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Soil-to-plant transfers of uranium series radionuclides in natural and contaminated settings

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Abstract. Uranium and related decay-chain radionuclides remain important subjects of study for a number of reasons. Uranium has the potential to be chemically toxic near mining and processing facilities, and the decay-chain radionuclides can contribute substantially to radiation dose. Establishing an air quality standard for U in Canada has also been tentatively based on its accumulation and toxicity in soil. This paper summarizes two studies. The first investigated the mobility in soil, uptake by plants and ecotoxicity of U near a U refining facility. Because of the presence of co-contaminants, a large number of other elements were measured to fully characterize the samples. In general, the soil solid/liquid partition coefficients, Kd, for U were high enough that leaching is not a dominant process. Plant/soil concentration ratios (CRs) were not consistently different compared to background sites. The second study measured plant/soil CRs for ^{210}Pb, ^{210}Po, ^{226}Ra, ^{228}Ra, ^{228}Th, ^{230}Th, ^{232}Th and ^{238}U on a series of sites across Canada, with emphasis on background sites with possible human food-chain connections. Secular equilibrium was rarely observed, especially in plants.

1. INTRODUCTION

Uranium (U) and U-series radionuclides are ubiquitous in the environment, and even natural levels not associated with contamination from industrial activities can reach levels of concern. For most of these radionuclides, radiological dose is the source of potential impact, but for U itself, chemical toxicity can supercede radiological dose [1]. The mobility of the U-series radionuclides is largely dependent on their chemical (elemental) properties. Generally, these elements are not very mobile, but several including U can form complexes, both inorganic and organic, that are mobile. For U, there can be substantial mobility in neutral to basic soils as a result of complexation with soluble carbonates [2].

This paper summarizes two studies – one referred to as the Port Hope U Refinery study, the other the Background Site study. The Port Hope U Refinery study dealt with the mobility in soil, transfer to plants, and chemical toxicity of U. The research site was around the U processing facility at Port Hope, Ontario. Mobility in soil is typically assessed with a Kd-based leaching model, and this study addressed the appropriateness of this approach. A previous paper by Sheppard [3] suggested that, at least near the surface, mobility may well be dominated by other processes. The underlying question about transfers from soil to plants was whether site-specific transfer parameters were required or even relevant to assess potential impacts. Sheppard [4] presented a case that site-specific parameter values may not be as useful as assessors often assume, and this study provided an opportunity to re-examine this suggestion. Finally, the issue of chemical toxicity of U has become complicated by the presence in the literature of reports of exceptional toxicity, as low as 0.5 mg U kg^{-1} dry soil. This study sought to establish credible toxicity thresholds by using established bioassay protocols. The toxicity results have been reported elsewhere [1], and although they included indications of greater sensitivity than previously obtained in Canada (about 100 mg U kg^{-1} affected one species of collembolan in one soil), they will not be re-iterated here.

The Background Sites study was broader in two dimensions, it dealt with many more radionuclides and there were 7 study sites across Canada. The emphasis here was on background sites, intended to provide background concentrations for risk assessments. The specific questions were: do the transfer parameters differ from those measured on contaminated sites, and where and to what extent can secular equilibrium be used to estimate concentrations of un-measured decay-series radionuclides.

2. METHODS

2.1 Port hope U refinery

The refinery is located in a small river valley on the shores of Lake Ontario, and is fully surrounded by the town site. Contamination in the area has resulted from operations over that last 60 years, and included dumping of ore waste, fugitive dust from the facility and stack emissions. In the past, there were other industrial activities, including a porcelain manufacturer, in the immediate area. Surrounding properties have been cleaned in several campaigns, each successive campaign with more stringent criteria. Current emissions are relatively low, but include fugitive dust and stack emissions. There remains a signature of elevated soil U concentrations, seldom above 100 mg kg^{-1}, centered on the facility and extending several hundred metres in all directions inland.

Two sets of 10 sites were chosen for the study. One set, to study mobility of U in soil, was intended to have relatively undisturbed soil profiles with soil U concentrations above 10 mg kg^{-1}. This resulted in the sites being relatively close to the facility. On these sites, the soil profiles were sampled every 4 cm in order to resolve in detail the depth distribution of U as well as potential co-contaminants, and to determine soil solid/liquid partition coefficients (Kd) for a large suite of elements. Soil layers were sampled horizontally from a pit wall (to 60-cm depth), in order to minimize cross-contamination. Below 60 cm and to 100 cm, samples were taken from vertical cores. Radium-226 was measured to indicate possible contamination by previous dumping of ore waste. Basic soil properties (pH, texture, carbonate content, organic matter content, bulk density) were measured on selected horizons. Soil samples from about 8 selected depths of each profile were analyzed, and intervening samples were analyzed when needed to resolve details of the depth distribution.

The other set of 10 sites, to study the soil-to-plant transfer of U and potential co-contaminants, could have U concentrations approaching background, and so included sites further from the facility. A few of these sites were common with those used for the soil profile analysis. The sites were chosen to have a useful range of vegetation present, particularly edible plants. Large samples of plants (several litres) were collected, to allow for thorough washing and thermal ashing. The plant samples were a composite from the defined site area (usually about 100 m^2), and corresponding composite soil samples of 0 to 30 cm and 30 to 60 cm were collected. Botanical specimens were archived to validate identification. The dilute-detergent wash solution was retained and filtered to analyze the dust removed from the plants. Plant moisture and ash contents were recorded.

Analysis was by inductively coupled plasma mass spectroscopy (ICP-MS), which provided results for about 50 analytes including U. Soils were extracted with a proprietary, strong 3-acid mixture, comparable to aqua regia. Plant ash and wash-water filters were fully digested prior to analysis. All results were statistically analyzed and are presented on a dry-weight basis. Plant/soil concentration ratios were computed, and log-transformed for statistical interpretation. Soil pore water was obtained by bringing aliquots of soil (about 60 mL) to field capacity moisture, allowing them to equilibrate for about a week, and then expressing the water by centrifugation. Concentrations in the pore water were also analyzed by ICP-MS and Kd values were computed for all analytes.

2.2 Background sites

Seven background sites were chosen to represent the three ecozones where most Canadian nuclear facilities are located: Atlantic Maritime (Nova Scotia), Mixed Wood Plains (Ontario), and Boreal Shield (Ontario and Manitoba). Specific soil types in these regions were targeted, but otherwise the

sites were selected as relatively undisturbed and populated with a diverse range of natural vegetation. The Mixed Wood Plains ecozone is intensively agricultural, so the sites chosen were areas between fields that had not been intensively managed. Similarly, one Boreal Shield site was an abandoned farmstead. Although past disturbance was not an intended criterion, it was observed that there was greater botanical diversity on these sites (because they were typical of forest margins), and they were more likely to include edible shrub species such as wild fruits.

Plant and soil samples were collected generally in the same way as for the soil-to-plant transfer sites of the Port Hope U Refinery study. The main plant samples were larger, about 20 L, because some of the intended radiochemical analyses require substantial amounts of plant ash. These large samples included some mixed tissues (e.g., leaves and first-year twigs), and could be considered samples of animal browse. Smaller samples and subsamples of specific tissues were also obtained. Only those plants with short stature and near bare soil were washed, most species collected were shrubs and trees and were free of soil splash. All samples were analyzed by ICP-MS. In addition, in the larger plant and all topsoil samples, ^{nat}U was measured by neutron activation delayed neutron counting (DNC); ^{228}Th, ^{230}Th, ^{232}Th, ^{226}Ra and ^{210}Po by alpha spectroscopy; ^{210}Pb by gas flow proportional counting; ^{228}Ra by beta counting; and ^{137}Cs by gamma spectroscopy. Most analyses were of ashed plant samples, the exception being ^{210}Po because of the potential for volatilisation. Plant/soil CR values for all analytes and soil Kd values for ICP-MS analytes were obtained and interpreted as before.

3. RESULTS

3.1 Mobility of U in soils (port hope U refinery study)

There are two dominant soil series in the contaminated area, but their chemical properties are very similar and overall the soils are quite uniform. They are all sandy loams with pH 7.1, 4.1% organic matter, 11% clay and contain 200 mg bicarbonate kg^{-1} dry soil. The geometric mean (GM) Kd values for U and selected other analytes are shown in Table 1. Although the intent was to sample sites that were relatively undisturbed for several decades, the area has been a townsite for over 100 years and all soils had some level of disturbance from the native state. In some cases, there was evidence of buried low-level contamination, and so these profiles were not useful. However, most showed monotonically decreasing U concentrations, with above background concentrations restricted to the top 40 to 60 cm (e.g., Figure 1). Although the total input and timing of the U contamination is not known in detail, the results suggest the centre of mass of the U is still in the top soil. This is consistent with expectation based on a leaching model and the measured Kd ranges.

Table 1. Geometric mean (GM) soil solid/liquid partition coefficients (m^3kg^{-1}) for soils from the Port Hope area.

Element	Number of observations	GM	GSD	Minimum	Median	Maximum
As	32	2.0	5.0	0.0	2.7	16.3
B	32	0.006	1.854	0.002	0.007	0.014
Bi	10	19.5	13.1	0.0	27.6	250.8
Cd	30	2.7	2.0	0.3	3.2	6.2
Cr	34	8.1	2.6	0.6	8.0	42.8
Cu	39	0.73	2.87	0.13	0.73	9.75
Mo	39	0.12	3.70	0.01	0.11	3.50
Ni	39	4.1	2.1	0.8	3.6	18.2
Pb	39	9.7	3.0	0.8	10.7	55.3
Sb	39	0.30	2.88	0.03	0.35	3.84
Sn	39	1.20	2.04	0.43	1.20	8.93
U	39	0.092	2.7	0.005	0.08	2.1
Zn	39	1.9	4.5	0.1	3.0	16.7

The most notable finding was that the depth distribution of U was very closely mirrored by the depth distribution of a large number of other elements. There were very strong positive correlations (significant at $P < 0.001$) in depth distribution between U and Ag, As, B, Bi, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Sn and Zn. Other elements were correlated, but to a lesser degree. These correlations included not only a general decrease with depth, but also to the detail of similarly elevated concentrations in specific horizons (see Figure 1 for example). This occurred despite the fact that the corresponding Kd values (Table 1) ranged from 0.006 m^3 kg^{-1} for B to 19.5 m^3 kg^{-1} for Bi, 15-fold lower and 200-fold higher than that for U (0.092 m^3 kg^{-1}). It is not clear that all these elements are from the same or similar sources as the U, but the exceptionally similar distributions in the soil profiles suggests some commonality in source and transport mechanism. Even without making the assumption that these elements are co-contaminants with U, it is evident that they have not been separated from the U by differential leaching. Because of the very large range in Kd values, the resulting implication is that leaching is not a dominant migration process in these soils. As suggested by the review of Sheppard [3], particle migration resulting from earthworm activity or mobilisation of clays may account for these results. Overall, the results support the common assessment practice of assuming the surface soil layer is uniformly mixed even if it is not cultivated.

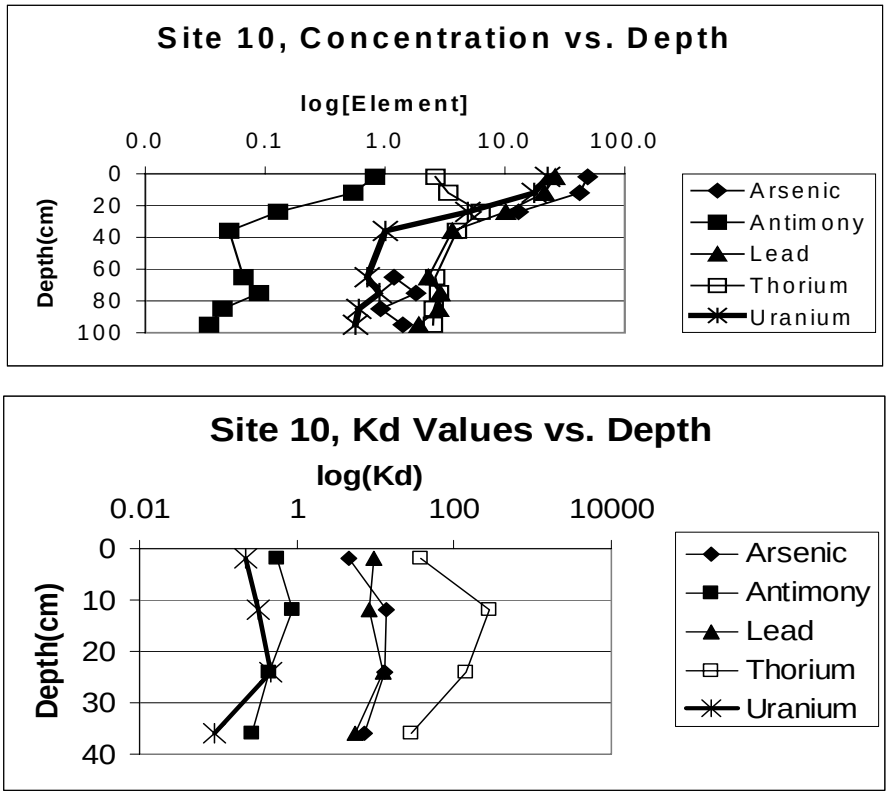

Figure 1. Example of concentration (mg kg^{-1}) and Kd (m^3 kg^{-1}) profiles for selected elements with depth in soil from the Port Hope area.

3.2 Plant/soil concentration ratios

Uranium was detectable in almost all plant and soil samples, resulting in a large number of plant/soil concentration ratio (CR) values. The overall GM values were remarkably consistent between the contaminated sites near Port Hope, the background sites and a review of values from around the world

(Table 2). With geometric standard deviations (GSD) in the order of 3 or more, CR values differing by less than about an order of magnitude are not significantly different. Thus, although there appear to be some differences for certain plant types, notably the trees, shrubs, annuals and forages, these may not be significant. In general, because there is a continued atmospheric emission of U in Port Hope, and washing of plants can never fully remove foliar contamination, higher CR values were expected for the Port Hope samples. However, the results suggest this effect, if present, was not large.

There were up to 151 plant samples from the background sites and up to 63 from Port Hope, and CR values for 49 elements were obtained. The ratios of CR between the background and Port Hope sites (background/Port Hope) were computed, and the median for all elements was 2.1 (for U it was 0.5). This supports the results in Table 2 indicating that CR values were not different between background and the contaminated Port Hope sites. In an assessment context, this implies site-specific parameter values may not be sufficiently different from global averages, given the inherent variability of the parameters, to warrant the emphasis some assessors place on measuring on-site values. This point is made by Sheppard [4].

Table 2. Geometric mean (GM) plant/soil concentration ratios for U (dry weight basis) for 10 sites near the Port Hope U Refinery, seven background sites from across Canada, and from a review of the literature.

Plant type	**Port Hope**	**Background sites**	**Global review [5] - Fine soils**
Overall GM (GSD)	0.0068 (4.9)	0.0035 (3.4)	0.0045
Trees	0.013	0.0041	0.0022
Shrubs	0.011	0.0044	
Annuals	0.017	0.0027	0.0076
Cereals			0.0014
Fruits	0.00076	0.0008	0.0025
Vegetable[1]	0.0041		0.0082
Root[1]	0.0093		0.0025
Forage	0.015	0.0022	0.0084

[1] 'Vegetable' refers to edible crops such as lettuce and beans, 'root' refers to root crops such as carrots and beets.

The CR values for the radionuclides measured at the background sites were few, because many were not detectable in either the soils or the plants (Table 3). Where there were sufficient data to do reliable statistical interpretations, there were significant differences among plant types and among soil types. Fruit tended to have lower CR values. Moss and lichen had especially high CR values for ^{210}Po and ^{210}Pb, probably reflecting that they accumulate these radionuclides from the atmosphere following the decay of radon.

Among the plant types, fruit samples had consistently lower CR values for U (Table 2) and for most other elements. At the background sites, various tissues were measured on the same plants and so direct comparisons were possible. For U and about 20 other elements, fruit had 3-fold lower CR values than the corresponding leaves and twigs. Bole wood (the centre of tree trunks as would be used in lumber or paper) had about 20-fold lower CR values for U and about 20 other elements than did leaves and twigs of the same trees. Leaves and twigs were not consistently different from each other.

3.3 Secular equilibrium in background samples

Secular equilibrium is where the activity concentrations of radionuclides in a decay series are the same. It results when the parent and progeny radionuclides remain in the same physical location long enough that sufficient ingrowth of the progeny occurs. For short half-life radionuclides, the time to reach secular equilibrium is relatively short. The ^{210}Po/^{210}Pb ratio is frequently used to infer the activity of one based on measurements of the other. In soils, the ratio was not different from unity (Table 4) implying secular equilibrium. For plants, with the exception of lichen, the ratio had a median of 0.6, and this was significantly less than unity. Clearly there was not enough time for ingrowth to reach secular equilibrium for most plant tissues. Lichens are an exception because they can accumulate dust with half-times for wash-off in the order of decades. The ^{210}Pb/^{226}Ra ratios were greater then unity, because ^{210}Pb is deposited on soils and plants after decay of radon, the volatile intermediate between ^{210}Pb and ^{226}Ra. This ratio was closer to unity in the subsoil samples, confirming that the excess ^{210}Pb comes from the atmosphere. There were fewer data for the ^{228}Th/^{232}Th ratio, it was unity in soils and tended to be greater than unity in plants. This may not be a reliable observation, but might be expected since ^{228}Th arises from alpha decay and alpha recoil might have the effect of making ^{228}Th more soluble and bioavailable than ^{232}Th in soils. Clearly, the ^{210}Po/^{210}Pb ratio could be used for assessment purposes to estimate unmeasured concentrations, but the other activity ratios are not similarly useful.

Table 3. Plant/soil concentration ratios on a dry weight basis for radionuclides at background sites.

Plant	^{210}Pb	^{210}Po	^{226}Ra	^{228}Ra	^{228}Th	^{230}Th	^{232}Th
Annual: fern, milkweed, sarsparilla, snakegrass strawberry	0.42	0.25	0.21		0.06		
Conifers: cedar, fir, hemlock, juniper, pine spruce		4.15	0.04		0.02	0.01	
Deciduous: apple, buckthorn, chokecherry, cranberry, hawthorn, hazel, locust, maple, oak, saskatoon, sumac, willow	0.58	0.53	0.075	0.35	0.03		
Shrub: blueberry, grape, raspberry, rose, wintergreen	0.43	0.55	0.053	0.25			
Forage: clover, grass, vetch	0.22	0.13	0.035				
Fruit: apple, berry, grape	0.019	0.010	0.022				
Lichen (n=1)		12					
Mushrooms	0.50	0.42	0.030		0.033		
Moss	27	28	0.15		0.020	0.023	0.030
Overall	**0.37**	**0.35**	**0.06**	**0.30**	**0.027**	**0.017**	**0.030**
ANOVA[1] plant type	**P<0.001**	**P<0.001**	**P<0.04**		**ns**		

[1] Results of Analysis of Variance, testing the effect of plant type on CR values.

Table 4. Isotope activity ratios at background sites.

Ratio	Soils	Plants
$^{210}Po/^{210}Pb$	0.95 (n = 11)	0.6 (n = 38) * 1.0 for lichen
$^{210}Pb/^{226}Ra$	2.5 (n = 11)	14 (n = 29) *
$^{228}Th/^{232}Th$	1.1 (n = 8)	4 (n = 3)

4. SUMMARY

Many concentration, CR and Kd values for primordial radionuclides and stable elements were obtained, both in a U-contaminated area and in background settings. At the U-contaminated sites, there was evidence of slow downward migration of U, but this was accompanied by very similar movement of a number of other elements with substantially lower and higher Kd values. This suggests that leaching was not the mechanism. Values of CR were different among plants, plant tissues and soils, but were not consistently different between background and contaminated sites. Finally, secular equilibrium was observed only in soils; plant tissues (apart from lichens) probably do not persist long enough for the $^{210}Po/^{210}Pb$ pair to reach secular equilibrium, and they receive ^{210}Pb from the atmosphere and so activity concentrations of ^{210}Pb in plants exceed that of ^{226}Ra.

References

[1] Sheppard S.C., Sheppard M.I., Gallerand M.-O. and Sanipelli B. Derivation of ecotoxicity thresholds for uranium. J. Environ. Radioactivity (in press) (2004).
[2] Echevarria G., Sheppard M.I. and Morel J. Effect of pH on the sorption of uranium in soils. J. Environ. Radioactivity **53** (2001) 257-264.
[3] Sheppard S.C. Assessment of long-term fate of metals in soils: Inference from analogues. Can. J. Soil Science (in press) (2004a).
[4] Sheppard S.C. Transfer parameters – are on-site data really better? Human and Ecological Risk Assessment (in press) (2004b).
[5] Sheppard S.C. and Evenden W.G. Critical compilation and review of plant/soil concentration ratios for uranium, thorium and lead. J. Environ. Radioactivity **8** (1988) 255-285.