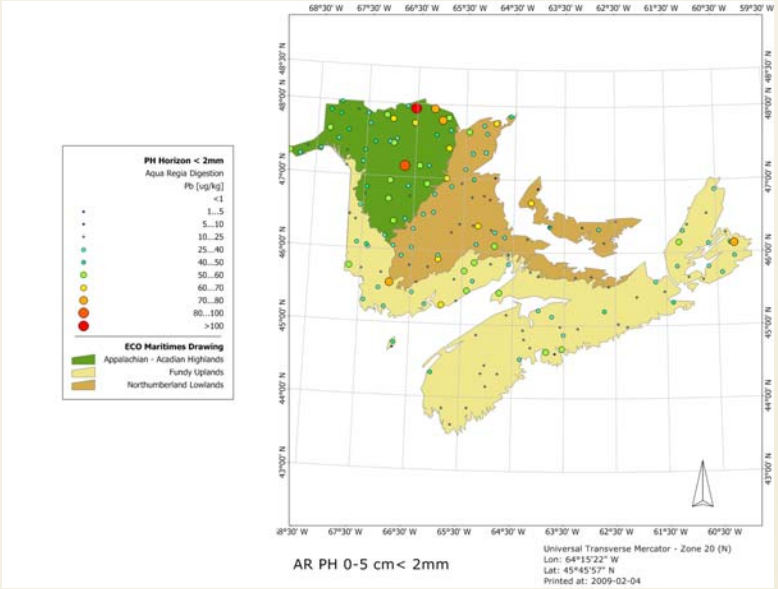
GEOCHEMICAL BACKGROUND – WHAT IT IS AND HOW IT VARIES



Robert G. Garrett and Eric C. Grunsky
Natural Resources Canada – Geological Survey of Canada

Workshop on the Role of Geochemical Data in Ecological and Human Health Risk Assessment, Halifax, Nova Scotia, March 17-18, 2010

BACKGROUND, WHAT IS IT?

- The concept of geochemical background was developed in the 1940s and 50s;
- It was introduced to differentiate between normal element concentrations and chemical anomalies that might be indicative of ore mineral occurrences;
- Definition (Hawkes and Webb, 1962):
  - "The normal abundance of an element in barren earth material"; and they concluded
  - "It is more realistic to view background as a range rather than an absolute value".

BACKGROUND

- Today geochemical surveys have equal applicability to environmental issues and concerns;
- Geochemically there is no immediate difference between an anomaly arising from a natural process, e.g., the formation of a mineral deposit, or as a result of contamination of the natural environment by an anthropogenic process;
- Both types of processes impose an ‘overprint’ on the natural regional geochemical background.

BACKGROUND … S

- Some would argue that natural background no longer exists, anthropogenic processes have distributed contaminants world-wide, thus the following terms are used:
  - Natural background; and
  - Ambient background;
- Thus ambient background is the sum of natural background levels and any anthropogenic additions;
- Regional geochemical maps demonstrate that natural processes still dominate the distribution of trace-elements on regional and continental scales.

CONTROLS ON BACKGROUND

- Background levels usually differ between sample media, thus levels in air, water, lake, stream/river and marine sediments, and soils will be different;
- However, all will be related to their source materials, i.e. rocks, and these will be modified by the physical, chemical and transport processes characteristic of the sample media;
- Difference in rock chemistry (geochemistry) for a single element may vary by orders of magnitude.

A TALE OF EIGHT ELEMENTS

Some average compositions of some rocks

	Hg (µg/kg)	Pb (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	As (mg/kg)	Cu (mg/kg)	Zn (mg/kg)
Earth's Crust	80	13	0.2	100	75	2	55	70
	90	12	0.2	110	89	2	63	94
Upper Continental Crust	*56*	20	0.1	35	20	1.5	25	71
	80	13	0.2	77	61	1.7	50	81
Igneous Rocks								
Ultramafic	*4*	1	0.1	1600	2000	1	10	50
Mafic	90	6	0.2	170	130	2	87	105
Intermediate	80	15	0.1	22	15	2	30	60
	30	10	*0.1*	55	30	*3*	60	*50*
Felsic	80	19	0.1	4	5	1	10	39
Sedimentary Rocks								
Sandstone	57	14	0.02	120	3	1	15	16
Limestone	46	16	0.05	7	13	2	4	16
Shale	270	80	0.2	423	29	9	45	130
Black Shale		15	4	18	68	22	50	189
		100		700	300		200	1500

Sources:
The Essentials of Medical Geology, Editor-in-Chief O. Selinus (2005), Chapter 2, Table 3
With additions from Chemical Elements in the Environment, Reimann, C.R. and de Caritat, P. (1998)

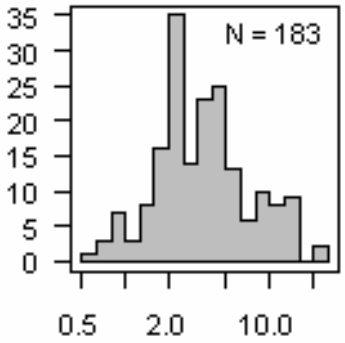
VIEWING BACKGROUND

- Statistically:
  - Various graphical displays of the data may – should – be prepared, e.g., cumulative frequency/probability plots, Tukey boxplots, histograms, etc.
  - Summary statistics may be used to help estimate the range of background variation.
- Spatially:
  - Geochemical maps can – should – be prepared.

ARSENIC AND LEAD

Earth Sciences Sector

Histogram

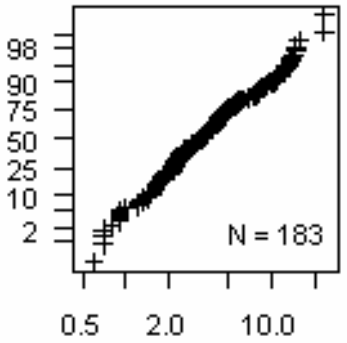


As (mg/kg) in <2 mm 0-5 cm soil
(US-EPA 3050B-AR_var)

Summary Statistics

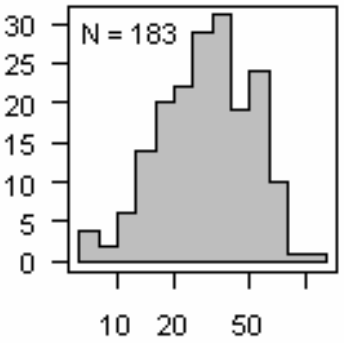
Maximum	23.4
98th Percentile	14.84
95th Percentile	13.34
90th Percentile	10.56
3rd Quartile	5.15
Median	3.3
1st Quartile	2.1
10th Percentile	1.42
5th Percentile	0.91
2nd Percentile	0.7
Minimum	0.6
Median Abs. Deviation	1.93
IQR Est. of Std. Dev.	2.25
Mean	4.53
Standard Deviation	3.9
Coeff. of Variation, %	86.2

% Probability Plot



As (mg/kg) in <2 mm 0-5 cm soil
(US-EPA 3050B-AR_var)

Histogram

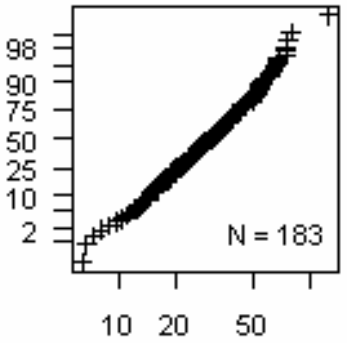


Pb (mg/kg) in <2 mm 0-5 cm soil
(US-EPA 3050B-AR_var)

Summary Statistics

Maximum	125.2
98th Percentile	75.4
95th Percentile	65.67
90th Percentile	56.77
3rd Quartile	43.24
Median	30.18
1st Quartile	19.92
10th Percentile	14.44
5th Percentile	12.17
2nd Percentile	7.195
Minimum	6.39
Median Abs. Deviation	16.8
IQR Est. of Std. Dev.	17.2
Mean	33.7
Standard Deviation	17.9
Coeff. of Variation, %	53.2

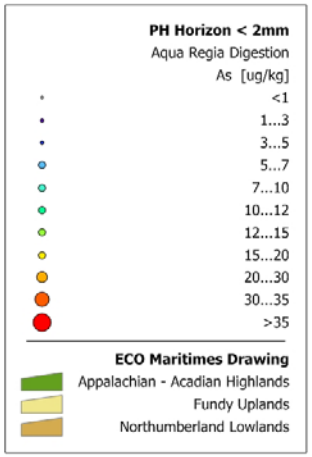
% Probability Plot

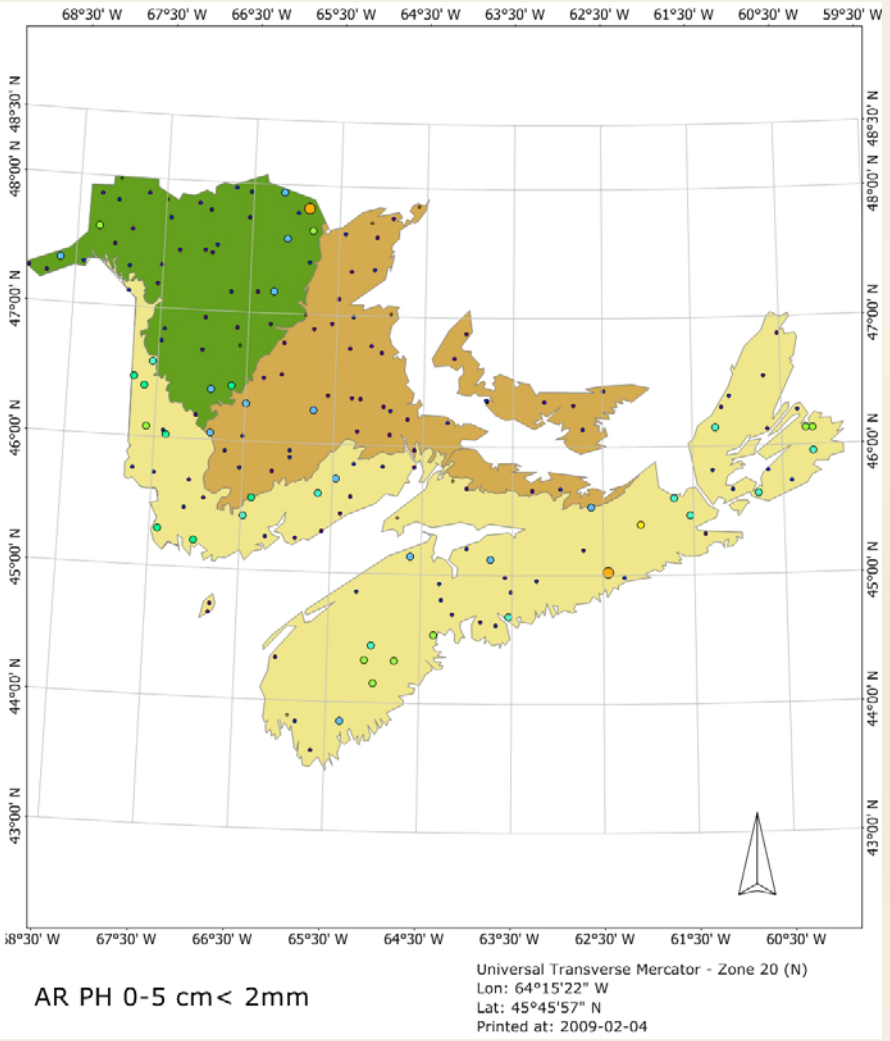


Pb (mg/kg) in <2 mm 0-5 cm soil
(US-EPA 3050B-AR_var)

ARSENIC

Earth Sciences Sector

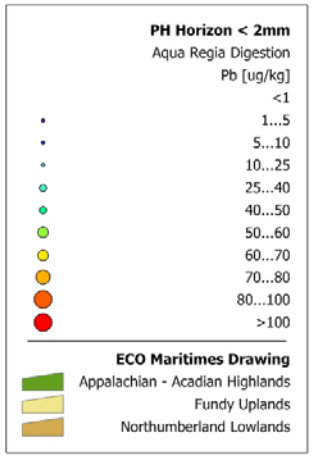


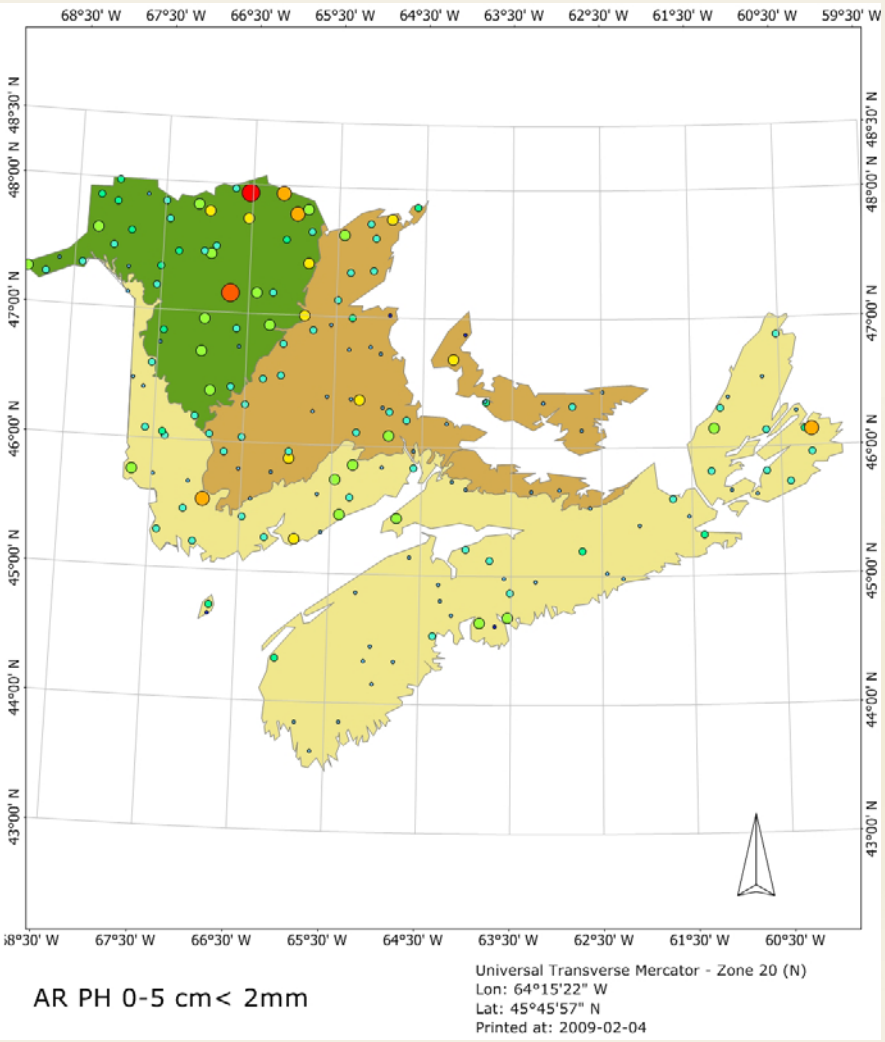


Interval: Public Health layer (0-5 cm)
Fraction: <2 mm
Digestion: USEPA 3050 B Aqua Regia variant
Analytical technique: ICP-MS

LEAD

Earth Sciences Sector





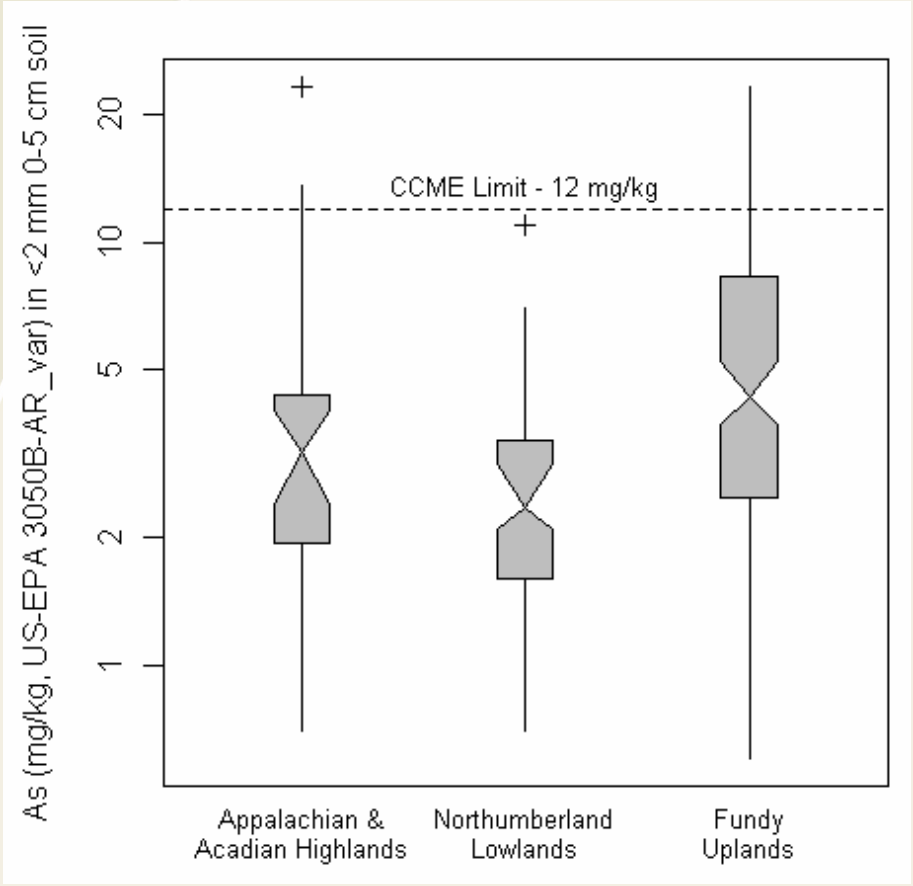
Interval: Public Health layer (0-5 cm)
Fraction: <2 mm
Digestion: USEPA 3050 B Aqua Regia variant
Analytical technique: ICP-MS

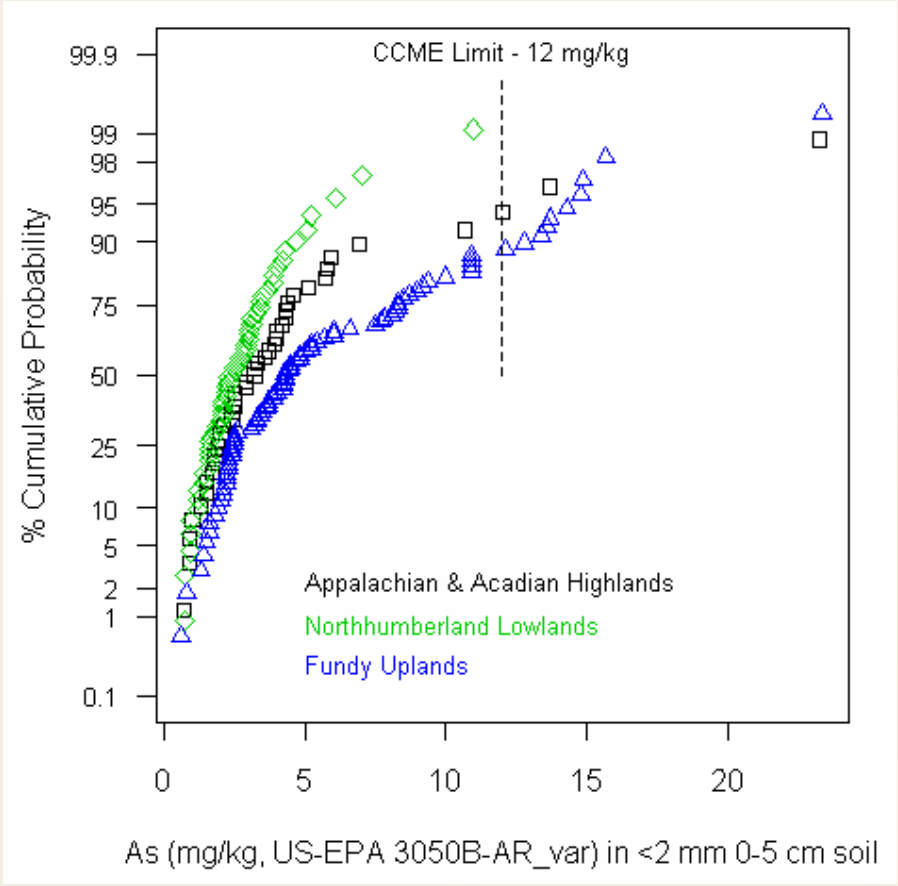
ARSENIC AND LEAD

- The histograms indicate the presence of more than one population in the data;
- The maps indicate that there are regional controls influencing the background levels;
- A breakdown of the data by the three ecoprovinces, Appalachian and Acadian Highlands, Northumber-land Lowlands, and Fundy Uplands, yields subsets of size 43, 56 and 84, respectively;
- Note, the cumulative probability plots do not clearly indicate the presence of multiple populations – not uncommon for mixtures of data with similar means.

ARSENIC

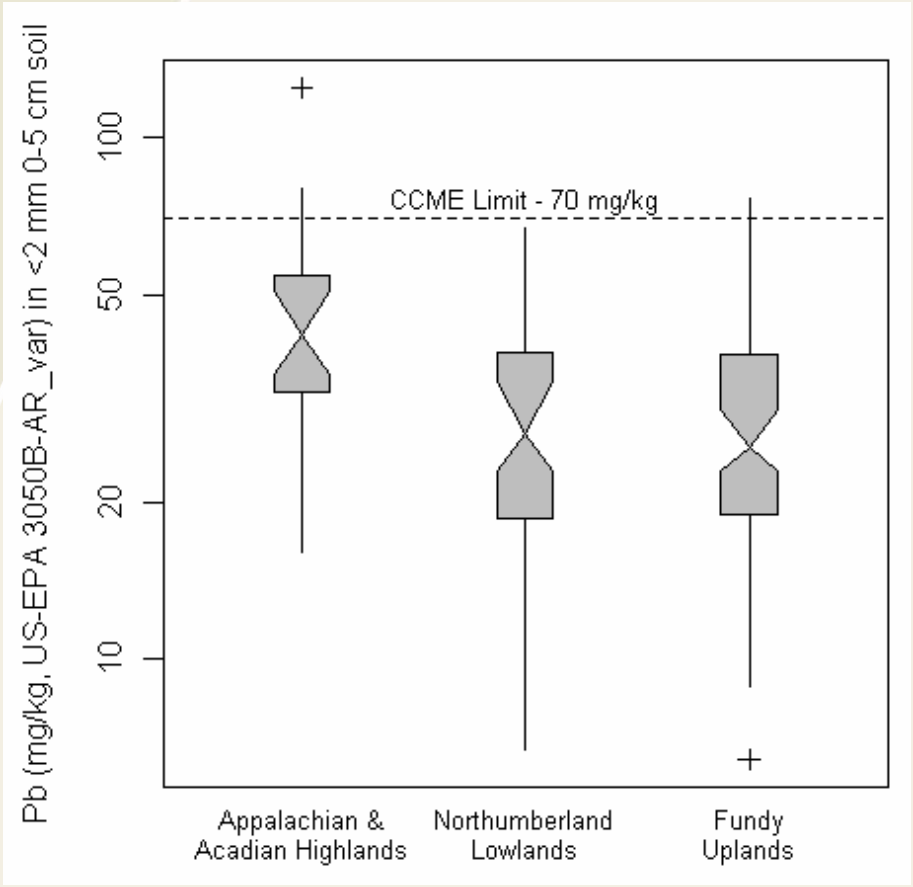
Earth Sciences Sector

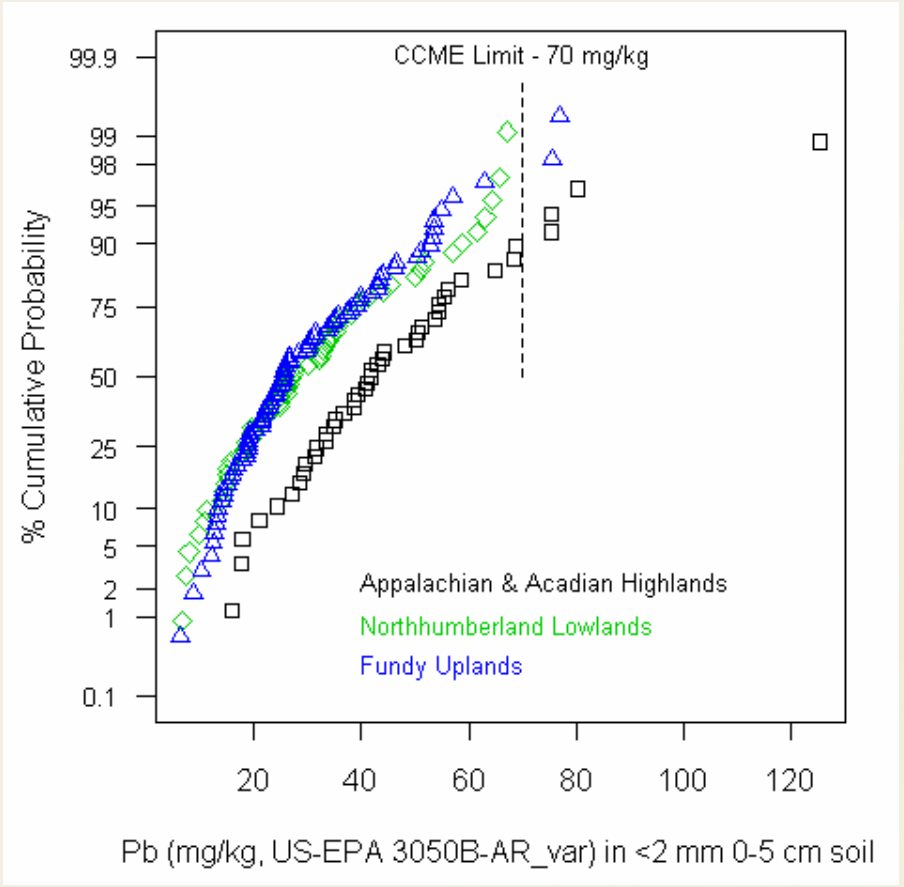




LEAD

Earth Sciences Sector





ESTIMATING BACKGROUND

- There are several methods:
  - Visual inspection of probability (Q-Q) plots;
  - Calculation; and
  - A combination (hybrid) of both.
- There are several methods of calculation:
  - Percentiles, cf. OTR98;
  - Mean ± 2 Standard Deviations (SD);
  - Median ± 2 Median Absolute Deviations (MAD); and
  - Tukey Boxplot ‘normal’ range.
- Mean ± 2 SD, is very sensitive to outliers.

CALCULATED ESTIMATES

Earth Sciences Sector

As (mg/kg) - Appalachian and Acadian Highlands — N = 43 — 2%ile = 0.868 — 98%ile = 15.2

	Mean	SD	Median	MAD		Mean±2SD	Med±2MAD	Tukey Fences (actual)
	4.16	4.08	3.2	1.78	+	12.3	6.76	7.95 (6.9)
					-	-4.01	-0.358	-1.65 (0.7)
Log10	0.492	0.321	0.505	0.3	+	13.6	12.7	14.5 (13.7)
					-	0.708	0.803	0.585 (0.7)

As (mg/kg) - Northumberland Lowlands — N = 56 — 2%ile = 0.72 — 98%ile = 6.91

	Mean	SD	Median	MAD		Mean±2SD	Med±2MAD	Tukey Fences (actual)
	2.79	1.74	2.35	1.11	+	6.27	4.57	6.1 (5.2)
					-	-0.696	0.126	-1.1 (0.7)
Log10	0.377	0.245	0.371	0.243	+	7.38	7.18	10.5 (7)
					-	0.77	0.769	0.517 (0.7)

As (mg/kg) - Acadian Uplands — N = 84 — 2%ile = 1.13 — 98%ile = 15.2

	Mean	SD	Median	MAD		Mean±2SD	Med±2MAD	Tukey Fences (actual)
	5.87	4.36	4.3	3.11	+	14.6	10.5	17.0 (15.7)
					-	-2.85	-1.93	-6.26 (0.6)
Log10	0.656	0.323	0.633	0.393	+	20.1	26.3	51.0 (23.4)
					-	1.02	0.703	0.403 (0.6)

Pb (mg/kg) - Appalachian and Acadian Highlands — N = 43 — 2%ile = 17.5 — 98%ile = 87.4

	Mean	SD	Median	MAD		Mean±2SD	Med±2MAD	Tukey Fences (actual)
	45.4	20.3	41.7	17.7	+	85.9	77.2	87.2 (80.2)
					-	4.88	6.26	-0.152 (15.9)
Log10	1.62	0.186	1.62	0.172	+	97.8	92.1	118.0 (80.2)
					-	17.6	18.9	15.1 (15.9)

Pb (mg/kg) - Northumberland Lowlands — N = 56 — 2%ile = 7.37 — 98%ile = 65.6

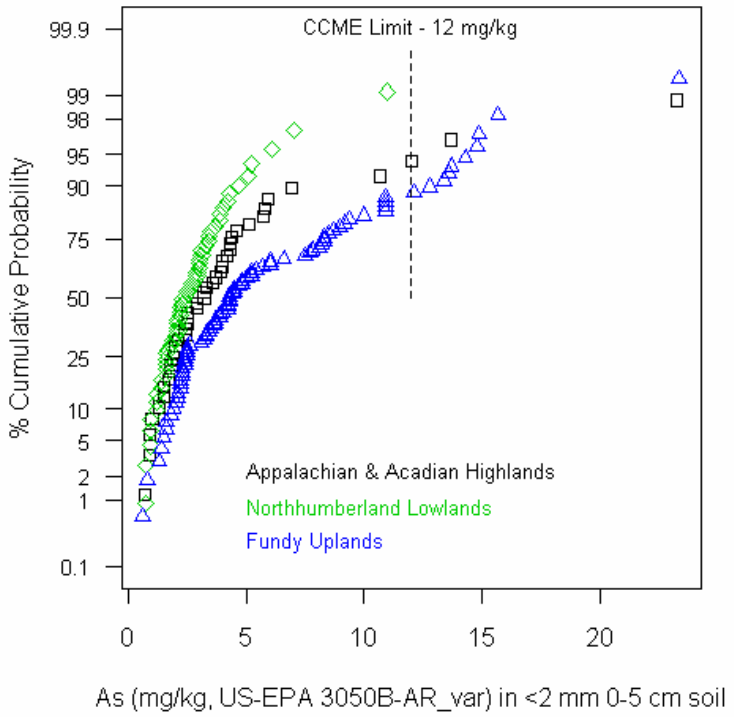
	Mean	SD	Median	MAD		Mean±2SD	Med±2MAD	Tukey Fences (actual)
	30.9	16.4	27.1	15.2	+	63.7	57.5	69.2 (67)
					-	-1.9	-3.22	-11.8 (6.67)
Log10	1.42	0.252	1.43	0.242	+	84.8	82.6	117.0 (67)
					-	8.31	8.92	6.15 (6.67)

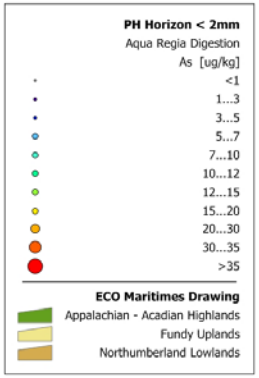
Pb (mg/kg) - Fundy Uplands — N = 84 — 2%ile = 9.82 — 98%ile = 67.2

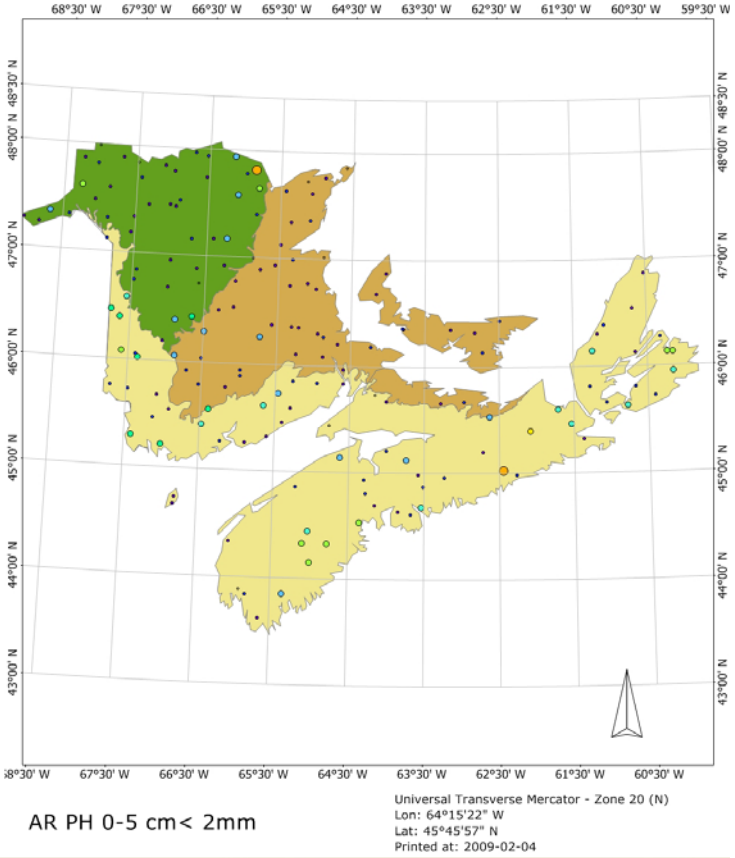
	Mean	SD	Median	MAD		Mean±2SD	Med±2MAD	Tukey Fences (actual)
	29.5	14.9	25.5	13.2	+	59.3	51.9	67.8 (62.9)
					-	-0.331	-0.9	-10.5 (6.39)
Log10	1.42	0.219	1.41	0.212	+	71.4	67.7	112.0 (76.9)
					-	9.55	9.59	6.47 (8.81)

BACKGROUND FOR As

Earth Sciences Sector

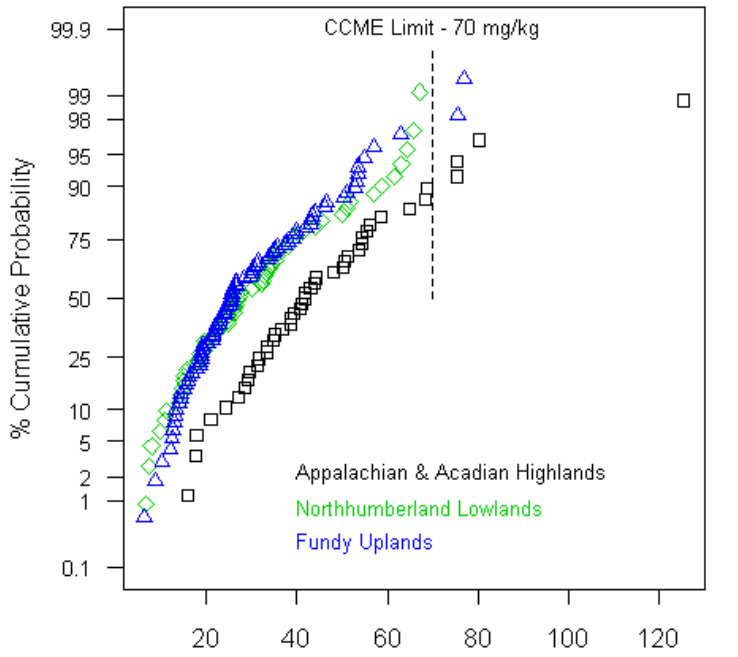




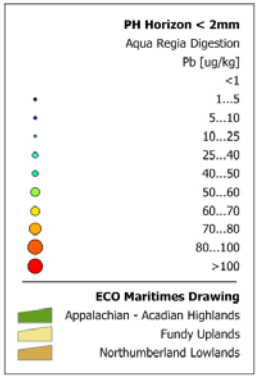


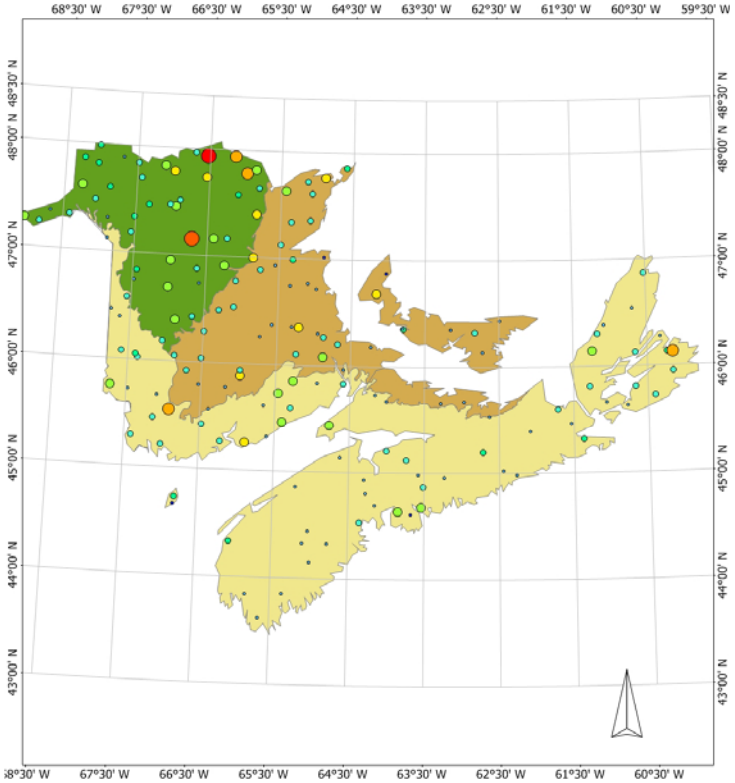
BACKGROUND FOR Pb

Earth Sciences Sector



Pb (mg/kg, US-EPA 3050B-AR_var) in <2 mm 0-5 cm soil





AR PH 0-5 cm< 2mm

Universal Transverse Mercator - Zone 20 (N)
Lon: 64°15'22" W
Lat: 45°45'57" N
Printed at: 2009-02-04

Natural Resources Canada | Ressources naturelles Canada

Canada

HYBRID ESTIMATES

Earth Sciences Sector

As - mg/kg	N	Min	Max	Cut-off	N	Min	98th %ile	Max
Appalachian and Acadian Highlands	43	0.7	23.3	8	39	0.7	6.1	6.9
Northumberland Lowlands	56	0.7	11	8	55	0.7	6	7
Acadian Uplands	84	0.6	23.4	16	83	0.6	14.8	15.7
Pb - mg/kg								
Appalachian and Acadian Highlands	43	15.9	125.2	100	42	15.9	76.2	80.2
Northumberland Lowlands	56	6.7	67	70	56	6.7	66	67
Acadian Uplands	84	6.4	76.9	70	82	6.4	55.7	62.8

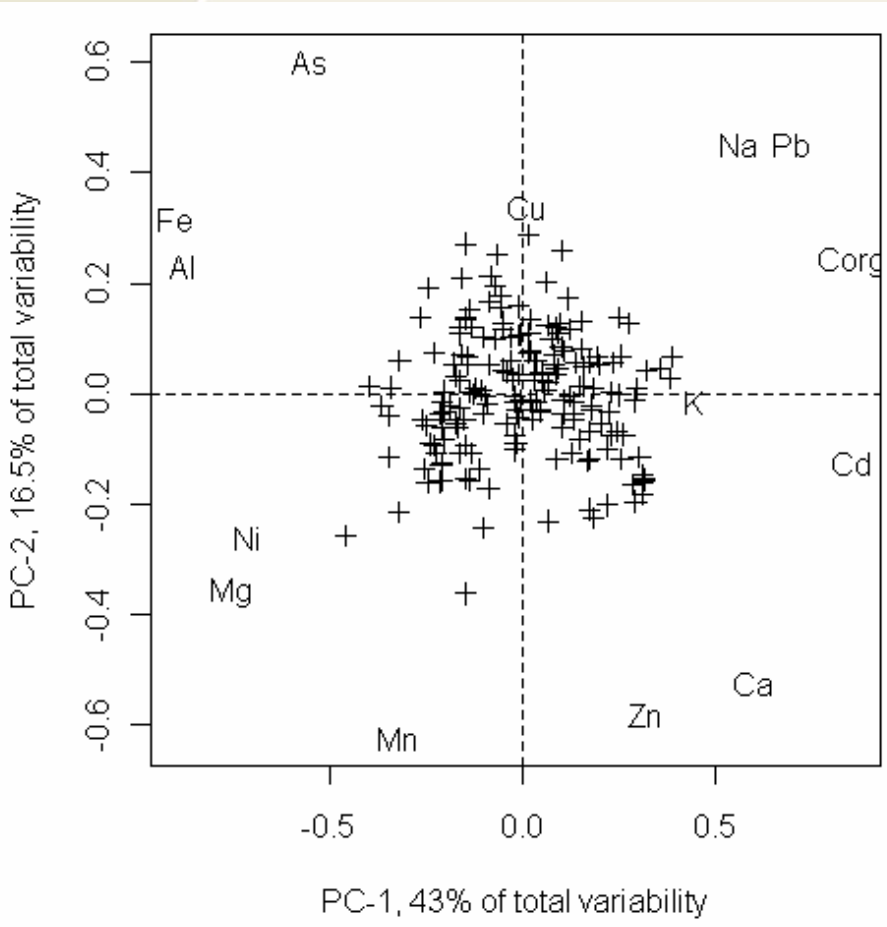
Estimates of background range for As in the Acadian Uplands are 0.6 to 15 mg/kg, and for Pb in the Appalachian and Acadian Highlands are 15 to 76 mg/kg

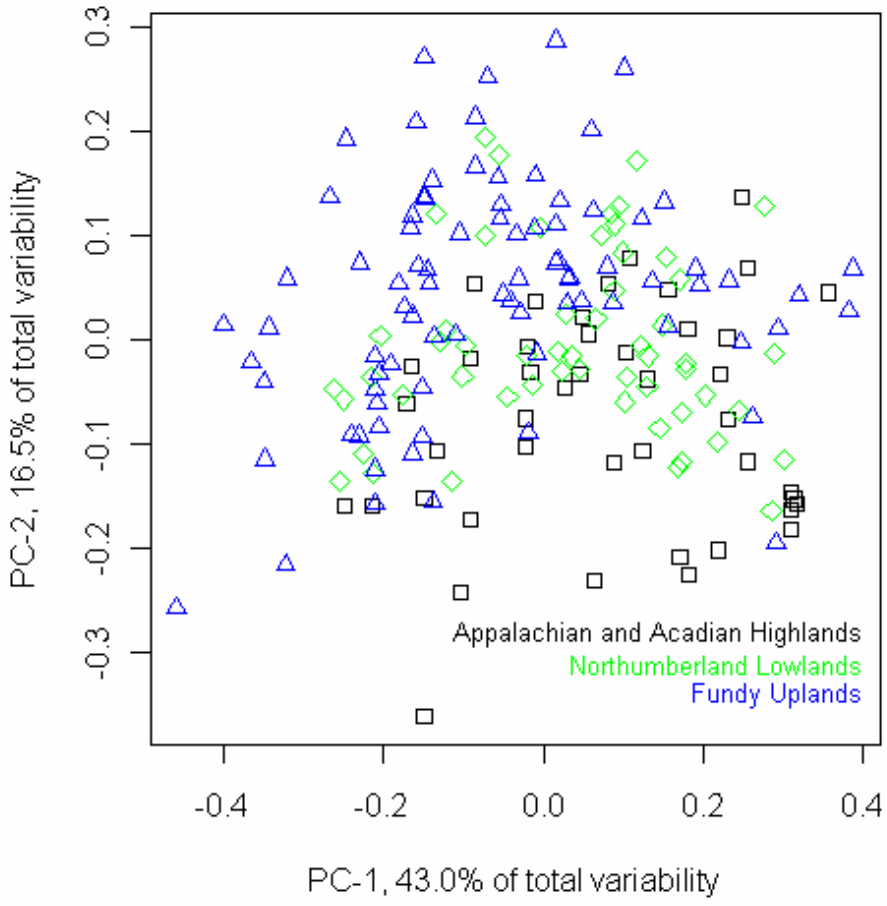
MULTI-ELEMENT APPROACHES

- Multivariate statistical approaches may sometimes help identify outliers, create outlier-free data subsets, understand the structure of the data, and identify groupings in the data;
- Some tools are Principal Components Analysis, multivariate probability – Chi-square – plots and cluster analysis; but
- Data (sub)sets should have sample sizes at least 8 to 9 times the number of variables studied

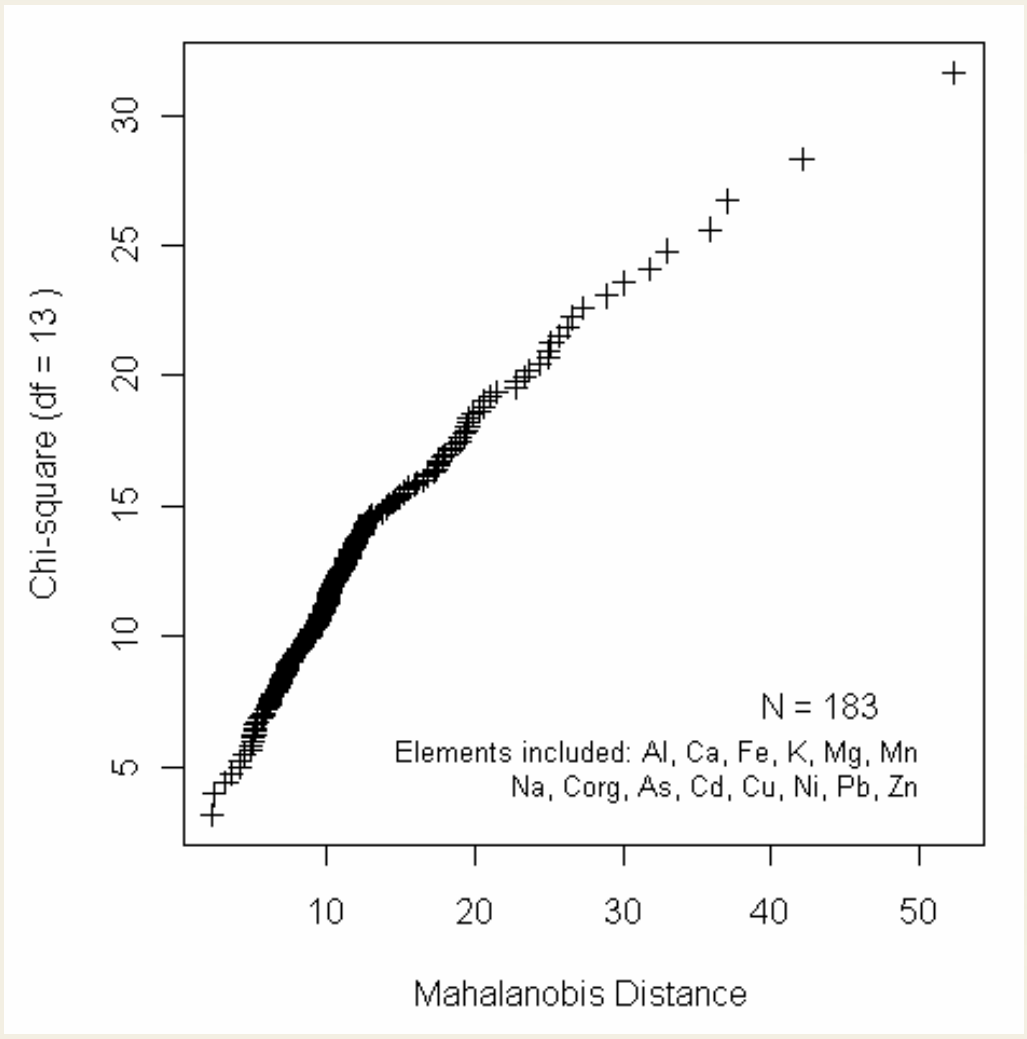
PCA

Earth Sciences Sector





CHI-SQUARE PLOT



RECOMMENDATIONS - 1

- To estimate background ranges:
  - Inspect the data as maps and statistical graphics displays;
  - If the data show evidence of falling into coherent regional patterns or of being poly-populational, decide whether to split the data into subsets;
  - Subsets should be a minimum of size 30; and
  - If multivariate procedures are to be used subsets should be a minimum size of 8 or 9 times the number of elements.

RECOMMENDATIONS - 2

- For the data set, or each data subset:
  - Use probability or Q-Q plots to identify outliers, individuals that do not appear to ‘belong’;
  - Select a ‘cut-off’ to remove the outliers;
  - Estimate the percentiles of the remaining, background, data;
  - Select from the percentiles, or even the minimum and maximum, a probable background range; and
  - Varying degree of ‘conservatism’ can be introduced by selecting different percentiles of the ‘background’ data.

REFERENCES

Hawkes, A.W. and Webb, J.S., 1962. Geochemistry in Mineral Exploration. Harper and Row, New York.

Selinus, O., 2005. Essentials of Medical Geology: Impacts of the Natural Environment on Public Health. Elsevier, Burlington, MA.

Reiman, C. and Caritat, P. de. 1998. Chemical Elements in the Environment. Factsheets for the Geochemist and Environmental Scientist; 398 pp. Springer-Verlag: Berlin, Heidelberg, etc.