Utilizing Isotopic Uranium Ratios in Groundwater Evaluations at FUSRAP Sites

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ABSTRACT

The U.S. Army Corps of Engineers Buffalo District is evaluating environmental radioactive contamination at several Formerly Utilized Sites Remedial Action Program (FUSRAP) sites throughout New York, Pennsylvania, Ohio, and Indiana. The investigations follow the process defined in the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). Groundwater data from the Niagara Falls Storage Site (NFSS) in Lewiston, New York were evaluated for isotopic uranium ratios, specifically uranium-234 versus uranium-238 (U-234 and U-238, respectively), and the results were presented at Waste Management 2006. Since uranium naturally occurs in all groundwater, it can be difficult to distinguish where low-concentration impacts from past releases differ from the high end of a site-specific natural background range. In natural groundwater, the ratio of U-234 to U-238 exceeds 1 (unity) due to the alpha particle recoil effect, in which U-234 is preferentially mobilized to groundwater from adjacent rock or soil. This process is very slow and may take hundreds to thousands of years before a measurable increase is seen in the natural isotopic ratio. If site releases are the source of uranium being measured in groundwater, the U-234 to U-238 ratio is commonly closer to 1, which normally reflects FUSRAP-related, uranium-contaminated wastes and soils. This lower ratio occurs because not enough residence time has elapsed since the 1940s and 1950s for the alpha particle recoil effect to have significantly altered the contamination-derived ratio. An evaluation of NFSS-specific and regional groundwater data indicate that an isotopic ratio of 1.2 has been identified as a signature value to help distinguish natural groundwater, which may have a broad background range, from zones impacted by past releases.

INTRODUCTION

Uranium is a naturally occurring radioactive metal that is fairly mobile in the subsurface environment. At least 54 former or current sites listed on the National Priorities List (i.e., Superfund sites) have uranium contamination [1]. In addition, there are several other sites that have uranium contamination in soils and groundwater which are being addressed as part of the Formerly Utilized Sites Remedial Action Program (FUSRAP). The Energy and Water Appropriations Act for Fiscal Year 1998 transferred responsibility for administering and executing FUSRAP from the USDOE to the USACE in October 1997. The Buffalo District of the USACE has responsibility for approximately 12 FUSRAP sites, several of which have elevated concentrations of uranium in the groundwater. These FUSRAP investigations follow the process defined in the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA).

Uranium is one of the more mobile radioactive elements [4]. At a contaminated site uranium can leach from a soil source term to the groundwater, resulting in not only elevated concentrations of uranium in groundwater, but also in altered ratios of U-234 to U-238 (denoted U-234:U-238) in groundwater. The site-specific U-234:U-238 ratio will be affected not only by whether or not the uranium soil contamination contains enriched or depleted uranium, but also the age and magnitude of the soil source term. Development of a site-specific groundwater ratio of U-234 to U-238 can assist at various stages of the CERCLA process, leading to more efficient site close-out. For example, a site-specific U-234:U-238 ratio can assist in differentiating groundwater locations that are impacted with site-related contamination versus those that contain only naturally occurring concentrations of uranium, including locations that are assumed to represent "background" or "reference" conditions, and (ii) supporting both risk and dose calculations for uranium, by reducing the number of different analysis that need to be performed by creating a site-specific conversion between uranium mass concentrations and uranium radioactivity concentrations (and vice-versa).

BACKGROUND

All soils and rock exhibit differing levels of radioactivity depending on varying levels of naturally-occurring potassium, uranium, thorium, and radium. In soil and radioactive wastes containing natural uranium, the ratio of U-234 to U-238 is essentially 1 or unity. However, naturally occurring uranium groundwater can have an elevated U-234:U-238 ratio that increases with time due to the alpha-particle recoil effect. This phenomenon occurs when a U-238 atom radioactively decays by emitting an alpha particle to form thorium-234 (Th-234), which then causes the nucleus to recoil in the opposite direction to conserve momentum. If this U-238 atom is adsorbed to rock or soil that is in contact with groundwater, the relatively short-lived (~24-day) daughter product Th-234 can have sufficient recoil energy to shortly enter the aqueous phase and then re-adsorb to the host soil or rock. This Th-234 atom transforms quickly to U-234 through two successive beta-particle decays and becomes more mobile than Th-234 in adjacent groundwater due to lower partitioning coefficients for uranium [5].

This mechanism is limited by the soil-groundwater phase interface and recoil geometry, although over considerable time, groundwater concentrations of U-234 can become much higher than those of U-238. The ratio of U-234 to U-238 in natural groundwater typically ranges from 1 to 3 and can reach 10 or more, which usually reflects hydrostratigraphy, location-specific hydrogeochemical factors, host rock mineralization, and chemical reactions along flow paths [7, 8, 9]. Since natural U-234:U-238 ratios and raw data may vary between water-bearing zones, this variability should be accounted for when evaluating uranium source term(s) against groundwater sampling results, especially for results at, or only slightly above, the high end of a background range.

The U-234:U-238 ratios in groundwater at FUSRAP sites with uranium groundwater contamination are commonly near 1, assuming depleted or enriched uranium are not present. This unity ratio reflects limited residence time in groundwater (<50 years), which should preclude the influence from the alpha particle recoil effect. Since background groundwater from upgradient or off-site sources may exhibit ratios higher than unity (or 1), especially from deeper hydrogeologic units, these data can produce signature ratios to more clearly bound contaminant plumes for cleanup decisions.

Groundwater at many FUSRAP sites contain elevated (i.e., above background) levels for a number of radioactive contaminants (including uranium) in several isolated plumes. The full delineation of these plumes can be complicated by variations in natural background groundwater, so the development of site-specific signatures for uranium ratios can help to better define the nature and extent of contamination at a site.

METHODS

Groundwater samples collected at FUSRAP sites were analyzed for isotopic uranium via alpha spectroscopy, following DOE method EML HASL-300. The U-234 and U-238 groundwater data were evaluated separately as a dissolved fraction dataset and total fraction dataset. In addition, background (upgradient or off-site) and site-related data also were evaluated statistically for trends and possibly signature values for U-234:U-238 ratios. Previous analyses [3] included the generation of background upper tolerance limits (UTLs) based on statistical or data-population results. The background UTLs were used to distinguish whether on-site sampling results indicated contamination (i.e., exceeded UTLs) and ensured that site contaminants did not unknowingly influence the background groundwater data. In Rhodes et al. [3], some slightly elevated background groundwater data were omitted from the UTL calculations due to near-unity ratios indicative of minor site influences.

RESULTS

Summaries of uranium isotopic concentrations for some FUSRAP sites investigated by the USACE Buffalo District are presented in the poster (see Poster Session 45, Topic B).

Niagara Falls Storage Site

The Niagara Falls Storage Site (NFSS) is a federally owned 191-acre site located in Lewiston, New York, approximately 10 miles north of Niagara Falls. The NFSS was used by the Manhattan Engineer District (MED) to store radioactive residues and wastes from uranium ore processing beginning in 1944, until the late 1950s. In 1982

the Department of Energy (DOE) began clean-up and consolidation of the radioactive wastes and residues into a 10-acre earthen containment cell constructed on the property, where they currently remain [10].

Rhodes et al. [3] produced a site-specific background UTL to screen on-site groundwater for contamination. Select wells exhibited marginal UTL exceedences in areas where either historical operations did not occur, migration would not have produced the exceedences, or other isotopes did not exceed UTLs. Consequently, a signature U-234:U-238 ratio value of 1.2, as derived from a tolerance limit evaluation, was compared to the data in question and the existence of suspect plumes were dismissed as an artifact of analysis uncertainty. The data evaluation and results in Rhodes et al. [3] generally support other FUSRAP site information regarding site contamination profiles and hydrostratigraphic variations in U-234:U-238 ratios.

Harshaw

The Former Harshaw Chemical Site is in Cleveland, Ohio on a 55-acre site along the Cuyahoga River and Big Creek, within an industrialized area of developed and undeveloped land parcels. Site parcels include former production areas with remaining facility buildings, former production area foundations, and parking areas associated with previously demolished buildings, and redeveloped privately-owned commercial properties. The Harshaw Chemical Company (HCC) refined uranium oxide feed material to produce numerous uranium based materials under contract to the Manhattan Engineer District (MED) and the Atomic Energy Commission (AEC) from 1942 through 1959 [11].

Luckey

The 40-acre Luckey site is located near Luckey, Ohio and comprised of a large production building and warehouse and minor structures surrounded by residential farmland. From 1949 to the early 1960s, the AEC contracted the Brush Beryllium Company to process beryllium from different types of source media or potential contaminants to support the national defense program. Primary source media at the Luckey site included materials delivered for processing or re-processing beryl ore from Africa and South America, scrap beryllium, and radiologically-contaminated scrap steel [12].

Linde

The Linde Site is now owned by Praxair, Inc. and comprises about 135 acres in the Town of Tonawanda, New York. The property contains various manufacturing and support structures for approximately 1,400 employees. During the early to middle 1940's, portions of the Linde Air Products Corp. were used for the separation of uranium ores under a MED/AEC contract, which resulted in elevated radionuclide levels in groundwater due to waste-fluid injection into portions of lower aquifer under the Linde property [13].

Shallow Land Disposal Area

The Shallow Land Disposal Area (SLDA) is located in Parks Township, Pennsylvania and received wastes from the nearby Apollo Nuclear Fuel Fabrication Facility, which was used to convert enriched uranium to naval reactor fuel. Waste streams from Apollo were disposed of in trenches at the SLDA between 1961 and 1970 in accordance with the United States Atomic Energy Commission (AEC) regulation in effect at the time, 10 CFR 20.304, "Disposal by Burial in Soil," which was subsequently rescinded in 1981. The 44 acre site is currently maintained under an NRC license (SNM-2001) and the USACE was tasked with remediating the radioactive wastes at SLDA under the FUSRAP, as a result of the Fiscal Year 2002 Defense Appropriations Act, Public Law (P. L.) 107-117, Section 8143 [14].

Joslyn

The Joslyn Manufacturing and Supply Co. is a 63 acre industrial site in Fort Wayne, Indiana that held a 1944 to 1949 contract with the University of Chicago to roll and machine uranium rods from billets. The USACE is currently performing a CERCLA site inspection in order to determine whether or not a radiological release occurred into site soils and groundwater [15].

DISCUSSION

Ranges of site-specific ratios can be explained by evaluating the various site data according to well depth or site hydrostratigraphy. One would expect U-234:U-238 ratios to be typically higher in lower confined aquifers, hydraulically tight units of low hydraulic conductivity, or bedrock units that would provide enough residence time for the alpha particle recoil effect to alter the ratios. Conversely, one would expect shallow and unconfined overburden aquifers that receive ample aerial recharge and then discharge to local surface drainages as having ratios reflecting natural uranium ratios near unity since the alpha-particle recoil effect is minimal.

CONCLUSIONS

The use of U-234:U-238 ratios can support decision making processes, especially where suspect groundwater sampling results originally considered impacted may be reclassified as unimpacted when the ratios are similar to or higher than a background-signature ratio value (i.e., ratio values indicative of background conditions).

Conversely, in situations where it is difficult to place upgradient wells that may be unequivocally unimpacted by site contamination, the use of the U-234:U-238 ratio can assist in the determination of whether or not the upgradient wells truly contain only background or naturally occurring concentrations of uranium in groundwater samples [3].

This technique could allow the USACE to more accurately assess the measured data in a timely manner and should reduce the remediation uncertainty, which will optimize remediation resources to best address site-related releases.

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REFERENCES

1. Agency for Toxic Substances and Disease Registry (ATSDR), 1999. *Toxicological Profile for Uranium*.
2. Environmental Protection Agency (EPA) 2000. *Federal Register Notice December 7, 2000. 40 CFR Parts 9, 141, and 142National Primary Drinking Water Regulations; Radionuclides; Final Rule*
3. Rhodes, M. C., et al 2006. Utilizing Isotopic Uranium Ratios in Groundwater Evaluations at NFSS. Proceedings for 2006 Waste Management Conference, Tucson Arizona.
4. EPA 1999. *Understanding Variation In Partition Coefficient, Kd, Values.* EPA 402-R-99-004A
5. Arndt, M.F., and L. West, 2005, "A Study of the Factors Affecting the Gross Alpha Measurement, and a Radiochemical Analysis of some Groundwater Samples from the State of Wisconsin Exhibiting an Elevated Gross Alpha Activity," http://www.slh.wisc.edu/ehd/radiochem/dnr_reports/dnrfinal.pdf, accessed January.
6. MacDonell, et al., 2005. "Using Isotopic Uranium Ratios as a Signature for Contaminated versus Uncontaminated Groundwater," 2005 International Conference of Environmental Remediation and Radioactive Waste Management. Glasgow, Scotland, September.
7. Hess, C.T., et al., 1985, "The Occurrence of Radioactivity in Public Water Supplies in the United States," Health Physics, 48:553-586.
8. Myrick, T.E., B.A. Berven, and F.F. Haywood, 1983, "Determination of Concentrations of Selected Radionuclides in Surface Soil in the U.S.," Health Physics, 45:631-642.
9. Cothern, C.R., and W.L. Lappenbusch, 1983, "Occurrence of Uranium in Drinking Water in the U.S.," Health Physics, 45:89-99.
10. USACE, November 2003. *Fact Sheet: Niagara Falls Storage Site*. http://www.lrb.usace.army.mil/fusrap/nfss/index.htm#Documents
11. United States Army Corps of Engineers (USACE), October 2006. *Remedial Investigation Report for the Former Harshaw Chemical Company FUSRAP Site, Cleveland, Ohio.* Prepared by Sciences Application International Corporation (SAIC), Twinsburg OH, for the Buffalo District USACE.
12. United States Army Corps of Engineers (USACE), June 2006. *Record of Decision for Soils Operarable Unit, Luckey FUSRAP Site, Luckey, Ohio.* Prepared by Sciences Application International Corporation (SAIC), Twinsburg OH, for the Buffalo District USACE.
13. United States Army Corps of Engineers (USACE), March 2006. *Proposed Plan for Groundwater Operarable Unit, Linde FUSRAP Site, Tonawanda, New York.* Prepared by Sciences Application International Corporation (SAIC), for the Buffalo District USACE.
14. USACE, November 2006. *Proposed Plan for the Shallow Land Disposal Area FUSRAP Site, Parks Township, Armstrong County, Pennsylvania.* Prepared by the Buffalo District USACE.
15. USACE, October 2005. *Preliminary Assessment for the Joslyn FUSRAP Site, Fort Wayne, Indiana.* Prepared by the Buffalo District USACE.