



Research Brief #2

1993

Mobility and Transport of Radium in Sediments and Waste Pits

To study what actually happens to radium in sediment and waste pits, researchers from Louisiana State University are using field samples in controlled microcosms, which allow them to monitor continuously the redox potential (Eh) and the acidity/alkalinity (pH) of the soil suspensions. These two parameters have been shown to affect significantly the solubility of heavy metals and what species of those metals are found (that is, whether they occur as sulfides, hydrides, oxides). Using selective extraction techniques, the researchers analyzed the microcosm samples for radium. In addition, they used a computer model, MINTEQ, to provide a theoretical look at aspects of the soil chemistry that are difficult to measure using standard lab techniques, such as reactions that are likely to occur and chemical species that are likely to form under certain conditions.

Current Findings

Researchers obtained samples from an oil-field waste pit in Quarantine Bay, Louisiana. These samples contained radium-226 in much higher concentrations (700 picocuries/gram) than are found as the average background activity of soils in Louisiana (less than 5 picocuries/gram). Researchers initiated several experiments using the waste-pit material in the microcosms. They used two treatment methods: a completely anaerobic treatment that approximates the condition of the material in the field at an Eh of -250 mV and pH of 7.2, and an aerobic treatment with an Eh of +250mV and pH of 5.2. The aerobic treatment represents the condition that would occur if the waste-pit material was dredged to the

surface and exposed to air. The researchers incubated the samples under these conditions for several months and then sampled, extracted, and analyzed them for radium-226.

The initial results indicated that very little (less than 10 percent) of the total radium was present in a form that was extractable or otherwise available from the waste-pit material (such forms include water-soluble, exchangeable, associated with carbonates, reducible, or organic/sulfide). More than 90 percent of the radium present was tied up in a residual form that could be extracted only with very strong acids; therefore, this radium will be released very slowly from the contaminated sediment.

In addition, the researchers could find no significant difference between the aerobic and anaerobic samples despite the large differences in pH. Low pH is associated with more mobility; therefore, it was hypothesized that the samples receiving aerobic treatment would have more radium that was in an extractable form and potentially mobile. This was not the case, however, which suggests that radium may be fixed or coprecipitated in a mineral form that is resistant to these extracts. The researchers are currently investigating the waste-pit material using techniques such as X-ray diffraction to determine the minerals that exist in the waste pit so they can find out what the radium is coprecipitating with.

The researchers entered chemical data about the interstitial water (subsurface water contained in the spaces or pores

Summary of the Problem

When oil companies drill, they bring large volumes of brine, called produced waters, to the surface. These produced waters contain heavy metals and radionuclides, including naturally occurring radium-226. Produced water and drilling muds are commonly stored in waste pits created at the production site. Some waste pits and surrounding soils and sediments emit so much gamma radiation that, in Louisiana, around 20,000 oil-production sites have enough radioactive contamination to require permitting.

Little is known about the fate of radium in sediment and waste pits. To improve our ability to predict its migration into aquatic environments and the food chain, we must understand the physical and chemical processes controlling solubility and movement.

The overall objective of this study is to determine factors governing transport and movement of radium in the environment. The ultimate goal is to minimize the release of radium from contaminated sediments and oil-pit materials. Specific objectives are:

- to determine the effect of sediment redox/pH conditions on radium movement;
- to evaluate the effect of adding other positively charged ions and of changing salinity on radium solubility and movement in sediments and waste pits;
- to determine the distribution of radium in waters and sediment;
- to develop budgets and models for transport and movement of radium in sediment-water systems.

These processes are being investigated experimentally using model sediment and dike materials, as well as representative confined disposal facility (CDF) construction and fill material.

continued on back

in sediment or soil) obtained from these microcosm experiments into the MINTEQ program. The model predicted that the water could contain several orders of magnitude more dissolved radium. Therefore, no solid radium mineral is likely to be forming. The model did predict supersaturation for several minerals, including gypsum and many iron-containing minerals. This is significant because gypsum has been shown to quantitatively coprecipitate radium; that is, when the gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) precipitates, trace amounts of radium substitute for the calcium. Consequently, the radium is incorporated or "fixed" within the gypsum and can only be released when the mineral is dissolved. Since gypsum is supersaturated, it will precipitate out and the researchers can extract it from the sediment. This evidence, along with the microcosm studies, suggests that radium in the waste-pit material is insoluble and likely is tied up in a co-precipitated mineral phase, possibly gypsum. Further work is being done to characterize this process. It is possible that a different set of conditions in contaminated sediments (for example, different mineralogy or composition) will affect radium solubility and sorption. These results may lead to a recommended practice of managing contaminant sediments and waste-pit material to prevent the release of radium.

Project Status

The researchers are completing experiments using the waste-pit material. They will continue to work to characterize the mineralogy and chemical properties of this material. Also, they are sampling at a second site in the Barataria basin in southeast Louisiana. This location is a bayou in a brackish marsh that has received produced-water inputs from an oil field and has been identified in a Louisiana Department of Environmental Quality report as containing high activities of radium-226. The researchers will conduct identical experiments and MINTEQ modeling with this sediment for comparison with the waste-pit material.

After determining the redox-pH chemistry of radium in these two representative materials, researchers will concentrate on two key questions. First, they will quantify the potential for the release of radium from both sediment and waste-pit material, using sediment cores to approximate the actual physical conditions at the sediment-water interface. Based on these studies and sorption data gathered in the first year, they will modify and use the models previously derived for radium in marine systems to describe the release of radium from these sediments. Second, they plan to further investigate the effect of radium releases, specifically looking for any change in the physical or chemical status of the contaminated materials that may result in a change in the solubility of radium (such as aeration and pH changes).



Director:

Danny D. Reible, Ph.D.

Louisiana State University
Baton Rouge, Louisiana 70803
Phone: 225/578-6770
FAX: 225/578-5043

Co-Directors:

F. Michael Saunders, Ph.D.

Georgia Institute of Technology
Atlanta, Georgia 30332
Phone: 404/894-2265
FAX: 404/853-3177

C. Herb Ward, Ph.D.

Rice University
Houston, Texas 77251
Phone: 713/527-4086
FAX: 713/285-5203

Training & Technology Transfer Director:

Leigh F. McCook

Georgia Tech Research Institute
Atlanta, Georgia 30332
Phone: 404/894-7898
FAX: 404/894-2184

Principal Investigators

Wetland Biogeochemistry Institute
Louisiana State University—

R.D. DeLaune
J.H. Pardue
W.H. Patrick, Jr.
C.W. Lindau

Research Brief #2, 1993