Influence of sample collection method on determination of trace element concentrations

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Influence of sample collection method on determination of trace element concentrations

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Influence of sample collection method on determination of trace element concentrations

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Contents

Summary

Project and Client

- This project to assess the influence of sample collection method on measured concentrations of a suite of trace elements was undertaken for Waikato Regional Council by Landcare Research in 2014.

Methods

- Five different methods were used to collect composite samples at four sites. At one site duplicate and triplicate samples were collected using selected methods.

- Samples were sent to Hills Laboratories for trace level analyses of an extensive suite of trace elements. Statistical analysis using R version 3.0.2 was used to determine differences in sampling methods.

Results

- Sample collection method significantly influenced the concentrations of some individual analytes, although there was no consistent trend in these differences.

- The average coefficient of variation (%CV) for analytes in samples collected using the same method at the same site ranged from 6% to 12% and ranged from 0 to 30% for individual analytes.

- The average %CV for analytes in samples collected using different methods at the same site was 15–22% and ranged from 0 to 50% for individual analytes.

Conclusions

- Sample collection method does not appear to consistently influence soil concentrations of trace elements in collected samples.

- However, the use of different sample collection methods increases the variability in concentrations determined at a given site. This increased variability may mask trends in trace element concentrations or relationships of trace element concentrations with other soil parameters.

Recommendations

- Samples should be collected using a consistent method to minimise variability between sample results obtained at different sites and at different times. No particular method appears to be better or worse than others for the sites examined.

1 Introduction

Various methods have been used to collect soil samples to determine background concentrations of trace elements in New Zealand (ARC 2000; URS 2003; Tonkin & Taylor 2006). These methods also differ from that typically used by regional councils for soil quality monitoring for state of environment reporting (Hill & Sparling 2009). While all these methods provide composite samples for analysis, the difference in results obtained from samples collected by the different methods is not known. Similarly, the variability in results between replicate samples collected at the same site using the same method has not been quantified. Understanding this variability is important in being able to use soil concentration data collected from different studies and at different times to robustly determine trends or to determine background concentrations of trace elements.

This project was undertaken for the Waikato Regional Council by Landcare Research in 2014 to assess the influence of sample collection method on measured concentrations of a suite of trace elements.

2 Methods

2.1 Sampling

Three methods previously used to determine background concentrations of various trace elements (ARC 2000; URS 2003; Tonkin & Taylor 2006) are compared with conventional soil quality monitoring as outlined by Hill and Sparling (2009), and with that currently being used by GNS Science in a grid-based survey (M.Rattenbury, GNS Science, pers. comm,)

Sampling methods (as described in the original references) are:

a)   80 × 80 m square, one sample (0–15 cm depth) collected randomly within quadrants using a hand-held auger(Tonkin & Taylor 2006)

b)   20 × 20 m square with one sample (0–20 cm[1]) collected from each corner and a fifth sample collected from the centre using a 100-mm-diameter auger (M. Rattenbury, GNS, pers. comm.)

c)   15 × 15 m square with one sample (0–15 cm) collected from each corner using a push-tube corer or hand-held auger where nature of soil prevented use of push-tube corer (URS 2003). To obtain enough sample for analysis and archiving, separate composite samples will be collected for analysis and archiving.

d)   15 × 15 m with four samples (0–15 cm) approximately 1 m apart collected from each corner using a push-tube corer (ARC 2000)

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[1] Samples were actually collected to a depth of 15cm

e)   50-m transect with sample (0–10 cm) collected every 2 m using 2.5-cm-diameter
       hand-held corer (Hill & Sparling 2009).

Samples were collected from four gently sloping sites with average slopes of 5–10 degrees
(Table 1) following the sample collection method layout shown in Figure 1 with GPS
location (WP) marking the south-west corner of the 80-m plot. At Site 3, duplicate samples
for methods a and c and triplicate samples for methods b and e were collected to provide an
indication of intra-site variation.

Table 1 GPS location and brief description of the four sampling sites

Site	Elevation	NZMG E	NZMG N	Description
1	340	2727616	6321480	Typic Orthic Allophanic soil under mixed tawa–podocarp forest with some evidence of cattle browsing and heavy deer browsing
2	484	2727227	6319784	Humic Orthic Podzol soil under mixed tawa–podocarp forest with heavy deer browsing
3	370	2688492	6340652	Acid Orthic Allophanic soil under mixed broadleaved (kāmahi dominant) regrowth forest with little evidence of browsing
4	552	2689946	6352302	Mottled Orthic Allophanic soil under mixed broadleaved forest with little evidence of browsing
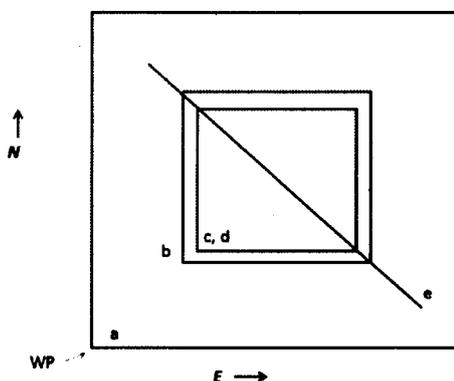
Figure 1 Layout of soil sampling quadrats.

For all samples, vegetative growth was removed from the surface prior to sampling, and all
individual samples were composited to form a single sample for each method and location.
Collected samples were dried and sieved (2-mm mesh size)prior to sending half the
composited sample to Hill Laboratories for analysis for an extensive suite of trace metals.
The remaining half of the sample was retained for archiving.
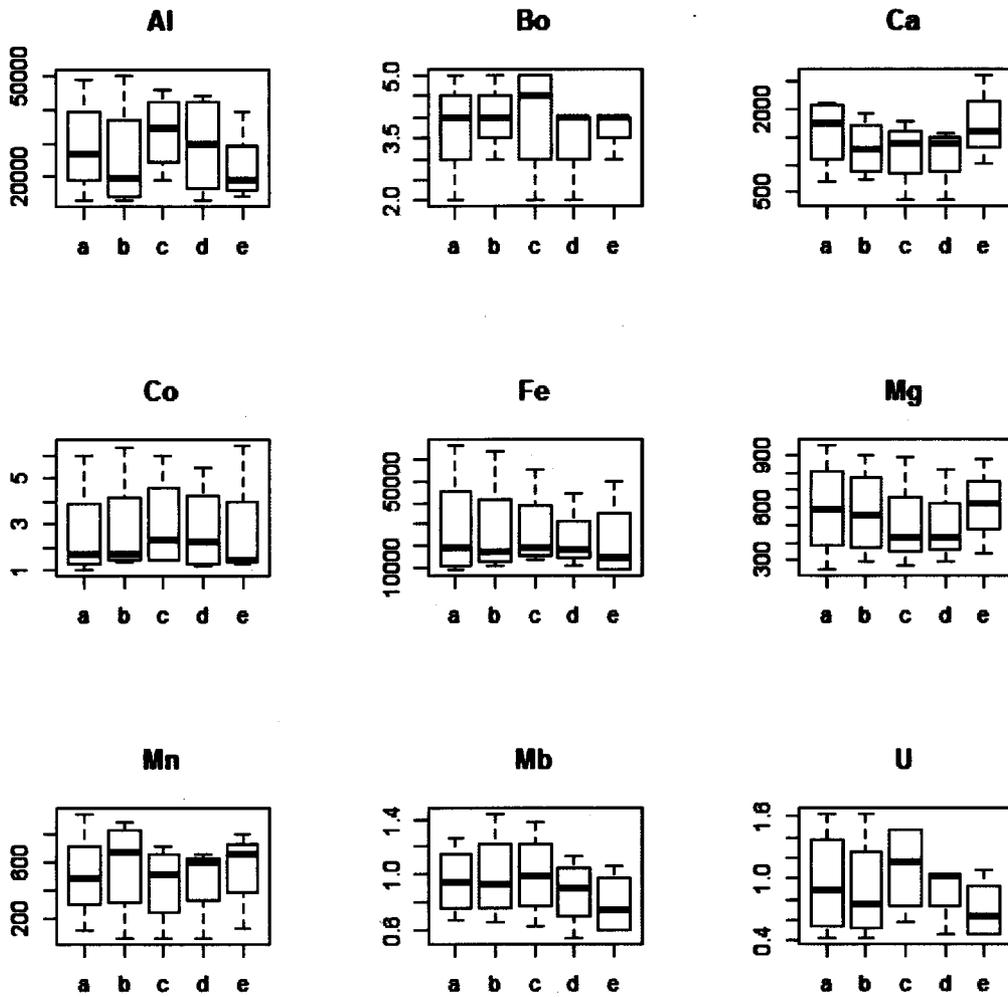
2.2   Statistical analyses

Statistical analyses were conducted using R version 3.0.2. One-way analysis of variance (ANOVA), with method as factor and site as blocks, was used to assess whether there were significant differences in concentrations of individual elements between samples collected using different methods. For this analysis only the first replicate of samples collected from Site 3 was used. A one-way ANOVA was used to determine intra-site differences using replicate samples collected from Site 3. Coefficients of variation (%CV) were determined for the concentration of individual analytes determined at each site using all methods, and with each method at Site 3.

3   Results

There were significant differences in the concentrations of some individual analytes from samples collected using the different methods, particularly for samples collected from Site 3 by the different methods (Table 2). However, as can be seen from Figures 2–5, there are no consistent trends in these differences, suggesting there is no influence of sampling method on analysed concentration. The mean concentrations of individual trace elements at each site from samples collected by all methods, and from replicate samples collected by the same method at Site 3, are shown in Appendix 1.

Table 2 Summary of differences in concentrations of individual trace elements with respect to method and site.

Analyte	Significant difference of sample collection method: all sites		Significant difference between sites		Significant difference between method: Site 3	
	$P < 0.05$	$P < 0.1$	$P < 0.05$	$P < 0.1$	$P < 0.05$	$P < 0.1$
Al			Y	Y	Y	Y
As			Y	Y		Y
Ba			Y	Y	Y	Y
Bi			Y	Y	Y	Y
Bo			Y	Y		
Cd						Y
Ce						Y
Ca		Y	Y	Y	Y	Y
Cr			Y	Y	Y	Y
Co			Y	Y	Y	Y
Cu			Y	Y		Y
Fe			Y	Y		Y
La			Y	Y	Y	Y
Pb			Y	Y	Y	Y
Li			Y	Y	Y	Y
Mg			Y	Y	Y	Y
Mn			Y	Y	Y	Y
Hg			Y	Y	Y	y
Mb	y		Y	Y	Y	Y
Ni			Y	Y	Y	y
P			Y	Y	Y	y
K		y	Y	Y	Y	y
Rb				y	y	y
Ag			Y	Y		y
Na					y	y
Sr			Y	Y	Y	y
Th			Y	Y	Y	y
Sn		y	Y	Y	Y	y
U			Y	Y	Y	y
V			Y	Y		y
Zn			Y	Y	y	y

Figure 2 Boxplots showing the variation in concentration of selected trace elements with sampling method (a–e). Refer to Methods section for description of individual sampling method.
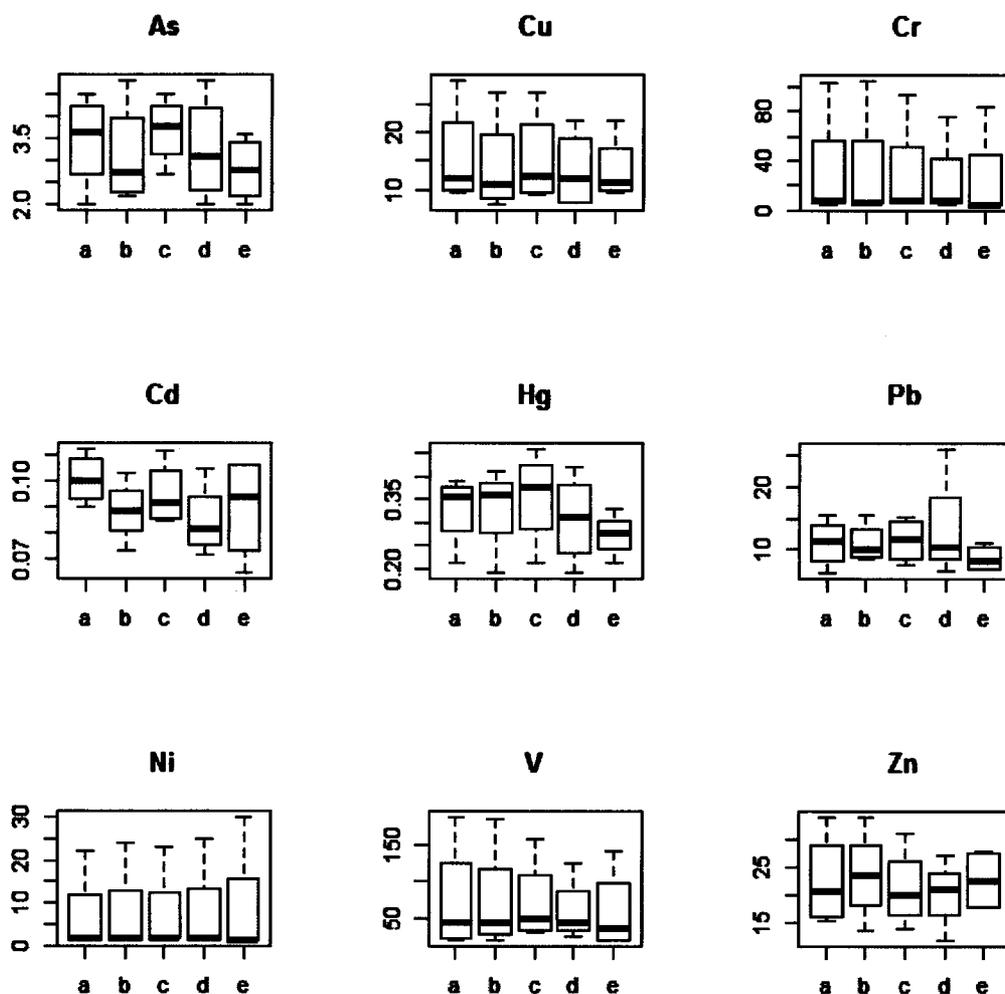
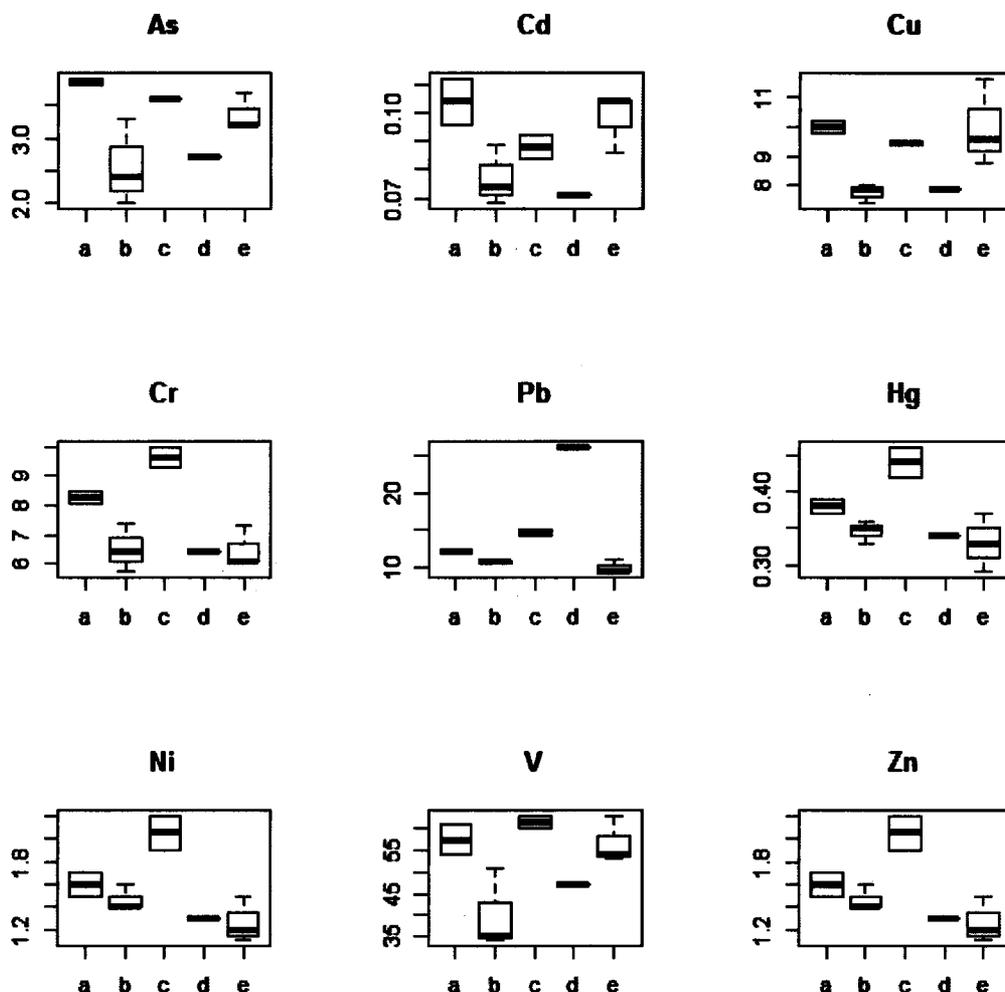**Figure 3** Boxplots showing the variation in concentration of selected trace element 'contaminants' with sampling method. Refer to Methods section for description of individual sampling method.
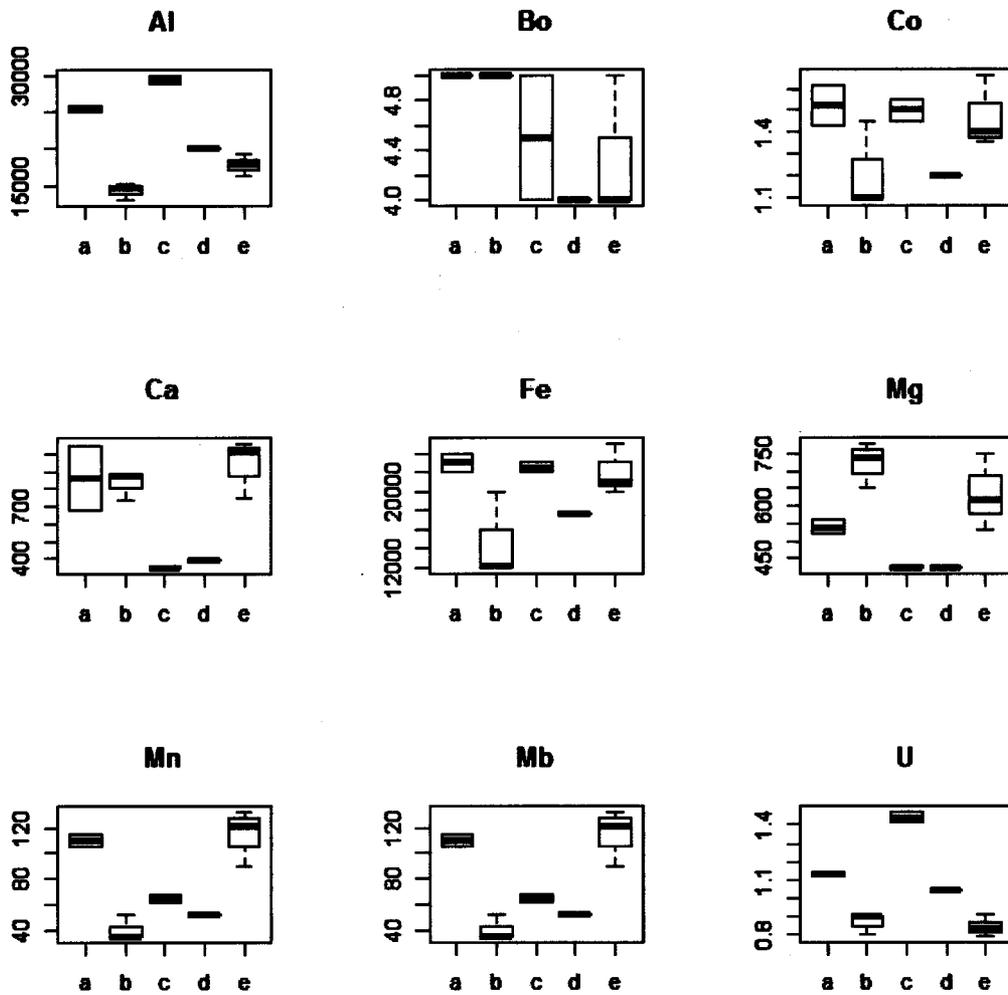
Figure 4 Boxplots showing the variation in selected trace element concentration in samples collected using different methods at Site 3. Refer to Methods section for description of individual sampling method.

Figure 5 Boxplots showing the variation in trace element 'contaminant' concentrations in samples collected using different methods at Site 3. Refer to Methods section for description of individual sampling method.

The concentrations of selected individual trace elements at the different sites are shown in Figures 6 and 7, with Site 4 having higher concentrations of a number of analytes. A summary of the mean concentrations of all analytes is provided in Appendix 1. To assess the influence of sampling collection methodology on the variability of sample results, the coefficient of variation (%CV) was determined for concentrations of analytes in samples collected by all methods for a given site, and for samples collected by selected methods for Site 3 (Appendix 1). The %CV was typically higher for concentrations determined at a given site using all samples (i.e. collected using different methods) than for the %CV for concentrations determined using samples collected using the same methods at an individual site (Table 3; Appendix 1). These results suggest that, on average, differences in sampling collection method will contribute about 20% of the variation in determined concentrations.
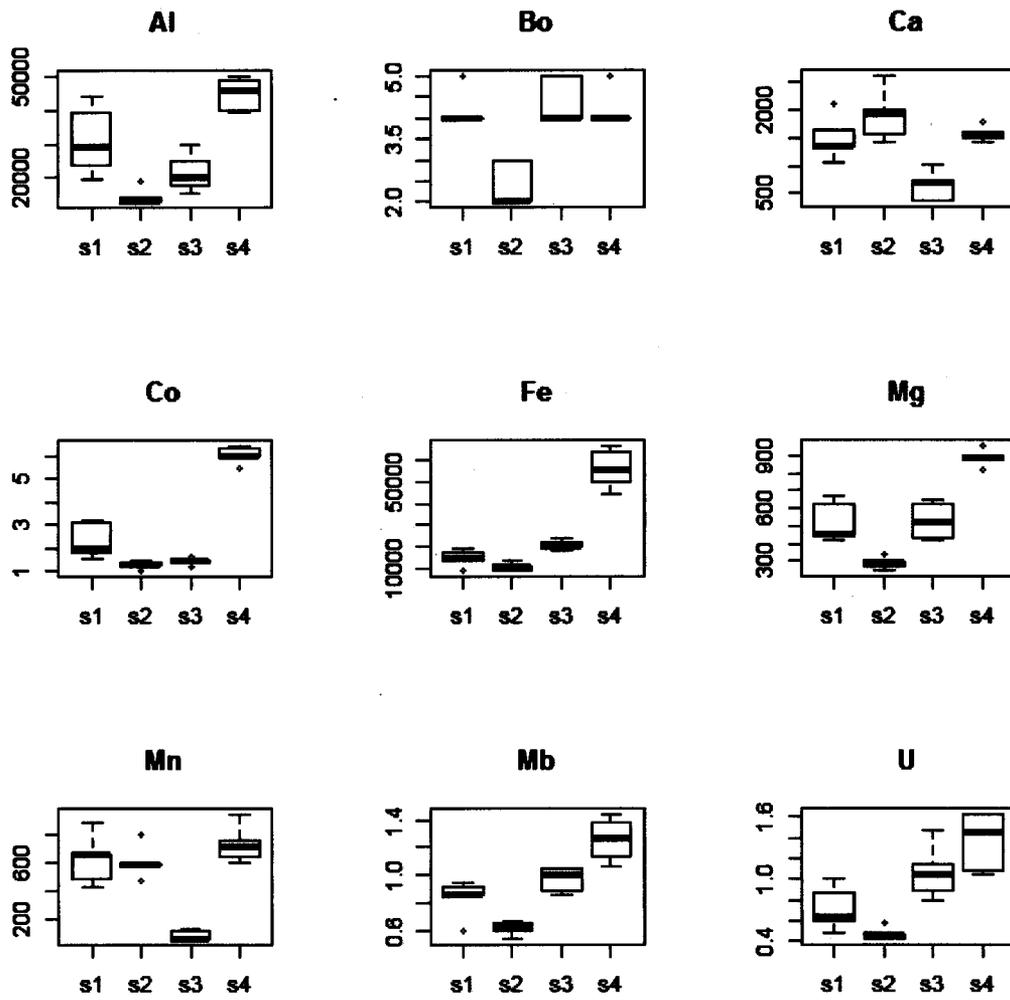
Figure 6 Boxplots showing the variation in selected trace element concentration with sites; samples collected by all methods.
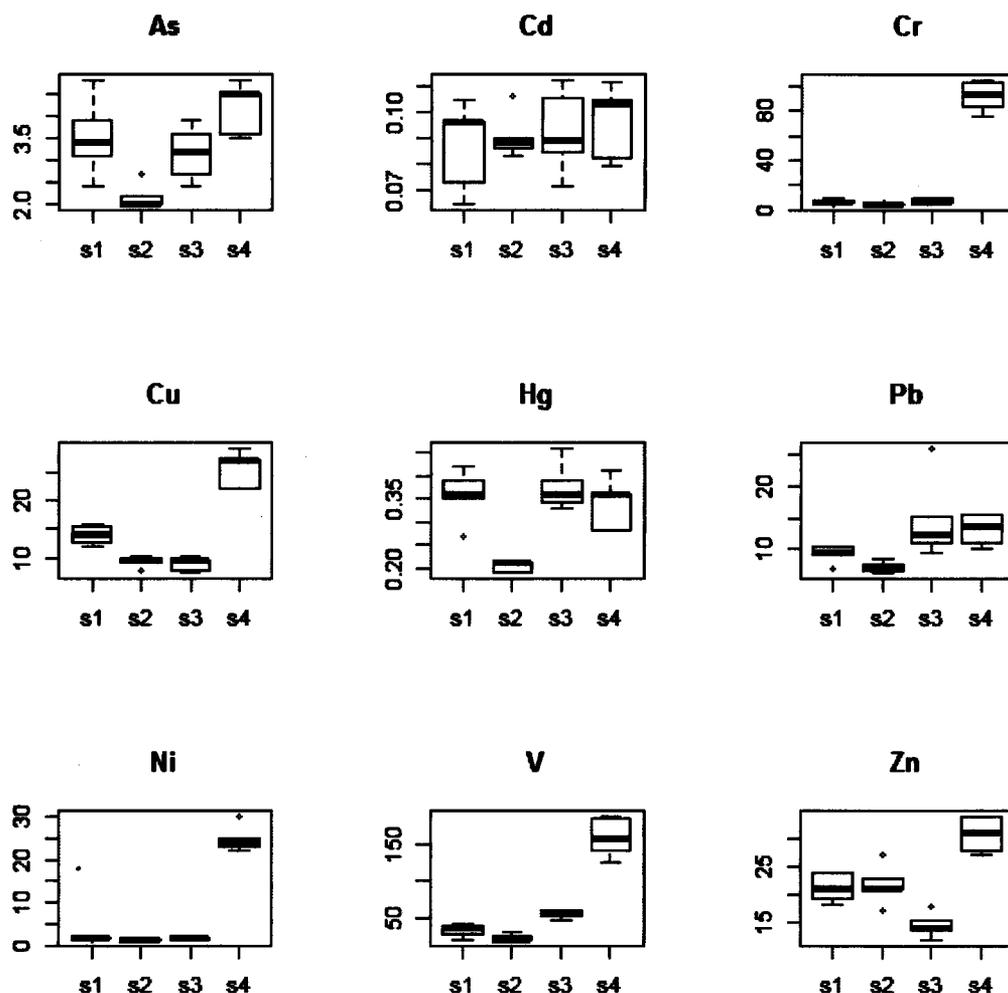
Figure 7 Boxplots showing the variation in concentration of selected trace element 'contaminants' with site; samples collected by all sampling methods.

Table 3 Mean and range of the coefficient of variation (%CV) for analytes determined from samples collected using all methods at the different sites and samples collected by different methods at Site 3

Site: all methods			*Method: Site 3*		
Site	Mean %CV	Range	Method	Mean %CV	Range
Site 1	21.51	8.6 – 49.5	a	6.23	0.0 – 30.2
Site 2	15.29	0.0 – 32.4	b	9.12	0.0 – 1.2
Site 3	20.60	10.9 – 45.3	c	4.67	0.0 – 15.7
Site 4	14.4	5.6 – 22.1	e	11.66	0.0 – 19.0

4 Conclusions

The concentrations of some individual analytes in samples collected by the different methods were significantly different; however, there were no consistent trends in these differences. This indicates that sample collection method does not significantly influence soil concentrations of trace elements in collected samples. However, the use of different sample collection methods increases the variability in concentrations (as assessed by the coefficient of variation) determined at a given site. This increased variability may mask trends in trace element concentrations or relationships of trace element concentrations with other soil parameters.

5 Recommendations

- Samples should be collected using a consistent method to minimise variability between sample results obtained at different sites and at different times. No particular method appears to be better or worse than another for the sites examined.

6 Acknowledgements

7 References

ARC 2001. Background concentrations of inorganic elements in soils from the Auckland Region. TP No. 153. Auckland Regional Council.

Hill RB, Sparling G P 2009. Soil quality monitoring. In: Land Monitoring Forum. Land and soil monitoring: a guide for state owned enterprise and regional council reporting. Hamilton, Land Monitoring Forum. Pp. 27–88.

Tonkin and Taylor 2006. Background concentrations of selected trace elements in Canterbury soils. Report for Environment Canterbury (Job 50875).

URS 2003. Determination of common pollutant background soil concentrations for the Wellington Region. Report prepared for Greater Wellington Regional Council.

Appendix 1 – Concentrations of individual trace elements

Table A1 Mean, standard deviation and % coefficient of variation of various trace elements collected from each site using all methods.

Site		Al	Sb	As	Ba	Bi	Bo	Cd	Ce	Ca	Cr	Co	Cu	Fe	La	Pb	Li	Mg
Site 1	Mean	31,160	0.05	3.52	77.0	0.22	4.20	0.09	0.84	1,492	6.52	2.33	14.0	14,480	23.52	9.3	2.14	520
	SD	10,140	0.01	0.90	10.8	0.06	0.45	0.02	0.11	399	1.64	0.76	1.7	4,012	11.64	1.5	0.63	116
	%CV	*32.5*	*16.1*	*25.5*	*14.0*	*25.4*	*10.6*	*19.8*	*13.4*	*26.7*	*25.1*	*32.6*	*11.9*	*27.7*	*49.5*	*15.7*	*29.3*	*22.3*
Site 2	Mean	14,440	0.04	2.18	81.0	0.19	2.40	0.09	1.02	1,896	4.22	1.27	9.4	10,220	17.78	7.2	1.42	286
	SD	2,713	0.00	0.30	26.2	0.03	0.55	0.01	0.22	461	0.63	0.18	0.8	1,941	3.55	1.0	0.29	36
	%CV	*18.8*	*0.0*	*13.9*	*32.4*	*15.5*	*22.8*	*9.9*	*21.8*	*24.3*	*14.9*	*14.4*	*8.9*	*19.0*	*20.0*	*13.3*	*20.8*	*12.8*
Site 3	Mean	20,564	0.05	3.22	25.5	0.31	4.64	0.09	0.75	741	7.38	1.39	9.1	19,873	8.12	12.9	4.73	584
	SD	5,998	0.01	0.61	6.5	0.05	0.50	0.01	0.14	273	1.44	0.19	1.2	4,383	1.25	4.7	1.13	135
	%CV	*29.2*	*17.5*	*19.0*	*25.4*	*15.2*	*10.9*	*16.2*	*18.3*	*36.8*	*19.5*	*13.8*	*13.7*	*22.1*	*15.3*	*36.2*	*23.9*	*23.1*
Site 4	Mean	44,800	0.05	4.18	43.0	0.26	4.20	0.10	0.90	1,556	92.40	6.02	25.4	56,200	7.06	13.2	5.16	890
	SD	5,070	0.01	0.59	6.0	0.05	0.45	0.01	0.20	139	12.93	0.39	3.2	9,550	0.93	2.5	0.90	50
	%CV	*11.3*	*9.5*	*14.1*	*13.9*	*18.6*	*10.6*	*15.0*	*22.1*	*9.0*	*14.0*	*6.5*	*12.6*	*17.0*	*13.2*	*19.1*	*17.4*	*5.6*

		Mn	Hg	Mb	Ni	P	K	Rb	Se	Ag	Na	Sr	Th	Sn	U	V	Zn
Site 1	Mean	624	0.36	0.83	1.60	556	366	2.74	3.00	0.21	112	26.40	0.25	1.00	0.73	32	21
	SD	176	0.06	0.14	0.29	60	76	0.28	0.71	0.05	10	4.51	0.05	0.27	0.21	9.44	2.71
	%CV	*28.2*	*15.7*	*17.1*	*18.2*	*10.8*	*20.9*	*10.2*	*23.6*	*23.9*	*8.6*	*17.1*	*19.6*	*27.1*	*28.7*	*29.3*	*12.7*
Site 2	Mean	606	0.20	0.61	1.28	384	237	2.19		0.21	115	27.40	0.12	0.87	0.47	22	22
	SD	120	0.01	0.05	0.15	60	36	0.27		0.01	9	5.86	0.02	0.13	0.07	5	4
	%CV	*19.8*	*5.7*	*8.4*	*11.6*	*15.7*	*15.3*	*12.1*		*5.3*	*8.0*	*21.4*	*15.7*	*15.3*	*14.4*	*20.6*	*16.5*
Site 3	Mean	79	0.36	0.95	1.53	408	294	2.17	3.45	0.16	141	14.03	0.07	1.53	1.03	52	14
	SD	36	0.05	0.11	0.32	66	44	0.26	0.69	0.02	37	4.64	0.01	0.34	0.23	10.17	2.57
	%CV	*45.3*	*12.8*	*11.9*	*20.7*	*16.2*	*14.9*	*12.1*	*19.9*	*11.4*	*26.4*	*33.1*	*17.1*	*22.0*	*22.8*	*19.5*	*17.8*
Site 4	Mean	730	0.34	1.25	24.80	578	358	2.32	4.40	0.18	130	23.40	0.11	1.90	1.37	160	31
	SD	133	0.06	0.16	3.11	47	58	0.49	0.55	0.02	13	2.30	0.02	0.38	0.28	27.31	3.27
	%CV	*18.2*	*16.8*	*12.8*	*12.6*	*8.1*	*16.1*	*21.2*	*12.4*	*11.8*	*10.3*	*9.8*	*15.2*	*19.8*	*20.8*	*17.0*	*10.6*

Table A2 Mean, standard deviation and % coefficient of variation for trace element concentrations in samples collected using different methods at Site 3.

Method		Al	As	Ba	Bi	Bo	Cd	Ce	Ca	Cr	Co	Cu	Fe	La	Pb	Li	Mg
a	Mean	25,500	3.85	31.5	0.35	5.00	0.10	0.91	865	8.30	1.52	10.0	23,000	7.20	12.1	6.50	540
N = 2	SD	707	0.07	2.1	0.01	0.00	0.01	0.01	262	0.28	0.13	0.3	1,414	0.42	0.3	0.14	28
	%CV	2.8	1.8	6.7	4.0	0.0	10.9	0.8	**30.2**	3.4	8.4	2.8	6.1	5.9	2.3	2.2	5.2
b	Mean	14,233	2.57	30.0	0.27	5.00	0.08	0.67	837	6.50	1.21	7.8	14,633	7.53	10.8	4.10	723
N = 3	SD	1,193	0.67	1.7	0.03	0.00	0.01	0.03	84	0.85	0.21	0.3	4,562	0.40	0.3	0.20	67
	%CV	8.4	**25.9**	5.8	9.8	0.0	14.0	3.9	10.0	13.1	16.9	4.1	**31.2**	5.4	2.8	4.9	9.2
c	Mean	29,500	3.60	16.6	0.38	4.50	0.09	0.94	350	9.65	1.50	9.5	22,500	10.45	14.8	5.60	425
N = 2	SD	707	0.00	1.0	0.01	0.71	0.01	0.01	14	0.49	0.07	0.1	707	0.35	0.6	0.28	7
	%CV	2.4	0.0	6.0	3.7	15.7	6.4	0.8	4.0	5.1	4.7	0.7	3.1	3.4	3.8	5.1	1.7
e	Mean	17,833	3.37	26.3	0.30	4.33	0.10	0.63	940	6.47	1.47	10.0	22,000	7.73	10.1	4.00	633
N = 3	SD	1,501	0.29	2.5	0.03	0.58	0.01	0.05	166	0.72	0.16	1.4	2,646	0.65	1.0	0.50	111
	%CV	8.4	8.6	9.6	9.7	13.3	10.9	7.5	17.7	11.2	11.1	14.4	12.0	8.4	9.8	12.5	17.5

Method		Mn	Hg	Mb	Ni	P	K	Rb	Se	Ag	Na	Sr	Th	Sn	U	V	Zn
a	Mean	111	0.38	0.98	1.60	400	285	2.50	3.50	0.16	130	13.2	0.07	1.76	1.13	58	15
N = 2	SD	6	0.01	0.11	0.14	14	7	0.14	0.71	0.01	0	2.5	0.00	0.08	0.01	4.95	0.92
	%CV	5.8	3.7	10.9	8.8	3.5	2.5	5.7	20.2	4.6	0.0	19.3	0.0	4.4	1.3	8.6	6.3
b	Mean	40	0.35	0.88	1.47	500	340	2.03	3.00	0.16	188	17.9	0.06	1.24	0.87	40	13
N = 3	SD	10	0.02	0.10	0.12	10	10	0.06	0.00	0.01	12	1.1	0.00	0.17	0.06	10	1
	%CV	**26.0**	4.4	11.5	7.9	2.0	2.9	3.2	0.0	3.7	6.3	5.9	0.0	13.8	7.0	**23.8**	8.0
c	Mean	65	0.44	1.09	2.05	375	250	2.40	4.50	0.20	100	7.4	0.09	2.05	1.44	62	14
N = 2	SD	5	0.03	0.05	0.21	7	14	0.00	0.71	0.01	1	0.5	0.00	0.22	0.04	2.12	0.21
	%CV	7.7	6.4	4.6	10.3	1.9	5.7	0.0	15.7	3.6	1.4	6.7	0.0	10.7	2.9	3.4	1.5
e	Mean	114	0.33	0.95	1.27	367	303	2.06	3.00	0.16	143	17.0	0.06	1.40	0.85	57	18
N = 3	SD	22	0.04	0.13	0.21	55	45	0.21	0.00	0.02	27	2.5	0.00	0.16	0.06	5.51	2.41
	%CV	19.0	12.1	14.2	16.4	15.0	14.9	10.4	0.0	13.3	18.7	14.4	0.0	11.5	7.1	9.7	13.6