

Development of speciation and separation techniques for radionuclides for the pre-assessment of their environmental mobility.

François Caron* and George Mankarios, Chemistry & Biochemistry Department, Laurentian University, 935 Ramsey Lake Rd., Sudbury, ON (Canada), P3E 2C6.

Abstract

Radionuclides of various natural or man-made origins all have the potential to migrate in groundwaters. Migration, among other factors, depends upon the aqueous speciation of the element. A key component affecting this speciation is natural organic matter (NOM). The latter consists of a mixture of hydrophilic and hydrophobic compounds, and contains weak acidic groups that can complex cationic radionuclides. These complexes can be mobile in soils.

In this work, we are testing a modified separation and speciation scheme, which is used as a pre-assessment tool for the mobility of two radionuclides of the actinide series, ^{241}Am and U. The ^{241}Am is artificial and it is present in a contaminated aquifer at the Chalk River Laboratories (CRL), whereas the U is of natural origin, as a part of the radioelements of the Elliot Lake Tailings Area (ELTA). The two sites are also of contrasting environments: the CRL sample has a low ionic strength, and it is near-neutral, whereas the ELTA sample is acidic and dominated by acid mine drainage of the pyritic-based material of the tailings.

Ion exchange extractions indicate that Am is predominantly present in anionic form (>98%), which is consistent with past work at CRL. Further analysis with Solid Phase Extraction (SPE) suggested that most of the Am could be associated with small molecular weight NOM or man-made organic, as opposed to hydrophobic NOM. The ELTA results suggested the predominance of cationic U species, likely as UO_2^{2+} .

1. Introduction

Radionuclide cycling in soils and in surface waters depend upon several factors related to the geochemistry of the environment surrounding the sources of contamination, and the flowpath of the water carrying the radionuclides. One key parameter affecting the chemical toxicity and mobility of the radionuclides is the chemical species present in waters. This depends strongly upon geochemical conditions such as the ions present, the redox potential, the presence of dissolved organics, to name just a few parameters. It is also important to understand that on an atomic or mole basis, unless exceptional circumstances are present, any radionuclide in the environment is at the trace or ultra-trace level, hence the geochemistry of the major or trace elements will dictate the species of radionuclides in water.

The parameter of interest is the impact of NOM on the speciation of selected radionuclides. For

our pre-assessment study, we have analyzed two samples from two drastically different sites, one from the Chalk River Laboratories (CRL), and one from the Elliot Lake Tailings Area (ELTA). We have also selected two different radioisotopes whose activity concentrations are similar, although in mole basis, they are drastically different: the target radioisotope is Am-241 from CRL, and Uranium from ELTA. These radioisotopes are in the post-actinium series, they are alpha emitters and they are an ingestion hazard when or if they are incorporated in the food chain.

To assess the mobility and/or the chemical toxicity of these elements, we are investigating whether a separation scheme previously used (Champ et al., 1984; Robertson et al., 2000; Caron et al., 2002) can be applied to these waters. In this scheme, two different aliquots of a sample are used (Figure 1). The first one is passed through a cation exchange resin, to isolate the anionic species of the radionuclides,

and the second one is passed through an anion exchange resin, to isolate the cationic species of the radionuclides. The relative proportion of these gives the predominant species, anionic vs cationic species. Am (oxidation state +3) has been reported to strongly bind to organics (Kim et al., 1989; Torres et al., 1984), however it has been suggested that its inorganic speciation may dominate under the conditions of the CRL sample (Caron et al., 2002). Uranium, in its +6 oxidation state (UO_2^{2+}), can associate with NOM (Li et al., 1980; Shanbag and Choppin, 1981), with a moderate to strong interaction.

The aim of our work is to develop a simple speciation and separation scheme for Am and U in samples of contrasting characteristics. The first point of information is to determine the predominance of anionic vs cationic species of radionuclides. The second point, for Am, is to use Solid Phase Extraction (SPE), to determine the extent of Am-NOM association.

2. Experimental

2.1. Sampling sites

The CRL site is located approximately 175 km West of Ottawa. The sample (LDA-22) was taken from a contaminated plume in a groundwater flow system adjacent to a former liquid dispersion area (LDA), used to discard low-level aqueous radioactive. The LDA sits in a sand dune, and it consists of a drainpipe, installed to feed liquid wastes into an excavated pit, backfilled with coarse aggregate. The pit overlies an aquifer that discharges to a perennial wetland ~100-200 m downstream. The aquifer material consists of sand, composed of quartz and feldspars (~30-40% each), and minor quantities of muscovite and ferromagnesian minerals. It was estimated that approximately $3.3 \times 10^5 \text{ m}^3$ of water was discarded in this pit, containing 230 TBq of various beta emitters and 0.31 TBq of alpha emitters. The pit was used for aqueous wastes from 1956 to 1992, with episodic discharges until its permanent closure in 1995. Several radionuclides have been measured (Rowat et al., 1998), and in this work, we will focus on ^{241}Am .

The ELTA site is located North of Huron Lake, approximately half way between Sault Ste Marie and Sudbury, Ontario, North of the Trans-Canada highway. The Elliot Lake ore zone occurs within a pyritic quartz-pebble conglomerate. The mineralogy is similar in the area, i.e., consisting of quartz and chert pebbles, in a matrix of feldspathic quartzite, containing pyrite and several uranium-bearing minerals (Robertson et al., 1987). Our sample was taken at station DS-2, downstream from the Stanrock Tailing Management Area (TMA; Denison Energy, 2002). This is approximately 15 km NE of the town of Elliot Lake. The TMA occupies a 61-ha area, and holds $\sim 6 \times 10^9$ kg of acid-generating tailings; the latter contain Ra, Th and U. In 2000 and 2001, 7000 m^3 of paper mill sludge were hauled and spread over the tailings to provide vegetation re-growth, and to improve the physical and chemical characteristics of the tailings seepage water. The drainage ditches of the TMA flow to a collection pond (DS-2), and a liming and treatment station before feeding to Moose Lake.

The water at the two sites have contrasting compositions (Table I). The Chalk River sample is circumneutral, with low but measurable TOC. The ion content reflects the expected compositions from the Canadian Shield, except for the elevated amounts of nitrate and phosphate. The Elliot Lake sample is acidic, with relatively high ionic strength. Its composition reflects acid mine tailings, with high sulfate and H^+ (low pH). MINTEQ runs indicate that the ELTA water is oversaturated with respect to ferric oxihydroxides minerals (hematite, goethite) and aluminum salts (gibbsite, alunite, and more).

2.2. Sampling

The Chalk River sample was taken in July 2002 from borehole LDA-22. The sample containers (2 collapsible plastic 20 L carboys) were covered with a dark plastic sheet, to prevent contact with direct sunlight. After collection, the samples were placed in an ice cooler and kept cold, in the dark, until filtering (within 48 h). Once filtered, the sample was allowed to warm up to room temperature. The sample was

always kept dark, either covered with a dark plastic sheet, or in a cooler.

The Elliot Lake sample was taken on November 2, 2001 by dipping a stainless steel tank (60 L) into the pond. The sample was allowed to stabilize to room conditions, in the dark, until processing (May 2002). At the time, iron oxide precipitate had settled and most of it was isolated prior to filtration with a 0.45 µm filter cartridge (A/G Technologies).

Table I: Major ion chemistry of the two sites.

Ion/parameter	CRL	ELTA
	CRL [§] LDA-22	ELTA [§] DS-2
	Concentration (mg/L)	
pH	6.80	2.80
TIC	7.10	-
TOC	3.2	2.2
CATIONS		
Na ⁺	33.2	9.8
Ca ²⁺	0.75	169
K ⁺	0.66	8.8
Mg ²⁺	0.250	25.1
Fe ³⁺	0.060	82.7
Mn ²⁺	0.005	2.5
Zn ²⁺	0.003	0.8
Al ³⁺	0.1	22.0
ANIONS		
Cl ⁻	0.5	-
F ⁻	0.4	-
SO ₄ ²⁻	17.1	884
NO ₃ ⁻	17.3	0.3
HCO ₃ ^{-*}	27.4	-
CO ₃ ^{2-*}	0.01	-
PO ₄ ³⁻	23.5	-
Dissolved Solids	124	1205
Conductivity (mS/cm)	140	1148
Ion imbalance **	+0.3 %	-0.4 %

*HCO₃⁻ and CO₃²⁻ are calculated from C_T and pH

** Imbalance = (C_{cations} - C_{anions}) / (C_{cations} + C_{anions}) × 100

[§] See Rowat et al. (1999) for CRL; Denison Energy (2002) for ELTA.

2.3. Speciation scheme and analysis

The speciation scheme was modified from (Robertson et al., 2000; Caron et al., 2002), to isolate the cationic and anionic fractions of the radionuclides (Figure I). A 1L sample of original (filtered) water was processed, and separate 3 L aliquots were passed through an anion exchange resin (Rohm & Haas IRN-78, converted to the Cl⁻ form), to isolate the cationic fraction, and a cation exchange resin (Purolite C-100, converted to the Na⁺ form), to isolate the anionic fraction. The samples and extracts (1 L of each) were placed in an evaporating dish pre-covered with a polyethylene sheet, and gently evaporated until dryness. The PE film was then folded and pressed in a 2-cm (dia.) dye (25 tons) to make a 2 cm × 0.5 cm thick PE disk. The disk was placed in a plastic dish and the sample was counted on a Canberra 1020 HP gamma spectrometer for 6 to 20 h (depending upon the sample activity). The Canberra Genie 2000 software was used for data processing.

The CRL sample was not passed through the anionic resin, as it is known that Am is predominantly anionic (Caron et al., 2002, and references therein). In addition, we proposed earlier that hydrophobic organics (retained on a C-18 chromatography column) retained a portion of radionuclides that have a strong affinity for organics (Caron et al., 1996). We are exploring a new step to confirm this, with a direct extraction. For this, triplicate aliquots of the CRL sample (0.34 to 0.5 L each) were passed through a SPE cartridge (Sep-Pak[®] C₁₈, Waters Corp.). This cartridge is hydrophobic, designed to concentrate hydrophobic organics, and elution with an organic solvent (methanol, MeOH) will desorb the organics. We expect that the ²⁴¹Am bound to hydrophobic NOM would be retained on the cartridge, while the ²⁴¹Am weakly bound, or not bound to this NOM would not be retained. The MeOH extract, the spent SPE cartridge and the evaporated extract (Figure 2a) were counted separately to check for the different Am fractions (Table IIa).

Similarly, mass balances of the DS-2 samples, before and after extraction with NaOH (anionic resin) and HCl (cationic resin), are shown in Figure 2b. The leached resin was counted, plus the aqueous extract was evaporated and pressed in a PE film as per above, for gamma counting.

3. Results and discussion

Table II shows the results of the radiological analyses for both samples (Table IIa for the CRL sample, Table IIb for the ELTA sample). The radiological results are in the same magnitude (~0.2 to 1.2 Bq/L) among radionuclides, and these values are just above the Minimum Detectable Activity (MDA).

Most of the Am is unretained by the cation exchange resin in the CRL sample (Table II a), which suggests that Am is present as “anionic”. Although we did not perform an anion exchange extraction on the sample, this is consistent with previous work (Caron et al., 2002). Calculations at mid-pH do not support the dominance of inorganic anionic complexes (hydroxo- or carbonato; see Artinger et al., 1998).

The CRL sample was further extracted with a set of SPE, done on separate subsamples. Although these volumes were smaller (0.34 to 0.5 L each), the relative distribution of solution extract (“solution only”) and leached cartridge is reproducible, with less than 2% standard deviation among replicates. No significant quantities of ^{241}Am were detected in the MeOH extract, suggesting that the ^{241}Am associated with hydrophobic NOM is a small proportion. Our findings contrast other studies, in which a large portion of Am is reported with humic/fulvic acids (Artinger et al., 1998). In our study, the majority of the Am (~65%) that has passed through the cartridge could be a combination of inorganic species, low molecular weight hydrophilic organics, or man-made organics (complexing agents such as EDTA). The meaning of the fraction left on the cartridge after leaching is difficult to interpret at the moment.

We were interested in Ra, U and Th in the Elliot Lake sample. We can analyze ^{235}U directly,

using its lines at 93.3 keV (Th- $\text{K}_{\alpha 1}$, 2.5% prob.), 185.7 keV (53%), 143 keV (10.5%), and 163 keV (4.7%). Although ^{235}U not an abundant U isotope, its half-life is shorter than that of ^{238}U , and their specific activities are comparable. In contrast, direct ^{238}U analysis is difficult, but it is possible through its ^{234}Th daughter (El-Daoushy and Hernandez, 2002), provided that the sample is at secular equilibrium. The ^{234}Th has emission lines at 63.3 keV (3.8%) and a doublet at ~92 keV (92.4 + 92.8 keV, ~2.7% each), which could interfere with the 93.3 keV line of ^{235}U . In addition, ^{226}Ra has a single line at 186.1 keV (3.3%), which is close to that of the ^{235}U line of 185.7 keV. There were also ^{235}U lines in the detector background. All these corrections were specified, and achieved with the Genie software.

Uranium-235 was the only readily identifiable parent radioisotope among the U, Ra, and Th. The cationic and anionic extracts were consistent: ^{235}U was extracted with the cation exchange resin, and not retained with the anion exchange resin (Table IIb). This is consistent with its expected species, UO_2^{2+} . It is doubtful that U is associated with organics at pH = 3, where the NOM functional groups are protonated. UO_2^{2+} has been reported to associate with NOM under different conditions (Li et al., 1980; Shanbag and Choppin, 1981).

Our attempt to analyze for ^{226}Ra and ^{238}U (^{234}Th) was not successful. The peak of the first ^{238}U daughter (^{234}Th , 63.3 keV) was in a region of high background. Similarly, the Ra peak at 186 keV was eliminated in the interference correction of ^{235}U . Alternatively, we also looked further down the secular equilibrium line, i.e., the ^{214}Bi and ^{214}Pb isotopes (4n + 2 series), and the ^{212}Bi and ^{212}Pb isotopes (4n series) (Table IIb). The analysis could be valid only if our sample was in secular equilibrium. This is achieved reasonably fast for the 4n series (only short-lived intermediates, including ^{220}Rn $t_{1/2} = 55.6$ s), but it is questionable for the (4n + 2) series (long-lived intermediates, particularly ^{226}Ra ($t_{1/2} = 1600$ a) and ^{222}Rn ($t_{1/2} = 3.82$ d)). Furthermore, one could use this approach only for the initial radionuclide, and not the fractionated sample (see the ambiguity for ^{212}Pb ,

Table IIb). To test the effectiveness of the separation with IX resins, other techniques should be used (e.g., ICP or alpha spectroscopy) to determine directly the amount of parent material (U, Th or Ra). It is only then that the speciation of these isotopes can be measured.

4. Conclusions

The speciation and separation scheme with ion exchange resins is just a first step in determining the species of radionuclides present in an aqueous system. This scheme needs to be further developed and hyphenated to other techniques to obtain specific information, as no single technique will determine the speciation. Our scheme was tested with two samples containing low levels of radionuclides, in the range of ~1 Bq/L (^{241}Am – CRL sample, and U + Th and daughter products – ELTA sample).

The predominance of the ^{241}Am species in the CRL sample was consistent with previous studies, and our results with SPE were very consistent among replicates. Thus, as a tool to determine the speciation and for a pre-assessment of mobility, the separation and speciation scheme used in this study yields useful information. Our results, however, do not give specific information as to the aqueous species of ^{241}Am . The inorganic species are unlikely to predominate at near-neutral pH (e.g., hydroxo- and carbonato- complexes). The SPE does not support the dominance of ^{241}Am association with humic/fulvic acids, while its presence with man-made complexing agents (EDTA, etc) or small organics is possible.

Uranium (^{235}U) was detected in most of the fractions isolated from the ELTA sample. Our results suggested a cationic species, which is consistent with its expected form UO_2^{2+} . Its association with NOM is unlikely at low pH. The separation/speciation scheme could not be successfully applied for ^{238}U , Th and Ra, because of the absence of measurable gamma lines. Our attempt at analyzing daughter radionuclides yielded ambiguous results, in part because the fractionation separates the sources from the daughter materials in our samples, and secular

equilibrium is likely disrupted. Other techniques (ICP, alpha spectroscopy) would need to be used to analyze the radioelements at the source.

5. Acknowledgements.

The authors wish to thank R.W.D. Killey (AECL) for field assistance at the CRL site and for data, G. Morgan (Elliot Lake Research Field Station) and N. Faubert (Laurentian University) for field sampling (ELTA site). We particularly thank G. Morgan for providing background information and data for site DS-2. We also thank C.C. Davison (AECL) for site access. This work was supported by the Natural Science and Engineering Research Council of Canada (NSERC). G.Mankarios was supported by the NSERC undergraduate student research award.

6. References.

- Artinger, R., B. Kienzler, W. Schussler, and J. I. Kim. 1998. *J. Contamin. Hydrol.* 35: 261-75.
- Caron, F., S. Elchuk, and Z. H. Walker. 1996. *J. Chromatogr.* 739: 281-94.
- Caron, F., et al. 2002. In: *Scientific Basis for Nuclear Waste Management XXV*, Eds. P.J. McGrail, and G.A. Cragnolino. Mat. Res. Soc. Symp. Ser., Vol. 713, p. 743-750.
- Champ, D.R., et al., 1984. *Water Poll. Res. J. Canada* 19: 35-54.
- Denison Energy. 2002. *Stanrock Biosolids Project*, C of A SSM0001. Denison Energy Inc.
- El-Daoushy, F., and F. Hernandez. 2002. *Analyst* 127: 981-89.
- Kim, J.I., et al. 1989. *Radiochim. Acta* 48: 135-43.
- Li, W. C., D. M. Victor, and C. L. Chakrabarti. 1980. *Anal. Chem.* 52: 520-523.
- Robertson, A. MacG. et al. 1987. *Canadian uranium mill waste disposal technology*, DSS 15SQ.23317-6-1730. Energy Mines and Resources Canada, Ottawa, Ont.
- Robertson, D.E. et al. 2000. NUREG/CR-6627, PNNL-12185. U.S. Nuclear Regulatory Commission, Washington, DC.
- Rowat, J.H. et al. 1999. AECL-MISC-403-98.

Atomic Energy of Canada Limited, Chalk River, ON.

Shanbag, P. M., and G. R. Choppin. 1981. *J.*

Inorg. Nucl. Chem. 43: 3369-72.

Torres, R. A., and G. R. Choppin. 1984. *Radiochim. Acta* 35: 143-48.

Table II: Analysis of the fractionation of the samples from the two sampling sites.

a.

CRL LDA-22	Aqueous solution - "original"			<u>Cationic IX resin extraction</u>		
	Conc. Bq/L	Std. Dev.* Bq/L	MDA** Bq/L	Unleached spent resin	Anionic solution extract	
Am-241 (1 L analyzed)	1.07	0.11	0.30	1.5%	98.5%	
				<u>SPE extraction</u>		
				Spent cartridge	Solution extract	MeOH extract
(0.5 L analyzed)	0.89	0.12	0.36	35.3%	64.7%	<0%
	Std. dev. of replicates (n = 3)			1.9%	1.8%	1.1%

b.

Elliot Lake DS-2	Aqueous solution - "original"			<u>Cationic IX resin extraction</u>		<u>Anionic IX resin extraction</u>	
	Conc. Bq/L	Std. Dev.* Bq/L	MDA* Bq/L	HCl Extract + spent resin	Anionic solution extract	NaOH Extract + spent resin	Cationic solution extract
<u>4n (²³²Th) series</u>							
Bi-212	0.54	0.10	0.28	~100%	< MDA	< MDA	< MDA
Pb-212	0.89	0.04	0.06	~100%	< MDA	86%	14%
<u>4n + 2 (²³⁸U) series</u>							
Bi-214	0.24	0.03	0.06	78%	22%	< MDA	< MDA
Pb-214	0.32	0.02	0.06	~100%	< MDA	< MDA	< MDA
<u>4n + 3 (²³⁵U) series</u>							
U-235	0.25	0.02	0.05	~100%	< MDA	< MDA	~100%

*Std. Dev.: based on the number of counts.

**MDA: Minimum Detectable Activity

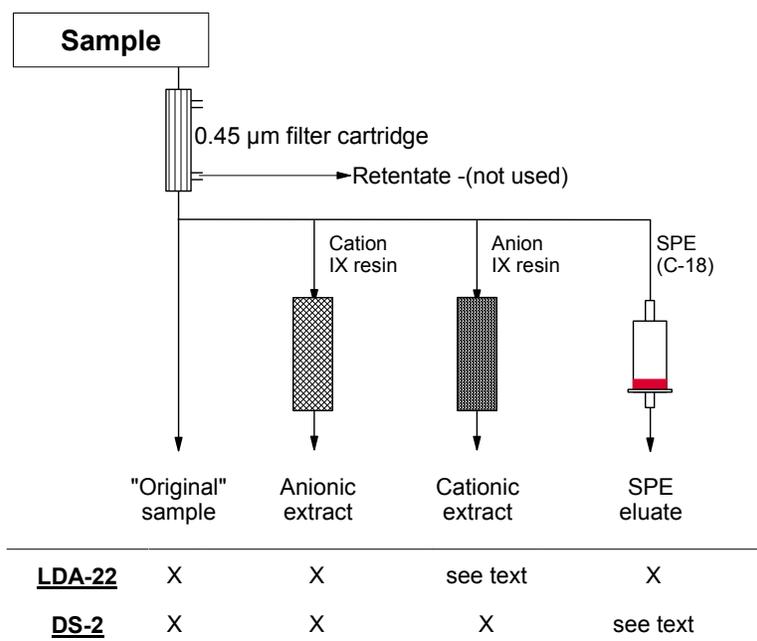


Figure 1: schematics of the sample extractions.

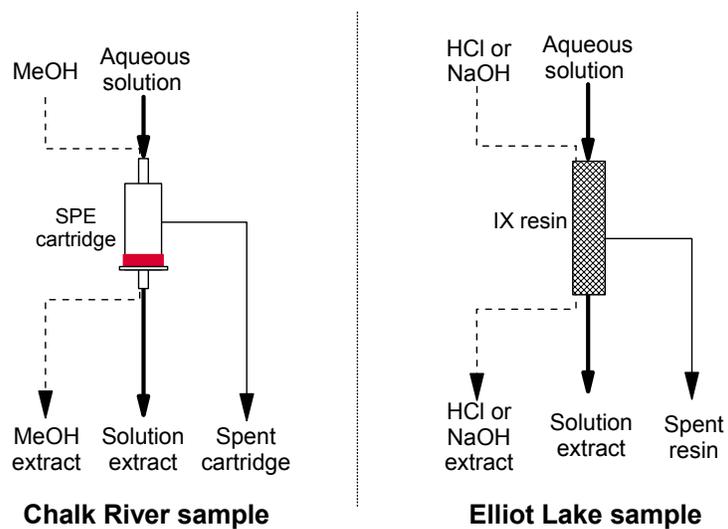


Figure 2: schematics of sample processing for the SPE cartridge and the IX columns.