiation/docs/tenorm/402-r-00-001.pdf

Evaluation of Guidelines for Exposures to Technologically Enhanced Naturally Occurring Radioactive Materials, Committee on Evaluation of EPA Guidelines for Exposure to Naturally Occurring Radioactive Materials, National Academy of Sciences, 1999
(http://www.nap.edu/books/0309062977/html/index.html)

Final Report: ISCORS Assessment of Radioactivity in Sewage Sludge: Radiological Survey Results and Analysis, NUREG-1775, EPA 832-R-03-002/DOE/EH-0669, November 2003
(http://www.iscors.org/FinalSurvey.pdf)

Implementation Guidance for Radionuclides, EPA 816-F-00-002, March 2002
(http://www.epa.gov/safewater/rads/final_rads_implementation_guidance.pdf)

Radioactive Material Regulations Overview, U.S. Department of Transportation, Research and Special Programs Administration
(http://hazmat.dot.gov/pubtrain/ramreview.pdf)

Radionuclides Rule (Final), Federal Register, Vol. 65, No. 36, December 7, 2000
(http://www.epa.gov/safewater/rads/radfr.pdf)

Radionuclides Rule: A Quick Reference Guide, EPA 816-F-01-003, June 2001
(http://www.epa.gov/safewater/radionuclides/pdfs/qrg_radionuclides.pdf)

Radionuclides in Drinking Water: A Small Entity Compliance Guide, EPA 815-R-02-001, February 2002
(http://www.epa.gov/safewater/rads/pdfs/rads-smallsyscompguide.pdf)

Radionuclides Notice of Data Availability, Technical Support Document, EPA, March 2000
(http://www.epa.gov/safewater/rads/tsd.pdf)

RCRA Orientation Manual, EPA 530-R-02-016, January 2003
(http://www.epa.gov/epaoswer/general/orientat/r02016.pdf)

Web sites

Conference of Radiation Control Program Directors, Inc. - http://www.crcpd.org

U.S. EPA Office of Air and Radiation:
Radiation Protection - http://www.epa.gov/radiation/index.html
Managing Radioactive Materials and Waste - http://www.epa.gov/radiation/tenorm/index.html

TENORM - http://www.epa.gov/radiation/tenorm/index.html

U.S. EPA Office of Ground Water and Drinking Water
Radionuclides in Drinking Water - http://www.epa.gov/safewater/radionuc.html
Underground Injection Control Program - http://www.epa.gov/safewater/uic.html

U.S. EPA Office of Solid Waste and Emergency Response
Hazardous Waste Identification - http://www.epa.gov/epaoswer/hazwaste/id/index.htm
Key Radiation Guidances and Reports - http://www.epa.gov/oerrpage/superfund/resources/radiation/index.htm
Non-Hazardous Waste (RCRA Subtitle D) - http://www.epa.gov/osw/
Paint Filter Liquids Test - http://www.epa.gov/epaoswer/hazwaste/test/pdfs/9095a.pdf

U.S. EPA Office of Wastewater Management
NPDES - http://cfpub.epa.gov/npdes/

The TENORM Page - http://www.tenorm.com/

Exhibit 7

The Science of the Total Environment, 31 (1983) 219—241
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

ESTIMATED DOSE TO MAN FROM URANIUM MILLING VIA THE BEEF/MILK FOOD-CHAIN PATHWAY*

DONALD R. RAYNO

*Division of Environmental Impact Studies, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439 (U.S.A.)***

(Received February 24th, 1983; accepted April 7th, 1983)

ABSTRACT

One of the major pathways of radiological exposure to man from uranium milling operations is through the beef/milk food chain. Studies by various investigators have shown the extent of uptake and distribution of ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb, and ^{210}Po in plants and cattle. These long-lived natural radioisotopes, all nuclides of the uranium decay series, are found in concentrated amounts in uranium mill tailings. In this paper, data from these investigations are used to estimate the dose to man from consumption of beef and milk from cattle that have fed on forage contaminated with the tailings. The estimated doses from this technologically enhanced source are compared with those resulting from average dietary intake of these radionuclides from natural sources.

INTRODUCTION

Processing of uranium ore began in the United States during the early 1950s with the establishment of production mills by such companies as Anaconda and Climax [1]. U.S. production of radium from uranium-containing ore predates uranium milling by more than 35 years, the first radium-processing plant having been founded in 1914 at Denver [2]. The tailings piles produced by these operations are located throughout the country, but mostly in the Southwest.

Recent attention has been directed toward estimating the potential health hazards due to the presence of these exposed tailings, particularly hazards to human populations living in the vicinity of these piles. Among the many considerations has been the contamination of the beef/milk food chain

---

* Supported by the U.S. Department of Energy, Uranium Mill Tailings Remedial Action Project.

**Presently with the Nuclear Measurements and Analysis Division, Department of Nuclear Engineering, North Carolina State University.

0048-9697/83/$03.00

with the long-lived radionuclides of the uranium series: ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb, and ^{210}Po, all present in uranium tailings.

Several computer codes have been developed to make theoretical predictions of the dose received by man due to radionuclide transport from nuclear facilities. Some of these codes, including AIRDOS-EPA [3], FOOD [4], UDAD [5], and MILDOS [6], include models of food-chain contamination by uranium-series nuclides as at least part of their overall scheme. In addition, measurements have been made of the parameters that control man's exposure to radionuclides in the uranium decay chain via the beef/milk food-chain pathway, including uptake coefficients (soil to forage plant), transfer coefficient (forage to beef and milk), and conversion factors relating food ingestion by humans to internal dose.

In this report, data from various investigators are examined in an effort to estimate the dose to man from beef/milk food-chain transport of tailings radionuclides as shown in Fig. 1. Contamination of this food chain through groundwater, wild game, locally grown vegetables, livestock other than cattle, and direct ingestion of contaminated plants by humans has not been considered because of a lack of data.

The first step in the food-chain movement of tailings radionuclides is the uptake of these radioelements from tailings (or tailings-contaminated soil) to forage plants. The most recent U.S. Environmental Protection Agency (EPA) standards state that the ^{226}Ra concentration in surface soil (top 15 cm) at abandoned uranium mill sites should not exceed 5 pCi/g* subsequent to remedial action, such as burial [7]. The Department of Energy (DOE) currently is outlining cleanup operations with the intent of performing remedial action on many of the inactive uranium mill tailings sites in the United States within the next several years. The 5-pCi/g post-remedial concentration proposed by the EPA therefore has been used in this paper to estimate the amount of radionuclide activity taken up by forage vegetation at such sites. In this report, equilibrium with ^{226}Ra is assumed for ^{230}Th, ^{210}Pb and ^{210}Po.

Tracking the transport of radionuclides from tailings to forage plants, and subsequently to cattle and human beings, is complicated by the fact that there are two modes of vegetation contamination: (1) root uptake of radionuclides from tailings, or from soil contaminated with tailings, and (2) foliar deposition and subsequent foliar absorption of airborne radionuclides from tailings, ore, yellowcake, or particulates containing radon decay products. However, data characterizing the extent of foliar deposition of these materials are lacking, since plants are generally washed prior to radiochemical analysis. Thus, the concentrations of radionuclides in forage reported in this paper are reflective only of root uptake and any foliar absorption that may take place. The potential for food-chain contamination via this dusting effect, however, indicates the need for further study.

---

* pCi/g = picocuries per gram. 1 curie = 3.7×10^{10} Bequerels.

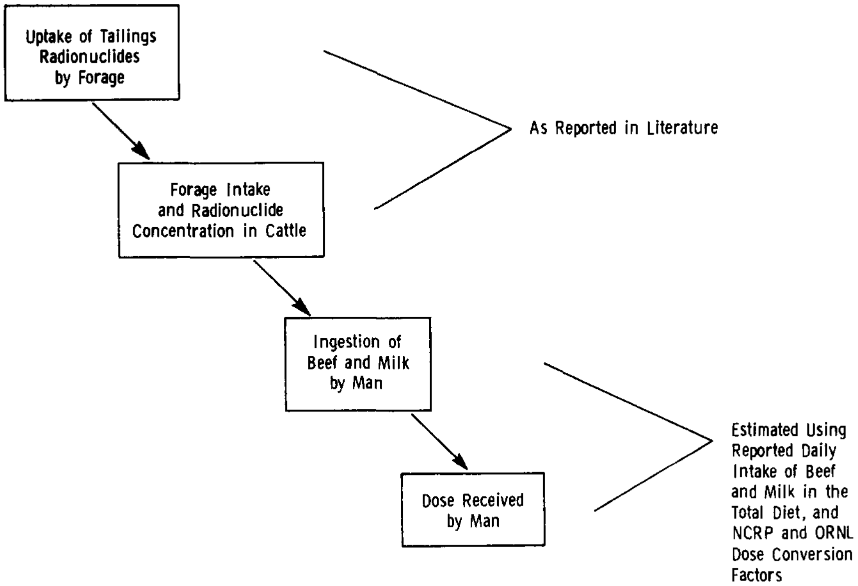


Fig. 1. Meat/milk food-chain exposure to man.

Following the accumulation of tailings radionuclides in forage, some plants may be consumed by grazing cattle. It has been conservatively assumed in this report that cattle graze throughout the year; however, it is recognized that the grassland ranges in the Southwest sometimes are not available for grazing during the winter or during severe drought. Only a small amount of data characterizing the transfer of uranium-series radionuclides from ingested forage to cattle muscle (beef) and milk has been reported. These data (transfer coefficients) were used to estimate the activity concentrations of tailings radioisotopes in beef and milk as a result of their transfer via the tailings—forage—cattle pathway.

Human intake of these contaminated foodstuffs was converted into estimated dose rates to bone and soft tissue using both National Council on Radiation Protection and Measurements (NCRP) [8] and Oak Ridge National Laboratory (ORNL) [9] dose conversion factors. Because of the wide variation in the reported values of beef/milk food-chain transfer parameters (Table 1), minimum and maximum estimates of dose, based on the lowest and highest set of transfer parameters available from the literature, are given for each radionuclide (Table 2). Presented for comparison in Table 2 are estimates of the dose to man from (1) the transport of uranium mill tailings radionuclides through the beef/milk food chain, and (2) normal dietary intake of these same radionuclides in the average diet, using values of radioisotope consumption reported in the literature. (The composition of a "normal" diet is often specific for a given geographic location. Dietary habits can also vary widely from individual to individual. The ranges of average rates of ingestion of uranium-series radionuclides in the United States (as reported in the literature) were used as the average "normal" dietary intake for this report.)

TABLE 1

REPORTED FOOD-CHAIN TRANSFER FACTORS FOR URANIUM-SERIES NUCLIDES: TAILINGS—FORAGE—CATTLE—MAN PATHWAY

Isotope	Plant uptake coefficient[a]				Transfer coefficient[b]			
	Minimum estimate	Reference[c]	Maximum estimate	Reference	Minimum estimate	Reference	Maximum estimate	Reference
$^{238}U/^{234}U$	10^{-5}	[10]	0.2	[11]	1.4×10^{-4} (milk)	[12, 13]	6.1×10^{-4} (milk) 3.4×10^{-4} (beef)	[5, 14] [5, 14]
^{230}Th	10^{-4} [d]	[15]	0.1	[16]			5.0×10^{-6} (milk) 2.0×10^{-4} (beef)	[17] [5, 14]
^{226}Ra	0.002	[18]	6.5	[19]	4.0×10^{-4} (milk) 5.1×10^{-4} (beef)	[20] [21, 21]	5.9×10^{-4} (milk) 4.0×10^{-3} (beef)	[21] [5]
^{210}Pb	0.08	[16]	2.8	[19]	2.6×10^{-6} (milk) 2.9×10^{-4} (beef)	[5] [5]	1.2×10^{-4} (milk) 1.0×10^{-3} (beef)	[20—22] [20]
^{210}Po	0.03	[23]	0.2	[23]	8.9×10^{-5} (milk) 1.2×10^{-2} (beef)	[24—26] [5]	2.9×10^{-4} (milk) 5.0×10^{-2} (meat)[e]	[24, 26, 27] [28]

[a] (pCi/g dry forage)/(pCi/g dry soil).

[b] Day/l for milk and day/kg for beef.

[c] References are listed at the end of this report.

[d] Reported for ^{232}Th.

[e] Reported for reindeer meat.

The estimates of the doses to man have been made in as conservative a manner as possible with the available data. Particularly conservative assumptions used in making these dose estimates are that (1) the cattle continually graze on rangeland contaminated with tailings and (2) all beef in the diet of a person living in the vicinity of a tailings pile would come from these cattle. However, only beef and milk have been examined as foods, and, as discussed above, any possible contamination from accumulated foliar dust has not been included in the dose estimates.

URANIUM-238/URANIUM-234

Uptake by forage plants from soil and tailings. Estimates of average uranium content in soil range from 1×10^{-4} to 3×10^{-4}% by weight (0.7 to 2.1 pCi/g) [39—41]. Some of this uranium is assimilated into vegetation, probably as the UO_2^{2+} ion [42], and measurements have been made of the concentration of this radionuclide in plants growing on "natural" soils [43, 44]. According to Laul et al. [44], the uranium content of various garden vegetables rooted in soil that contained about 2 pCi/g of uranium activity ranged from 5.6×10^{-4} to $<7.0 \times 10^{-4}$ pCi/g.

Much attention has been given to uranium uptake by vegetation growing in uranium-rich locations. Plants exhibiting a high uptake of uranium have been used as uranium indicators in botanical prospecting [45—49], and the assimilation of uranium by vegetation growing in the vicinity of coal mines, phosphate mills, copper ore beds, the Russian taiga region, and nuclear test sites has been studied [50—59].

The absorption of uranium isotopes into edible vegetation has also been examined using soils spiked with known amounts of radioactivity [60—63]. These studies indicate that the uptake coefficient, the ratio of radionuclide activity in the plant to that in root-zone soil, is dependent on several variables, including the plant species and the fraction of soil uranium available for root uptake (not ionically bound). (In the literature, this ratio is also referred to variously as the concentration factor (ratio), uptake factor, bioaccumulation factor, and observed concentration ratio. Unless otherwise specified, uptake coefficients are reported for dry plants and soil.) The greatest concentrations of uranium in plants tend to be in the roots.

Several studies have focused on the uptake of uranium by forage plants growing on or near uranium mine spoils or mill tailings. (^{238}U and ^{234}U are found in lower abundance in the tailings than are their long-lived daughter products [^{230}Th, ^{226}Ra, ^{210}Pb, and ^{210}Po] since the mill extraction processes remove 91—93% of the uranium in the ore [64].) The uptake coefficients for aboveground plant tissue obtained from these studies vary widely. Moffett and Tellier [65], Morishima et al. [10], and Dreesen and Marple [66] report estimated uptake coefficients ranging from 10^{-5} to 10^{-3}, while Rayno et al. [16] and Winsor and Whicker [11] report higher values, ranging from 0.01 to 0.2; Winsor and Whicker also report an average

TABLE 2

ESTIMATED DOSE RATES TO MAN FROM INGESTION OF URANIUM-SERIES RADIONUCLIDES

Isotope	Dose rate from food-chain transport of tailings radionuclides[a] (mrem/y)		Dose rate from normal dietary intake[b] (mrem/y)	
	Minimum estimate	Maximum estimate	Minimum estimate	Maximum estimate
^{238}U/^{234}U				
Bone[c]				
NCRP[e]	6×10^{-4}	90	20	30
ORNL[f]	2×10^{-4}	30	8	11
Soft tissue[d]				
NCRP	4×10^{-5}	6	1	2
ORNL	3×10^{-5}	5	1	2
^{230}Th[g]				
Bone				
ORNL	1×10^{-3}	1		0.2
Soft tissue				
ORNL	1×10^{-4}	1×10^{-2}		3×10^{-2}
^{226}Ra[h]				
Bone				
NCRP	0.6	8×10^{3}	8	30
ORNL	0.9	1×10^{4}	10	40
Soft tissue				
NCRP	8×10^{-3}	90	0.1	0.3
ORNL	1×10^{-2}	1×10^{2}	0.2	0.5
^{210}Pb[i]				
Bone				
Holtzman	0.3	50		1
ORNL	0.4	5×10^{2}		10
Soft tissue				
Holtzman	4×10^{-3}	5		0.1
ORNL	6×10^{-3}	7		0.2
^{210}Po[j]				
Bone				
NCRP	2×10^{2}	7×10^{3}	50	60
ORNL	1	30	0.2	0.3
Soft tissue				
NCRP	20	7×10^{2}	5	6
ORNL	1	30	0.2	0.3
Total dose rate from U-series ingestion				
Bone				
NCRP, Holtzman	200	1.5×10^{4}	80	120
ORNL	2.3	1.1×10^{4}	18	62
Soft tissue				
NCRP, Holtzman	20	800	6.1	8.4
ORNL	1.0	140	1.4	3.0

coefficient of 3.3 for phlox, but this seems exceptionally high. (All uptake coefficients are for dry plant matter, except that from Morishima et al. [10].) As reported by Whicker [19], a number of parameters affect radionuclide assimilation by vegetation, including climate, soil type, plant structure, and experimental conditions. The effects of one or more of these parameters thus may be responsible for the extreme variation of uranium uptake coefficients reported by various investigators.

In their study of the effects of soil containing elevated concentrations of uranium on the ecological system of the Los Alamos test sites, Hanson and Miera [67] suggest that resuspension of soil (by wind or rain spattering, for example) could be an important agent of radionuclide transfer to plants through foliar deposition and possible subsequent incorporation into the plant tissue. This is particularly true in the arid Southwest (where most of the uranium mines and mills are located) since drier soil would be more susceptible to wind erosion.

Concentration in cattle. Concentrations of ^{238}U and ^{234}U found in grazing livestock (sheep and cattle) have been reported in the literature [68, 69]. However, the actual transfer of these isotopes from forage to grazing animal has not been studied extensively. Data are particularly sparse for beef and dairy cattle, which are strategic links in the terrestrial food-chain exposure pathway. Some measurements and estimates have, however, been made. The transfer coefficients (pCi/l or pCi/kg in milk or meat per pCi/day intake by cattle) reported are low, with estimates ranging from 1.4×10^{-4} to 6.1×10^{-4} day/l for milk [5, 12—14]. The only value for beef found in the literature was 3.4×10^{-4} day/kg [5—14]. These values are based on an assumed equilibrium of radionuclide intake and excretion.

---

[a] Calculated using transfer factors given in Table 1, 18.1 kg/day dry forage intake by cattle, food ingestion rates of 0.5 l/day (milk) and 0.2 kg/day beef per person, and both the NCRP and ORNL dose equivalent rates as given in References [8, 9, 29]. Concentrations of radionuclides in soil following remedial action of tailings were assumed to be 0.7—2.1 pCi/g ($^{238}U/^{234}U$) and 5 pCi/g (^{230}Th, ^{226}Ra, ^{210}Pb, ^{210}Po), according to the proposed standards set by the EPA for cleanup [7].

[b] Average dietary intakes used to make these estimates were 0.7—1.0 pCi/day ($^{238}U/^{234}U$), 0.1 pCi/day (^{230}Th), 0.7—2.4 pCi/day (^{226}Ra), 1.3—1.6 pCi/day (^{210}Pb), and 1.3—1.6 pCi/day (^{210}Po) [8, 29—38].

[c] Specifically osteocytes.

[d] Represented by gonads.

[e] Dose equivalent rates from the National Council on Radiation Protection and Measurements [8] used.

[f] Dose equivalent rates from Oak Ridge National Laboratory [9] used.

[g] No NCRP rate available.

[h] Dose from ingested ^{226}Ra and ^{222}Rn and daughters (assuming 30% retention of Rn).

[i] Dose conversion factors given by Holtzman [29] are for ^{210}Pb only; those from ORNL [9] are for ^{210}Pb and ingrown ^{210}Po.

[j] Dose conversion factors given by the NCRP [8] are based on ^{210}Pb intake and retention (with subsequent ingrowth of ^{210}Po); those from ORNL reflect only intake of ^{210}Po.

Estimated dose to man: Tailings—forage—cattle—man pathway. Based on the U.S. EPA's recent recommendation that the average radium concentration of soil at a mill-tailings site after remedial action should not exceed 5 pCi/g for the top 15-cm depth [7], if the $^{238}U/^{234}U$ content of tailings is assumed to be 7% of that of ^{226}Ra [64], then the uranium activity concentration in the root soil after remedial action would be reduced to within the range of average background concentrations (0.7 to 2.1 pCi/g) [39—41]. This is based on an initial ^{226}Ra concentration in tailings of 280 pCi/g [70]. Using the lowest (10^{-5}) and highest (0.2) values of uptake coefficients for tailings forage reported above, this range of $^{238}U/^{234}U$ concentrations in soil would result in minimum and maximum concentrations of 7×10^{-6} and 0.4 pCi/g, respectively, in plants supported by that soil. This extreme range demonstrates the necessity for improved estimates of the uptake coefficient for uranium.

According to Comar [71], a cow consumes 8 to 20 kg/day of dry feed; while Heath et al. [72] report that a grazing dairy cow ingests an average of 11.3 to 18.1 kg/day of dry pasture forage. Based on an intake of 18.1 kg/day and the uranium concentration values for contaminated forage given above, the range of $^{238}U/^{234}U$ ingested by a cow feeding on this vegetation would be 0.1 to 8000 pCi/day. By applying the previously reported transfer coefficients for milk (minimum of 1.4×10^{-4} day/l, maximum of 6.1×10^{-4} day/l), one can calculate that these ingestion rates would result in estimated minimum and maximum $^{238}U/^{234}U$ concentrations in milk of 2×10^{-5} and 5 pCi/l, respectively. Similarly, the transfer coefficient for beef reported above (3.4×10^{-4} day/kg) would result in estimated minimum and maximum uranium concentrations of 4×10^{-5} and 3 pCi/kg, respectively, in meat. According to Fisenne and Keller [73], the human diet includes about 0.2 kg/day of meat and 0.5 l/day of milk; so on the basis of the above estimations, persons living in the vicinity of the mill and consuming these foodstuffs would ingest a minimum of 2×10^{-5} and a maximum of 3 pCi/day of $^{238}U/^{234}U$.

Intake of $^{238}U/^{234}U$ can be translated into an estimated dose to man by use of conversion factors supplied by the National Council on Radiation Protection and Measurements [8, 29] and Oak Ridge National Laboratory [9]. The NCRP conversion factors are based on a quality factor of 10 for alpha particles, and ORNL uses a quality factor of 20.

Based on the NCRP dose—equivalent rates of 12 mrem/y to bone (specifically osteocytes) and 0.8 mrem/y to soft tissue (represented by gonads) from an intake of 0.4 pCi/day of $^{238}U/^{234}U$ [8, 29], ingestion of 2×10^{-5} to 3 pCi/day of these isotopes (as a result of radionuclide transport through the beef/milk food chain from tailings subsequent to remedial action) can be translated into minimum and maximum estimated dose rates to man of 6×10^{-4} to 90 mrem/y bone and 4×10^{-5} to 6 mrem/y soft tissue. The dose rates to man can also be estimated using the ORNL dose conversion factors [9]. The estimates derived by use of both sets of conversion factors are represented in Table 2.

It should be noted that the large difference between the maximum and minimum dose-rate values is primarily a result of the marked variability in the reported uranium uptake coefficients for vegetation. This variability, as given in various literature references, is illustrated in Table 1.

Estimated dose to man: Normal dietary intake. The uranium content of various foodstuffs has been reported in the literature [34, 35, 38, 39, 74–77]. Dietary items with the highest uranium concentrations are tubers (e.g., potatoes and turnips), fruits and vegetables, shellfish, and certain cooking additives, such as salt, fat, and oil. Accoding to Hamilton [34] cereals and grains, tubers, fruits, and vegetables comprise 83% of the uranium intake through the human diet. Estimated normal dietary intake of uranium ranges from 1 to 1.4 μg/day (0.7 to 1.0 pCi/day) [34, 38]. Estimates of the dose to man from this daily intake of $^{238}U/^{234}U$ are given in Table 2.

THORIUM-230

Uptake by forage plants from soil and tailings. Less beef/milk food-chain transport data are available for ^{230}Th than for any of the long-lived uranium-series radionuclides. The background concentration of this isotope in soil ranges from 0.1 to 0.6 pCi/g [78]. Comar [79] and Russell [80] have stated that thorium is not readily assimilated by vegetation. Most investigations of the uptake of thorium into plants have focused on the most abundant isotope, ^{232}Th, as well as ^{228}Th, one of its daughters [15, 33, 53, 59, 81]. Bondietti and Sweeton [15] calculated vegetation uptake coefficients for ^{232}Th ranging from 1×10^{-4} to 7×10^{-3}.

A few investigators have examined the uptake of ^{230}Th by plants [16, 57, 82]. An uptake coefficient of 0.91 for ^{230}Th assimilation in kidney beans (*Phaseolus vulgaris*), as obtained by D'Souza and Mistry [82], demonstrates that aboveground vegetation can absorb thorium to a greater extent than indicated above. However, the beans were grown in a nutrient solution, and thus any effects of soil-binding on root uptake were excluded. According to Russell and Smith [83], soil-binding may be the primary factor inhibiting the movement of thorium into plants. The small amount of data available indicates that thorium can be absorbed by roots but is not mobile within the plant structure, and thus is not readily translocated to the aboveground biomass (shoots). Of special interest, however, are the only available data for ^{230}Th assimilation into vegetation growing on uranium mill tailings [16]. These data indicate an uptake coefficient of 0.1 for Indian ricegrass (*Oryzopsis hymenoides*). It may be that translocation of thorium from soil to plant is strongly species-dependent, but more data are required to verify this.

Concentration in cattle. Few data have been reported describing the transfer of ^{230}Th from forage plants to cattle meat and milk. Since it is estimated that only 0.03–0.6% of ingested thorium is absorbed into the blood from the intestine of a dairy cow [13], ^{230}Th transfer coefficients are probably quite low for beef and milk. According to Ng et al. [17], the equilibrium value for milk is about 5.0×10^{-6} day/l. The equilibrium transfer coefficient for beef has been estimated to be 2.0×10^{-4} day/kg [5, 14]. However, there are insufficient data to fully support these values.

Estimated dose to man: Tailings—forage—cattle—man pathway. To estimate the dose rate to man due to ^{230}Th transport from uranium tailings via the beef/milk food chain, it was assumed that root soil at a mill site would contain not more than 5 pCi/g of ^{230}Th following remedial action. This is in keeping with the proposed EPA standards [7], if one assumes equilibrium between ^{230}Th and ^{226}Ra. Minimum and maximum estimates of dose rates were made using the transfer factors listed in Table 1 and the grazing and dietary assumptions used in making analogous dose estimates for ^{238}U/^{234}U ingestion (Table 2).

Estimated dose to man: Normal dietary intake. The average amount of ^{230}Th taken in through the normal diet is reported to be about 0.1 pCi/day [8, 29, 84]. Much of this may come from root vegetables, such as carrots and potatoes, since thorium movement to shoots is slight, as is any subsequent transfer to beef or milk. Specific sources of ^{230}Th in the diet, however, have not been identified. The estimated doses are given in Table 2.

RADIUM-226

Uptake by forage plants from soils and tailings. The translocation of ^{226}Ra into plants has been extensively studied. It has been reported as being one of the natural radioelements most readily incorporated into vegetation [40].

According to Fisenne [85], the average concentration of ^{226}Ra in soil is about 1 pCi/g. In some areas, however, the soil content of this isotope may be naturally of artificially enhanced. Increased concentrations of ^{226}Ra in soil and its subsequent assimilation by plants have been observed in the Soviet Union [52, 53, 57–59], India [86], Brazil [33], Iran [87], Poland [88], and the United States [78, 89]. The areas studied in the Soviet Union, Brazil, and Iran are considered to have naturally elevated amounts of ^{226}Ra in the soil, while the sites in India, Poland, and the United States that were studied have been contaminated with this radionuclide through industrial activity.

The specific behavior of radium in vegetation has been examined through laboratory and greenhouse studies. Much of the radium within most (but not all) plants is concentrated in the roots, and to a lesser extent in the leaves [82, 90]. Popova, Kodaneva, and Vavilov [90, 91] have proposed the existence of an acropetal gradient of ^{226}Ra in plants, the concentration in leaves decreasing in successive steps from oldest to youngest foliage.

The uptake of radium from soil by plants is highly dependent on the organic content of the soil, since organic material tends to bind radium, making it unavailable for root uptake [92]. Radium uptake by plants is to some extent species-dependent as well. The Brazil nut tree, for example, is known to concentrate relatively large amounts of ^{226}Ra, particularly in the edible nuts [28, 80] (little of the ^{226}Ra ingested in this form is absorbed through the gastro-intestinal tract when the nuts are consumed by humans [93]).

Movement of ^{226}Ra into vegetation growing on uranium mill tailings has been investigated, particularly in relation to vegetative stabilization of tailings piles [94, 95]. Reported plant uptake coefficients for ^{226}Ra, as with the other uranium-series isotopes, vary widely, ranging from 0.002 to 6.5 [11, 16, 18, 19, 65, 66]. (The highest coefficient observed, 6.5, was for sagebrush (*Artemisia tridentata*), a common desert browse.)

Concentration in cattle. The uptake of ^{226}Ra by sheep, pigs, and cattle has been reported in the literature [29, 96—98]. Transfer coefficient values for dairy cow milk reported in the literature range from 4.0×10^{-4} to 5.9×10^{-4} day/l; those for beef have been estimated at between 5.1×10^{-4} and 4.0×10^{-3} day/kg, assuming an equilibrium of radium intake and excretion and, again, based on sparse data [5, 16, 28, 98].

Estimate dose to man: Tailings—forage—cattle—man pathway. Estimates of the maximum and minimum dose rates to humans due to ingestion of ^{226}Ra transported from tailings through the beef/milk food chain are presented in Table 2. These dose rates were estimated the same way as was done for dose rates from ^{238}U/^{234}U ingestion. The transfer factors given in Table 1 and the EPA standard of 5 pCi/g of ^{226}Ra in surface soil following remedial action were used for the calculations.

Estimated dose to man: Normal dietary intake. Concentrations of ^{226}Ra in various foods have been reported widely in the literature [8, 35, 36, 75, 79, 83, 99—104]. According to these reports, the foodstuffs that contain the highest ^{226}Ra concentrations are Brazil nuts, some breakfast cereals, cockles, bakery products, root vegetables, flour (particularly wheat), and eggs.

The average dietary intake of ^{226}Ra has been estimated for several countries of the world, as well as for various U.S. cities [8, 29, 73, 75, 83, 105—112]. Ingestion of ^{226}Ra through the diet varies considerably from location to location, a good example of this being the reported threefold difference between intakes in Puerto Rico and the United States [106]. Even within the United States, dietary intake of ^{226}Ra can vary by a factor of 2 to 3 [29].

According to Holtzman et al. [29], the intake of ^{226}Ra from the diet ranges from 0.7 to 2.4 pCi/day. Estimates for dose rates to humans based on this average range of intake are given in Table 2.

Uptake by forage plants from soils and tailings. ^{210}Pb originates from the disintegration of the gaseous decay product of ^{226}Ra, ^{222}Rn, and its short-lived daughters. Thus, this radioactive lead isotope is not only present in tailings, but also can be found in soil distant from the pile as a result of the atmospheric dispersion of radon. Vegetative uptake of ^{210}Pb can, therefore, occur by the same mechanisms involved in uptake of uranium, thorium, and radium (i.e., root uptake and dust suspension of soil, ore, tailings, etc.), plus the additional mode of atmospheric washout and subsequent foliar absorption.

Root uptake of ^{210}Pb has been examined by D'Souza and Mistry [82, 113] by use of spiked nutrient solutions. These studies indicate that in the absence of soil binding, lead is strongly assimilated by plants, concentrating particularly in the roots. Attempts have also been made to investigate the extent of foliar absorption of ^{210}Pb [114—117]. According to Athalye and Mistry [114], over 90% of foliar-applied ^{210}Pb (as nitrate solution) was absorbed by tested plants.

One particular plant that has been extensively studied because of its tendency to take up ^{210}Pb (and other radionuclides) is tobacco [118—121]. These studies have led to investigations of the ^{210}Pb and ^{210}Po content of cigarettes and, because of their volatility, the concentration of these nuclides in cigarette smoke [119, 122, 123].

Concentrations of ^{210}Pb in vegetation growing in various geographical locations are given in the literature [124—127]. In the arctic regions, lichens (which grow extremely slowly) are significant accumulators of fallout ^{210}Pb and other radionuclides. Several investigators have examined the contamination of the lichen—reindeer—man food-chain with this radioisotope [128—133]. (^{210}Pb uptake in this ecosystem has been summarized by Holtzman [134]).

Despite these numerous ^{210}Pb uptake studies, the translocation of this radionuclide from uranium tailings to vegetation has not been extensively examined. The available literature, however, indicates that ^{210}Pb uptake coefficients for plants growing on tailings vary from 0.08 to 2.8 [11, 16, 19, 66], compared to the currently accepted coefficients of 9×10^{-2} and 6.8×10^{-2} used for predictive modeling [5, 20, 22].

Concentration in cattle. Calculated values of the transfer coefficient of ^{210}Pb to milk vary widely, ranging from 2.0×10^{-6} to 1.2×10^{-4} day/l [5, 20, 22, 135, 136]. Estimates of the transfer coefficient to beef range from 2.9×10^{-4} to 1.0×10^{-3} day/kg, based on sparse data [5, 20, 22].

Estimated dose to man: Tailings—forage—cattle—man pathway. The minimum and maximum estimates of the dose to human beings from the ingestion of beef and milk contaminated through the food-chain transport of ^{210}Pb from tailings are listed in Table 2. As with the other radionuclides, these doses were calculated on the basis of the transfer coefficients listed in Table 1 and assuming a maximum ^{210}Pb concentration of 5 pCi/g (if ^{210}Pb is in equilibrium with ^{226}Ra) subsequent to tailings cleanup [7].

Estimated dose to man: Normal dietary intake. Concentrations of ^{210}Pb in dietary foodstuffs are reported in several sources [30—32, 35, 37]. As with ^{226}Ra, the normal dietary intake of ^{210}Pb has been extensively studied [29, 36, 39, 84, 137, 138]. Most of the dietary ^{210}Pb is probably from vegetables and cereals [29, 36]. Data presented by Holtzman [36] indicate that ^{210}Pb intake in the human diet probably range from 1.3 to 1.6 pCi/day. Estimates of the dose to man from such ^{210}Pb intake are given in Table 2.

POLONIUM-210

Uptake by forage plants from soils and tailings. ^{210}Po, the 138-day half-life decay product of ^{210}Pb, is present both in the atmosphere (attached to dust particles) and the soil [139]. Thus, as with ^{210}Pb, aerial contamination of foliage is of possible significance. Work by Popova and Taskaev [116] and Athalye and Mistry [114] confirms that ^{210}Po can be absorbed through aboveground plant tissue and subsequently distributed throughout the plant. Athalye and Mistry [114] indicate that under laboratory conditions, about 30% of ^{210}Po (nitrate solution) applied to a plant surface is incorporated into the plant.

D'Souza and Mistry [82, 113] report that when assimilated through the roots, ^{210}Po concentrates there rather than distributing more evenly throughout the plant (as apparently occurs following foliar deposition of polonium). Root uptake of ^{210}Po from soil has been examined in plants growing under both greenhouse and outdoor conditions [23, 125, 126, 140—143]. The uptake coefficients obtained from these studies ranged from 1.2×10^{-6} to 0.23. The coefficients were considerably higher for outdoor plants (from 0.03 to 0.23) than for greenhouse vegetation (from 3×10^{-6} to 3×10^{-2}) [23]. It is possible that this difference is due to foliar contamination of the outdoor plants with airborne $^{210}Pb/^{210}Po$ (either through dust deposition or rainfall), considered by some to be the principal mode of ^{210}Po uptake in vegetation [26, 141].

There is little information concerning the transport of ^{210}Po from uranium mill tailings to vegetation, but some data are available from Holtzman et al. [29]. The authors did not measure uptake coefficients, but did report ^{210}Po concentrations of 2.8—4.1 pCi/g in grass (shoots) growing on tailings piles, compared to a control grass content of 0.7 pCi/g. Moffett and Tellier [65] reported concentrations of ^{210}Po ranging from 0.03 to 0.13 pCi/g in four species of grass (shoots) growing on tailings. These value are probably aberrant, since the plants were dry-ashed in a muffle furnace at 750°C, a temperature that would volatilize some of the polonium.

Concentration in cattle. Transfer of ^{210}Po from cattle fodder to milk has been studied by McInroy et al. [24] and Watters and McInroy [27]. The degree of transfer apparently depends on the chemical form of the ingested polonium. Reported ^{210}Po transfer coefficients for milk range from 8.9×10^{-5} to 2.9×10^{-4} day/l for PoO_2 and $PoCl_4$, respectively [24–27].

Based on an estimate of 0.05 day/kg given by Garner [28] for reindeer, the transfer coefficient for ^{210}Po from forage to meat appears to be higher than that for the other uranium-series radionuclides. The only transfer coefficient estimate reported for beef, however, is 0.012 day/kg [5].

Estimated dose to man: Tailings—forage—cattle—man pathway. Estimates of the minimum and maximum dose rates to man from beef/milk food-chain transport of ^{210}Po are presented in Table 2. These estimates were based on the data of Table 1 and on an assumed concentration limit of 5 pCi/g in root soil after remedial action (^{210}Po in equilibrium with ^{226}Ra) [7].

Estimated dose to man: Normal dietary intake. The ^{210}Po content in a variety of common foods is reported in the literature [31, 32, 35, 144]. As with ^{210}Pb, it appears that most dietary intake of ^{210}Po is from cereals and vegetables [29, 36]. Although some meats and seafoods contain concentrations of ^{210}Po similar to concentrations in cereals and vegetables, the meat and seafoods are consumed in smaller quantities. An estimate of the range of dietary intake of ^{210}Po is reported as 1.3 to 1.6 pCi/day [36]. Maximum and minimum dose estimates are given in Table 2 for this range of daily ^{210}Po intake. However, most of this dose arises from ^{210}Po generated from ^{210}Pb already present in the body, rather than from ingested ^{210}Po [145]. In Table 2, the dose rates due to ^{210}Po intake in a normal diet, using NCRP dose-conversion factors, are based on intake and retention of ^{210}Pb and subsequent ingrowth of ^{210}Po. These estimated dose rates are much higher than the analogous estimates made using ORNL dose-conversion factors, which were based solely on normal dietary intake of ^{210}Po.

SUMMARY

An effort was made to relate radioactive contamination of cattle near uraniun mills to radiation doses to people living in the vicinity of those mills by tracking radionuclide transfer through successive levels of the beef/milk food chain and then converting the estimated amounts of contaminants ultimately consumed by man into dose equivalents by use of NCRP and ORNL dose-conversion factors. The major portion of this effort consisted of an extensive literature search to glean data on food-chain uptake and transport coefficients for long-lived nuclides in the uranium series. Because of the lack of information in the literature, this process could be carried out only for direct uptake/consumption of radionuclides from mill tailings piles through the crucial forage vegetation → cattle → beef/milk → man pathway (Table 1).

The doses to man estimated in this report are considered highly conservative for the beef/milk pathway. However, these estimates did not take into account any other food-chain exposures attributable to mill tailings (e.g., drinking of contaminated water or consumption of locally grown vegetables contaminated with tailings nuclides). Even for the beef/milk pathway, the available data on uptake and transfer coefficients (particularly the former) were so variable (ranging over several orders of magnitude in some cases) and the methods by which they were determined were so inconsistent, that a minimum and maximum range of possible doses to man were calculated (Table 2). Estimated doses from average total dietary intake of the same radionuclides were presented for comparison.

Based on the data in Table 2, the minimum dose rates from beef/milk food-chain transport of $^{238}U/^{234}U$, ^{230}Th, ^{226}Ra, and ^{210}Pb in tailings are below the expected dose from a normal diet. However, the minimum dose rates from food-chain transport of ^{210}Po in tailings exceed those predicted for normal dietary intake. The primary reason for this is that the transfer coefficients (meat) reported for ^{210}Po are higher than for the other uranium-series radionuclides discussed in this paper (see Table 1). The maximum estimates for dose rates from beef/milk food-chain transport of tailings radionuclides in nearly all instances exceed those expected via a normal diet, substantially so for ^{210}Po, as can be seen in Table 2.

The great variability in the vegetation uptake coefficients reported in the literature was a principal reason for the wide range of the final minimum and maximum estimated doses to man. Among the many factors that influence radionuclide uptake into plants are plant species, composition of soil, and climate. In addition, the methods used to determine uptake coefficients can have considerable bearing on the findings. For example, greenhouse studies of the intake of uranium-series radionuclides by plants do not account for outdoor effects such as tailings resuspension by wind and rain, and the deposition of radon progeny on foliage. Even in reported determinations of uptake coefficients for field vegetation, these effects are often neglected. Ideally, of course, such avenues of radionuclide transfer as resuspension and aerial deposition should be examined independent of the root uptake mechanism. Such studies, however, have not been done.

The uptake of uranium-series radionuclides specifically from uranium mill tailings by forage has not been extensively studied. The small amount of data available from the literature, however, indicates that uptake coefficients for plants growing in tailings or soil contaminated with tailings are higher than those for other vegetation. This is possibly a result of dusting of aboveground foliage by windblown ores, tailings, yellowcake, or radon decay products, followed by incorporation of the radionuclides into the plant structure. This effect has not been verified by measurements. However, this does demonstrate that uptake coeffcients, often taken to be solely an indication of the soil-to-plant movement of radionuclides, can in some instances be a reflection of a number of contamination processes.

In summary, the dearth of field data characterizing forage-plant assimilation of uranium-series radionuclides from mill tailings, as well as the high degree of variability in the data that are available, makes it difficult to predict the dose to man due to beef/milk food-chain transport of these isotopes. Data pertinent to other exposure pathways, such as consumption of locally grown vegetables contaminated with tailings nuclides and drinking of contaminated water, are even more scarce. Thus, there is at present insufficient information available to completely assess the consequential dose to man as a result of food-chain contamination by radionuclides from mill tailings.

ACKNOWLEDGEMENTS

The author wishes to thank Richard Holtzman, Walter Kisieleski, Norbert Kretz, and Phillip Zelle for their helpful suggestions and discussion. Special appreciation is extended to John DePue for his editorial assistance.

REFERENCES

1 R. C. Merritt, The Extractive Metallurgy of Uranium, Colorado School of Mines Research, Golden, CO, 1971, pp. 379, 390.

2 V. M. Vdovenko and Yu. V. Dubasov, in D. Malament (Ed.), Analytical Chemistry of Radium, John Wiley and Sons, New York, 1975, pp. 14.

3 U.S. Environmental Protection Agency, AIRDOS-EPA: A computerized methodology for estimating environmental concentrations and dose to man from airborne releases of radionuclides, Report ORNL-5532, Oak Ridge National Laboratory for USEPA, 1979.

4 D. A. Baker, G. R. Hoenes and J. K. Soldat, FOOD—An interactive code to calculate internal radiation doses from contaminated food products, in W. R. Ott (Ed.), Environmental Modeling and Simulation, Report EPA-600/9-76-015, U.S. Environmental Protection Agency, 1976, pp. 204—208.

5 M. H. Momeni, Y. Yuan and A. J. Zielen, The Uranium Dispersion and Dosimetry (UDAD) Code, Report NUREG/CR-0553, ANL/ES-72, Argonne National Laboratory for U.S. Nuclear Regulatory Commission, 1979.

6 U.S. Nuclear Regulatory Commission, MILDOS computer code user's manual, Report NUREG/CR-2011, 1980.

7 U.S. Environmental Protection Agency, standards for remedial actions at inactive uranium processing sites (40 CFR 192), Final rule, Federal Register, Vol. 48, No. 3, Jan. 5, 1983.

8 National Council on Radiation Protection and Measurements, Natural background radiation in the United States, NCRP Report No. 45, 1975.

9 D. E. Dunning, Jr., S. R. Bernard, P. J. Walsh, G. G. Killough and J. C. Pleasant (Compilers), Estimates of internal dose equivalent to 22 target organs for radionuclides occurring in routine releases from nuclear fuel facilities, Report NUREG/CR-0150 Vol. 2, ORNL/NUREG/TM-190/V2, Oak Ridge National Laboratory for U.S. Nuclear Regulatory Commission, 1979.

10 H. Morishima, T. Koga, H. Kawai, Y. Honda and K. Katsurayama, Studies on the movement and distribution of uranium in the environment-distribution of uranium in agricultural products, J. Radiat. Res., 18 (1977) 139—150.

11 T. F. Winsor and F. W. Whicker, ^{238}U, ^{226}Ra and ^{210}Pb in soil and vegetation at the Lucky Mc Uranium Mine and Mill, in Environmental Report to Accompany Source Material License Application, Utah International, Inc. (U.S. Nuclear Regulatory Commission Docket No. 40-2259), 1975.

12 T. S. Chapman and S. Hammons, Jr., Some observations concerning uranium content of ingesta and excreta of cattle, Health Phys., 9 (1963) 79—81.

13 C. T. Garten, Jr., A review of parameter values used to assess the transport of plutonium, uranium and thorium in terrestrial food chains, Environ. Res., 17 (1978) 437—452.

14 U.S. Nuclear Regulatory Commission, Final generic environmental impact statement on uranium milling, Report NUREG-0706, 1980, Vol. 2, Appendix G-3.

15 E. A. Bondietti and F. H. Sweeton, Transuranic speciation in the environment, in Transuranics in Natural Environments, Report NVO-178, Nevada Applied Ecology Group, U.S. Energy Research and Development Administration, Las Vegas, NV, 1977, pp. 449—476.

16 D. R. Rayno, M. H. Momeni and C. Sabau, Forage uptake of uranium series radionuclides in the vicinity of the Anaconda Uranium Mill, in Proceedings of the 3rd Symposium on Uranium Mill Tailings Management, Colorado State University, Fort Collins, CO, 1980, pp. 57—66.

17 Y. C. Ng, C. S. Colsher, D. J. Quinn and S. E. Thompson, Transfer coefficients for the prediction of the dose to man via the forage-cow-milk pathway from radionuclides released to the Biosphere, Report UCRL-51939, Lawrence Livermore Laboratory, 1977.

18 D. R. Dreesen, M. L. Marple and N. E. Kelley, Contaminant transport, revegetation, and trace element studies at inactive uranium mill tailings piles, in Proceedings of the First Symposium on Uranium Mill Tailings Management, Colorado State University, Fort Collins, CO, 1978, pp. 111—139.

19 F. W. Whicker, Biological interactions and reclamation of uranium mill tailings, in Proceedings of the First Symposium on Uranium Tailings Management, Colorado State University, Fort Collins, CO, 1978. pp. 141—153.

20 L. M. McDowell-Boyer, A. P. Watson and C. C. Travis, A review of parameters describing terrestrial food chain transport of lead-210 and radium-226, Nucl. Saf., 21 (1980) 486—495.

21 L. M. McDowell-Boyer, A. P. Watson and C. C. Travis, Review and recommendations of dose conversion factors and environmental transport parameters for ^{210}Pb and ^{226}Ra, Report NUREG/CR-0574, ORNL/NUREG-56, Oak Ridge National Laboratory for U.S. Nuclear Regulatory Commission, 1979.

22 L. M. McDowell-Boyer, A. P. Watson and C. C. Travis, Food-chain transport of ^{210}Pb resulting from uranium milling activities, Report IAEA-SM-237/43, Oak Ridge National Laboratory, 1979.

23 W. R. Hansen and R. L. Watters, Plant uptake of ^{210}Po from soil, Radiat. Bot., 10 (1970) 371—375.

24 J. F. McInroy, R. L. Watters and J. E. Johnson, Polonium oxide metabolism in ruminants, Health Phys., 19 (1970) 333.

25 B. B. Moroz and Yu. D. Parfenov, Metabolism and biological effects of polonium-210, At. Energy Rev., 10 (1972) 175—232.

26 Yu. D. Parfenov, Polonium-210 in the environment and in human organism, At. Energy Rev., 12 (1974) 75—143.

27 R. L. Watters and J. F. McInroy, The transfer of ^{210}Po from cattle feed to milk, Health Phys., 16 (1969) 221—225.

28 R. J. Garner, Transfer of Radioactive Materials from the Terrestrial Environment to Animals and Man, CRC Press, Cleveland, OH, 1972.

29 R. B. Holtzman, P. W. Urnezis, A. Padova and C. M. Bobula, III, Contamination of the human food chain by uranium mill tailings piles, Report NUREG/CR-0758, Argonne National Laboratory for U.S. Nuclear Regulatory Commission, 1979.

30 T. Baltakmens, Lead-210 in New Zealand milk, Aust. J. Sci., 31 (1968) 111—114.

31 T. M. Beasley, C. L. Osterburg and Y. M. Jones, Natural and artificial radionuclides in seafoods and marine protein concentrates, Nature (London), 221 (1969) 1207—1209.

32 T. M. Beasley, T. A. Jokela and R. J. Eagle, Radionuclides and selected trace elements in marine protein concentrates, Health Phys., 21 (1971) 815—820.

33 M. Eisenbud, H. Petrow, R. T. Drew, F. X. Roser, G. Kegel and T. L. Cullen, Naturally occurring radionuclides in foods and waters from the Brazilian areas of high radioactivity, in The Natural Radiation Environment, Univeristy of Chicago Press, Chicago, IL, 1964, pp. 837—854.

34 E. I. Hamilton, The concentration of uranium in man and his diet, Health Phys., 22 (1972) 149—153.

35 C. R. Hill, Identification of α-emitters in normal biological materials, Health Phys., 8 (1962) 17—25.

36 R. B. Holtzman, Normal dietary levels of radium-226, radium-228, lead-210 and polonium-210 for man, in T. F. Gesell and W. M. Lowder (Eds.), The Natural Radiation Environment III, Report CONF-780422, U.S. Department of Energy, 1980, Vol. 1, pp. 755—782.

37 B. Y. Lalit, T. V. Ramachandran and S. Rajan, Lead-210 content of food samples in India, Radiat. Environ. Biophys., 18 (1980) 13—17.

38 G. A. Welford and R. Baird, Uranium levels in human diet and biological materials, Health Phys., 13 (1967) 1321—1324.

39 A. W. Klement, Jr., Natural radionuclides in foods and food source materials, in E. B. Fowler (Ed.), Radioactive Fallout, Soils, Plants, Foods, Man, Elsevier, Amsterdam, 1965, pp. 121.

40 W. S. Osburn, Primordial radionuclides: Their distribution, movement, and possible effects within terrestrial ecosystems, Health Phys., 11 (1965) 1275—1295.

41 L. A. Pertsov, The natural radioactivity of the biosphere, Report AEC-tr-6714, Israel Program for Scientific Translations, Jerusalem, 1967, pp. 77.

42 R. O. Hansen, R. D. Vidal and P. R. Stout, Radioisotopes in soils: Physical-chemical composition, in R. S. Caldecott and L. A. Snyder (Eds.), A symposium on Radioisotopes in the Biosphere, University of Minnesota, Minneapolis, MN, 1960, pp. 23—36.

43 M. H. Dean, A survey of the uranium content of vegetation in Great Britain, J. Ecol., 54 (1966) 589—595.

44 J. C. Laul, W. C. Weiner and L. A. Rancitelli, Biogeochemical distribution of rare earths and other trace elements in plants and soils, Report BNWL-SA-6078, Battelle, Pacific Northwest Laboratory, 1977.

45 H. L. Cannon, The effect of uranium—vanadium deposits on the vegetation of the Colorado Plateau, Am. J. Sci., 250 (1952) 735—770.

46 H. L. Cannon and W. H. Starrett, Botanical prospecting for uranium on La Ventana Mesa, Sandoval County, New Mexico, U.S. Geol Surv. Bull, 1009-M (1956).

47 H. L. Cannon, The development of botanical methods of prospecting for uranium on the Colorado Plateau, U.S. Geol. Surv. Bull. 1085-A (1960).

48 A. J. Froelich and F. J. Kleinhampl, Botanical prospecting for uranium in the Deer-Flat Area, White Canyon District, San Juan County, Utah, U.S. Geol. Surv. Bull. 1085-B (1960).

49 K. L. Gulati, S. C. Goswami and K. K. Nagpaul, Mineral element compositon of natural vegetation and its relation to soil of Puga Valley, Ladakh, India, Plant Soil, 52 (1979) 345—351.

50 R. N. W. DiLabio and A. N. Rencz, Relationship between levels of copper, uranium, and lead in glacial sediments and in *Vaccinium uliginosum* at an Arctic site enriched with heavy metals, Can. J. Bot., 58 (1980) 2017—2021.

51 J. A. Erdman and R. J. Ebens, Element content of crested wheatgrass grown in reclaimed coal spoils and on soils nearby, J. Range Manage., 32 (1979) 159—161.

52 V. V. Kovalsky, I. E. Vorotnitskaya and V. A. Lekarev, Biogeochemical food chains of uranium in aquatic and terraneous organisms, in B. Aberg and F. P. Hungate (Eds.), Radioecological Concentration Processes, Pergamon Press, London, 1967, pp. 329—332.

53 V. I. Maslov, K. I. Maslova and R. M. Alexakhin, Redistribution of natural radioactive elements resulting from animal and plant life activity in regions with high radioactivity, in T. F. Gesell and W. M. Lowder (Eds.), The Natural Radiation Environment III, Report CONF-780422, U.S. Department of Energy, 1980, Vol. 1, pp. 738—754.

54 F. R. Miera, Jr., W. C. Hanson, E. S. Gladney and P. Jose, Mobility of elevated levels of uranium in the environment, in T. F. Gesell and W. M. Lowder (Eds.), The Natural Radiation Environment III, Report CONF-780422, U.S Department of Energy, 1980, Vol. 1, pp. 681—699.

55 W. L. Nees and J. P. Corley, Environmental Surveillance at Hanford for CY-1973, Report BNWL-1811, Battelle, Pacific Northwest Laboratory, 1974.

56 R. C. Severson and L. P. Gough, Concentration and distribution of elements in plants and soils near phosphate processing factories, Pocatello, Idaho, J. Environ. Qual., 5 (1976) 476—482.

57 N. A. Titaeva, A. I. Taskaev, V. Ya. Ovchenkov, R. M. Aleksakhin and I. I. Shuktomova, Content and characteristics of U, Th, Ra and Rn uptake in plants growing under different radioecological conditions, Ekologiya, 4 (1978) 37—44.

58 P. P. Vavilov, B. I. Gruzdev, V. I. Maslov, V. Ya. Ochenkov and A. I. Taskaev, Results of an experiment over many years in decontaminating radium-bearing pollutants in the central taiga, Ekologiya, 6 (1977) 32—38.

59 I. N. Verkhovskaja, P. P. Vavilov and V. I. Maslov, The migration of natural radioactive elements under natural conditions and their distribution according to biotic and abiotic environmental components, in B. Aberg and F. P. Hungate (Eds.), Radioecological Concentration Processes, Pergamon Press, London, 1967, pp. 313—328.

60 W. H. Adams, J. R. Buchholz, C. W. Christenson, G. L. Johnson and E. B. Fowler, Studies of plutonium, americium and uranium in environmental matrices, Report LA-5661, Los Alamos Scientific Laboratory, 1975.

61 K. L. Gulati, M. C. Oswal and K. K. Nagpaul, Assimilation of uranium by wheat and tomato plants, Plant Soil, 55 (1980) 55—59.

62 R. G. Schreckhise and J. F. Cline, Uptake and distribution of ^{232}U in peas and barley, Health Phys., 38 (1980) 341—343.

63 T. Yamamoto and K. Masuda, Studies on environmental contamination by uranium; 4. Uranium absorption by Chinese cabbage, J. Radiat. Res., 15 (1974) 1—6.

64 M. B. Sears, R. E. Blanco, R. C. Dahlman, G. S. Hill, A. D. Ryon and J. P. Witherspoon, Correlation of radioactive waste treatment costs and the environmental impact of waste effluents in the nuclear fuel cycle for use in establishing 'as low as practicable' guides — milling of uranium ores, Report ORNL-TM-4903, Oak Ridge National Laboratory, 1975, Vol. I.

65 D. Moffett and M. Tellier, Uptake of radioisotopes by vegetation growing on uranium tailings, Can. J. Soil Sci., 57 (1977) 417—424.

66 D. R. Dreesen and M. L. Marple, Uptake of trace elements and radionuclides from uranium mill tailings by four-wing saltbush (*Atriplex canescens*) and alkali sacaton (*Sporobolus airoides*), in Proceedings of the 2nd Symposium or Uranium Mill Tailings Management, Colorado State University, Fort Collins, CO, 1979, pp. 127—143.

67 W. C. Hanson and F. R. Miera, Jr., Long-term ecological effects of exposure to uranium, Report LA-6269, Los Alamos Scientific Laboratory, 1976.

68 D. D. Smith, S. C. Black, K. R. Giles, D. E. Bernhardt and R. R. Kinnison, Tissue burdens of selected radionuclides in beef cattle on and around the Nevada test site, Report NERC-LV-539-29, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Las Vegas, NV, 1976.

69 D. D. Smith, K. R. Giles and D. E. Bernhardt, Animal investigation program, 1973 annual report: Nevada test site and vicinity, Report ESML-LV-0539-3, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Las Vegas, NV, 1977.

70 U.S. Nuclear Regulatory Commission, Final generic environmental impact statement on uranium milling, Report NUREG-0706, 1980. Vol. 1, pp. 5—6.

71 C. L. Comar, Radioactive materials in animals — entry and metabolism, in R. S. Russell (Ed.), Radioactivity and Human Diet, Pergamon Press, London, 1966, pp. 129—157.

72 M. E. Heath, D. S. Metcalfe and R. F. Barnes, Forages: The Science of Grassland Agriculture, Iowa State University Press, Ames, IA, 1978, pp. 667.

73 I. M. Fisenne and H. W. Keller, Radium-226 in the diet of two U.S. cities, in E.P. Hardy, Jr. (Ed.), Fallout Program, Quarterly Summary Report, Dec. 1, 1969—May 1, 1970, Report HASL-224, U.S. Atomic Energy Commission. Health and Safety Laboratory, 1970, pp. I-2—I-8.

74 S. K. Chakarvarti, J. Dhiman and K. K. Nagpaul, Uranium trace analysis of a chewable betel-leaf preparation and tea leaves, Health Phys., 40 (1981) 78—81.

75 J. H. Harley, Radionuclides in food, in Biological Implications of the Nuclear Age, Lawrence Radiation Laboratory, U.S. Atomic Energy Commission, Livermore, CA, 1969, pp. 189—200.

76 J. B. Hursh and N. L. Spoor, Data on man, in H. C. Hodge, J. N. Stannard and J. B. Hursh (Eds.), Uranium, Plutonium, Transplutonic Elements, New York, Springer-Verlag, 1973. Chap. 4, Part IV B, pp. 231—233.

77 T. Yamamoto, E. Yunoki, M. Yamakawa, M. Shimizu and K. Nukada, Studies on environmental contamination by uranium; 5, Uranium contents in daily diet and in human urine from several populations around a uranium mine in Okayama Prefecture, J. Radiat. Res., 15 (1974) 156—162.

78 H. W. Dickson, G. S. Hill and P. T. Pardue, Weldon spring dose calculations, Report ORNL/TM-6272, Oak Ridge National Laboratory, 1978.

79 C. L. Comar, Natural radioactivity in the biosphere and foodstuffs, in Toxicants Occurring Naturally in Foods, National Academy of Sciences, National Research Council, Publication 1354, 1966.

80 R. S. Russell, The extent and consequences of the uptake by plants of radioactive nuclides, An. Rev. Plant. Physiol., 14 (1963) 271—294.

81 P. F. Gustafson and A. M. Brues, A study of the radioactivity found in grass grown on thorium-bearing (Monazite) sand, in Biological and Medical Research Division Semiannual Report, January—June 1958, Report ANL-5916, Argonne National Laboratory, 1958.

82 T. J. D'Souza and K. B. Mistry, Comparative uptake of thorium-230, radium-226, lead-210 and polonium-210 by plants, Radiat. Bot., 10 (1970) 293—295.

83 R. S. Russell and K. A Smith, Naturally occurring radioactive substances: The uranium and thorium series, in R. S. Russell (Ed.), Radioactivity and Human Diet, Pergamon Press, London, 1966, pp. 367—379.

84 United Nations Scientific Committee on the Effects of Atomic Radiation, Sources and Effects of Ionizing Radiation, United Nations, New York, 1977, pp. 35—144.

85 I. M. Fisenne, Distribution of ^{210}Pb and ^{226}Ra in soil, in Proceedings of the 13th Annual Bioassay and Analytical Chemistry Meeting, Report UCRL-18140, Lawrence Radiation Laboratory, University of California, Berkeley, CA, 1968, pp. 145—158.

86 P. R. Kamath, M. A. R. Iyengar and I. S. Bhat, The changing radiation environment in India, in J. A. S. Adams, W. M. Lowder and T. F. Gesell (Eds.), The Natural Radiation Environment II, Report CONF-720805-P2, U.S. Energy Research and Development Administration, 1972, Vol. 2, pp. 917—928.

87 B. Khademi, A. A. Alemi and A. Nasseri, Transfer of radium from soil to plants in an area of high natural radioactivity in Ramsar, Iran, in T. F. Gesell and W. M. Lowder (Eds.), Natural Radiation Environment III, Report CONF-780422, U.S. Department of Energy, 1980, Vol. 1, pp. 600—610.

88 S. Wlodek, D. Grzybowska and M. Bysiek, The effect of human activity upon migration of radium-226 in the environment, Nukleonika, 15, 9 (1970) 80—86 (Eng. trans.).

89 G. L. Murphy, J. D. Spaulding and J. E. Noakes, Decommissioning of a luminous dial painting facility, Health Phys., 39 (1980) 593—600.

90 O. N. Popova, R. P. Kodaneva and P. P. Vavilov, Distributions in plants of radium absorbed from the soil, Plant Physiol., 11 (1964) 371—375.

91 P. P. Vavilov, O. N. Popova and R. P. Kodaneva, On the behavior of radium in plants, Akad. Nauk SSSR Proc. Bot. Sci., 157 (1964) 134—136.

92 D. Grzybowska, Uptake of ^{226}Ra by plants from contaminated soils, Nukleonika, 19, 1 (1974) 62—68 (Eng. trans.).

93 J. J. Gabay and N. I. Sax, Retention of radium due to ingestion of Brazil nuts, Health Phys., 16 (1969) 812—813.

94 N. E. Kelley, Vegetational stabilization of uranium spoil areas, grants, New Mexico, Report LA-7624-T (PhD. Thesis, University of New Mexico), Los Alamos Scientific Laboratory, 1979.

95 W. J. Shelley, personal communication, February, 1979.

96 B. Khademi and A. Mahdavi, Increase of ^{226}Ra in the water intake by sheep, Health Phys., 27 (1974) 522—524.

97 N. S. Nelson and J. H. Rust, Distribution of and discrimination against naturally occurring ^{226}Ra in swine, in B. Aberg and F. P. Hungate (Eds.), Radioecological Concentration Processes, Pergamon Press, London, 1967, pp. 573—588.

98 B. F. Sansom and R. J. Garner, The metabolism of radium in dairy cows. Biochem. J., 99 (1966) 677—681.

99 M. DeBortoli and P. Gaglione, Radium-226 in environmental materials and foods, Health Phys., 22 (1972), 43—48.

100 G. G. Mastinu and G. P. Santaroni, ^{226}Ra levels in Italian drinking waters and foods, Report RT/PROT(78)14, Comitato Nazionale Energia Nucleare, 1978.

101 H. Muth, B. Rajewsky, H. J. Hantke and K. Aurand, The normal radium content and the Ra-226/Ca ratio of various foods, drinking water and different organs and tissues of the human body, Health Phys., 2 (1960) 239—245.

102 T. W. Oakes and K. E. Shank, Concentrations of radionuclides and selected stable elements in fruits and vegetables, Report CONF-770676-1, Oak Ridge National Laboratory, 1977.

103 Z. Pietrzak-Flis, Radium-226 in Polish diet and foodstuffs, Nukleonika, 17 (1972) 227—321.

104 R. C. Turner, J. M. Radley and W. V. Mayneord, The naturally occurring α-ray activity of foods, Health Phys., 1 (1958) 268—275.

105 N. A. Hallden, I. M. Fisenne and J. H. Harley, Radium-226 in human diet and bone, Science, 140 (1963) 1327—1329.

106 N. A. Hallden and J. H. Harley, Radium-226 in diet and human bone from San Juan, Puerto Rico, Nature (London), 204 (1964) 240—241.

107 Public Health Service, Radionuclides in institutional diet samples, October—December and annual averages, 1964, Radiological Health Data Report 6, Division of Radiological Health, 1965, pp. 371—377.

108 Public Health Service, Radionuclides in institutional diet samples, January—March 1965, Radiological Health Data Report 6, Division of Radiological Health, 1965, pp. 548—554.

109 Public Health Service, Food and diet surveillance activities, Radiological Health Data Report 7, Division of Radiological Health, 1966, pp. 398—403.

110 Public Health Service, Food and diet surveillance, Radiological Health Data Report 8, National Center for Radiological Health, 1967, pp. 591—599.

111 Public Health Service, Food and diet surveillance, Radiological Health Data Report 9, National Center for Radiological Health and National Center for Urban and Industrial Health, 1968, pp. 359—363.

112 Northeastern Radiological Health Laboratory, Evaluation of radium-226 in total diet samples, 1964 to June 1967, Radiological Health Data Report 10, Bureau of Radiological Health, 1969, pp. 547—549.

113 T. J. D'Souza and K. B. Mistry, Preliminary studies on the absorption and translocation of polonium-210 and lead-210 in plants, in Proceedings of the All India Symposium on Radioactivity and Meteorology of Radioluclides, Atomic Energy Establishment Trombay, Bombay, 1966, pp. 381—401.

114 V. V. Athalye and K. B. Mistry, Foliar retention, transport and leaching of polonium-210 and lead-210, Radiat. Bot., 12 (1972) 287—290.

115 R. C. Chadwick and A. C. Chamberlain, Field loss of radionuclides from grass, Atmos. Environ., 4 (1970) 51—56.

116 O. N. Popova and A. I. Taskaev, Investigation of routes of contamination of plants with polonium-210 and lead-210, Radiobiology (USSR), 6 (1977) 147—151.

117 J. Rule, D. Hemphill and J. O. Pierce, The use of ^{210}Pb and ^{109}Cd isotopes in a preliminary study of their uptake and translocation by plants, in Trace Contaminants in the Environment, Report LBL-3217, Lawrence Berkeley Laboratory, Berkeley, CA, 1974, pp. 333—339.

118 V. V. Athalye and K. B. Mistry, Uptake and distribution of polonium-210 and lead-210 in tobacco plants, Radiat. Bot., 12 (1972) 421—425.

119 E. S. Ferri and H. Christiansen, Lead-210 in tobacco and cigarette smoke, Public Health Rep., 82 (1967) 828—832.

120 T. C. Tso, N. Harley and L. T. Alexander, Source of lead-210 and polonium-210 in tobacco, Science, 153 (1966) 880—882.

121 T. C. Tso and I. Fisenne, Translocation and distribution of lead-210 and polonium-210 supplied to tobacco plants, Radiat. Bot., 8 (1968) 457—462.

122 E. A. Martell, Radioactivity of tobacco trichomes and insoluble cigarette smoke particles, Nature (London), 249 (1974) 215—217.

123 A. Mogro-Campero and R. L. Fleischer, Upper limits of a α-radioactivity per particle of cigarette smoke, Health Phys., 32 (1977) 39—40.

124 R. F. Dushauskene-Duzh and V. A. Urbonas, Migration of ^{210}Pb and ^{90}Sr in terrestrial biogeocenoses, Sov. J. Ecol., 9 (1978) 480—482.

125 C. R. Hill, Lead-210 and polonium-210 in grass, Nature (London), 187 (1960) 211—212.

126 L. A. Ladinskaya, Yu. D. Parfenov, R. S. Arutyunov and D. K. Popov, Natural Concentrations of ^{210}Pb and ^{210}Po in plants of steppe phytocenoses, Sov. J. Ecol., 7 (1976) 21—24.

127 N. Margocsy, H. Feraru, R. Pomoje, P. Plavosin, Fl. Gavrila, N. Racoveanu and Gh. Furnica, The study of the absorption of natural U and ^{210}Pb concerning a lot of population in connection with the radioactivity of the environment in an area with increased natural background of Romania, in E. Bujdoso (Ed.), Health Physics Problems of Internal Contamination, Akademiai Kiado, Budapest, 1973, pp. 401—406.

128 R. L. Blanchard and J. B. Moore, ^{210}Pb and ^{210}Po in tissues of some Alaskan residents as related to consumption of caribou or reindeer meat, Health Phys., 18 (1970) 127—134.

129 R. B. Holtzman, Natural levels of lead-210, polonium-210 and radium-226 in humans and biota of the Arctic, Nature (London), 210 (1966) 1094—1097.

130 P. Kauranen and J. K. Miettinen, ^{210}Po and ^{210}Pb in environmental samples in Finland, in B. Aberg and F. P. Hungate (Eds.), Radioecological Concentration Processes, Pergamon Press, London, 1967, pp. 275—280.

131 P. Kauranen and J. K. Miettinen, ^{210}Po and ^{210}Pb in the Arctic food chain and the national radiation exposure of Lapps, Health Phys., 16 (1969) 287—295.

132 P. Kauranen, J. K. Miettinen and E. Pulliainen, Polonium-210 and lead-210 in some terrestrial animals in Finland, Ann. Zool. Fenn., 8 (1971) 318—323.

133 R. B. R. Persson, Stable lead and ^{210}Pb in the food chain lichen—reindeer—man, in Comparative Studies of Food and Environmental Contamination, Report STI/PUB/348, International Atomic Energy Agency, Vienna, 1974, pp. 231—247.

134 R. B. Holtzman, Application of radiolead to metabolic studies, in J. Nriagu (Ed.), The Biogeochemistry of Lead in the Environment, Elsevier, Amsterdam, 1978, Vol. 1B, pp. 37—96.

135 G. D. Potter, D. R. McIntyre and G. M. Vattuone, The fate and implications of ^{203}Pb ingestion in a dairy cow and a calf, Health Phys., 20 (1970) 650—653.

136 R. E. Stanley, A. A. Mullen and E. W. Bretthauer, Transfer to milk of ingested radiolead, Health Phys., 21 (1971) 211—215.

137 P. J. Magno, P. R. Groulx and J. C. Apidianakis, Lead-210 in air and total diets in the United States during 1966, Health Phys., 18 (1970) 383—388.

138 R. S. Morse and G. A. Welford, Dietary intake of ^{210}Pb, Health Phys., 21 (1971) 53—55.

139 S. Abe and M. Abe, Chemical properties of ^{210}Po in the atmosphere, in Physical Behavior of Radioactive Contaminants in the Atmosphere, Report STI/PUB/354, International Atomic Energy Agency, 1974, pp. 367—373.

140 K. C. Berger, W. H. Erhardt and C. W. Francis, Polonium-210 analyses of vegetables, cured and uncured tobacco, and associated soils, Science, 150 (1965) 1738—1739.

141 C. W. Francis, G. Chesters and W. H. Erhardt, ^{210}Polonium entry into plants, Environ. Sci. Technol., 2 (1968) 690—695.

142 C. R. Hill, Polonium-210 in man, Nature (London) 208 (1965) 423—428.

143 R. L. Watters and W. R. Hansen, The hazards implication of the transfer of unsupported ^{210}Po from alkaline soil to plants, Health Phys., 18 (1970) 409—413.

144 R. N. Khandekar, Polonium-210 in Bombay diet, Health Phys., 33 (1977) 148—150.

145 R. B. Holtzman, The source of unsupported Po-210 (RaF) in tissue, Health Phys., 10 (1964) 763—764.

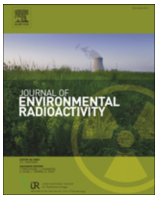
Exhibit 8

Journal of Environmental Radioactivity 110 (2012) 64–68

Contents lists available at SciVerse ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvrad



Transfer of natural radionuclides from hay and silage to cow's milk in the vicinity of a former uranium mine

Marko Štrok, Borut Smodiš*

Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

ARTICLE INFO

Article history:
Received 29 September 2011
Received in revised form
2 February 2012
Accepted 9 February 2012
Available online 1 March 2012

Keywords:
Natural radionuclides
Milk
Concentration ratio
Alpha spectrometry
Proportional counter

ABSTRACT

After the closure of the former Žirovski Vrh uranium mine in Slovenia, mining and milling wastes were deposited on two waste piles, which are located close to the mine. These wastes contain elevated levels of natural radionuclides from the uranium decay chain. Due to different migration processes (erosion, aerial deposition, through groundwater), these radionuclides can be transported via fodder into cow's milk, which is an important foodstuff for Slovenian people. Therefore, natural radionuclides were analysed in the transfer food chain from soil to cow's fodder and cow's milk. After sampling, ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po were determined using radiochemical separation methods and alpha spectrometry or proportional counting. Hay and silage to milk concentration ratios (kg dry weight L^{-1}) were calculated and were 0.260 for ^{238}U, 0.255 for ^{230}Th, 0.070 for ^{226}Ra, 0.021 for ^{210}Pb and 0.019 for ^{210}Po. The calculated annual ingestion dose due to milk consumption for the natural radionuclides analysed was 9 μSv/year for adults and 389 μSv/year for infants with the highest contribution of ^{210}Po (51% for adults and 63% for infants) and ^{210}Pb (36% for adults and 24% for infants). This study provides new data quantifying the transfer of natural radionuclides to milk, which is a parameter for which there have been very few previously reported values.

1. Introduction

Wastes with enhanced natural radionuclide concentrations, such as uranium mining and milling wastes, are often situated close to agricultural areas. This is the case for the former uranium mine at Žirovski Vrh, in Slovenia, where, amongst other agricultural crops, farmers produce fodder for dairy cows. In addition, phosphate fertilizers used in fodder production usually contain a higher content of natural radionuclides compared to the environmental background (Ghosh et al., 2008). This can additionally enhance activity concentrations in the soil used for producing fodder (Ioannides et al., 1997). Due to the relatively high human milk consumption, especially of infants, it is important (i) to measure the activity concentration of natural radionuclides in milk, and (ii) to quantify the transfer of natural radionuclides through the food chain from soil via fodder to milk. Whereas there are many studies concerning natural radionuclide activity concentrations in milk (Pietrzak-Flis et al., 1997; Ababneh et al., 2010; Al-Masri et al., 2004; Giri et al., 2011), there is a lack of data which enable the calculation of transfer parameter values for natural radionuclides in milk (IAEA, 2010; Fesenko et al., 2007). Therefore, in this study natural radionuclides were analysed in soil from fields used for fodder production, in the fodder produced (hay and silage) and in cow's milk, and the data used to estimate the transfer parameter values.

This study provides new data quantifying the transfer of natural radionuclides to milk, which is a parameter for which there have been very few previously reported values (Howard et al., 2009a, 2009b).

2. Materials and methods

2.1. Sampling and sample preparation

All samples were collected from a farm which lies about 500 m from the former U concentrate production plant (Fig. 1). Soil samples were obtained from three fields where fodder for cows was produced (Fig. 1). A pooled sample covering the whole of each field was obtained by random sampling with a corer designed to sample about 200 g at once at the depth from 0 to 15 cm. This gave about 5 kg in total of each soil sample. Pre-treatment of the soil samples was carried out according to ISO 11464 (1994). The sample was dried at 80 °C to constant weight. Then the larger stones and roots were removed and the sample was sieved through a 2-mm screen sieve. The fraction which passed through the sieve was then

---

* Corresponding author. Tel.: +38615885363; fax: +38615885346.
E-mail addresses: Marko.Strok@ijs.si (M. Štrok), Borut.Smodis@ijs.si (B. Smodiš).

0265-931X/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jenvrad.2012.02.009

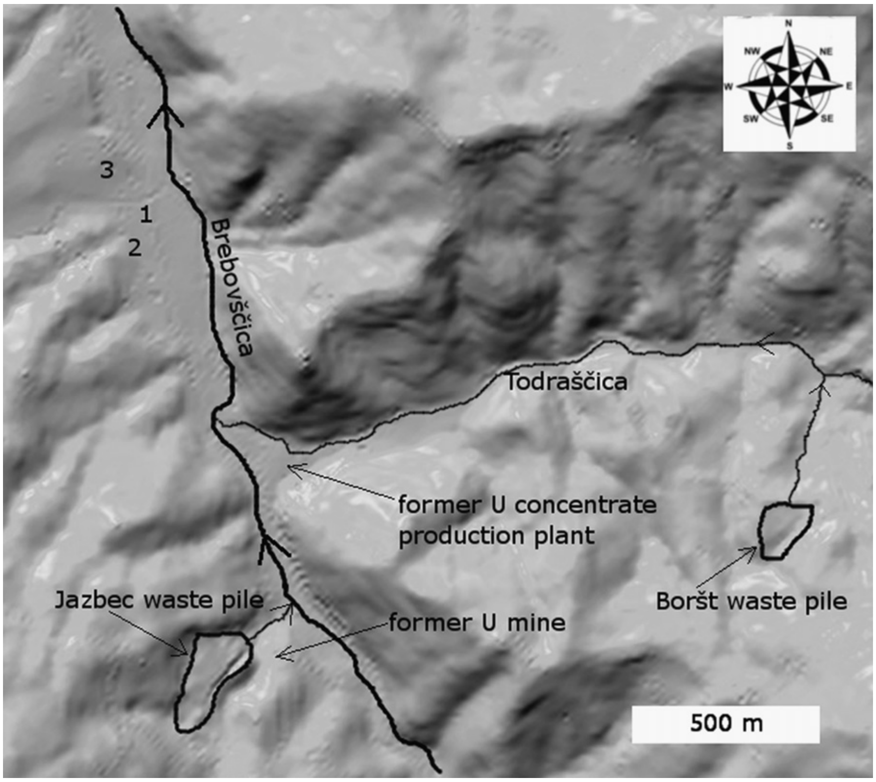


Fig. 1. Soil sampling locations (1–3) and area of the former uranium mine Žirovski Vrh.

homogenised and a subsample for the analysis was taken by hand quartering.

Sampling of fodder took place at the time when the cows were being fed. Due to possible variations in natural radionuclide activity concentrations in hay and silage, samples of hay and silage were randomly taken directly from the fodder bin of each cow. About 5 kg of hay and 5 kg of silage was collected and dried to constant weight. Hay and silage samples were not washed due to the fact that cows ingested hay and silage that is not washed and the transfer of radionuclides could not be assessed properly, if the samples would be washed.

Milk was collected from two cows (each with a weight about 500 kg), which were always kept indoors and were fed with hay and silage. About 2.5 L of milk was collected from each cow during milking and both samples were combined to get one sample of about 5 L of milk. Afterwards, the milk sample was weighed and then dried at 60 °C and reweighed to determine the dry matter content. The dried milk sample was homogenised and stored until analysis.

2.2. Radiochemical separation procedure for ^{238}U, ^{234}U, ^{232}Th, ^{230}Th, ^{226}Ra

The radiochemical separation procedure for ^{238}U, ^{234}U, ^{232}Th, ^{230}Th and ^{226}Ra is outlined below and the detailed procedure can be found in Štrok et al. (2010). All samples were analysed in duplicate. The radiochemical separation procedure was the same for soil, hay, silage and milk samples. Dried sample was first ashed at 650 °C in a muffle furnace to remove organic matter. After that, the sample was fused with Na_2O_2 and Na_2CO_3 at 900 °C. Then ^{232}U, ^{229}Th and ^{133}Ba tracers were added. The fusion cake was then dissolved by the addition of concentrated HNO_3, and transferred to a Teflon beaker. Then, the sample was further digested by the addition of concentrated HCl, HNO_3 and HF acids and H_2O_2. Finally, concentrated H_2SO_4 was added and evaporated until incipient dryness.

After final evaporation, radionuclides were co-precipitated on $Fe(OH)_3$. After washing, the precipitate was dissolved with 3 M HNO_3/1 M $Al(NO_3)_3$ and thorium was separated from uranium and radium on a TEVA separation column.

The uranium and radium-containing eluate obtained from the separation on the TEVA column was transferred to a UTEVA separation column, where uranium was separated from radium.

Radium and barium were co-precipitated from the radium-containing eluate with $PbSO_4$. Then the precipitate was dissolved in 0.1 M EDTA/0.5 M NaOH. Afterwards a $Ba(Ra)SO_4$ precipitate was formed by a consecutive addition of Ba carrier, pH 0–5 indicator, 1:1 acetic acid, a saturated solution of Na_2SO_4 and 0.125 mg/mL $BaSO_4$ substrate. After 30 min, the solution was filtered through a 0.1 μm filter. Finally, the filter was dried and mounted on a stainless steel planchet and dried again.

Thorium was microprecipitated from the thorium-containing eluate with NdF_3. Uranium from the uranium-containing eluate was firstly reduced with 15% $TiCl_3$ and then microprecipitated with NdF_3. Both thorium and uranium microprecipitates were placed in an ice bath for 30 min into an ice bath prior to filtration. Filtration was carried out through a 0.1 μm filter that was previously rinsed twice with 10 μm/mL NdF_3 substrate solution. Finally, the filter was mounted on a stainless steel disc and dried.

2.3. Radiochemical separation procedure for ^{210}Pb

Samples for ^{210}Pb were not ashed. In a similar manner as for uranium, thorium and radium, ^{210}Pb was also extracted using a radiochemical separation procedure adopted from Štrok et al. (2010) and is therefore only briefly summarised here. All samples were analysed in duplicate and the radiochemical separation

Table 1
Activity concentrations of ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po in soil, silage, hay and milk samples (Fresh milk mass to dry milk mass ratio was 7.9).

Sample	Activity concentration (Bq/kg dry mass)					
	^{238}U	^{234}U	^{230}Th	^{226}Ra	^{210}Pb	^{210}Po
Soil 1	65.0 ± 3.6	62.9 ± 3.5	58.1 ± 2.9	83.1 ± 4.0	51.3 ± 1.9	59.6 ± 2.0
Soil 2	65.1 ± 3.6	69.0 ± 3.8	65.2 ± 3.2	74.6 ± 3.7	48.7 ± 1.8	59.5 ± 2.2
Soil 3	60.5 ± 3.2	60.1 ± 3.2	64.6 ± 3.2	79.6 ± 2.9	119 ± 4	134 ± 5
Silage	0.213 ± 0.021	0.320 ± 0.027	0.561 ± 0.028	1.28 ± 0.08	14.7 ± 0.9	22.6 ± 0.85
Hay	0.218 ± 0.017	0.209 ± 0.017	0.125 ± 0.010	0.602 ± 0.036	14.4 ± 0.9	4.54 ± 0.19
Milk	0.0561 ± 0.0080	0.0622 ± 0.0085	0.0874 ± 0.0043	0.0659 ± 0.0052	0.302 ± 0.087	0.251 ± 0.019

procedure was the same for soil, hay, silage and milk samples. Firstly, Pb tracer was added to the sample and then the sample was digested with concentrated HNO_3 and HCl acids and H_2O_2. After digestion, the sample was evaporated and dissolved in 2 M HCl and Pb was separated on a Sr Resin separation column. Then the Pb-containing eluate was evaporated to dryness, dissolved with deionised water and a $PbSO_4$ precipitate was formed by the addition of concentrated H_2SO_4. Subsequently, the precipitate was transferred to a counting planchet, dried and weighed to gravimetrically determine the radiochemical recovery.

2.4. Radiochemical separation procedure for ^{210}Po

Samples for ^{210}Po were not ashed, All samples were analysed in duplicate and the radiochemical separation procedure was the same for soil, hay, silage and milk samples. The procedure for the separation is based on the procedure developed by Flynn (1968). Firstly, ^{209}Po tracer was added to determine the radiochemical recovery. Then the sample was digested overnight at room temperature with addition of 25 mL of conc. HNO_3 and 5 mL of conc. HCl. The next day, the sample was digested for 30 min at 200 °C. After cooling, 10 mL of H_2O_2 were added and heated for 10 min at 100 °C. When the sample had cooled to room temperature, it was filtered through a black ribbon filter paper. The residue was again introduced into the same Erlenmeyer flask and the whole digestion procedure was repeated. Both filtrates were combined and evaporated until dryness at 100 °C. Then 2 mL of concentrated HCl was added and the sample was again evaporated to dryness. This step was repeated once more. After that, 2 mL of concentrated HCl, 0.5 g of ascorbic acid and 0.5 g of hydroxylammonium chloride were added and the sample diluted to 100 mL with deionised water. Po was spontaneously deposited onto silver disc at 80 °C for 4 h.

2.5. Measurement system

The radionuclides ^{238}U, ^{234}U, ^{232}Th, ^{230}Th, ^{226}Ra and ^{210}Po were measured in a Canberra Alpha Analyst alpha spectrometry system with PIPS (Passivated implanted planar silicon) detectors. The radiochemical recovery for ^{226}Ra was determined via ^{133}Ba measurement on an HPGe spectrometer. The ^{210}Pb was measured in a low-background gas-flow proportional counter, which was previously calibrated to take into account self-absorption and ^{210}Bi in-growth (Štrok et al., 2008). Measurement uncertainties were propagated according to EURACHEM/CITAC Guide CG 4 (2000) and are reported as combined standard uncertainties with a coverage factor 1. All results are reported as mean values of two replicates and accompanied with the combined standard uncertainty. The differences between duplicates were within combined standard uncertainties.

3. Results and discussion

3.1. Activity concentrations of natural radionuclides in soil, silage, hay, and milk samples

Activity concentrations of ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po in soil, silage, hay and milk samples are shown in Table 1. Fresh mass to dry mass ratio for the milk sample was 7.9. It is evident that the activity concentrations of ^{238}U, ^{234}U, ^{230}Th and ^{226}Ra among the three soil samples did not differ substantially (one-way ANOVA P value was 0.427 for ^{238}U, 0.171 for ^{234}U, 0.172 for ^{230}Th and 0.194 for ^{226}Ra). However, ^{210}Pb and ^{210}Po activity concentrations were more than twice as high in the third soil sample (one-way ANOVA P value was <0.0001 for both ^{210}Pb and ^{210}Po). Activity concentrations of ^{230}Th and ^{210}Po were almost five times higher in silage than in hay, for ^{226}Ra they were about twice as high and for ^{238}U and ^{210}Pb they were comparable (Table 1). This could be attributed to the fact that at the same fields, grass was harvested in different time periods for hay as well as for silage, as well as in different growth stages, which are required to acquire the best grass characteristics for hay or silage. Since the grass for hay is dried on the sun, it is a few days longer exposed to the atmospheric deposition of ^{210}Pb and ^{210}Po, which could cause higher activity concentrations of these radionuclides in hay compared to silage. However, grass for silage is collected when it is still wet and the capacity for collecting the dust and possibly also soil particles during the harvesting and packing into bales is much higher comparing to hay, which is collected dry and actually a lot of deposited ^{210}Pb and ^{210}Po could deposit during the process of collection and transportation.

Table 2
Transfer factors (F_v) soil – silage and hay, concentration ratios (CR) silage and hay – milk and feed transfer coefficients (F_m) for ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po.

Radionuclide	F_v (soil – silage and hay)	CR (silage and hay – milk)	F_m (d/L)	
	This work	This work	This work	IAEA (2010)
^{238}U	0.00340 ± 0.00039	0.260 ± 0.048	3.2E-3 ± 0.6E-3	5.0E-4 – 6.1E-3
^{234}U	0.00413 ± 0.00078	0.235 ± 0.040	2.9E-3 ± 0.5E-3	/
^{230}Th	0.00548 ± 0.00053	0.255 ± 0.024	3.1E-3 ± 0.3E-3	/
^{226}Ra	0.0119 ± 0.0011	0.0703 ± 0.0077	8.6E-4 ± 0.9E-4	9.0E-5 – 1.4E-3
^{210}Pb	0.199 ± 0.016	0.0207 ± 0.0061	2.6E-4 ± 0.7E-4	7.3E-6 – 1.2E-3
^{210}Po	0.161 ± 0.014	0.0185 ± 0.0018	2.3E-4 ± 0.2E-4	8.9E-5 – 3.0E-4

For soil samples, the average ^{234}U/^{238}U isotopic ratio was about 1, for silage about 1.5, for hay about 1 and for milk about 1.1. These isotopic ratios are in accordance with expectations. Because of different time when the grass for the hay or silage was harvested, the level of groundwater, which has higher ^{234}U/^{238}U ratios than 1 due to recoil effect (Suksi et al., 2006), could be higher in the case of grass for silage, which is harvested in more wet period of the year and lower in the case of hay, which is harvested in the dry period of the year. The ^{234}U/^{238}U ratio in milk is between the ratios found in hay and silage, presumably because the cows ingested both feed at the same time. The ^{210}Po and ^{210}Pb in the soil and milk samples were almost in equilibrium, which was not the case for silage, where ^{210}Po activity concentrations were about 1.5 times higher and, in the case of hay, about 3 times lower than ^{210}Pb. Although lower ^{210}Po activity concentrations could be explained by ^{210}Po volatility (Mabuchi, 1958), it is not likely that the temperatures during drying of hay by the sun were higher than 80 °C, at which temperature ^{210}Po is still non-volatile. Therefore, the reason for ^{210}Po and ^{210}Pb discrepancy in hay and silage is unclear for us.

3.2. *Transfer factors (F_v), concentration ratios (CR) and feed transfer coefficients (F_m)*

For the calculation of transfer factors, the average values for soil samples were used. Results for silage and hay were combined, because cows were fed with about 50% of silage and 50% of hay during the collection of the milk sample. Soil – to – silage and hay transfer factors (plant/soil concentration ratios on a dry weight basis) are presented in Table 2. The highest soil to vegetation transfer factors were for ^{210}Pb, followed by ^{210}Po, ^{226}Ra, ^{230}Th, ^{234}U and ^{238}U. The reason for the substantially higher transfer factors for ^{210}Pb and ^{210}Po is probably atmospheric deposition of ^{210}Pb and ^{210}Po onto the surface of the grass, which would have been directly ingested by the cows. Therefore, transfer factors for ^{210}Pb and ^{210}Po calculated in our study should be regarded as a transfer of ^{210}Pb and ^{210}Po from soil, together with atmospheric deposition of ^{210}Pb and ^{210}Po onto grass.

Concentration ratios were calculated as milk/(silage and hay) and were calculated on a dry mass basis. As was done for transfer factors, the activity concentrations for silage and hay were combined, because cows were fed with 50% silage and 50% hay. It is evident from Table 2 that the concentration ratios for ^{238}U, ^{234}U and ^{230}Th are similar at about 0.25 (one-way ANOVA P value was 0.794). Concentration ratios for ^{226}Ra, ^{210}Pb and ^{210}Po were much smaller and were about 0.07 for ^{226}Ra and 0.02 for ^{210}Pb and ^{210}Po. The reason for that is most probably because ^{226}Ra is competing with Ca for the uptake into cows and that substantial amount of ^{210}Pb and ^{210}Po are in less available form adsorbed on particles, as a result of atmospheric deposition of these two radionuclides.

Feed transfer coefficients were also calculated and are presented in Table 2. This coefficient is calculated as the activity concentration in milk divided by the daily intake of a certain radionuclide with feed and is expressed in d/L. For calculation of the volume of milk, a milk density 1.03 kg/L was used. The data on daily intake of hay and silage was provided by the farmer and was about 10 kg dry mass. Similar as for concentration ratios, it can be concluded that the feed transfer coefficients for ^{238}U, ^{234}U and ^{230}Th were similar and for ^{226}Ra, ^{210}Pb and ^{210}Po they were much smaller (Table 2). Feed transfer coefficients for ^{238}U, ^{226}Ra, ^{210}Pb and ^{210}Po were within the range of those reported by the IAEA (2010) (Table 2).

Table 3
Committed effective dose per unit of intake by ingestion for adults and infants (IAEA, 2003).

Radionuclide	Committed effective dose per unit of intake by ingestion (Sv/Bq)	
	Adults	Infants (≤1 year)
^{238}U	4.5*10^{-8}	3.4*10^{-7}
^{234}U	4.9*10^{-8}	3.7*10^{-7}
^{226}Ra	2.8*10^{-7}	4.7*10^{-6}
^{230}Th	2.1*10^{-7}	4.1*10^{-6}
^{210}Pb	6.9*10^{-7}	8.4*10^{-6}
^{210}Po	1.2*10^{-6}	2.6*10^{-5}

Table 4
Annual effective ingestion doses due to milk ingestion for adults and infants.

Radionuclide	Adults		Infants (≤1 year)	
	E_{ing} (μSv/year)	Percentage	E_{ing} (μSv/year)	Percentage
^{238}U	0.039 ± 0.006	0.4	0.712 ± 0.103	0.2
^{234}U	0.047 ± 0.007	0.5	0.859 ± 0.120	0.2
^{226}Ra	0.285 ± 0.024	3.2	11.6 ± 1.0	3.0
^{230}Th	0.807 ± 0.046	8.9	38.1 ± 2.2	9.8
^{210}Pb	3.21 ± 0.93	35.6	94.4 ± 27.9	24.3
^{210}Po	4.64 ± 0.36	51.4	243 ± 19	62.5
Total	9.03 ± 1.37	100	389 ± 50	100

3.3. *Calculation of annual ingestion dose due to milk consumption*

For calculation of the annual effective ingestion dose due to radionuclides in milk, Eq. (1) was used.

$$E_{\mathrm{ing}} = h(g)_{\mathrm{ing}} a m \tag{1}$$

where E_{ing} is the annual effective ingestion dose due to a particular radionuclide in Sv/year, $h(g)_{\mathrm{ing}}$ is the committed effective dose per unit of intake by ingestion in Sv/Bq, a is the activity concentration of a particular radionuclide in the sample in Bq/kg dry weight and m is the annual intake of milk for certain group of individuals in kg/year. For the calculation, the data from Tables 1 and 3 were used. The committed effective doses per unit of intake by ingestion were taken from the IAEA International Basic Safety Standards (IAEA, 2003). Annual effective ingestion doses were calculated for adults and infants consuming milk from the farm where the sample was collected. The annual effective ingestion dose due to milk strongly depends on the milk consumption. In our study the mass of milk consumed annually by adults was 122 kg fresh weight and by infants 295 kg fresh weight (Omahen et al., 2006). In our study it was supposed that all annual milk consumption by the specific individual comes from the selected farm, which is rather conservative approach, because milk producers are selling the raw milk to dairies where it is mixed with other milk and most of the people consume milk and milk products, which are purchased from the shops and not from the farms directly. Nevertheless, it could be considered that the farmers are not purchasing milk from shops and are consuming their own milk.

The calculated annual effective ingestion doses are presented in Table 4 where it is evident that the highest contribution to the total annual effective ingestion is due to ^{210}Po (51.4% for adults and 62.5% for infants). This is mainly because the committed effective dose per unit of intake for ^{210}Po is much higher than for the other radionuclides analysed (Table 3). In addition, activity concentrations of ^{210}Po were higher than those of the other radionuclides, with the exception of ^{210}Pb (Table 1). The total annual effective ingestion dose due to ingestion of milk from the selected farm was about 9 μSv/year for adults and 389 μSv/year for infants.

4. Conclusions

The highest transfer factors from soil to silage and hay were for ^{210}Pb and the lowest for ^{238}U. Concentration ratios between cow's fodder and milk were the highest for ^{238}U and the lowest for ^{210}Po. A similar situation existed with feed transfer coefficients, which were comparable with already reported results (IAEA, 2010). The highest contribution to the total annual effective ingestion dose was due to ^{210}Po (51.4% for adults and 62.5% for infants).

Acknowledgements

We would like to thank the staff of the Rudnik Žirovski Vrh company for their cooperation and assistance. The financial support of the Slovenian Research Agency (Grant No. P2-0075) is highly appreciated.

References

Ababneh, Z.Q., Alyassin, A.M., Aljarrah, K.M., Ababneh, A.M., 2010. Measurement of natural and artificial radioactivity in powdered milk consumed in Jordan and estimates of the corresponding annual effective dose. Radiat. Prot. Dosim. 138, 278–283.

Al-Masri, M.S., Mukallati, H., Al-Hamwi, A., Khalili, H., Hassan, M., Assaf, H., Amin, Y., Nashawati, A., 2004. Natural radionuclides in Syrian diet and their daily intake. J. Radioanal. Nucl. Chem. 260, 405–412.

EURACHEM/CITAC Guide CG 4, 2000. Quantifying Uncertainty in Analytical Measurement, second ed.

Fesenko, S., Howard, B.J., Isamov, N., Voigt, G., Beresford, N.A., Sanzharova, N., Barnett, C.L., 2007. Review of Russian language studies on radionuclide behaviour in agricultural animals: part 2. Transfer to milk. J. Environ. Radioact. 98, 104–136.

Flynn, W.W., 1968. The determination of low levels of polonium-210 in environmental materials. Anal. Chim. Acta 43, 221–227.

Giri, S., Singh, G., Jha, V.N., Tripathi, R.M., 2011. Risk assessment due to ingestion of natural radionuclides and heavy metals in the milk samples: a case study from a proposed uranium mining area, Jharkhand. Environ. Monit. Assess. 175, 157–166.

Ghosh, D., Deb, A., Bera, S., Sengupta, R., Patra, K.K., 2008. Measurement of natural radioactivity in chemical fertilizer and agricultural soil: evidence of high alpha activity. Environ. Geochem. Health 30, 79–86.

Howard, B.J., Beresford, N.A., Barnett, C.L., Fesenko, S., 2009a. Radionuclide transfer to animal products: revised recommended transfer coefficient values. J. Environ. Radioact. 100, 263–273.

Howard, B.J., Beresford, N.A., Barnett, C.L., Fesenko, S., 2009b. Quantifying the transfer of radionuclides to food products from domestic farm animals. J. Environ. Radioact. 100, 767–773.

IAEA, 2003. International Basic Safety Standards for Protection against Ionizing Radiations and for the Safety of Radiation Sources. Safety Series No. 115.

IAEA, 2010. Handbook of Parameter Values for the Prediction of Radionuclide Transfer in Terrestrial and Freshwater Environments. Technical Report Series no. 472.

Ioannides, K.G., Mertzimekis, T.J., Papachristodoulou, C.A., Tzialla, C.E., 1997. Measurements of natural radioactivity in phosphate fertilizers. Sci. Total Environ. 196, 63–67.

ISO 11464:1994(E), 1994. Soil Quality – Pretreatment of Samples for Physico-Chemical Analyses. International Organization for Standarisation, Geneve.

Mabuchi, H., 1958. On the volatility of polonium compounds. Bull. Chem. Soc. Jpn. 31, 245–246.

Omahen, G., Benedik, L., Repinc, U., 2006. Measurements of the Radioactivity in the Žirovski Vrh Uranium Mine Environment and Assessment of Its Environmental Impacts – Results for 2005. Jožef Stefan institute, Ljubljana. IJS-DP-9342 (in Slovene).

Pietrzak-Flis, Z., Chrzanowski, E., Dembinska, S., 1997. Intake of ^{226}Ra, ^{210}Pb and ^{210}Po with food in Poland. Sci. Total Environ. 203, 157–165.

Suksi, J., Rasilainen, K., Pitkänen, P., 2006. Variations in ^{234}U/^{238}U activity ratios in groundwater – a key to flow system characterisation? Phys. Chem. Earth 31, 556–571.

Štrok, M., Repinc, U., Smodiš, B., 2008. Calibration and validation of a proportional counter for determining beta emitters. J. Power Energy Syst. 2, 573–581.

Štrok, M., Smodiš, B., Petrinec, B., 2010. Natural radionuclides in sediments and rocks from Adriatic Sea. J. Radioanal. Nucl. Chem. 286, 303–308.

Exhibit 9

Journal of Food Composition and Analysis 64 (2017) 198–202

Contents lists available at ScienceDirect

Journal of Food Composition and Analysis

journal homepage: www.elsevier.com/locate/jfca

Original research article

Uranium, polonium and thorium in infant formulas (powder milk) and assessment of a cumulative ingestion dose

Miha Trdin*, Ljudmila Benedik

Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia

ARTICLE INFO

Keywords:
Food analysis
Food composition
Infant formulas
Polonium
Uranium
Thorium
Dose assessment

ABSTRACT

It is well known that all food and foodstuffs contain naturally occurring radionuclides originating from uranium and thorium decay chains. Since a dose coefficient is always related to a specific radionuclide, it is therefore necessary to determine the activity concentrations of particular radionuclides when completing a radiological risk assessment. Dose coefficients, however, are age dependent, with the highest values being prescribed for infants. Due to the fact that the data on particular radionuclide content in infant formula are scarce, the aim of our research was their determination in infant formulas available on the Slovenian market. ^{238}U, ^{234}U, ^{230}Th and ^{210}Po activity concentrations were determined in five samples and dose assessment was carried out with dose coefficients listed in the IAEA International Basic Safety Standards (2014). The results obtained show that the main contributors to the estimated cumulative radiation dose (230 to 350 μSv y^{-1}) is ^{210}Po.

1. Introduction

According to the data available online (UNICEF, 2014; CDC, 2014; WHO, 2015) less than 40% of infants worldwide under six months are exclusively breastfed. The reasons for this low percentage vary, with the most common being a lack of mother's milk and socio-economic conditions (e.g. working mothers).

The diets of infants that are not exclusively breastfed are supplemented or completely comprised of powdered milk (baby formula) which is a special synthetic supplement designed to provide nutrients necessary for the normal development of infants. Depending on the infant's needs several different types of infant formulas are available on the market. Among the most common are those based on cow's milk (most infants do not have a problem ingesting cow's milk). However, for infants with strong sensitivity to cow's milk and for infants with other formula related medical or digestive conditions there are many special products available on the (Slovenian) market. (Novalac, 2016; Aptamil, 2016; Hipp, 2016)

The research on alpha-emitting radionuclides in infant formulas are scarce. Prabhath et al. (2015) reported ^{210}Po activity concentrations and the committed effective dose associated with it in Mumbai, India. The results showed that activity concentrations of ^{210}Po vary from 0.08 to 0.23 Bq/kg and that the average annual effective dose by ingestion of infant formulas is 150 μSv. Uwatse et al. (2015) determined ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs in 14 brands of powdered milk for infants from various regions around the world. The estimated annual effective doses for infants under 1 year was 635.13 μSv y^{-1}. Additionally, Štrok and Smodiš (2011) reported activity concentrations of ^{238}U, ^{234}U, ^{226}Ra, ^{210}Pb and ^{210}Po in infant formulas available on the Slovenian market. Their results showed that the highest combined annual effective ingestion dose for infants is 648 ± 98 μSv with the main contribution originating from ^{210}Po and ^{210}Pb.

For infants (< 1 years old), who form one of the most sensitive segments of the population, it is important to consider their exposure to different food contaminants, including various naturally occurring radionuclides. Infants in particular have a greater intestinal absorption and lower threshold for adverse effects than adults (Tripathi et al., 2001; Fergusson, 1990). In light of this information, we have decided to analyze activity concentrations of the natural alpha-emitting radionuclides (^{238}U, ^{234}U, ^{230}Th and ^{210}Po) in the most commonly used infant formulas available on the Slovenian market.

2. Materials and methods

All reagents used in the analysis were of analytical grade. The tracer solutions ^{232}U (SRS 82712-482), ^{209}Po (SRS 82710-482) and ^{229}Th (SRS 82711-482) and used in the study were prepared from calibrated solutions purchased from Analytics, Inc. (Analytics, Inc., Atlanta, GA, USA). The producer maintains traceability to the NIST (NIST, Gaithersburg, MD, USA). Uranium (U) standard solution (SRM 3164) was obtained from NIST. The extraction resins employed in this work was UTEVA®, available from Triskem International (Triskem

---

* Corresponding author.
E-mail address: miha.trdin@ijs.si (M. Trdin).

http://dx.doi.org/10.1016/j.jfca.2017.09.005
Received 4 January 2017; Received in revised form 27 July 2017; Accepted 9 September 2017

International, Brus, France).

Five samples (S1–S5) of infant formulas for infants aged 0–12 months from two different producers (Nutricia Zakłady Produkcyjne sp. z o.o., Poland (Aptamil) and UP Medi-Europa SA, Swiss (Novalac)) were analyzed.

Tap water from Ljubljana, Slovenia was also analyzed.

An alpha spectrometer (CANBERRA's Alpha Analyst™; Canberra Industries, Meriden, CT, USA) with passivated implanted planar silicon (PIPS) semiconductor detectors with an active area of 450 mm^2 and 28% efficiency for 25-mm diameter discs was used for alpha-particle spectrometry measurements. The measured source was placed in a parallel plane, centered at the symmetry axis of the detector at a distance (varying a bit amongst chambers) of about 5.0 ± 0.5 mm. The calibration of the detectors was made with a standard radionuclide source containing ^{238}U, ^{234}U, ^{239}Pu and ^{241}Am (code 67978-121), obtained from Analytics, Inc.

Water samples (~3 mL) were irradiated in the Institute's TRIGA MK II reactor in the pneumatic tube (rabbit system) at a neutron fluence rate of $4 \cdot 10^{12}$ $ncm^{-2} s^{-1}$ for up to 5 min with a uranium standard (~100 ng, NIST, Gaithersburg, MD, USA).

Infant formula samples (~ 0,5 g) were irradiated in the Institute's TRIGA MK II reactor in the pneumatic tube (rabbit system) at a neutron fluence rate of $4 \cdot 10^{12}$ $ncm^{-2} s^{-1}$ for 90 s with a uranium standard (~100 ng).

When ^{238}U is irradiated in a reactor the following capture reaction takes place:

$$^{238}U(n,\gamma)^{239}U(t_{1/2} = 23.5 \text{ min}) \rightarrow {}^{239}Np\ (t_{1/2} = 2.35 \text{ d}) \rightarrow$$

Gamma-ray measurements of isolated uranium fraction after irradiation and added U-235 for determination of recovery s were conducted by well-type HPGe detector with an active volume of 277 cm^3 (well diameter 26 mm, well depth 45 mm), having an absolute efficiency of 5.6% at 122 keV. Direct gamma-ray measurements of samples (approx. 30 g) were conducted with a coaxial HPGe detector (ORTEC GEM-30, 37% relative efficiency and 1.8 keV resolution for ^{60}Co at 1332 keV line). The detector was calibrated with a certified reference material "simulated vegetation" 85344-443 obtained from Eckert & Ziegler (Eckert & Ziegler, Berlin, Germany). The reference material and samples were measured in identical cylindrical containers. The density corrections were applied using EFFTRAN software (Vidmar et al., 2011; Vidmar, 2005). All spectra were evaluated using Genie-2000® software (Canberra Industries, Meriden, CT, USA).

For thermal fusion dissolution, a Cleise LeNEO furnace (Corporation Scientifique Claisse, Ville de Québec, QC, Canada) in combination with a platinum crucible and a Teflon beaker was used.

2.1. Radiochemical procedures

2.1.1. Determination of uranium mass concentration by radiochemical neutron activation analysis (RNAA)

Each sample (0.4–0.6 g) was sealed in a clean polypropylene container and irradiated simultaneously with a uranium standard (100 ng U/g) for 90 s at the Jožef Stefan institute's TRIGA Mark II reactor (Ljubljana, Slovenia).

Immediately after irradiation, the irradiated sample was rapidly wet-ashed over a glass flame in a 100 mL long-necked silica Kjeldahl flask already containing 3 mL of 9 mol L^{-1} sulphuric acid (Sigma-Aldrich, Steinheim, Germany) and 50 mg of natural uranium (prepared from $(UO_2)(NO_3)_2 \cdot 6H_2O$, Merck, Darmstadt, Germany) by heating with repeated additions of concentrated nitric acid (Sigma-Aldrich, Steinheim, Germany)until a pale yellow-green colour was obtained which did not darken on heating. The flask was then cooled by plunging into water, 1–2 mL of concentrated perchloric acid (Sigma-Aldrich, Steinheim, Germany) was added, and the flask reheated to evaporate the perchloric acid as dense white fumes. After dissolution the contents were transferred to a 50 mL separatory funnel with 20 mL of 5 mol L^{-1} nitric acid, split into two rinses. Uranium was extracted by vigorous shaking for 30 s with 50% tri-*n*-butylphosphate (TBP) (Sigma-Aldrich, Steinheim, Germany)in toluene (Sigma-Aldrich, Steinheim, Germany). The organic phase was briefly cleaned up with two washes of 5 mol L^{-1} nitric acid containing 0.2% hydrofluoric acid (Sigma-Aldrich, Steinheim, Germany). This washing helps to strip daughters decay products from natural uranium. The organic phase was drawn off by pipette, run into a measuring vial and measured directly in a Ge well-type detector (Byrne and Benedik, 1988; Repinc and Benedik, 2008). To avoid bias in the measurements, sample and standard were prepared in the same matrix and the measuring geometries.

2.1.2. Determination of ^{234}U, ^{238}U and ^{230}Th activity concentrations

For determination of thorium and uranium radioisotopes by alpha-particle spectrometry the samples (15–30 g) were ignited at 650 °C for 4 h and the remaining material was decomposed by lithium borates thermal fusion. The decomposed samples were loaded directly on the UTEVA® resin (Eichrom Technologies Inc., 2001) preconditioned in 3 mol L^{-1} HNO_3. The beakers were then washed twice with 3 mol L^{-1} HNO_3 (5 mL). After the sample was loaded the column was consecutively washed with 3 mol L^{-1} HNO_3 (20 mL) and 9 mol L^{-1} HCl (5 mL). In the next step thorium radioisotopes were stripped with 5 mol L^{-1} HCl with 0.5 mol L^{-1} oxalate (25 mL). In the final step the uranium radioisotopes were stripped with 1 mol L^{-1} HCl (15 mL). The sources for alpha-particle spectrometric measurement were prepared by microcoprecipitation with NdF_3 (Neodymium (III) Oxide) (Merck, Darmstadt, Germany) (Hindman, 1983; Sill and Williams, 1981). The neodymium fluoride suspension was filtered through a 0.1-µm polypropylene filter with a 25-mm diameter Resolve® filter (Eichrom Technologies, Lisle, IL, USA). The microcoprecipitate was dried under an infrared lamp, mounted on an aluminum disc, and measured on an alpha spectrometer.

2.1.3. Determination of ^{210}Po activity concentration

Determination of ^{210}Po was conducted according to the procedure described by Benedik and Vreček (2001). Each sample (5–6 g) to which Po-209 tracer was added was digested in a glass beaker at temperatures lower than 160 °C by mineral acids (HNO_3, $HClO_4$ and HF). The Po radioisotopes were deposited on a silver disc (Thessco B.V., Amsterdam-Zuidoost, Netherland). The measurements were conducted by an alpha spectrometer.

3. Results and discussion

In this study, 5 different types of infant formula for infants under 1 year of age from two of Slovenia's most popular producers of infant formulas were analyzed. It is worth mentioning that the analyzed infant formulas are widely available in pharmaceutical shops and supermarkets all over Slovenia. Samples 1–4 represent "normal" milk based infant formula with no modifications while sample 5 is a special formula that reduces the colonic fermentation which is responsible for bloating and excessive gas. Table 1 summarizes the details of the analyzed infant formulas and gives the date of ^{210}Po measurement. For the cumulative consumption calculation, the fact that infant diets should be supplemented with additional foods after the infant's 4th month was taken into account, as recommended by the producers. The cumulative consumption for each infant formula was calculated using the data available on the product's declaration.

To determine the activity concentrations of gamma-emitting radionuclides, the samples (approx. 30 g) were sealed in 100 mL plastic containers and after one month measured on a coaxial HPGE detector for 300 000 s. Inspection of the obtained spectra revealed that with the exception of ^{40}K and ^{210}Pb, no other gamma-emitting radionuclides had a high enough activity concentration to be accurately determined by direct gamma-ray spectrometry. Due to the low activity concentration

Table 1
Details about infant formulas samples and date of ^{210}Po activity concentration measurement as derived from each infant formula's declaration.

Sample	Type of sample	Date of manufacture	Expiration Date	Age of infant [month]	Cumulative consumption [kg/period]	Date of ^{210}Po measurement
S1	Milk Powder	n/a	5.10.2018	0–6	15.7	18.03.2016
S2	Milk Powder	n/a	14.06.2018	0–6	16.5	28.03.2016
S3	Milk Powder	14.01.2016	14.07.2017	0–6	19.4	18.04.2016
S4	Milk Powder	13.02.2016	13.08.2017	0–6	16.1	15.04.2016
S5	Milk Powder	n/a	7.09.2018	0–12	37.4	15.04.2016

Table 2
Activity concentrations of selected radionuclides in infant formula in Bq/kg. The uncertainty is given as an extended uncertainty at $k = 2$.

	S1	S2	S3	S4	S5
^{238}U [Bq/kg] *	0.0160 ± 0.0070	0.0296 ± 0.0070	0.0289 ± 0.0064	0.0335 ± 0.0082	0.0097 ± 0.0049
^{238}U [Bq/kg] **	0.0135 ± 0.0013	0.0194 ± 0.0028	0.0254 ± 0.0022	0.0201 ± 0.0025	0.0087 ± 0.0016
^{238}U [ng/g] **	1.09 ± 0.05	1.58 ± 0.11	2.06 ± 0.09	1.63 ± 0.10	0.71 ± 0.06
^{234}U [Bq/kg] *	0.0109 ± 0.0041	0.0358 ± 0.0081	0.0289 ± 0.0064	0.0371 ± 0.0084	0.0070 ± 0.0034
^{210}Po [Bq/kg] *	0.33 ± 0.14	0.358 ± 0.086	0.187 ± 0.066	0.162 ± 0.057	0.28 ± 0.11
^{230}Th [Bq/kg] *	0.577 ± 0.064	0.66 ± 0.24	0.462 ± 0.048	0.527 ± 0.054	0.292 ± 0.058

*Results were obtained by alpha-particle spectrometry.
**Results were obtained by RNAA (1 Bq/kg = 80.4 μg kg^{-1})

of ^{210}Pb in the samples and related possible interferences with background radiation, however, its activity concentration could not be accurately determined. The ^{40}K activity concentration on the other hand was between 200 and 300 Bq/kg.

The activity concentrations for the alpha-emitting radionuclides of interest are tabulated in Table 2. In light of the facts that for three samples the production date could not be derived from the product declaration and that all of the obtained samples were produced in the near past before obtaining them, the ^{210}Po activity concentration is given as measured on the day of the measurement (Table 1).

As illustrated in Fig. 1 the activity concentrations for each radionuclide of interest vary by up to 75% of the average value. The lowest uranium content (^{234}U and ^{238}U) was detected in samples 1 and 5. The highest uranium content was detected in infant formulas 2 and 4 which are meant for infants aged 6–12 months (these two infant formulas were made by two separate producers). The ^{210}Po content was higher in samples 1,2 and 5 which interestingly all originate from the same producer. For ^{230}Th, the lowest value was measured in a special powdered milk formula (S5) while the activity concentrations detected in other samples are comparable. The differences between ^{238}U activity concentrations obtained by RNAA and alpha-particle spectrometry are suspected to originate from differences in the sample mass used for the analysis: 0.5 g for RNAA vs. 15–30 g for determination by alpha-particle spectrometry.

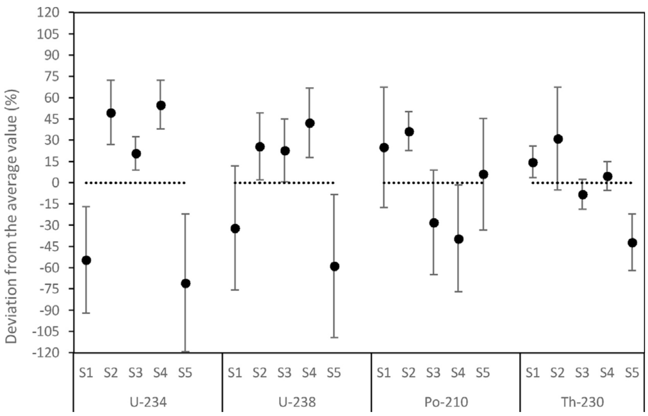


Fig. 1. Deviation of results from the average value for each individual radionuclide. The uncertainty is given as an extended uncertainty at $k = 2$.

For calculation of the cumulative effective ingestion dose, the following equations were used:

$$E = \sum E_{ing} \qquad (1)$$

$$E_{ing} = e(g)_{ing} am \qquad (2)$$

Where E is the cumulative effective dose, E_{ing} is the cumulative effective dose due to the particular radionuclide, $e(g)_{\mathrm{ing}}$ is the committed effective dose coefficient for a particular radionuclide per unit of intake by ingestion in *Sv/Bq*, *a* is the activity concentration of a particular radionuclide in *Bq/kg* and m is the cumulative intake of powdered milk in kg per unit period. The committed effective dose coefficients per unit of intake by ingestion are from the IAEA International Basic Safety Standards (2014). The committed effective dose coefficients are tabulated in Table 3.

As can be seen in Fig. 2, the main contribution to the estimated cumulative dose for infants originates from ^{210}Po (66–86%) and ^{230}Th (14–34%) while the contribution of uranium radioisotopes is negligible. On the other hand, if radioactive equilibrium between ^{210}Pb and ^{210}Po is assumed, the main contribution still comes from ^{210}Po (54–63%) while ^{210}Pb (18–20%) and ^{230}Th (17–28%) also present a significant part of the estimated cumulative dose (Fig. 3).

The estimated annual effective cumulative dose from the ingestion of the analyzed radionuclides can vary from 230 to 350 μSv y^{-1} and depends on the combination of infant formulas ingested by the infant since a specific infant formula can only be used at a specific age. On the other hand, if radioactive equilibrium between ^{210}Pb and ^{210}Po is assumed, the annual cumulative dose varies from 330 to 460 μSv y^{-1} depending on the combination of infant formulas used. The cumulative doses are tabulated in Table 4.

Table 3
Half-life ($t_{1/2}$) and Committed effective dose coefficient ($h(g)_{\mathrm{ing}}$) for infants (age ≤ 1 y) for the radionuclides of interest.

	$t_{1/2}$	$e(g)_{\mathrm{ing}}$ [Sv/Bq]
^{210}Po	133 d	2.60E − 05
^{210}Pb	22.3 a	8.4E − 06
^{230}Th	7,70E4 a	4.10E − 06
^{234}U	2,44E5 a	3.70E − 07
^{238}U	4,47E9 a	3.40E − 07

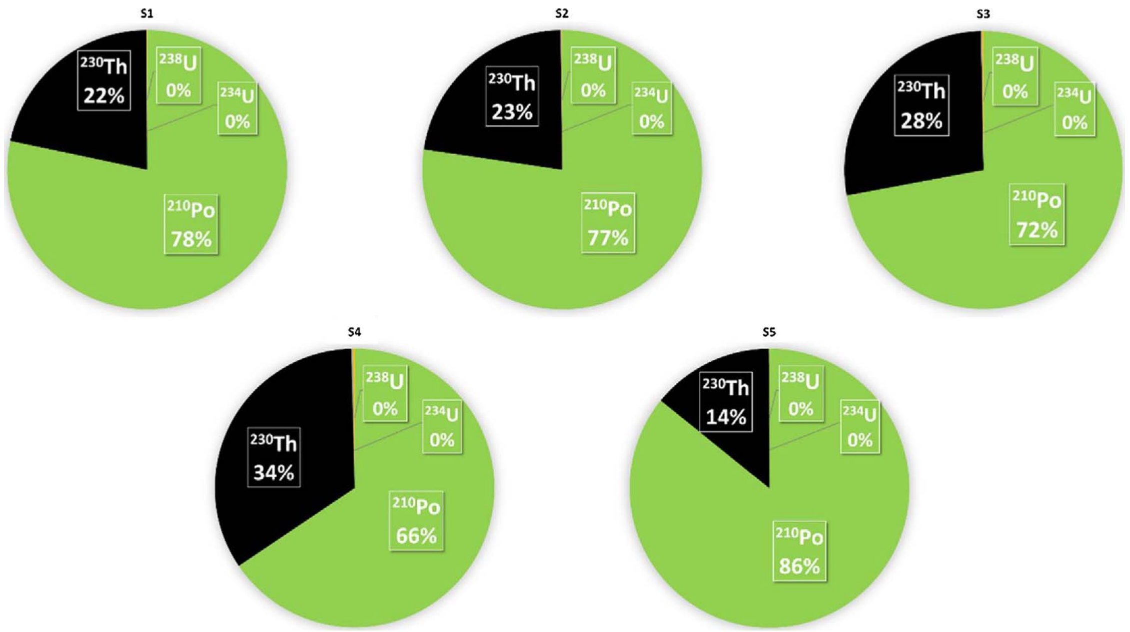


Fig. 2. Relative contribution of selected, analyzed radionuclides to the cumulative dose for infants from infant formulas.

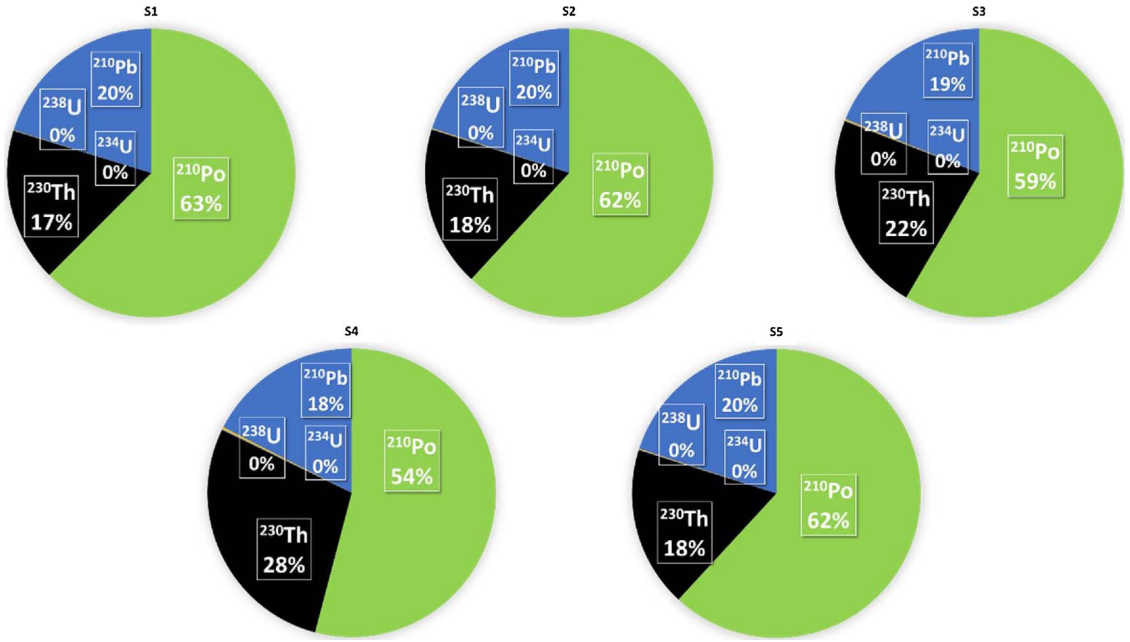


Fig. 3. Relative contribution of selected, analyzed radionuclides to the cumulative dose for infants from infant formulas if radioactive equilibrium between ^{210}Po and ^{210}Pb is presumed.

Table 4
Cumulative consumption in the period listed, as derived from the infant formula declaration and the cumulative dose during the same period. The uncertainty is given as an extended uncertainty at k = 2.

	Age of infant [month]	Cumulative consumption [kg]	Cumulative dose [μSv/per period]	Cumulative dose [μSv/per period]*
S1	0–6	15.7	**172 ± 26**	**215 ± 32**
S2	6–12	16.5	**198 ± 29**	**248 ± 37**
S3	0–6	19.4	**132 ± 22**	**164 ± 24**
S4	6–12	16.1	**102 ± 17**	**124 ± 19**
S5	0–12	37.4	**317 ± 49**	**404 ± 61**

The values are derived from the recommended daily intake provided by the producers.
* The cummulative dose if radioactive equilibrium between ^{210}Pb and ^{210}Po is presumed.

Table 5
Activity concentrations of radionuclides of interest in tap water from Ljubljana, Slovenia. The uncertainty is given as an extended uncertainty at k = 2.

^{210}Po	1.74E − 04	±	5.2E − 05	Bq/L
^{210}Pb	2.0E − 03	±	6.0E − 04	Bq/L
^{230}Th	1.78E − 03	±	1.2E − 04	Bq/L
^{234}U	6.11E − 03	±	4.8E − 04	Bq/L
^{238}U	4.76E − 03	±	3.9E − 04	Bq/L

In light of the fact that the infant formulas have to be dissolved in water before ingestion, the tap water from the Slovenian capital of Ljubljana was also analyzed to determine the contribution of the naturally present ^{210}Po, ^{210}Pb, ^{234}U, ^{238}U and ^{230}Th to the cumulative annual dose. The results show that the contribution to the annual cumulative dose is essentially negligible, reaching up to 8.5 μSv per year

Table 6
Volume of the tap water consumed with infant formula by an infant per period and the estimated cumulative dose.

Sample	age of infant [months]	Volume of tap water consumed [L]	Cumulative dose per period [μSv per period]
S1	0–6	110	3.6
S2	0–6	115	3.7
S3	0–6	129	4.2
S4	0–6	99	3.2
S5	0–12	261	8.5

(up to 5% of the estimated cumulative dose). The activity concentrations are tabulated in Table 5 and the resulting annual cumulative doses for the radionuclides of interest are tabulated in Table 6. The results obtained are in agreement with our previous study (Benedik and Jeran, 2012) where we determined the effective doses for adults, children (7–12 y) and infants (1–2 y). The values obtained, however, are well below the recommended reference dose level set by WHO of < 100 μSv y^{-1}. (WHO, 2011)

4. Conclusion

The obtained results show that ^{210}Po and ^{230}Th are responsible for more than 99% of the combined annual cumulative dose (230 to 350 μSv y^{-1}) derived from the activity concentrations of the selected radionuclides. Additionally, if radioactive equilibrium between ^{210}Pb and ^{210}Po is assumed, the combined annual cumulative dose reaches between 330 and 460 μSv y^{-1}. The tap water in which infant formula is dissolved, however, does not contribute noticeably to the estimated cumulative dose. The assessed dose from the radionuclides analyzed presents half of the effective dose allowed for public exposure. The latter is limited by council directive 2013/59/EURATOM to 1 mSv per year (EURATOM, 2014).

Author contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Acknowledgements

This work was financially supported by the Ministry of Education, Science and Sport of Slovenia (Project P1-0143). The research represents a part of the ERA Chair ISO-FOOD project for isotope techniques in food quality, safety and traceability.

References

Štrok, M., Smodiš, B., 2011. Natural radionuclides in milk from the vicinity of a former uranium mine. Nucl. Eng. Des. 241, 1277–1281.
Aptamil, 2016. Retrieved December 27, 2016 from: https://www.aptaclub.co.uk/products.
Benedik, L., Jeran, Z., 2012. Radiological of natural waters in Slovenia. Radiat. Prot. Dosim. 151, 306–313.
Benedik, L., Vreček, P., 2001. Determination of 210Pb and 210Po in environmental samples. Acta Chim. Slovenica 48, 199–213.
Byrne, A.R., Benedik, L., 1988. Evaluation of uranium at trace levels by radiochemical neutron activation analysis employing radioisotopic yield evaluation. Talanta 35, 161–166.
CDC, 2014. Breastfeeding Report Card United States/2014. Retrieved December 27, 2016 from: https://www.cdc.gov/breastfeeding/pdf/2014breastfeedingreportcard.pdf.
EURATOM, 2014. Council directive 2013/59/EURATOM. Off. J. Eur. Union L 13, Brussels, 1e73.
Eichrom Technologies Inc., 2001. Uranium and Thorium in water. Analytical Procedures ACW01 Rev. 1.7.
Fergusson, J.E., 1990. The Heavy Elements Chemistry, Environmental Impact and Health Effects. Pergamon Press.
Hindman, F.D., 1983. Neodymium fluoride mounting for alpha spectrometric determination of uranium: plutonium and americium. Anal. Chem. 55, 2460–2461.
Hipp, 2016. Retrieved December 27, 2016 from: http://www.hipp.de/milchnahrung/.
IAEA, 2014. Radiation Protection and Safety of Radiation Sources: International Basic Safety Standards. General Safety Requirements. IAEA Safety Standards Series No. GSR Part 3.
Novalac, 2016. Retrieved December 27, 2016 from: http://www.novalac.net/.
Prabhath, Ravi K., Sreejith, Sathyapriya R., Nair, Madhu G., Rao, D.D., Pradeepkumar, K.S., 2015. Determination of ^{210}Po concentration in commercially available infant formulas and assessment of daily ingestion dose. J. Radiat. Res. Appl. Sci. 8 (3), 470–476.
Repinc, U., Benedik, L., 2008. Development of the procedure for simultaneous determination of vanadium, uranium and manganese in biological materials using RNAA. Acta Chim. Slovenica 55, 653–659.
Sill, C.W., Williams, R.L., 1981. Preparation of actinides for alpha spectrometry without electrodeposition. Anal. Chem. 53, 415–421.
Tripathi, R.M., Raghunath, Radha, Mahapatra, Suchismita, Sadasivan, S., 2001. Blood lead and its effect on Cd, Cu, Zn: Fe and hemoglobin levels of children. Sci. Total Environ. 277, 161–168.
UNICEF, 2014. A post-2015 world fit for children: Issue brief: Breastfeeding. Retrieved December 27, 2016 from: https://www.unicef.org/agenda2030/files/Breastfeeding_2pager_FINAL1_web.pdf.
Uwatse, O.B., Olatunji, M.A., Khandaker, M.U., Amin, Y.M., Bradley, D.A., Alkhorayef, M., Alzimami, K., 2015. Measurement of natural and artificial radioactivity in infant powdered milk and estimation of the corresponding annual effective dose. Environ. Eng. Sci. 32, 1–9.
Vidmar, T., Kanisch, G., Vidmar, G., 2011. Calculation of true coincidence summing corrections for extended sources with EFFTRAN. Appl. Radiat. Isot. 69, 908–911.
Vidmar, T., 2005. EFFTRAN—a Monte Carlo efficiency transfer code for gamma-ray spectrometry. Nucl. Instrum. Methods Phys. Res. Sect. A 550, 603–608.
WHO, 2011. Guidelines for drinking water quality. 4th edition, Geneva, Switzerland. Retrieved December 27, 2016 from: http://www.who.int/water_sanitation_health/publications/.
WHO, 2015. 10 facts on breastfeeding. Retrieved December 27, 2016 from: http://www.who.int/features/factfiles/breastfeeding/en/.