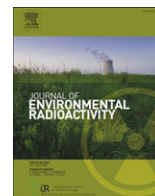




Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvrad

Plant/soil concentration ratios for paired field and garden crops, with emphasis on iodine and the role of soil adhesion

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ARTICLE INFO

Article history:

Received 29 January 2010

Received in revised form

6 August 2010

Accepted 10 August 2010

Keywords:

Kd

Partition coefficient

Risk assessment

Selenium

Arsenic

ABSTRACT

In the effort to predict the risks associated with contaminated soils, considerable reliance is placed on plant/soil concentration ratio (CR) values measured at sites other than the contaminated site. This inevitably results in the need to extrapolate among the many soil and plant types. There are few studies that compare CR among plant types that encompass both field and garden crops. Here, CRs for 40 elements were measured for 25 crops from farm and garden sites chosen so the grain crops were in close proximity to the gardens. Special emphasis was placed on iodine (I) because data for this element are sparse. For many elements, there were consistent trends among CRs for the various crop types, with leafy crops > root crops ≥ fruit crops ≈ seed crops. Exceptions included CR values for As, K, Se and Zn which were highest in the seed crops. The correlation of CRs from one plant type to another was evident only when there was a wide range in soil concentrations. In comparing CRs between crop types, it became apparent that the relationships differed for the rare earth elements (REE), which also had very low CR values. The CRs for root and leafy crops of REE converged to a minimum value. This was attributed to soil adhesion, despite the samples being washed, and the average soil adhesion for root crops was 500 mg soil kg⁻¹ dry plant and for leafy crops was 5 g kg⁻¹. Across elements, the log CR was negatively correlated with log Kd (the soil solid/liquid partition coefficient), as expected. Although, this correlation is expected, measures of correlation coefficients suitable for stochastic risk assessment are not frequently reported. The results suggest that $r \approx -0.7$ would be appropriate for risk assessment.

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1. Introduction

Plant/soil concentration ratios (CRs) are used to estimate food contamination in situations where there is potential for soil-to-plant transfer of contaminant (Carini, 2009; Vandenhove et al., 2009; Sheppard et al., 2006). The ratios are empirical, ideally measured in settings similar to those where the estimates are required. Typically, the estimates must encompass a suite of plant types all of which could be grown and could contribute to the diet of the people dependent on the site for food. However, often there is a scarcity of appropriate data and extrapolation is required. For extrapolation among soil types, it is often possible to rely on functions that relate CR to soil properties (e.g. Absalom et al., 2001; Massas et al., 2002). These functions are possible because the soil properties are considered continuous variables.

Extrapolation from one plant type to another is not as easy, because instead of belonging to multidimensional continua as do soils, plants belong to more discrete categories by species. For

practical purposes, CR values are often grouped into plant categories, such as grains, leafy vegetables, root crops and fruits. However, it is very rare that data from each of these categories are measured in the same setting. The objective of this study was to find locations where cereal crops and garden crops were grown on adjacent soils, in order to more rigorously determine how CRs for such crops differ.

This study deals only with indigenous elements, in contrast to many studies designed to measure soil-to-plant transfer of radionuclides in which the radionuclide of interest is deliberately added to the soil or which use previously contaminated soils. Clearly, there are circumstances where the radionuclide will behave differently than its indigenous stable-element counterpart. For example, ¹³⁷Cs undergoes progressive sorption reactions in soils, and so if CR data are needed to describe transfer of ¹³⁷Cs to foods in the first year after contamination, then data from stable Cs measurements are probably not appropriate. In contrast, in the context of nuclear waste management where soil contamination (if any) may be spread over decades to millennia, then the contaminant radionuclides in soil will be in chemical and physical states very similar to the indigenous elements. For such long-term

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assessments, CRs based on indigenous elements may be the most appropriate. In addition to this argument, it is possible to simultaneously measure CRs for >60 elements when indigenous elements are used.

Although assessment of nuclear waste management requires data for many elements, a few are especially important and are not often measured in relation to other industries. In nuclear fuel waste, especially of fuel that has not been reprocessed, ^{129}I and ^{36}Cl are important because they are long-lived, environmentally mobile and the elements I and Cl are biologically essential. Their stable isotopes are also relatively abundant, so that isotopic mixing occurs in the biosphere and radiological dose impacts from ^{129}I and ^{36}Cl are closely linked to transfer of the stable isotopes. As a result, plant/soil CR values for I and Cl are needed, and yet are not commonly measured, in part because of analytical limitations. Sheppard et al. (2006) reviewed what literature there is for these and several other elements important to nuclear fuel waste assessments. Thus, an important aspect of the present study was to include analytical techniques specific to and especially sensitive to I and Cl.

2. Methods and materials

2.1. Sampling and sample handling

The basic strategy was to sample 10 sites where field crops (usually wheat, *Triticum aestivum*) were grown in close proximity to a garden with a wide range of vegetables and fruits. The intent was that the crops within a site were sampled close enough together that the corresponding soil properties would be consistent, and on the sites sampled there were no visually apparent discontinuities in soil type. The species available for sampling varied somewhat from garden to garden. The sites were located in southern Manitoba and near Thunder Bay, Ontario. Plant samples were collected by hand in a manner consistent with normal harvest, and generally only edible portions were sampled. In a few cases such as cabbage, corn and peas, outer tissues exposed to the atmosphere and interior tissues were sampled separately. Plant samples were refrigerated and shipped fresh to the laboratory. In the laboratory, samples that may have contacted soil were washed with deionised water. Beet roots were peeled and only the interiors were retained (because the rind is seldom consumed), whereas carrot roots, onion bulbs and potato tubers (collectively called root crops) were thoroughly scrubbed but not peeled. Cereal grains and interior tissues such as sweet corn kernels and interior cabbage leaves were not washed. Grain samples were cleaned of chaff by hand, and the chaff retained as a separate sample.

Soil samples were collected as a composite of the top 30 cm of the soil in the area encompassed by the plant sampling, usually less than 1 ha. In most cases, separate soil samples for the field crop and garden crop areas were collected, despite there being no other obvious differences between these soils. Fertilizer amendments were probably different between field and garden areas.

Wherever possible, laboratory gloves were worn to reduce contamination of samples by skin contact. All samples were weighed fresh, spread thinly on no-stick (silicone-coated) aluminum foil and dried in a plastic domestic food dehydrator with forced air at <35 °C. Drying usually continued for several days or until there was no further weight loss. Once dried, the samples were weighed again and ground in a small knife mill.

2.2. Analysis and data handling

All analyses of I, Cl and trace elements were done by Activation Laboratories, Ancaster, Ontario. Iodine in plant samples was determined using alkaline extraction with tetramethylammonium hydroxide (TMAH) (Fecher et al., 1998). This method was proven in preliminary studies to be sufficiently sensitive to enable quantification of I in most biological tissues at ambient environmental concentration levels. The method involved 3 to 4 separate analyses of the TMAH plant extract by inductively coupled plasma – mass spectrometry (ICP-MS), using standard addition of known aliquots of I to account for matrix effects. Iodine in soil samples and Cl in both soil and plant samples were analysed by instrumental neutron activation analysis (INAA), because concentrations were in the quantifiable range by this method and INAA requires less sample preparation. Trace elements other than I and Cl were analysed in plant samples using ICP-MS after digestion in HNO_3 , H_2O_2 , HCl and HF. Up to ~60 elements were reported. Care was taken to minimize sample dilution so that the best available detection limit for each element was achieved.

Physical properties and pH of soils were measured by ALS Laboratories, Saskatoon, Saskatchewan. Particle size fractionation of the mineral material was into clay, silt and sand fractions by the hydrometer method. Organic carbon was by the Walkley Black wet oxidation method. Soil pH was determined in water from saturated paste extracts of the soil.

The plant/soil concentration ratio (CR) was computed as the concentration in the dry plant tissue divided by the concentration in the dry soil to 30-cm depth. The solid/liquid partition coefficient (Kd) for soil was the concentration on the dry solids divided by the concentration in the pore water, where pore water field capacity was extracted by centrifugation (Sheppard et al., 2007). The resulting units for Kd are L kg^{-1} . The default assumption for the data frequency distributions of CR and Kd was lognormal, consistent with previous experimental evidence and with the Central Limit Theorem. All statistical tests were of log-transformed data, and geometric means (GMs) and geometric standard deviations (GSDs) are reported. Because the sampling was not of a balanced factorial design (not all species could be sampled at all sites and there were different numbers of samples at each site), the statistical tests were by analysis of variance with categories of plant types as the main factor.

3. Results and discussion

3.1. Soil properties and plant species

The ten sites had a range of soil clay contents from 15% to 56% (by weight), pH from 6.3 to 7.8 and organic carbon from 1.7% to 8.5%, properties that are typical of highly productive agricultural soils. The plants sampled and the plant-type categories they were assigned are indicated in Table 1.

3.2. Iodine concentration ratios

The CR values for I (Table 1) are generally consistent with the literature (Sheppard et al., 2006). The cereal chaff had significantly higher CRs than the corresponding grain samples, by about 2.5-fold. This may be because the chaff at earlier stages was capable of

Table 1

Plant/soil concentration ratios (CR) for I, separated by crop type and crop. Overall analysis of variance showed differences among crop types were statistically significant ($P < 0.001$), and plant types that were statistically different from seed ($P < 0.05$) are indicated by*. The residual GSD (after accounting for plant type) was 2.6.

Crop/sample type	Crop (n)	GM by crop	GM by crop type		
Field crop seed	Barley (1)	0.004	0.008		
	Canola (2)	0.005			
	Corn (3)	0.005			
	Wheat (8)	0.012			
Field crop chaff	Barley (1)	0.021	0.020*		
	Corn (2)	0.016			
	Wheat (8)	0.023			
Tree fruit	Apple (1)	0.006	0.006		
Bush fruit	Pepper (1)	0.004	0.004		
	Tomato (2)	0.003			
Ground fruit	Cucumber (6)	0.008	0.008		
	Zucchini (1)	0.005			
Fruit flesh only	Watermelon (1)	0.002	0.002		
Exposed leafy	Basil (1)	0.082	0.036*		
	Beet leaves (2)	0.020			
	Cabbage outer leaves (2)	0.046			
	Carrot leaves (2)	0.024			
	Chard (2)	0.054			
	Dill (1)	0.022			
	Lettuce (3)	0.053			
	Onion tops (3)	0.031			
	Parsley (1)	0.027			
	Spinach (1)	0.028			
	Interior leafy	Kale (1)		0.009	0.024*
		Cabbage (2)		0.032	
	Exposed pods	Bean (3)		0.006	0.015
Pea pods (3)		0.040			
Pod interiors	Peas (4)	0.019	0.019		
Roots	Beet interior (2)	0.005	0.010		
	Carrot (5)	0.009			
	Onion (3)	0.012			
	Potato (6)	0.011			
Overall	(90)		0.013		

photosynthesis, which has attendant micronutrient demands and photosynthetic chemical reduction that tend to sequester elements such as I. The chaff also provides an upper-canopy surface from which evapotranspiration takes place, and so may accumulate salts left behind as the water evaporates. Higher concentrations in the chaff may also indicate that some I was derived from deposition from the atmosphere. The sampling sites were mid-continent so that deposition of marine aerosol I was likely to be minimal, but deposition of soil dust was possible. Other elements with significantly higher concentrations in chaff than grain included several rare earth elements (REE), which suggests a contribution from soil dust. For several essential elements (Cu, Mg and Zn), the grain had significantly higher CR values, which is consistent with these elements being physiologically concentrated in the seed as reserves for the germinating embryo.

All the fruits sampled had CR values comparable to seed (Table 1), conceptually consistent in that both seeds and fruit are reproductive organs. In contrast, all exposed leafy vegetables had higher CR values than did seed. For many elements (Table 2), the leaves have the highest concentrations and CRs, related to the trace element demands of the photosynthetic apparatus, the concentration of elements left behind as water evaporates from stomates on leaves, and the accumulation of dust on leaves. For I, interior leaves of

cabbage and peas inside the pod had CRs comparable to the outer leaves and to other exposed leafy vegetables, suggesting that dust was not an important source of I. The CR values for roots other than beets (which were peeled) could have been influenced by residual soil, but the values for all the root crops were similar and were intermediate between seed and leafy vegetables.

3.3. Correlation of CR among plant types

One of the questions to be addressed in this project is whether it is possible to predict CRs by extrapolating from one plant type to another, especially between field and garden crops. The ideal would be to demonstrate a correlation between species growing in the same soil and weather conditions. In Fig. 1, the CR values for fruit, leaf, pod, root and garden-seed crops are plotted versus the CR values for field grain crops from the same farm/garden settings. For I (upper plot in Fig. 1), there is no clear pattern and the correlation coefficient was not significant. This apparent lack of correlation was true for many of the elements, and does not support extrapolation from one plant type to another. However, the soil concentration range for I was ~30-fold and may have been too narrow to demonstrate the correlation. For Cs (lower plot in Fig. 1), there was a larger range in soil concentrations, there is a trend, and the correlation between (log) CR values for all garden crops versus (log) CR for field grains was statistically significant ($P < 0.05$). This result for Cs supports extrapolation from one crop type to another, although obviously caution is required and the correlation may only be relevant when there is a wide range in soil concentrations. Certainly there remains considerable residual unexplained variation in CRs.

Across elements, the correlation is more obvious (Fig. 2). This plot is the log CR for root crops and leafy crops versus the log CR for

Table 2

Geometric mean CR values for other elements, separated by crop type. Analysis of variance by element showed differences among crop types were statistically significant ($P < 0.05$) except where indicated by 'ns' in the 'overall' column. For each element, plant types that were statistically different from seed ($P < 0.05$) are indicated by*.

Element	N	Overall	Leafy	Fruit	Root crop	Seed crop	Overall GSD
Ag	103	0.055	0.12*	0.070	0.037	0.039	2.8
As	91	0.012	0.007*	0.004*	0.004*	0.027	5.0
B	106	0.57	2.5*	1.3*	0.75*	0.19	4.2
Ba	93	0.049	0.20*	0.028	0.075*	0.026	3.5
Ca	106	0.064 ns	0.079	0.13	0.071	0.048	5.6
Cd	106	0.20	0.78*	0.21*	0.26*	0.12	3.2
Ce	97	0.00059	0.0062*	0.00021	0.00067*	0.00016	5.8
Cl	71	7.9	25*	12*	7.8*	3.2	3.2
Co	106	0.0044	0.012*	0.0077*	0.0045*	0.0016	2.9
Cr	105	0.007	0.013*	0.002	0.003	0.004	5.2
Cs	105	0.0053	0.022*	0.0054	0.0050	0.0028	4.9
Cu	106	0.20	0.27*	0.27*	0.20	0.20	1.8
K	105	0.71	0.10*	0.12*	1.4	1.8	8.3
La	95	0.00075	0.0068*	0.00035	0.00075*	0.00021	5.3
Li	96	0.0037	0.055*	0.0054*	0.0030	0.0010	7.7
Mg	106	0.21	0.73*	0.27*	0.14	0.19	2.5
Mn	106	0.039	0.10*	0.027	0.017*	0.045	2.6
Mo	106	1.2	3.8*	1.5	0.7	1.0	5.0
Na	84	0.28	3.2*	0.22	0.56*	0.04	11.2
Nb	96	0.0032	0.017*	0.0015	0.0025	0.0015	3.5
Nd	106	0.00038	0.0043*	0.00021	0.00054*	0.00010	5.8
Ni	104	0.024 ns	0.018	0.029	0.017	0.017	2.7
Pb	81	0.0024	0.0049*	0.0010	0.0020	0.0022	2.5
Pr	85	0.00080	0.0054*	0.00032	0.00078*	0.00023	4.2
Rb	106	0.25	0.62*	0.36	0.25	0.16	3.5
Sb	93	0.0074	0.017*	0.0055	0.0049	0.0033	3.5
Se	57	1.0	1.0	0.38*	0.66*	1.6	2.5
Sm	106	0.00042	0.0045*	0.00020	0.00064*	0.00011	5.1
Sn	31	0.25	0.12	0.97*	1.2*	0.14	3.7
Sr	106	0.15	1.1*	0.18*	0.11	0.07	4.4
Tb	106	0.0010	0.0072*	0.0005	0.0013*	0.0004	4.0
Th	55	0.0071 ns	0.0136	0.0036	0.0042	0.0090	3.0
Tl	68	0.029 ns	0.116	0.012	0.016	0.055	8.2
U	90	0.0019	0.0052*	0.0007	0.0032	0.0011	3.1
V	84	0.0019	0.0088*	0.0004*	0.0020	0.0013	5.3
Y	106	0.00064	0.0055*	0.00036	0.00080*	0.00021	4.6
Yb	82	0.0019	0.0080*	0.0010	0.0020*	0.0008	3.0
Zn	106	0.25	0.28	0.23	0.17*	0.37	2.1
Zr	106	0.015	0.087*	0.012	0.014	0.007	4.5

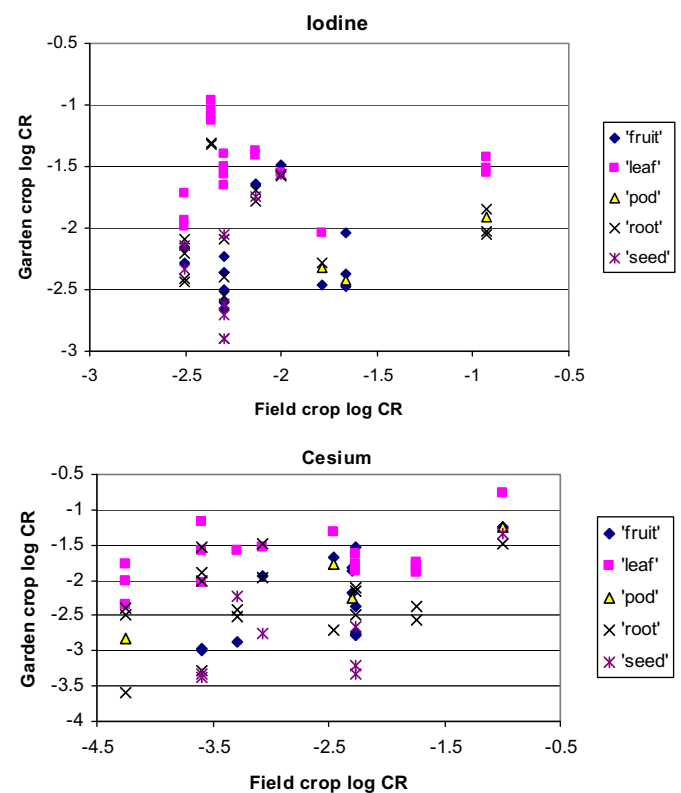


Fig. 1. Correlation of log CR values for fruit, leafy, pod, root and garden-seed (pea) crops to those of their paired field crops (mostly wheat grain), showing data for iodine (upper plot) and cesium (lower plot).

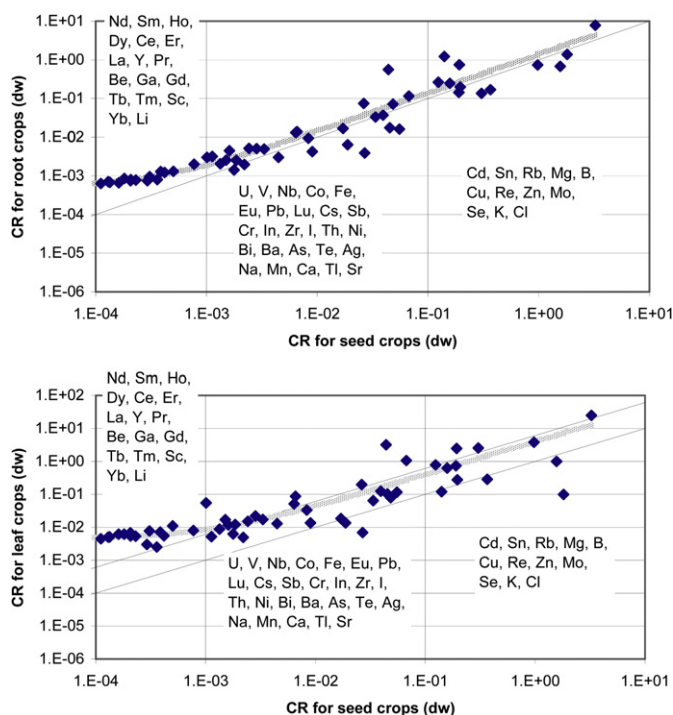


Fig. 2. Correlations between log CR for root (upper plot) and leafy (lower plot) crops versus log CR for seed crops. Each point is a different element, listed from left to right within each section. The 1:1 line is shown and for leafy crops a line representing the average leaf/seed ratio of 6 is also shown. The grey lines are the lines accounting for soil adhesion, as described in text.

seed crops, and each point represents a different element, the corresponding elements are indicated in Fig. 2. Because the log–log data are parallel to the 1:1 line, it indicates that in general the untransformed CR for these tissues were linearly correlated. This supports the hypothesis that extrapolation from one crop type to another is useful, but it is clear that variation about the best-fit line was often at least tenfold. The slopes differ from 1:1 below CR values of about 0.001, as discussed below.

3.4. Contribution of soil adhesion to CR

Between CR values of 0.001 and 0.0001, a range largely populated by REE, the root and leaf CR values diverge from and are higher than those for seed (Fig. 2). The presence of REE, which are not readily absorbed by plants, suggests a direct contribution from residual soil particles, perhaps microscopic amounts that resisted scrubbing. Sheppard and Evenden (1995) noted REE and other evidence for soil contamination in many types of plant samples, despite washing. Recall from above that REE were high in chaff relative to grain, and we speculated that soil dust may provide and explanation for this. A more direct comparison is for cabbage, and the REE had on average 13-fold higher concentrations in outer than in inner leaves. Similarly, REE in corn husks were at 12-fold higher concentrations than in kernels.

With a few assumptions, it is possible from the data in Fig. 2 to estimate an average soil load on the root and leaf crops. With adhering soil, the concentration of any element on the root or leaf sample (C_r) is:

$$C_r = CR_r^* \cdot C_s + SL \cdot C_s \quad (1)$$

Where C_r is the concentration of the element in the root or leaf, CR_r^* is the true CR attributed only to root uptake of that element into root or leaf, C_s is the concentration of the element in the soil,

and SL is the soil load (mass dry soil per mass dry plant) on the root or leaf. Assuming that elements with $CR > 0.001$ are mostly taken up by roots and that the seed has negligible soil dust, the CR for seeds above 0.001 are true CR_r^* indicative of only root uptake. From Fig. 2 it is evident that root and leaf CR are linearly related to seed CR above 0.001: in this range root/seed ratio $R_{r/s}$ is 1.4-fold and the leaf/seed ratio $R_{l/s}$ is 4-fold. From this, one can estimate the CR^* for root crops as $CR_r^* = CR_{seed} \cdot R_{r/s}$ and for leaf crops as $CR_l^* = CR_{seed} \cdot R_{l/s}$. From equation (1), SL for root (SL_r) and leaf (SL_l) can be computed as:

$$SL = CR_R - CR_{seed} \cdot R_{r/s} \quad (2)$$

and

$$SL_l = CR_l - CR_{seed} \cdot R_{l/s} \quad (3)$$

where CR_r and CR_l are the observed or net CR values for root and leaf crops. Among the REE, the median soil load on root crops was 0.0005 in units of CR, or 500 mg kg^{-1} . For leafy crops, the soil load was 0.005 or 5 g kg^{-1} . Although it may seem counter intuitive, it is logical that the soil load on washed roots was lower than on leaves because soil load is a surface phenomenon, and the surface per unit mass of the leaf is much higher than for the thickened roots and tubers. Sheppard and Evenden (1995), using a variety of techniques and plant types, found soil loads on washed leafy vegetables of 20 g kg^{-1} ($GSD = 3.3$). For pods, cucumber and strawberries, the value was lower at 2 g kg^{-1} ($GSD = 3.3$), again because these tissues have a lower surface per unit mass than do leafy tissues. Although these estimates of soil load may seem high for leaves, it is probable that the adhering soil consists of clay-sized particles that are of similar size to the wax particles and surface roughness features of the leaf, and so may be quite effectively entrained on the plant surfaces. Beresford et al. (2002) used Ti to indicate soil load on pasture vegetation, and from their data one could estimate they had soil loads in spring and summer of $25\text{--}50 \text{ g kg}^{-1}$ dry plant. Hinton et al. (1995) reported soil loads on unwashed vegetation of $10\text{--}20 \text{ g kg}^{-1}$. More relevant to food plants, Amaral et al. (1994) reported soil loads on lettuce of $130\text{--}340 \text{ g kg}^{-1}$. Clearly soil adhesion to leaves can predominate over root uptake for insoluble elements. Additionally, as indicated by Sheppard (1995), the soil particles most likely to resiliently adhere to plant leaves are clay-sized, and for many elements the concentrations on clay-size particles can be 20-fold or more higher than the bulk soil.

The implication of these levels of soil loading is that ~ 0.001 is the detection limit for CR to represent root uptake. The CR values below ~ 0.001 are valid for assessment modeling, and there is a component of root uptake involved, but the mechanism becomes dominated by surface adhesion of soil dust. There is potential for double accounting of soil ingestion in risk assessments that use CRs below 0.001 and separately compute soil ingestion from soil adhering to food items.

3.5. Relative CR values for other elements

The CR values for 39 elements in leafy, fruit, root and seed crops are contrasted in Table 2. There were overall significant differences between geometric mean CRs for these plants types for all elements except Ca, Ni, Th and Tl. The latter two were near detection limits and were not detectable in all samples, and so the lack of significant differences for Th and Tl may reflect analytical limits. Calcium is a macronutrient largely associated with cell wall structures, and so may be at relatively constant concentrations per unit dry matter, because most of the dry matter is composed of cell walls. An explanation for Ni is not as obvious.

Although other statistical tests among plant types are possible, the analysis of variance results shown contrast leafy, fruit and root

crops versus seed. As noted above, for most elements the CR for leafy crops was higher than for seed. Often, root crops also had higher CR than seed, and for some elements CR for fruit was higher than for seed. There were notable exceptions, and As, K, Se and Zn appeared to be preferentially concentrated in seed, having higher CR values for seeds than for other tissues. Both K and Zn are essential elements, and so this may explain why they are concentrated in the seed. A related explanation may apply to As and Se, because they are chemical analogues of P and S. Phosphorus is concentrated in many seeds as phytic acid and S in cysteine and related proteins. Ferri et al. (2004), Galeas et al. (2007) and Vogrinčić et al. (2009) all noted Se at higher concentrations in seed than the corresponding foliage. Porter and Peterson (1975) also noted this for As, but others such as Murillo et al. (1999) did not find As concentrated in the seed.

3.6. Relationship of CR to Kd

There is an a priori assumption about the relationship between CR and Kd: the lower the Kd, the more soluble the element in soil pore water and hence the greater potential for uptake by the plant resulting in a higher CR (Sheppard and Sheppard, 1989; Baltreinaite and Butkus, 2007). This implies a negative correlation between CR and Kd, as shown empirically by Watmough et al. (2005) and Vandenhove and Van Hees (2007), among others. In this study, there were too few soils with too narrow a range of properties to meaningfully examine this correlation for each element. However, the correlation across elements has value.

The GM Kd values measured in this study for I was 0.073 L kg^{-1} with a GSD of 2.3. For the other elements, the GM Kd (L kg^{-1}) values were – As: 400, Ba: 87, Ca: 250, Ce: 5200, Cl: 45, Cr: 4000, Cu: 1200, Fe: 76000, K: 2200, Li: 620, Mg: 460, Mn: 25000, Mo: 68, Na: 12, Ni: 2900, Pb: 1600, Rb: 990, Sr: 180, U: 90, V: 3200 and Zn: 250, with a median GSD for these elements of 2.3. The correlation of log CR to log Kd is shown in Fig. 3, with the plant-essential elements and their analogues differentiated from the other elements. For the plant-essential element group, the correlation coefficient was $r = -0.83$, $P < 0.001$, and for the other elements it was $r = -0.64$, $P < 0.05$. These are consistent with the correlation invoked for each element by Sheppard and Sheppard (1989), and their results indicated that correlations of this magnitude will affect (probably lower) the upper percentile dose estimates in stochastic risk assessment. This effect on the upper percentile of dose arises because the negative correlation limits the stochastic co-occurrence of high CR and high Kd: high CR and high Kd each increase

dose and in combination they would markedly increase dose. In addition, invoking such a correlation explicitly links CR to soil properties, and may be the most logical way to model the expected change in CR from one soil to another (although this implies that Kd is known for the required range of soils).

4. Conclusions

There are few studies that compare CRs among plant types that encompass both field and garden crops. Here, CRs for 40 elements were measured for 25 crops from farm and garden sites chosen so the grain crops were in close proximity to the gardens. Special emphasis was placed on I because data for this element are sparse. The results indicated:

- The correlation of CRs from one plant type to another was evident only when there was a wide range in soil concentrations.
- CRs for most elements were ordered leafy crops > root crops \geq fruit crops \approx seed crops.
- Exceptions included CR values for As, K, Se and Zn which were highest in the seed crops.
- Soil adhesion occurred on root and leafy crops despite the samples being washed, the average soil adhesion for roots was $500 \text{ mg soil kg}^{-1}$ dry plant and for leafy crops was 5 g kg^{-1} , and these imply minimum detection limits for root uptake for these plant types.
- Across elements, the log CR was negatively correlated with log Kd, and $r \approx -0.7$ would be appropriate for probabilistic risk assessment.

Overall, these results will support risk assessment of contaminants from many situations, although they were intended for and are especially relevant to stochastic assessment of the potential long-term impacts of nuclear fuel waste management.

Acknowledgements

Funding was provided by the Canadian Nuclear Waste Management Organization. The analytical method for I was developed and managed by Yakov Kapusta of ActLabs, Ancaster, Ontario. Sampling near Thunder Bay, Ontario was done by Dr. Tarlok Singh and associates. The cooperation of the producers (farmers and gardeners), who are not named on promise of confidentiality, is especially appreciated.

References

- Absalom, J.P., Young, S.D., Crout, N.M.J., Sanchez, A., Wright, S.M., Smolders, E., Nisbet, A.F., Gillett, A.G., 2001. Predicting the transfer of radiocaesium from organic soils to plants using soil characteristics. *J. Environ. Radioact* 52, 31–43.
- Amaral, E.C.S., Paretzke, H.G., Campos, M.J., Pires do Rio, M.A., Franklin, M., 1994. The contribution of soil adhesion to radiocaesium uptake by leafy vegetables. *Radiat. Environ. Biophys.* 33, 373–379.
- Baltreinaite, E., Butkus, D., 2007. Modelling of Cu, Ni, Zn, Mn and Pb transport from soil to seedlings of coniferous and leafy trees. *J. Environ. Eng. Landscape Manage.* 15, 200–207.
- Beresford, N.A., Barnett, C.L., Coward, P.A., Howard, B.J., Mayes, R.W., 2002. A simple method for the estimation of the bioavailability of radiocaesium from herbage contaminated by adherent soil. *J. Environ. Radioact* 63, 77–84.
- Carini, F., 2009. Radionuclide transfer to fruit in the IAEA TRS 364 Revision. *J. Environ. Radioact* 100, 752–756.
- Fecher, P.A., Goldmann, I., Nagengast, A., 1998. Determination of iodine in food samples by inductively couple plasma mass spectrometry after alkaline extraction. *J. Anal. Spectrom.* 13, 977–982.
- Ferri, T., Coccioli, F., De Luca, C., Callegari, C.V., Morabito, R., 2004. Distribution and speciation of selenium in *Lecythis ollaria* plant. *Microchem. J.* 78, 195–203.
- Galeas, M.L., Zhang, L.H., Freeman, J.L., Wegner, M., Pilon-Smits, E.A.H., 2007. Seasonal fluctuations of selenium and sulfur accumulation in selenium hyper-accumulators and related nonaccumulators. *New Phytol.* 173, 517–525.

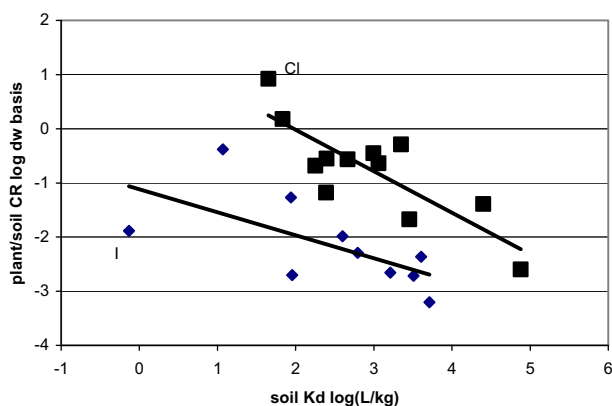


Fig. 3. Correlation of log CR for all plant types versus log Kd. Each point is a different element, and the points for I and Cl are labelled. The large squares are plant-essential elements and their analogues (Ca, Cl, Cu, Fe, K, Mg, Mn, Mo, Ni, Rb, Se, Sr and Zn) and the smaller diamonds are the other elements.

- Hinton, T.G., Stoll, J.M., Tobler, L., 1995. Soil contamination of plant surfaces from grazing and rainfall interactions. *J. Environ. Radioactivity* 29, 11–26.
- Massas, I., Skarlou, V., Haidouti, C., 2002. Plant uptake of ¹³⁴Cs in relation to soil properties and time. *J. Environ. Radioact* 59, 245–255.
- Murillo, J.M., Marañón, T., Cabrera, F., López, R., 1999. Accumulation of heavy metals in sunflower and sorghum plants affected by the Guadamar spill. *Sci. Total Environ.* 242, 281–292.
- Porter, E.K., Peterson, P.J., 1975. Arsenic accumulation by plants on mine waste (United Kingdom). *Sci. Tot. Environ.* 4, 365–371.
- Sheppard, M.I., Sheppard, S.C., Grant, C.A., 2007. Solid/liquid partition coefficients to model trace element critical loads for agricultural soils in Canada. *Can. J. Soil Sci.* 87, 189–201.
- Sheppard, S.C., 1995. A model to predict concentration enrichment of contaminants on soil adhering to plants and skin. *Environ. Geochem. Health* 17, 13–20.
- Sheppard, S.C., Evenden, W.G., 1995. Systematic identification of analytical indicators to measure soil load on plants for safety assessment purposes. *Intl. J. Environ. Anal. Chem.* 59, 239–252.
- Sheppard, S.C., Sheppard, M.I., 1989. Impact of correlations on stochastic estimates of soil contamination and plant uptake. *Health Phys.* 57, 653–657.
- Sheppard, S.C., Sheppard, M.I., Tait, J.C., Sanipelli, B.L., 2006. Revision and meta analysis of selected biosphere parameter values for chlorine, iodine, neptunium, radium, radon and uranium. *J. Environ. Radioact* 89, 115–137.
- Vandenhove, H., Olyslaegers, G., Sanzharova, N., Shubina, O., Reed, E., Shang, Z., Velasco, H., 2009. Proposal for new best estimates of the soil-to-plant transfer factor of U, Th, Ra, Pb and Po. *J. Environ. Radioact* 100, 721–732.
- Vandenhove, H., Van Hees, M., 2007. Predicting radium availability and uptake from soil properties. *Chemosphere* 69, 664–674.
- Vogrincic, M., Cuderman, P., Kreft, I., Stibilj, V., 2009. Selenium and its species distribution in above-ground plant parts of selenium enriched buckwheat (*Fagopyrum esculentum Moench*). *Anal. Sci.* 25, 1357–1363.
- Watmough, S.A., Dillon, P.J., Epova, E.N., 2005. Metal partitioning and uptake in central Ontario forests. *Environ. Pollut.* 134, 493–502.