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Environmental Applications of Stable Xenon and Radioxenon Monitoring

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Characterization of transuranic waste is needed to make decisions about waste site remediation. Soil-gas sampling for xenon isotopes can be used to define the locations of spent fuel and transuranic wastes. Radioxenon in the subsurface is characteristic of transuranic waste and can be measured with extreme sensitivity using large-volume soil-gas samples. Measurements at the Hanford Site showed ^{133}Xe and ^{135}Xe levels indicative of ^{240}Pu spontaneous fission. Stable xenon isotopic ratios from fission are distinct from atmospheric xenon background. Neutron capture by ^{135}Xe produces an excess of ^{136}Xe in reactor-produced xenon providing a means of distinguishing spent fuel from separated transuranic materials.

Introduction

Nuclear weapon and nuclear energy production have left a legacy of radioactive waste and contaminated soil. Transuranic waste, defined as material with > 3,700 Bq/g (100 nCi/g) of man-made isotopes with atomic number greater than uranium (> 92), is of particular concern due to generally long half-lives, high toxicity, and stringent regulatory requirements for disposal. Advanced characterization techniques that are minimally

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invasive are desirable to locate buried waste and to evaluate the extent of environmental releases.

Monitoring of xenon as a surrogate for transuranic waste is attractive because xenon is a relatively non-reactive gas with a high environmental mobility. Fission xenon is isotopically distinct from atmospheric xenon. Due to the short half-lives (< 1 week), the radioxenon isotopes in legacy waste materials can be attributed to in-situ spontaneous fission. The stable isotopes may be from spontaneous fission or remain from original nuclear reactor exposure.

Monitoring of xenon gas in the subsurface is analogous to soil gas monitoring for volatile organic compounds. Either temporary or permanent sampling points are installed near suspected source locations. Gas-sample concentrations are interpreted to provide indication of the proximity and concentration of the source material.

This paper describes the theory and example results of stable and radioxenon monitoring in waste sites at U.S. Department of Energy facilities. The work consists of the following activities: 1) Sampling of radioxenon and stable xenon isotopes at a liquid waste disposal facility that received large amounts of transuranic waste at the U.S. Department of Energy's Hanford Site in southeastern Washington State, 2) sampling of stable xenon isotopes at a solid waste burial ground with unknown transuranic inventory at the Hanford Site, and 3) modeling of xenon gas transport and distribution for evaluation of the applicability to waste site characterization at the Idaho National Laboratory in southeastern Idaho.

The gas composition of the atmosphere is the standard for rare gas stable isotopic measurements and is considered fixed, although isotopic ratios may vary in minerals and

deep subsurface fluids due to natural fission and mantle contributions[1,2]. The deep
subsurface sources are unlikely to shift the shallow soil gas from atmospheric
composition. ^{131}Xe, ^{132}Xe, ^{134}Xe, and ^{136}Xe are naturally occurring stable isotopes and
are also produced through fission reactions[3]. Thus, anthropogenic inputs may affect the
stable xenon isotopic composition of soil gas near waste sources if exchange with the
atmosphere is sufficiently restricted. The differences in thermal neutron fission yield for
^{235}U and ^{239}Pu are not large for the xenon isotopes of interest.

Radioxenon is a sensitive indicator of nuclear production due to the insignificant
natural background[4,5,6]. Anthropogenic sources of atmospheric radioxenon background
include releases from nuclear power plants, medical facilities, and potentially, nuclear
weapons testing. ^{133}Xe (5.243 day half life) and ^{135}Xe (9.10 hour half life) are of interest
for environmental monitoring of transuranic wastes.

EXPERIMENTAL

Sampling and Analysis

Proof-of-principle sampling of xenon was performed at one liquid waste disposal
facility, the 216-Z-1A tile field, and at the 618-11 radioactive waste burial ground at the
Hanford Site (Figure 1). Both radioxenon and stable xenon samples were collected at the
216-Z-1A tile field but only stable xenon isotopes could be sampled at the 618-11 burial
ground because the previously installed sampling points were not of sufficient diameter
to collect the large volume of gas needed for the radioxenon analysis.

The 216-Z-1A tile field received liquid waste containing approximately 57 kg of
weapons grade plutonium. The waste was from the final stages of processing so it
contained minimal fission products or uranium. Gas for radioxenon analysis was

collected from two pre-existing 15-cm-diameter, open-bottom, carbon-steel vadose well casings within the 216-Z-1A tile field. The samples were composited for analysis. The casing extended approximately 6.1 m below the ground surface or 1.5 m below the waste discharge. The maximum plutonium contamination was found at the bottom of the boreholes during geophysical logging[7].

The 618-11 burial ground received a wide variety of contact and remote handled research waste. The disposal was poorly documented. The burial ground contains 3 trenches. Numerous vertical caissons and "vertical pipe units" located in the northeast part of the burial ground were used for disposal of remotely handled waste. The samples were collected from three existing soil gas monitoring points consisting of 0.25-cm-interior diameter plastic tubing connected to an ~ 20-cm-long fine mesh stainless steel screen The points were located outside the burial ground fence line and installed to a depth of ~ 6 m below ground surface using a Geoprobe® direct-push rig. The installation method returns no cuttings to the surface thereby reducing contamination concerns.

The sampling vessels for stable xenon isotopes were 50-ml stainless steel cylinders. Each vessel was evacuated to less than 667 Pa before sampling. The flow was adjusted to 1 L per minute, and the soil gas sampling point was allowed to purge for a minimum of 15 minutes. The sampling cylinder was pressurized to a gauge pressure of ~140 kPa.

When sampling for the radioactive xenon isotopes a SCUBA-type compressor was used to pressurize two ~43.8-L gas cylinders to a gauge pressure of ~14,000 kPa for each sample, giving a total gas volume of ~12,000 L at standard temperature and pressure. Assuming a soil porosity of 0.3, this represents a 2.1 m radius of interrogation.

Stable xenon isotopes were analyzed by rare gas mass spectrometry at Lawrence Berkeley National Laboratory on an all-metal, high-resolution magnetic sector mass spectrometer. The samples were purified by passing over a series of cold traps and metal alloy getters to remove other air components. The residual rare gas fraction was sorbed onto activated carbon at 77 K and sequentially desorbed into the mass spectrometer.

Radioactive xenon isotopes were analyzed on an Automated Radioxenon Sampling and Analysis (ARSA) system developed for Comprehensive Test Ban Treaty verification. The ARSA uses a series of chillers and sorbants to separate and concentrate xenon from air then quantifies the xenon isotopes in a gas cell scintillation counter using beta-gamma coincidence counting.[8]. The removal of radon is important because radon background is about 10 mBq/m^3 in the atmosphere and certainly greater in soil gas. Make-up nitrogen containing no radioactive xenon was introduced for the duration of the 8-hour analytical cycle.

Transport Calculations

A two-dimensional, multi-phase flow and transport model was developed to evaluate the applicability of xenon soil-gas monitoring and to assess whether sampling would likely be effective adjacent to buried waste or in the cap above the waste. Sampling schemes that avoid direct penetration of waste trenches would better safeguard workers and lead to considerable cost savings. The model was developed for a generic waste trench in a semi-arid environment using parameters representative of buried transuranic waste at the Idaho National Laboratory[9]. Although this is not the location of proof-of-principle testing described above, it provides a conceptual basis for the interpretation of the results and for guiding future studies. A major difference between

the model parameters and the Hanford Site experimental locations is the presence of basalt below the waste in the model, whereas at Hanford, unconsolidated sediments are present for tens to hundreds of meters below the bottom of the waste material.

The Subsurface Transport Over Multiple Phases (STOMP) model[10,11] was used to simulate the steady-state diffusion of xenon gas from a source represented by a 2-dimensional vertical cross section through the right half of a symmetric waste trench. ^{133}Xe and ^{135}Xe were simulated. The xenon source was released uniformly over the waste portion of the model domain at production rates based on ^{240}Pu inventory estimate shown in Table 1. ^{240}Pu is considered most likely source of fission production in the subsurface at most nuclear waste sites. Weapons-grade plutonium contains less than 7 weight % ^{240}Pu[13]. In practice, the ^{240}Pu content of weapons grade plutonium is approximately 6 atom percent. Further details on model parameterization are provided in DRESEL and WAICHLER. (2004).[12]

A base case and six additional cases to evaluate sensitivity or check assumptions were simulated. The additional cases used the base case input values except for the particular input being changed (Table 2).

A recent critical review of spontaneous fission half-lives gives a ^{240}Pu spontaneous fission half-life of 1.14E11[PED1] yr[14].   The fission yield for xenon isotopes from spontaneous fission of ^{240}Pu is not readily obtained from literature tabulations. HYDE (1964)[15] gives total chain yields for the ^{131}I, ^{133}I, and ^{135}I parents of xenon isotopes of the same mass as 2.34%, 8.20%, and 6.94 % but ^{240}Pu spontaneous fission yields are not included in the ENDF/B-VI data review[16]. SCHILLEBEECKX et al. (1992)[17] indicate that the mass distribution for ^{240}Pu spontaneous fission is somewhat

narrower than that of ^{239}Pu thermal neutron fission but they do not provide the fission yield data for ^{240}Pu post-neutron spontaneous fission. For this paper the ^{240}Pu spontaneous fission yield was estimated to be equal to the thermal neutron fission yield for ^{239}Pu.

From the ^{240}Pu spontaneous fission half-life, 1.14E11 yr or 3.60E18 s, the effective decay constant for ^{133}Xe and ^{135}Xe production, $\lambda^{Xe-133}{}_{Pu-240}$ and $\lambda^{Xe-135}{}_{Pu-240}$ is calculated by multiplying the decay constant for ^{240}Pu fission, $\lambda^{\eta}{}_{Pu-240}$, by the isotope's fission yield:

$$\lambda^{Xe-133}{}_{Pu-240} = \lambda^{\eta}{}_{Pu-240} * 0.0702 = 1.58\text{E-}20 \text{ s}^{-1}$$

$$\lambda^{Xe-135}{}_{Pu-240} = \lambda^{\eta}{}_{Pu-240} * 0.076 = 1.34\text{E-}20 \text{ s}^{-1}$$

RESULTS AND DISCUSSION

Isotopic Sampling

The composite radioxenon sample collected at the 216-Z-1A tile field contained 16,400 mBq/m^3 of ^{133}Xe (at standard pressure) and 1,811 mBq/m^3 of ^{135}Xe. The instrument detection limit was approximately 0.58 mBq/m^3 of ^{133}Xe and 3 mBq/m^3 of ^{135}Xe. The concentrations above are not decay-corrected to the time of sampling because the analysis was carried out on the same day as sampling.

At secular equilibrium between ^{240}Pu and radioxenon, the decay rate of each xenon isotope equals the production rate. Thus, the atoms ^{133}Xe or ^{135}Xe present per atom ^{240}Pu is:

$$\lambda^{Xe-133}{}_{Pu-240} / \lambda^{\beta}{}_{Xe-133} = 1.0\text{E-}14$$

$$\lambda^{Xe-135}{}_{Pu-240} / \lambda^{\beta}{}_{Xe-135} = 6.32\text{E-}16$$

It is clear that the sediments are not at secular equilibrium since the fission yields

for ^{133}Xe and ^{135}Xe are nearly the same but the activity of ^{135}Xe is about an order of

magnitude lower. Decay correction for the time between sampling and analysis (~8-10

hours) would not account for the difference.

The average time between xenon production and analysis can be calculated from

the measured atom ratio, $^{135}N/^{133}N$, the reciprocal ratio of the fission yields, $^{133}N_0/^{135}N_0$,

and the decay constants for each isotope, $^{133}\lambda$ and $^{135}\lambda$,

$$t = \frac{\ln\left(\frac{^{135}N}{^{133}N} \bullet \frac{^{133}N_0}{^{135}N_0}\right)}{^{133}\lambda - ^{135}\lambda}$$

Thus, for the 216-Z-1A composite sample the average time from production to

analysis was 66 hours. Decay correcting the gas concentrations for this time gives a

concentration at t_0 of 23.61 Bq/m^3 of ^{133}Xe. Since a Becquerel equals a decay per

second, dividing by the effective decay constant, $\lambda^{Xe\text{-}133}_{Pu\text{-}240}$, gives 1.49E21 atoms

^{240}Pu/m^3, the number of atoms of ^{240}Pu needed to produce the ^{133}Xe in a m^3 of soil gas. A

lower-bound plutonium concentration in the soil is obtained by assuming the plutonium is

present in the same soil volume as the ^{133}Xe. Thus, with a porosity of 0.3, a soil bulk

density of 2.65, and 6 atom % ^{240}Pu in weapons grade plutonium, the plutonium

concentration is 2,990 Bq/g (80.7 nCi/g). Diffusion and dilution with background soil

gas will tend to dilute the sample radioxenon concentrations so this amount indicates that

the contaminated sediments likely would meet the definition of transuranic waste.

The results of the stable xenon analysis at the 216-Z-1A tile field and the 618-11

burial ground are listed in Table 3 using delta notation with the reference isotope ^{129}Xe

and an atmospheric standard. ^{129}Xe was chosen as the reference isotope because its

fission yield is effectively blocked by ^{129}I. Figure 2 plots δ^{136}Xe vs. δ^{134}Xe. Background air would plot at the origin. One of the tile field samples and all the burial ground samples show a fission component. The lines show the relationships for uranium thermal neutron fission, plutonium thermal neutron fission, and average values calculated for two types of Hanford reactor fuel[18]. One sample from the tile field shows isotopic ratios consistent with spontaneous fission. However, the two burial ground samples with the greatest shift from background show an excess of ^{136}Xe over the fission yield, consistent with irradiated Hanford reactor fuel. It is difficult to say whether the third burial ground sample represents spontaneous or reactor fission due to the error bars.

The excess ^{136}Xe in reactor fission is the result of neutron capture on ^{135}Xe (cross section of 2.6E6 barns[3]). The stable xenon isotopic data provide evidence for the likely presence of unseparated, irradiated fuel in the burial ground.

Transport Model

The model domain and the base case steady-state gas concentrations for ^{133}Xe and ^{135}Xe are shown in Figure 3. Steady-state gas concentrations were attained within 0.1% of the final concentration within 4 to 11 days. The ^{135}Xe concentrations fall off more rapidly with distance from the waste form than the ^{133}Xe concentrations due to the shorter ^{135}Xe half life.

Of all the results, the greatest sensitivity was found in the response of ^{133}Xe to changing the tortuosity (Table 2). The tortuosity had a much smaller effect on ^{135}Xe. The tortuosities range estimated for the site and used in Cases 5 and 6 was lower than the base case and led to higher xenon concentrations. Linear scaling to lower source concentration in Case 2 had the next greatest impact, but modeled concentrations

decreased by less than an order of magnitude. Cases 3 and 4 had only small effect on the modeled concentrations for ^{133}Xe but increased ^{135}Xe concentrations. Inducing atmospheric pumping in Case 7 decreased concentrations for both isotopes slightly.

The model results show xenon concentrations extending laterally beyond the trench boundary and upward into the cap at many orders of magnitude above instrument minimum detection limits (~ 1 mBq/m^3).

CONCLUSIONS

Proof-of-principle sampling results show successful analysis of radioxenon and fission stable xenon isotopes in soil gas at radioactive waste sites. The reactor-fission can be distinguished from spontaneous fission in the stable isotopes because excess ^{136}Xe was produced from neutron capture on ^{135}Xe. The greatest sensitivity is seen in the radioxenon sampling due to lower background and the ability to concentrate large volume samples. In principle, the ARSA system can be deployed in the field simplifying sampling, eliminating the need for make-up gas, and increasing the sensitivity by ~ 3 times.

Model results show that the diffusion through sediments is likely to be sufficiently rapid, relative to decay rates, and sampling within the cap or adjacent to waste trenches is promising. This is confirmed by the stable xenon sampling at the 618-11 burial ground where the samples were collected outside the burial ground fence at a minimum of ~30 m from the waste units. Shallow sampling points have a limitation for large-volume radioxenon sampling since breakthrough of air from the surface could occur.

Since the xenon sampling is an indirect indicator, it requires release from the waste form and waste containers. Given past disposal practices, it is likely that many

containers have been breached; however, the results are necessarily semi-quantitative due to the unknowns in release rate and transport properties. Information on average time from generation can be obtained if both radioxenon isotopes are detected. Due to the current limitations on analytical throughput, the method is best suited to targeted or random sampling design rather than sampling at a large number of grid locations. However, analytical modifications could greatly increase throughput.

ACKNOWLEGMENTS

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TABLES

Table 1. Spontaneous Fission Production Rates for Transport Model

Case	^{240}Pu		^{133}Xe production		^{135}Xe production	
	Bq/m^3	g/m^3	atom/(m^3*s)	mBq/(m^3*s)	atom/(m^3*s)	mBq/(m^3*s)
Base Case	1.25E+10	1.49E+00	5.05E+01	7.72E-02	5.46E+01	1.16E+00
Case 2	1.50E+09	1.79E-01	6.06E+00	9.27E-03	6.56E+00	1.39E-01

Table 2. Results at end of simulation for a node located 75 cm below ground surface at waste center

Case	Description	Moisture Content (m3/m3)	^{133}Xe 5 day (mBq)	^{135}Xe 9 hour (mBq)
		Concentrations (per m^3 of air)		
		Results		
1	Baseline case (1.499 g/m^3 ^{240}Pu)	0.303	39,053	4,162
		Percent change from base case		
2	Test of linear scaling (0.179 g/m^3 ^{240}Pu)	0	-88.0	-88.0
3	Infiltration rate = 10 mm/yr	-8.9	0.3	51.5
4	Residual saturation index in sediments = 0.20	-8.5	-0.3	44.1
5	Small tortuosity (factors: sediments = 1/3, basalt = 1)	-0.1	26.4	417
6	Large tortuosity (factors: sediments = 1/5, basalt = 1/2)	-0.1	28.1	215
7	Atmospheric pumping	0	-2.6	-2.7

Table 3. Results of stable xenon analysis for isotopes with significant fission yields

Site	Sample ID	δ (^{131}Xe)	+/-	δ (^{132}Xe)	+/-	δ (^{134}Xe)	+/-	δ (^{136}Xe)	+/-
618-11	C3225	11.077	3.481	17.181	2.223	71.714	3.410	132.272	5.017
618-11	C3229	7.037	3.301	10.440	2.126	34.403	3.287	64.667	4.649
618-11	C3236	1.985	4.044	5.147	2.946	11.473	4.076	13.459	5.184
216-Z1-A	299-W18-76	3.494	3.350	3.985	2.218	7.424	3.455	7.825	4.476
216-Z1-A	299-W18-80	0.039	3.462	1.237	2.288	0.616	3.200	2.641	4.669

Data Normalized to ^{129}Xe   Potential fission isotopes only

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FIGURES

Figure 1. 216-Z-1A Tile Field and 618-11 Burial Ground Sample Locations

Figure 2. δ^{136}Xe vs. δ^{134}Xe for Samples from the 216-Z-1A Tile Field and the 618-11

Burial Ground. The reference isotope is ^{129}Xe and atmospheric xenon is the

standard.

Figure 3. Model Domain (top) and Steady-State [133]Xe (middle) and [135]Xe (bottom)
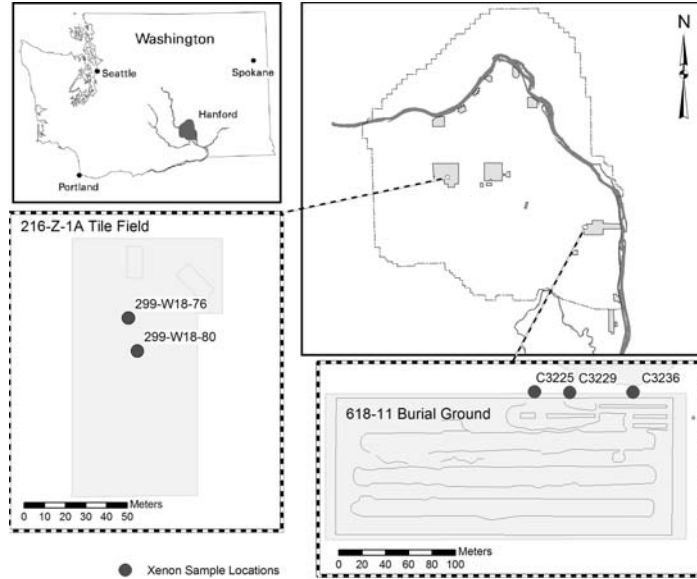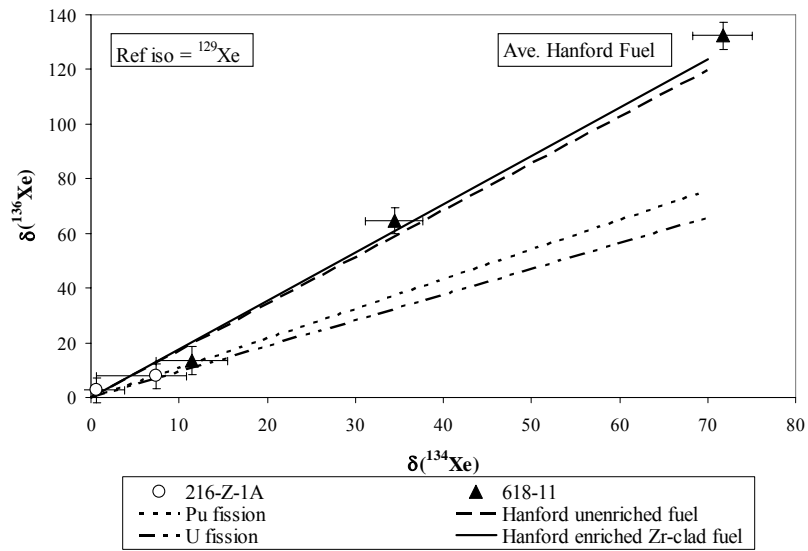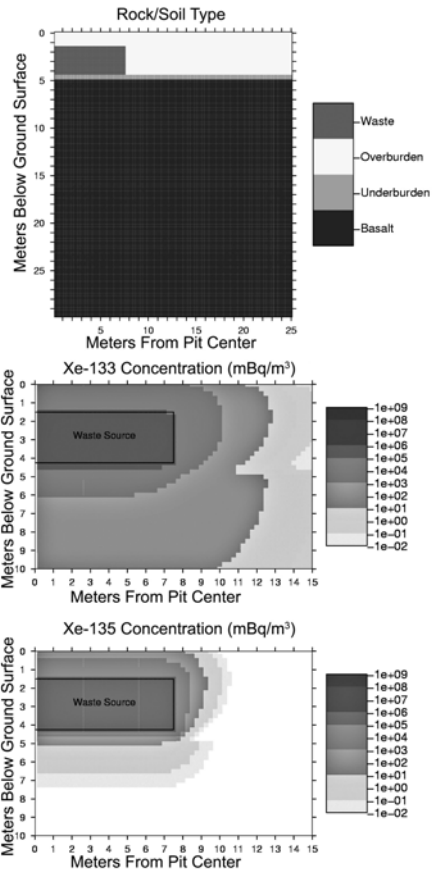
Concentrations