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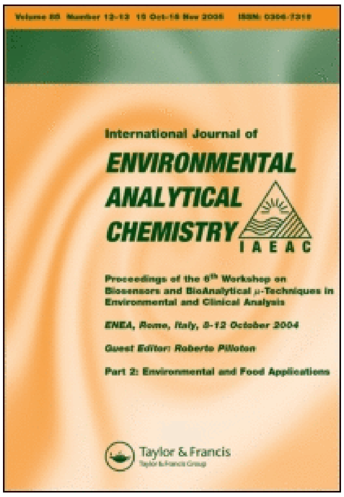

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Systematic Identification of Analytical Indicators to Measure Soil Load on Plants for Safety Assessment Purposes

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SYSTEMATIC IDENTIFICATION OF ANALYTICAL INDICATORS TO MEASURE SOIL LOAD ON PLANTS FOR SAFETY ASSESSMENT PURPOSES

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Contaminants in soil can be transferred to humans and other biota when soil dust on plants is ingested as food. Measuring how much soil is on plants, in the absence of artificial tracers or contaminants, is difficult because of the very small amounts involved and the confounding effect of absorption of elements through roots. However, measurements of soil load are essential for assessment modelling. We compared the ability of several analysis strategies, involving naturally occurring elements, to predict the soil load on plants. Large samples of 12 vegetable and fruit crops were collected, along with corresponding soil samples. An independent measure of soil load on the crop samples was derived from a combination of gravimetric measurements, including loss on washing and the acid-insoluble ash content. The best agreement between the elemental-abundance and the gravimetric methods was for Sr in the plant acid-insoluble ash. Through a systematic process of elimination, we conclude that analyses of the acid-insoluble ash fraction of the plant samples for Al, Ba, Fe, Si, Sr and Ti are most reliable. If analyses are to be restricted to the full plant ash, then the choice of analytes is restricted to Al, Fe, Si and Ti. Soil loads in our study averaged 20 mg soil kg^{-1} dry plant for leafy tissues and 2 mg soil kg^{-1} for fruits, and washing decreased soil loads about 1.5 fold.

KEY WORDS: Soil load, mass loading, dust loading, soil ingestion.

INTRODUCTION

Estimating the health and environmental impacts of soil contamination is a complex task[1,2]. One part of this task is the estimation of contaminant delivery to the affected organisms. In doing this, it is imperative to consider both the obvious and the less obvious routes of exposure. The less-obvious routes are especially important for contaminants that are not very mobile in either the abiotic or biotic parts of the environment. For these, exposure will often be dominated by direct ingestion and inhalation of contaminated soil[3].

Contaminated soil may adhere to plants and be inadvertently ingested. Kitchen and industrial food hygiene will not remove all the contaminated soil adhering to plants. There may even be soil imbedded in the plant tissues[4,5,6]. Animals consume plants directly regardless of adhering contaminated soil[3,7]. Data on the amount of soil ingested with food are required to quantitatively assess impacts. However, for this, as for many other of the less-obvious pathways, the data are not readily available. Hinton[8] highlighted this paucity of data in a recent review article.

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Hinton[8] also commented on the diversity of methods and results in studies of soil load on plants. Pinder and coworkers[9] have provided much of the data using the opportunity provided by Pu releases from a nuclear fuel production centre in the southern U.S.A. However, few other sites have such wide-spread release of a suitable anthropogenic tracer for soil. Other researchers have used indigenous tracers of soil such as Ti, and these allow the opportunity to obtain a much broader survey of soil load on plants in many settings.

Mitchell[10] suggested that Ti was a suitable tracer for soil load on plants, largely because it is present in soils at 10 000–fold higher concentrations than in plants. Others[11] provided advice for analysis of Ti for this usage, and Ti has subsequently been used to estimate soil contamination in order to correct elemental analyses of plant samples[12,13] and to estimate soil ingestion by animals[14] and humans[15,16]. Mañkovská[17] found Ti useful to differentiate mineral dust on plant leaves from other particulates.

Aluminum, Ba, Fe, Hf, Mn, Si, V, Y and Zr have also be used as tracers for soil[11,15,18]. Acid-insoluble ash content has been used as a measure of soil in faeces[16], and it is potentially a useful tracer for soil load on plants. Van Wijnen[16] also used a most-limiting-tracer method, where they used several tracers to estimate soil load and then selected the lowest value. Although this may seem arbitrarily conservative, it is equivalent to a fingerprint analysis based on element ratios. The underlying concept of the fingerprint analysis is that ratios of element concentrations are unique to the soil material, and deviations are attributable to other sources or to selective bioaccumulation by the plant. The relative merits of the various tracers and the use of combinations of tracers and methods have not been investigated.

The objective of this study was to identify the best analytical indicators among indigenous soil elements that could be used to measure the amount of soil adhering to plant surfaces. This would ultimately lead to improvements in the accuracy of contaminant pathways analyses because, with reliable indicators, data on ingestion of soil with plants could be obtained from almost any setting. It would also facilitate estimation of contaminant enrichments on adhering particles[19] because the technique is independent of contaminant concentrations. The basic plan was to collect several plant samples, subject subsamples to differing washing protocols and measure a series of potential indicators of soil load. Systematic criteria for evaluating the indicators were developed and included the correlation to gravimetric indicators.

METHODS AND MATERIALS

Collection of plant samples

Plants chosen to collect were vegetable and fruit crops where soil contact was likely. Twelve samples, each 1 – 5 kg fresh weight, included bean leaves and pods, beet and chard leaves, cucumber and strawberry fruits and cabbage outer and inner leaves. The vegetable plants were collected in two private gardens with markedly different soils, and the strawberries were collected from a commercial pick-your-own operation. These sites were within 50 km of Pinawa, Manitoba. A > 5-L sample of the surface soil was also obtained from each site. Each site had been tilled, which assured vertial homogenization, and each sample was a composite of multiple scoops representative of the area where plant samples had been collected.

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Sample processing

The plant samples were split into three and weighed. One third was left unwashed, another third was washed by hand in distilled water, and the remaining third was washed by hand in a solution of soil dispersant (a flowchart is shown in Table 1). The volume of wash solution was 3 ± 2 L kg^{-1} fresh plant. The soil dispersant was Calgon, a commercial preparation of $NaPO_3$ and Na_2CO_3, at 0.5 g L^{-1} (0.14 g Na L^{-1}) routinely used in soil mechanical analysis[20]. The individual pieces of the washed samples were rubbed by hand with an intensity meant to emulate typical household practices. The wash solutions were collected, concentrated by evaporation to 100 mL and filtered through pre-tared Whatman #41 paper.

The plant samples were dried at 50°C for 24 h and weighed. The samples were then ashed at 500°C for > 24 h and the ash was weighed. To measure the acid-insoluble residue (AIR), we followed published methods[16]. Aliquots of up to 1 g the ash were accurately weighed, moistened with distilled water and suspended with 5 mL of concentrated HCl. This was evaporated to dryness overnight at 50°C, and the residue was suspended in 10 mL of 2 N HNO_3. After heating for 30 min, the volume was brought to 20 mL with distilled water and the suspension was filtered through pre-tared Whatman #541 paper. The filtrate was analysed for Al, Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, Gd, Hf, Mg, Mn, Ni, Pb, Ru, Sb, Si, Sn, Sr, Te, Ti, V, Zn and Zr by inductively coupled plasma – atomic emission spectroscopy (ICP-AES) The filter paper containing the AIR was dried 24 h at 105°C, and then ashed at 500°C overnight. The residue was moistened slightly with water and treated with 2 mL of concentrated HCl, evaporated to dryness and

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Table 1 Flow chart indicating preparation of the 12 plant and corresponding soil samples. All sample fractions were ultimately analysed as liquids by inductively coupled plasma - atomic emission spectroscopy (ICP-AES). Details are provided in the text.

Original material	*Materials after washing*	*Materials after filtration of wash water*	*Materials after partial acid dissolution of ash*
Plant washed in dispersant	Plant	–	Plant acid-insoluble ash (AIR)[1] Plant soluble ash
	Wash water	Retentate	Adhering-soil AIR Adhering-soil soluble ash
		Filtrate	
Plant washed in distilled water	Plant	–	Plant AIR Plant soluble ash
	Wash water	Retentate	Adhering-soil AIR Adhering-soil soluble ash
		Filtrate	
Plant not washed	Plant	–	Plant AIR Plant soluble ash
Original soil	–	–	Original-soil AIR Original-soil soluble ash
Processed soil[2]	–	–	Processed-soil AIR Processed-soil soluble ash

[1] The AIR materials were fully decomposed in HF prior to analysis by ICP-AES

[2] The processed soil, as described in the text, was soil fines removed from the original soil by suspension/sedimentation in water.

weighed. The residue was then digested using 50 mg residue in 1 mL aqua regia and 10 mL concentrated HF[21]. Care was taken to ensure that the plastic containers were well sealed to minimize loss of Si. The digests were neutralized with 100 mL saturated boric acid, diluted to 200 mL with deionized water and analysed by ICP-AES as above.

The soil residue filtered from the plant-wash water was weighed and was ashed as above. The ash weight was recorded and the AIR in the ash was determined as described above, with subsequent analyses of soluble and insoluble fractions by ICP-AES.

Aliquots of the soil samples were vigorously stirred in distilled water and the suspensions allowed to settle for 60 s. The supernatant was decanted to a depth of 7.2 cm below the suspension surface. Based on Stokes law, the soil material in this supernatant had particles less than 40-μm diameter. The supernatant was dried, and we term the soil residue the processed soil. The processed soil and aliquots of the original soil were dried at 105°C for 24 h, weighed, ashed at 500°C for 24 h and weighed. The AIR in the ash was determined as described above, with subsequent analyses of soluble and insoluble fractions by ICP-AES.

All elemental analyses are expressed on the basis of dry plant or soil weight unless specified otherwise. Most variables spanned several orders of magnitude and tended to be lognormally distributed. As a result, geometric means (GM) and standard deviations (GSD) are used to summarize the data unless specified otherwise, and are shown with the numbers (n) of observations as (GM x ÷ GSD, n). Statistical significance was assigned to a probability level of ≤ 0.05 by two-tailed tests, and probability levels of < 0.1, < 0.05, < 0.01 and < 0.001 are reported. The 0.1 probability level by two-tailed test is equivalent to a 0.05 level by one-tailed test, and is reported where one-tailed tests would be considered appropriate.

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Computations from the data

Plant dry matter content was computed as the dry weight per unit fresh weight. The dry matter content is not discussed further, the overall GM was 0.11 kg kg^{-1} (x ÷ 1.6, n = 36). Plant and soil ash contents (AC) were the ash weights per unit dry weight. Plant and soil acid-insoluble ash contents (AIAC) were the weights of AIR per unit weight of original dry (unashed) material.

Soil load on the plants was expressed as weight of dry whole soil per unit plant dry weight. There were gravimetric and elemental-abundance methods to estimate soil load, as discussed with the results. The gravimetric estimates were the AC and the amount of soil washed off the plants. The elemental-abundance estimates were computed as the weight of soil which would have an amount of element equivalent to the amount found per unit dry weight of the plant. In effect, it is the ratio of plant to soil concentrations both expressed per unit dry weight. These elemental-abundance estimates of load were computed for both the total (soluble plus insoluble) analyses of the plant and soil and the analyses of the plant and soil AIR.

Loads can also be based on element ratios, assuming that adhering soil will have the same ratios as the original soil and that deviations from the ratios in the plants reflect bioaccumulation of one (in the case of two-element ratios) or more (in the case of multi-element ratios) of the elements. In effect, a load based on element ratios is equal to the lowest elemental-abundance load of the elements included in the ratio. That element is assumed to not bioaccumulate, whereas the others are assumed to bioaccumulate. Ratios of the structural elements of minerals such as Al:Si:Ti are especially appropriate to consider.

Soil loads were also estimated based on differences between washing treatments, assuming that the Calgon wash removed all the soil and that the unwashed samples did not lose soil. We did observe some loss of soil particles from the unwashed samples as they dried, and this was not fully recovered.

RESULTS AND DISCUSSION

Gravimetric measurements of soil load

Gravimetric measurements of soil load were essential for comparison of the elemental tracers, because the gravimetric data were the best possible independent measurements. The AC, AIAC and the amounts of soil collected from the wash water all responded in the expected manner to the washing treatments (Table 2). The values of AC and AIAC for the plants significantly decreased as washing intensity increased, reflecting that these are correlated to soil load. The AC is not a direct measure of soil load because it contains all of the non-volatile elements from the plant, not just the soil minerals. Although some researchers have assumed that the AIAC is a direct measure of soil load, we again interpret it as an overestimate because there may be acid-insoluble residues from the plant ash that were not soil-derived. Examples might be Al and Si oxides formed during ashing from organically-bound Al and Si. Silicate clay minerals may actually be formed inside root epidermis[22].

The amount of soil washed off the plants tended to be slightly greater for the dispersant wash than for the distilled water wash, which was the expected trend. We interpret the measurement of soil washed off the plants to be an underestimate of the true soil load, because some very small soil particles may be effectively trapped on or in the plant surfaces and not removed by washing. These smaller particles, because of their high specific surface area, may be especially contaminated[19]. To detect these, elemental analyses may be particularly useful because these small particles may also be enriched in the analyte element.

Given our interpretations of AIAC and the amount of soil washed off the plant, there is no acceptable single direct measure of soil load. We used two approaches to provide

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Table 2 Response to the washing treatments of several gravimetric indicators of soil load (g soil kg^{-1} dry plant) measured on plant samples.

Indicator of soil load	*Wash treatment*			p^1	GSD^1
	None	*Water*	*Dispersant*		
Ash matter content (AC)	141	139	136	+	1.1
Acid-insoluble ash content (AIAC)					
Plant only[2]	17.3	13.9	13.9	**	1.2
Corrected for soil AIAC[2]	21.5	17.2	17.2	**	1.2
Soil removed by washing	–	5.5	7.4		1.5

[1] P is the probability level corresponding to a test of the effect of washing within a two-way analysis of variance, coded as + ($P < 0.1$) and ** ($P < 0.01$). The geometric standard deviation (GSD) was based on the error term from the analysis of variance.

[2] AIAC for plant only assumes all of the acid-insoluble residue from the plant samples is soil, whereas the plant AIAC corrected for soil AIAC adjusts for the fraction of the original soil that is not retained in the soil acid-insoluble residue.

an independent measure of soil load. The first was to assume that the geometric mean of the two gravimetric methods that under- and overestimate load represents the true soil load. For this, we considered the AIAC of the unwashed plant sample as the overestimate, and the soil washed off the paired plant sample by the dispersant as the underestimate. The overall soil load based on the mean of these values was 13 x ÷ 3.5 g soil kg^{-1} plant (n = 12). We term this the gravimetric best-estimate of load. The second approach was based on comparing the differences in measurements among the washing treatments with the amount of soil removed by the washing treatments. For example, the dispersant wash removed 7.4 x ÷ 1.1 g soil kg^{-1} plant (n = 12). This should be correlated with the difference in load between the unwashed and dispersant-washed samples computed by the elemental abundance methods we investigated.

Criteria for comparison of tracers

Our data provide numerous ways to compute soil load on plants, and a systematic process of elimination was employed to identify the most useful tracers. The impact of each criterion is discussed in the following sections. The criteria for a good tracer were that it:

- be readily detectable in soil,
- be predominantly in the insoluble ash of soil,
- be subject to low bioaccumulation by plants,
- differ in concentration among the plant washing treatments in an expected manner,
- result in soil loads in agreement with gravimetric measurements, and
- have relatively homogenous concentrations among broad ranges of soils.

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Concentrations of elements in soil

For an element to be a useful indicator of soil load on plants, it must be measurable in very small quantities of soil. It is likely that the most useful indicator elements will be predominantly found as part of soil mineral structures, and hence in the insoluble ash of both the soil and the plant.

The analytical methods we used could not detect Gd, Hf, Ru, Sb, Sn or Te in the soils, where detection levels for these elements were about 10 mg kg^{-1}. The concentrations of the other elements ranged considerably (Tables 3), with Si and Al being the most abundant. The relationship between concentrations in the whole soil and concentrations in the AIR of that soil varied element to element (Table 3). Elements such as Si, Ti and Zr were not solubilized from the ash, and hence were slightly more concentrated in the soil AIR than in the whole soil. Other elements, such as Ca, Fe, Mg, Mn, and Zn, were solubilized from the ash, and hence were at lower concentrations in the soil AIR than in the whole soil. We expected that the better indicators of soil load would not be solubilized and, therefore, would be in the AIR.

The processed soil had only slightly higher concentrations of elements than the original soil (Table 3). The overall ratio was 1.2-fold more concentrated, which was statistically significant when all elements were considered. This enrichment likely reflects the different mineralogy of finer soil particles and their greater capacity for retaining sorbed elements. Although the soil retained on plant leaves will likely have undergone some particle size selection, we opted to use the analyses of the original soils for further interpretation in this study because the elemental concentrations were not

Table 3 Weighted[1] geometric mean concentrations (g kg^{-1}) of elements in the three original soils, with related ratios, and in the processed soil where aggregate and single-grain particles larger than 40 μm diameter were excluded.

	Original soil				
Element	*Dry weight basis*[2] *(n in brackets if less than 3)*	*Insoluble ash (AIR) basis*[3] *(n in brackets if less than 3)*	*Fraction of element in ash that was insoluble*[4] *(%)*	*Ratio of plant/soil insoluble ash concentrations*	*Processed soil, insoluble ash (AIR) basis*[3] *(n =3)*
Al	51	53	84	0.20*[5]	58
Ba	0.50	0.51	83	0.34	0.54
Ca	21	11	44	3.2*	9.7
Cd	0.001	nd[6]	nd	nd	nd
Ce	0.032	0.05(1)	70	nd	nd
Co	0.005	nd	nd	nd	nd
Cr	0.035	0.028	64	4.3*	0.039
Cu	7.0	nd	nd	9.8*	0.009
Fe	18	9.2	42	0.22*	12
Mg	7.6	3.5	39	2.5*	4.8
Mn	0.68	0.18	22	1.4*	0.17
Ni	0.011	nd	nd	8.7*	0.033
Pb	0.003(1)	nd	nd	nd	nd
Si	180	220	100	0.62*	220
Sr	0.21	0.22	87	0.65*	0.17
Ti	1.9	2.3	97	0.14*	3.2
V	0.049	0.048	79	0.21*	0.079
Zn	0.11	0.031	24	4.8*	0.040
Zr	0.17	0.21	100	0.68	0.16

[1] Means are weighted by the number of plant samples obtained on each site, so that plant and soil concentrations can be compared.

[2] Concentrations on a dry weight basis include the analyses of both soluble and insoluble fractions of the soil ash.

[3] Concentrations in soil insoluble ash only.

[4] Fraction calculated as the amount of insoluble element in the ash divided by the total amount of element in the ash.

[5] The * indicates the elements where the mean concentration in the plant insoluble ash differed significantly ($P<0.05$) from that in the insoluble ash of the original soil.

[6] The nd indicates non detectable.

very different from the processed soils, and because the unprocessed original soil is the more practical to measure in future applications.

Concentrations of elements in plant insoluble ash

An ideal indicator will be an element that is not strongly bioaccumulated by plants. Because the plant AIR will contain the adhering soil, we compare analyses of the soil and plant AIR (by ratios in Table 3). The concentrations in the plant AIR differed significantly from those in the soil AIR, indicating that the plant AIR is not solely composed of soil residues. Again, the relationship varied from element to element, with the difference apparently related to the bioaccumulation of the element by the plants. Plant-essential elements such Ca, Cu, Mg, Mn, and Zn were at higher concentrations in the plant AIR than in the soil AIR. Chromium and Ni, although not essential to the plants collected,

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were also at higher concentrations in the plant AIR than the soil AIR. Elements not strongly bioaccumulated were at lower concentrations in the plant AIR than in the soil AIR; they were effectively diluted in the plant AIR by the elements that were bioaccumulated. Based on the ratios in Table 3, Al, Ba, Fe, Si, Sr, Ti, V, and Zr were not strongly bioaccumulated, and hence may be better choices as indicators of soil load. This is in agreement with the concept of tracer detection limits used by Calabrese and Stanek[23].

Response of plant elemental concentrations to washing

An important criterion for selecting an elemental indicator of soil load was that the concentration in the plant ash varied systematically with the washing treatments. Table 4 lists those elements where concentrations in the unwashed samples were higher than those in one or both of the wash treatments. Few of these differences were statistically significant. Aluminum, Fe, Ni, Si, Ti, V, and Zr had concentrations in unwashed samples higher than both wash treatments on a plant analysis basis, whereas only Fe, Ni and Ti showed this trend consistently for analyses of both the plants and the plant AIR. Of these, Ni was not always detectable and Fe was not statistically significant. This suggests that Ti may be the superior indicator. The other elements, where there was no trend with wash treatments (Table 5), were not considered further.

Soil loads based on elemental abundance

The soil loads based on elemental abundance, for the elements considered at this stage (Table 6), spanned a broad range. Those based on Cr were markedly higher than the

Table 4 Concentrations of elements in plants and in plant insoluble ash, showing only those elements where unwashed samples had higher concentrations than either the water- or dispersant-washed treatments (n=36 except where indicated). Units are mg kg^{-1} except for Al and Si where they are g kg^{-1}.

	Plants, on dry weight basis[1]						*Plant insoluble ash*[2]					
Element	*Wash treatment*				*P*[3]	*GSD*[3]	*Wash treatment*				*P*	*GSD*
	n	*None*	*Water*	*Disp.*			*n*	*None*	*Water*	*Disp.*		
Al		0.266	0.248	0.226		1.7		13.5	13.7	8.79		2.1
Ba		11.1	11.2	9.2		1.5		187	205	134		2.0
Cr		2.78	2.19	3.40		2.1		147	141	221		2.4
Cu		no systematic trend					18	102	107	83.0		1.3
Fe		179	179	151		1.4		2940	2790	2540		1.6
Ni	33	2.77	1.34	2.40		2.8	10	729	51	165		2.7
Si		2.490	2.050	1.750	*	1.4		141	144	123		1.3
Sr		13.9	14.9	11.0		1.8		118	122	98.6		1.6
Ti		12.7	8.28	6.69	***	1.4		566	455	359	**	1.4
V	6	0.848	0.746	0.656		1.8		not sufficiently detectable				
Zr	16	4.64	4.54	1.72		2.1	16	157	173	75.9		1.9

[1] Concentrations on a dry weight basis include the analyses of both soluble and insoluble fractions of the plant ash.

[2] Concentrations in plant insoluble ash only.

[4] P is the probability level corresponding to a test of the effect of washing within a two-way analysis of variance, coded as* ($P < 0.05$), ** ($P < 0.01$) and *** ($P < 0.001$). The geometric standard deviation (GSD) was based on the error term from the analysis of variance.

Table 5 Concentrations of elements in plants and in plant insoluble ash, showing those elements where concentrations did not vary systematically with the washing treatment. Units are mg kg^{-1} except for Ca and Mg where they are g kg^{-1}.

Element	*Plants, on dry weight basis*[1]			*Plant insoluble ash*[2]		
	GM[3]	*GSD*[3]	*n*	*GM*	*GSD*	*n*
Ca	7.9	1.2	36	31	1.2	36
Cd	0.09	1.3	5	nd[4]		0
Ce	1.8	1.7	31	930	–	1
Co	0.14	2.1	5	nd		0
Cu	4.9	1.2	36	102	1.3	18
Mg	3.3	1.2	36	11.8	1.2	36
Mn	27	1.2	36	220	1.7	36
Sb	0.38	2.4	6	220	–	1
Sn	2.5	1.8	36	270	1.3	2
V	0.78	1.8	6	16	1.1	2
Zn	19	1.6	36	190	1.7	35

[1] Concentrations on a dry weight basis include the analyses of both soluble and insoluble fractions of the plant ash.

[2] Concentrations in plant insoluble ash only.

[3] The geometric mean (GM) is of all observations. Where there were more than 17 observations, the geometric standard deviation (GSD) was based on the error term from the two-way analysis of variance. Where there were insufficient data in the categories for analysis of variance, the GSD was computed directly from the observations.

[4] The nd indicates non detectable.

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Table 6 Soil load (g soil kg^{-1} dry plant) in response to the washing treatments based on several elemental indicators of load measured on plant samples.[1] Loads were computed based on elemental analyses of either plants and soil, or of the plant and soil insoluble ash.

	Based on plant					*Based on insoluble ash*				
	Wash treatment			*P*[3]	*GSD*[3]	*Wash treatment*			*P*	*GSD*
	None	*Water*	*Dispersant*			*None*	*Water*	*Dispersant*		
Al	8.0	6.9	5.4		1.8	6.3	5.1	3.2	*	2.3
Ba	22	23	18		1.5	7.8	6.9	4.4	+	2.0
Cr	79	62	93		2.1	110	87	140		2.2
Fe	10	10	8.4		1.4	6.9	5.3	4.8	*	1.5
Si	14	12	10	*	1.4	14	11	9.7	*	1.4
Sr	67	72	70		1.2	11	9.4	7.7	+	1.6
Ti	8.9	5.4	4.4	***	1.4	5.4	3.5	2.7	***	1.4
Zr		insufficient data				25	24	9.2		2.1

[1] Although concentrations of Cu, Ni and V in plants responded systematically to the wash treatments (Table 4), when combined with the soil analysis (Table 3) there were insufficient data to interpret further.

[2] P is the probability level corresponding to a test of the effect of washing within a two-way analysis of variance, coded as + ($P < 0.1$), * ($P < 0.05$) and *** ($P < 0.001$). The geometric standard deviation (GSD) was based on the error term from the analysis of variance.

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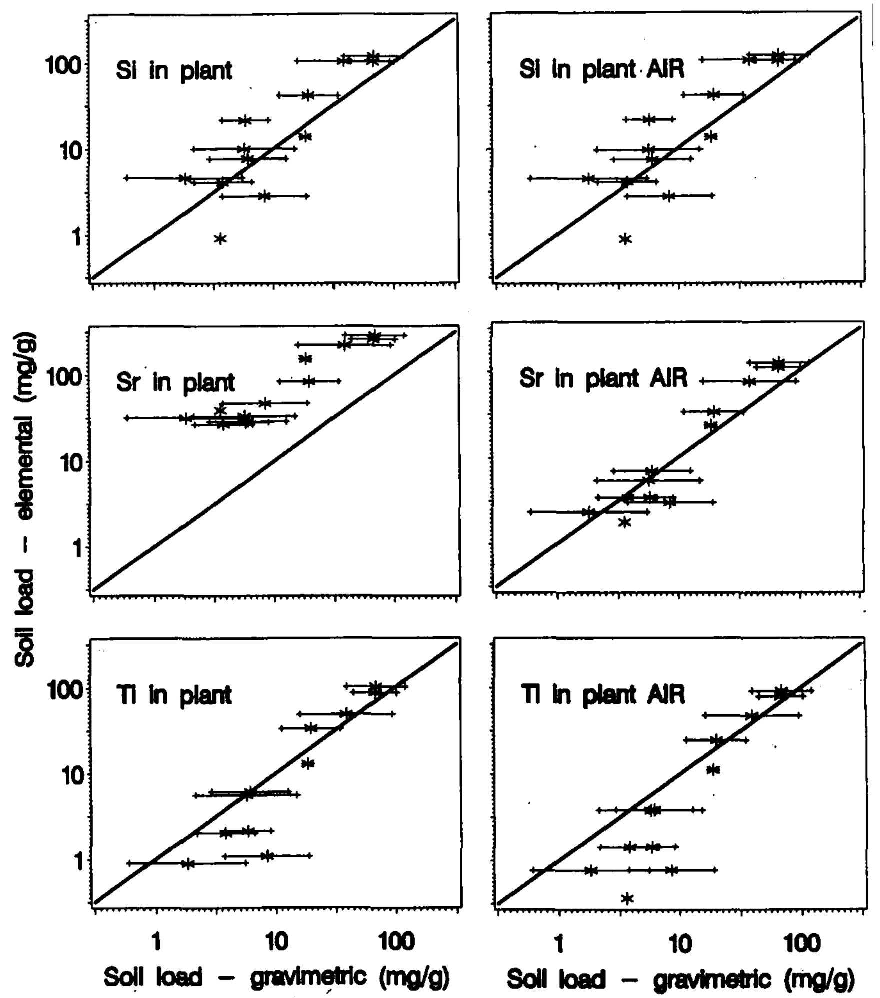

Figure 1 Relationship between estimates of soil load derived from elemental abundance methods and those determined gravimetrically. Results for Si, Sr and Ti in both the plant and in the plant acid-insoluble ash (AIR) are shown. As explained in the text, there were two gravimetric measurements: one tended to over- and the other to underestimate soil load. The horizontal lines connect these values and the geometric mean is indicated by the*. The 1:1 line representative of perfect agreement is shown.

others in Table 6 and the gravimetric indices in Table 2, so Cr was not considered further. We previously noted evidence of bioaccumulation of Cr. The loads based on analyses of insoluble ash tended to be lower than those based on analysis of the plant. This reflects that the difference, the acid-soluble ash, may include amounts of element that were bioaccumulated.

The elemental-abundance loads were plotted versus the gravimetric best-estimate loads, shown for selected elements in Figure 1. Both plant analysis and plant AIR analyses were considered, but for Al, Fe, Si and Ti there was little difference between these methods. This is likely because the bulk of these elements was present only in the plant AIR. For Ba and Sr, the load estimates based on the plant analysis were too high, but these elements did provide useful load estimates when based only on analysis of the plant AIR.

The comparison between the elemental-abundance loads and the gravimetric best-estimate loads is most easily interpreted as the ratio of the two measurements, and ratios statistically different from unity would be undesirable. For loads based on plant AIR, the ratios increased in the order of Sr (1.0), Si (1.3), Ba (1.4), Fe (1.6), Al (1.9) and Ti (2.0). The ratios for Ti and Al were significantly greater than unity, indicating them to be poor estimates of the gravimetric best-estimate loads. These data indicate that the traditional use of Ti as a tracer for soil could be improved, and that Sr in the plant AIR is an excellent tracer. For loads based on the full plant, the ratios were Fe (1.1), Si (1.3), Ti (1.4), Al (1.5), Ba (2.0) and Sr (6.2), with the ratios for Ba and Sr as significantly different from unity.

We conclude that Al, Ba, Fe, Si, Sr and Ti were all useful when analysed in the plant AIR, whereas only Al, Fe, Si and Ti were useful when analysed in the full plant. Most soil mineral particles adhering to plants will be resistent to ashing and acid solubilization and, therefore, will be part of the plant AIR. Analysis of the plant AIR is expected to be the most reliable method, and here our data suggests that elements other than Ti may be more useful. However, the acid extraction step in obtaining AIR is time consuming, and if it is not done, then Al, Fe, Si and Ti are the best choices.

The elemental abundance methods were highly correlated element to element across the full range of soil load values. Most were linearly related to the gravimetric measurements at soil loads above about 10 mg kg^{-1} dry plant (Figure 1). At lower soil loads, many of the elemental abundance methods deviated from linear in the same manner and some gave lower soil load values than the gravimetric best estimate. In this range, the values were more similar to the gravimetric measurement of soil washed off the plants, which we considered an underestimate of true soil load.

The most-limiting-tracer method, which is effectively an element ratio method, was considered for Al, Si and Ti (Figure 2). Here, the deviation from the gravimetric estimates at low soil loads was especially marked, and the element ratio method gave values even lower than the gravimetric measurement of soil washed off the plants. Clearly, the most-limiting-tracer method underestimates soil load.

Another evaluation of elemental abundance versus gravimetric methods was possible by comparing the differences in elemental-abundance loads between wash treatments with the corresponding measurement of the amount of soil removed by the washing. This comparison was less precise because the measurements were less direct. However, the conclusions were much the same. The exception was for soil loads based on Fe, which were consistently poor.

Overall best indicators of soil load, and use of generic soil data

No one of the various criteria we applied to judge the estimates of load is absolute, and the decision about best estimator must be based on several factors. Aluminum, Fe, Si and Ti are expected to be good indicators because they were present dominantly in the AIR, they were not strongly bioaccumulated by the plants and they were well correlated to our best-estimate gravimetric indicator of load. Barium and Sr are very good indicators, but only when analysed in the plant AIR. Ideal elemental-abundance indicators would have relatively narrow concentration ranges in soils. Sheppard[24] reported concentrations of Al, Ba, Fe, Sr and Ti in samples from a broad geographic range, using HF digestions of

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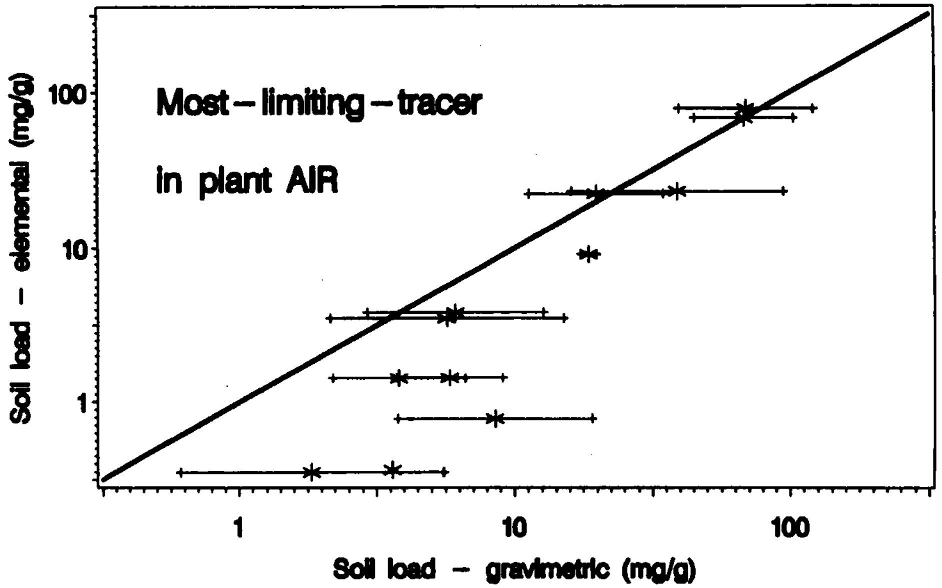

Figure 2 Relationship between estimates of soil load derived from the most-limiting-tracer or ratio method for Al:Si:Ti and those determined gravimetrically. Plot symbols and lines have meanings as described for Figure 1.

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the whole soils. The GM concentrations (n=64) were 63 a Al kg^{-1} (x ÷ 1.6), 0.63 g Ba kg^{-1} (x ÷ 1.6), 20 g Fe kg^{-1} (x ÷ 2.0), 0.20 g Sr kg^{-1} (x ÷ 2.0) and 2.5 g Ti kg^{-1} (x ÷ 2.5), all in good agreement with the present study. He[24] also reported Si at 1.3 g Si kg^{-1} (x ÷ 4.0), but these values are likely low and variable because of incomplete trapping of Si in the HF digestion. With GSD values of 1.6 to 2.5, soil load estimates using generic values of soil elemental concentrations would result in errors of less than threefold. In the context of many assessment issues, this is an acceptable degree of uncertainty. An additonal advantage of using generic or regional means of soil concentrations is that the soil on plants may come from a relatively broad fetch because of atmospheric dust transport, and therefore site-specific soil data may not be appropriate. If generic soil concentrations are used, soil load on plants could be estimated based on analyses of plants only, and for Al, Fe, Si and Ti, these could be analyses of the plant ash and not necessarily the plant AIR. We expect greater precision with analysis of the plant AIR.

Variation of soil load among plant types, and effects of washing

Using the elemental-abundance methods, estimates of load were possible for all our samples, whether washed or not. Here we report loads based on geometric mean loads from analyses of plant AIR. Among our plant samples, the major classification was planar, leafy tissues versus spherical or cylindrical fruit tissues. After hand washing in distilled water, the leafy samples still had 20 x ÷ 3.3 g soil kg^{-1} dry plant (n = 6) and the fruits (green pods, cucumber and strawberry) had 2 x ÷ 3.3 g soil kg^{-1} dry plant (n = 5). The soil loads on the fruits were lower because of their low surface area per unit weight, and this dominated over the counterbalancing effect of their low dry matter content. The sequestered inner leaves of cabbage had a soil load of 0.6 g soil kg^{-1} dry plant (n = 1). Developmentally, these tissues would not be exposed to soil splash and deposition. However, the samples would have been exposed to some dust in the laboratory, just as they might in a home setting. Alternatively, this load level could be considered a detection limit for the elemental abundance methods.

Washing the plants by hand with distilled water decreased soil loads of all samples, compared to unwashed pairs, by 1.5 fold, with a range of nil to 2.6 fold. There was a further reduction from water-washed to dispersant-wasted of 1.2 fold, with a range of nil to 2.0 fold. Clearly, soil loads may be decreased by washing but not entirely eliminated.

CONCLUSIONS

Soil ingestion by humans and other biota is an important route for exposure to contaminated soil. One pathway in this is the inadvertant ingestion of soil on plant tissues. Measurements of soil load on plants have been made, especially for animal feed and forage. However, one of the difficulties has been to measure the small amounts of soil on plants. Through extensive analysis on a number of markedly different plant samples, we have recommended a strategy. The most reliable estimates of soil load will result from analysis of HF digestions of the acid-insoluble fraction of the ash in the plants. Most mineral material deposited on plants will become part of this fraction. The analyte that gave the best agreement to gravimetric measures of soil load was Sr in the acid-insoluble fraction. Overall, Al, Ba, Fe, Si, Sr and Ti gave good results. In the HF digestion, care must be taken to quantitatively recover Si. Simplification of the method to analysis of plant material, as opposed to acid-insoluble ash, is possible but restricts the choice of analytes to Al, Fe, Si, and Ti. We compared estimates of soil load using these elements to best-estimate gravimetric values and found good agreement. Among our samples, leafy tissues had soil loads, after nominal washing, of 20 mg soil kg^{1} dry plant, and fruits had soil loads an order of magnitude lower. Washing decreased soil loads by only about 1.5 fold. These estimates of soil load, and the methods we have developed, will serve to improve the accuracy of exposure models for contaminated soil.

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