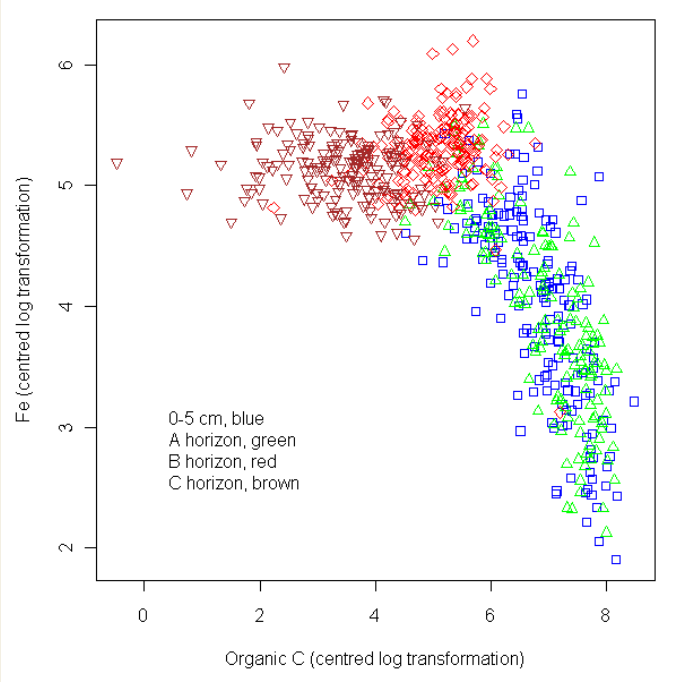
THE TRI-NATIONAL (2007) MARITIMES DATA

Earth Sciences Sector

Some Important and Interesting Observations



Robert G. Garrett
Natural Resources Canada – Geological Survey of Canada

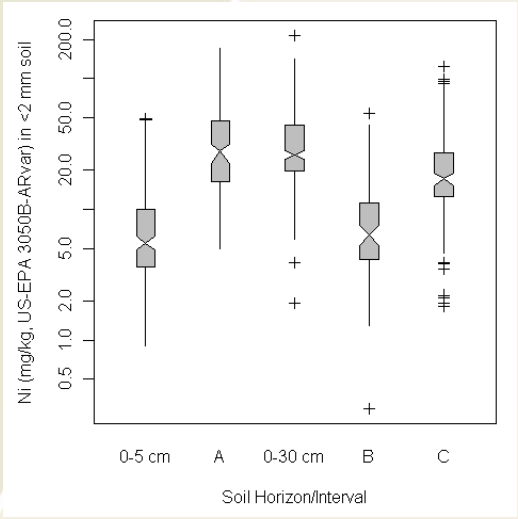
Workshop on the Role of Geochemical Data in Ecological and Human Health Risk Assessment; Halifax, Nova Scotia, March 17-18, 2010

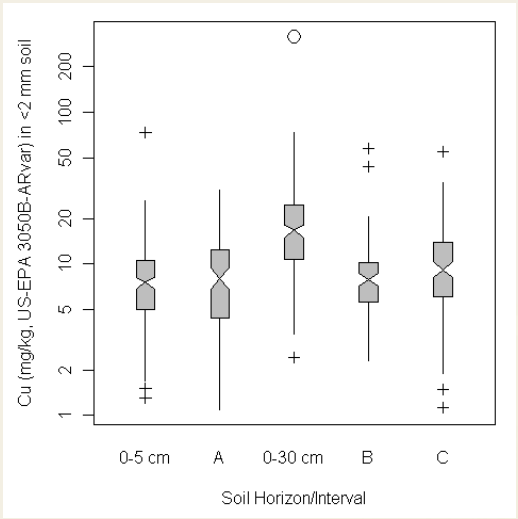
INTRODUCTION

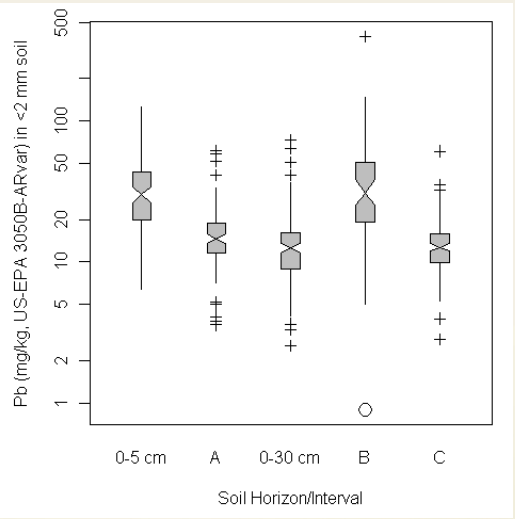
- Data for six elements, As, Cd, Cu, Ni, Pb and Zn, in the <2 mm fraction of five soil horizons/intervals were investigated with several analytical protocols, varying from a water leach to a 'total' acid (HF-$HClO_4$-HNO_3-HCl) decomposition;
- For core work the US-EPA 3050B Aqua Regia variant (4:1 HCL-HNO_3) was selected.
- The questions were:
  - What influences trace element levels?
  - How critical is soil horizon/interval? &
  - What are the relevance of these data to ecosystem and human health risk assessment and management?

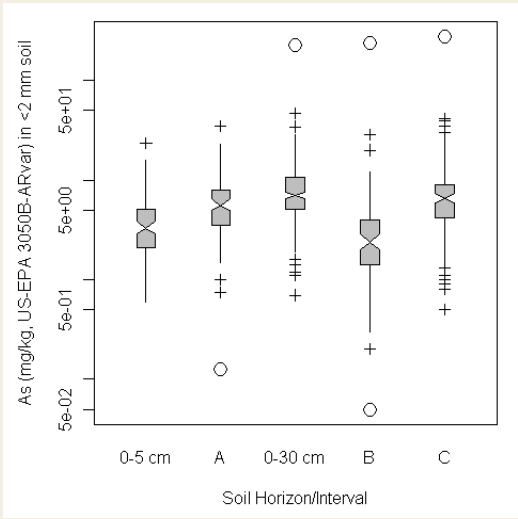
A TALE OF FIVE HORIZONS

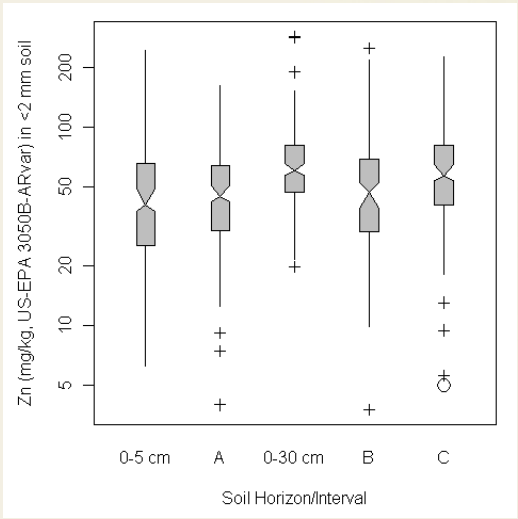
Earth Sciences Sector

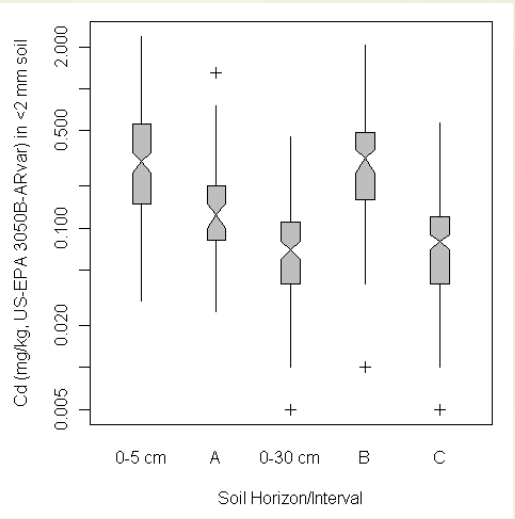












OBSERVATIONS

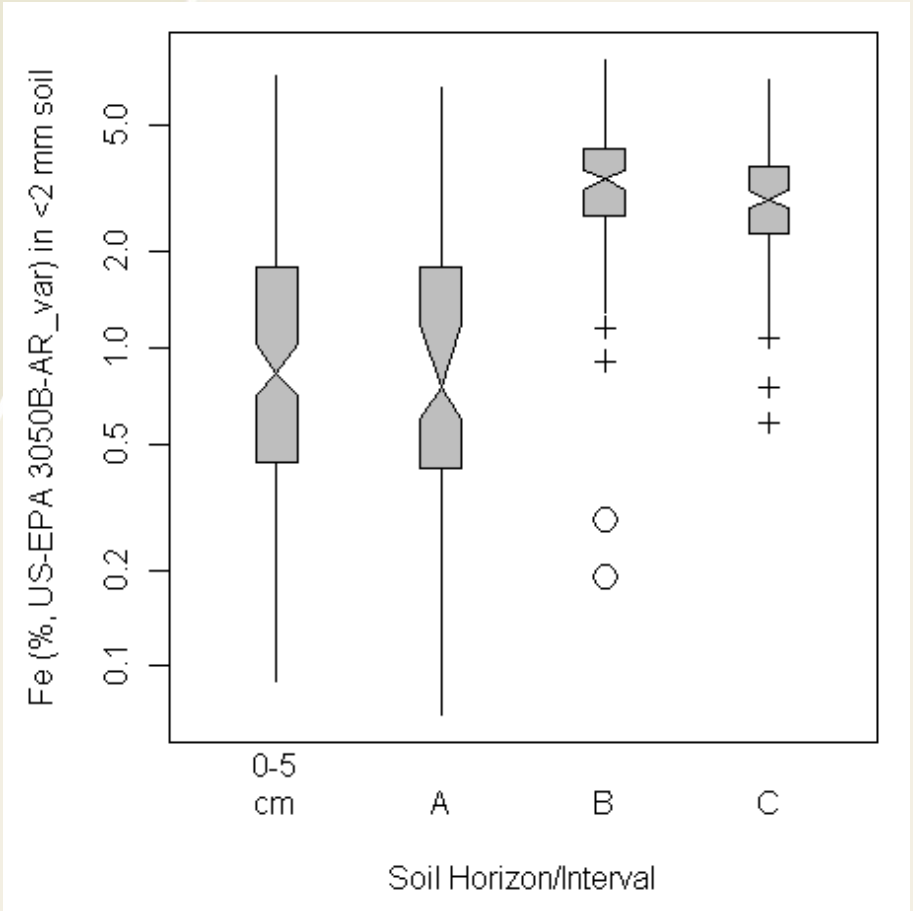
- The data divide into two groups on the basis of their distribution across soil horizons/intervals:
  - Ni, Cu, Zn and As levels increase with depth through the 0-5 cm, A and 0-30 cm ‘horizons’, then decrease to the B-horizon before increasing to the C-horizon - the weathered soil parent material; &
  - Pb and Cd levels decrease downwards from the surface layers before rising again in the B-horizon and then falling to the C-horizon.
- In general:
  - Levels in the 0-5 cm interval and B-horizon are similar; &
  - Levels in the 0-30 cm interval and C-horizon are similar.

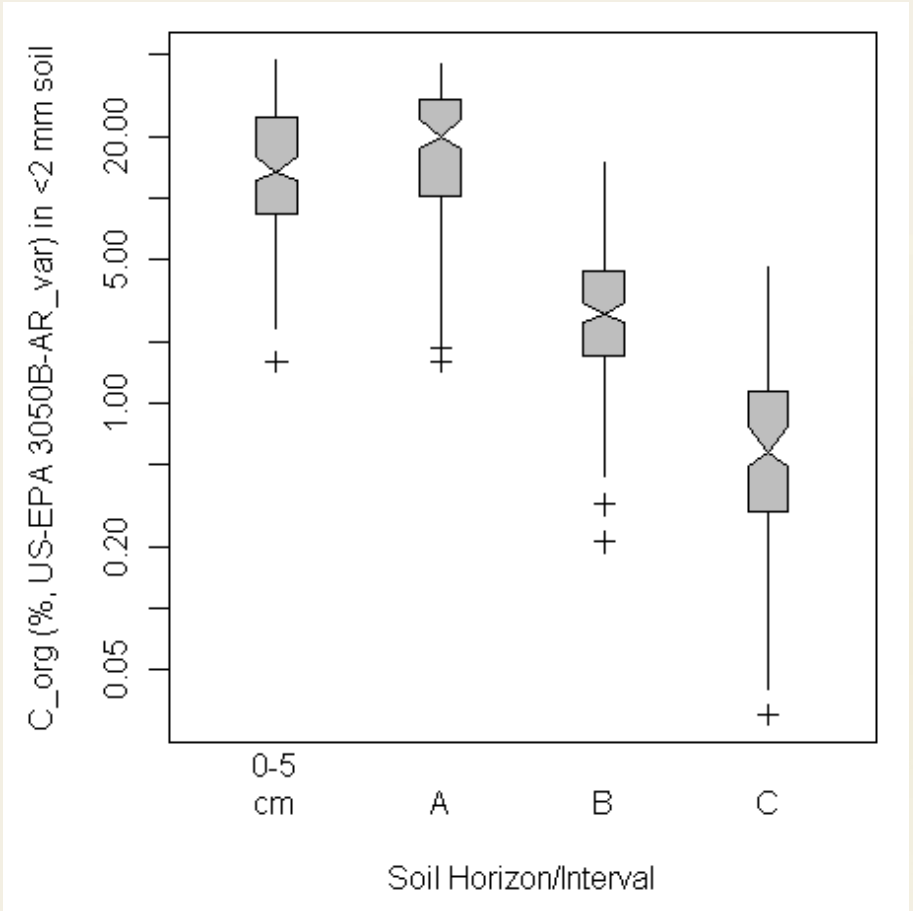
WHY?

- Trace elements only form a small part of the soil composition, generally they total to less than 1%;
- They are influenced by at least four factors:
  - The geochemistry of the soil parent material;
  - Any additions due to anthropogenic processes, i.e. contamination; &
  - Soil forming processes where major soil components such as iron (Fe), manganese and aluminium oxy-hydroxides, clays, and organic carbon (C_org) play an important role through their ability to sequester and form stable ligands with trace elements.

IRON AND ORGANIC CARBON

Earth Sciences Sector



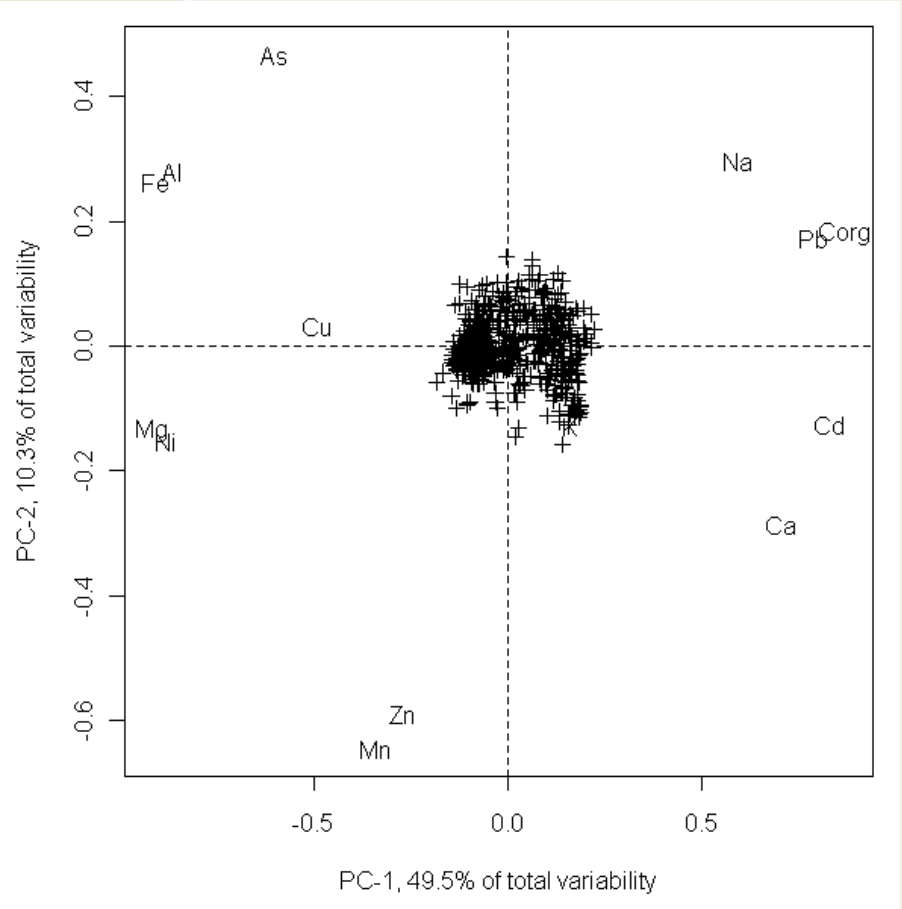


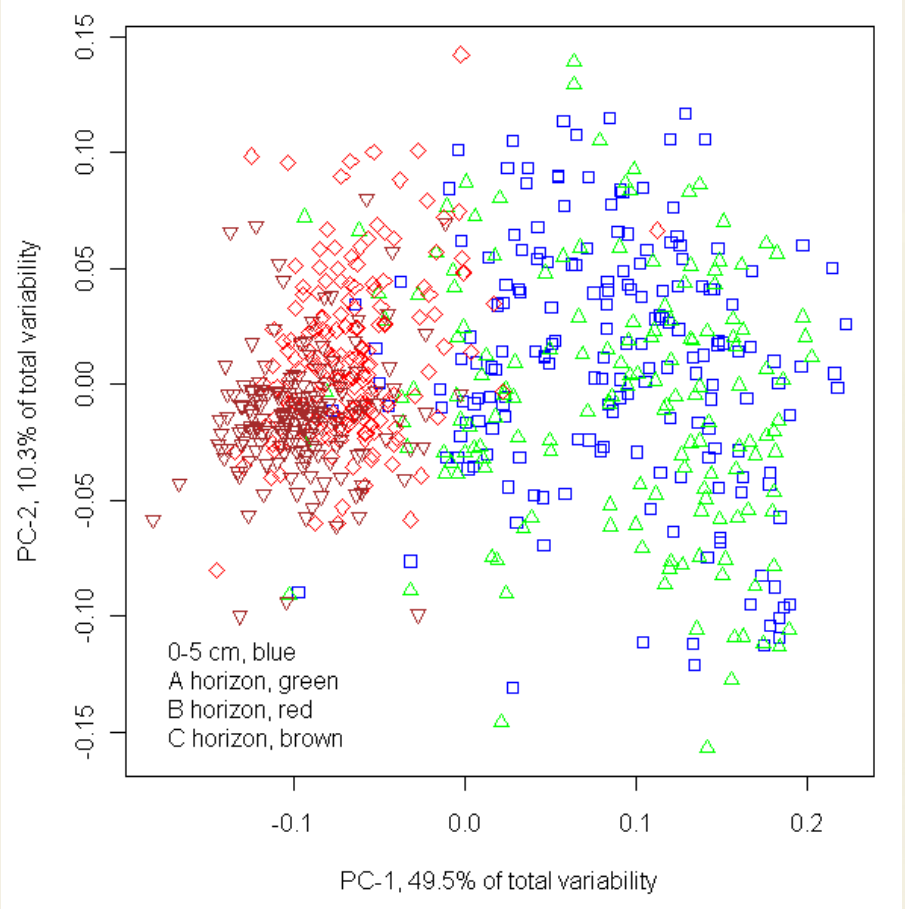
WHY?

- The major soil components, Fe-compounds and organic_C, vary significantly with depth:
  - Fe increases with depth, peaking in the B-horizon, a zone of Fe-sesquioxide, clay and organic_C accumulation; &
  - Organic_C decreases with depth.
- Trace elements behave differently depending upon the stability of the ligands formed with the ‘major components’ in the soil environment;
- A Principal Component Analysis (PCA) can help identify the relationships.

PRIMARY CONTROLS

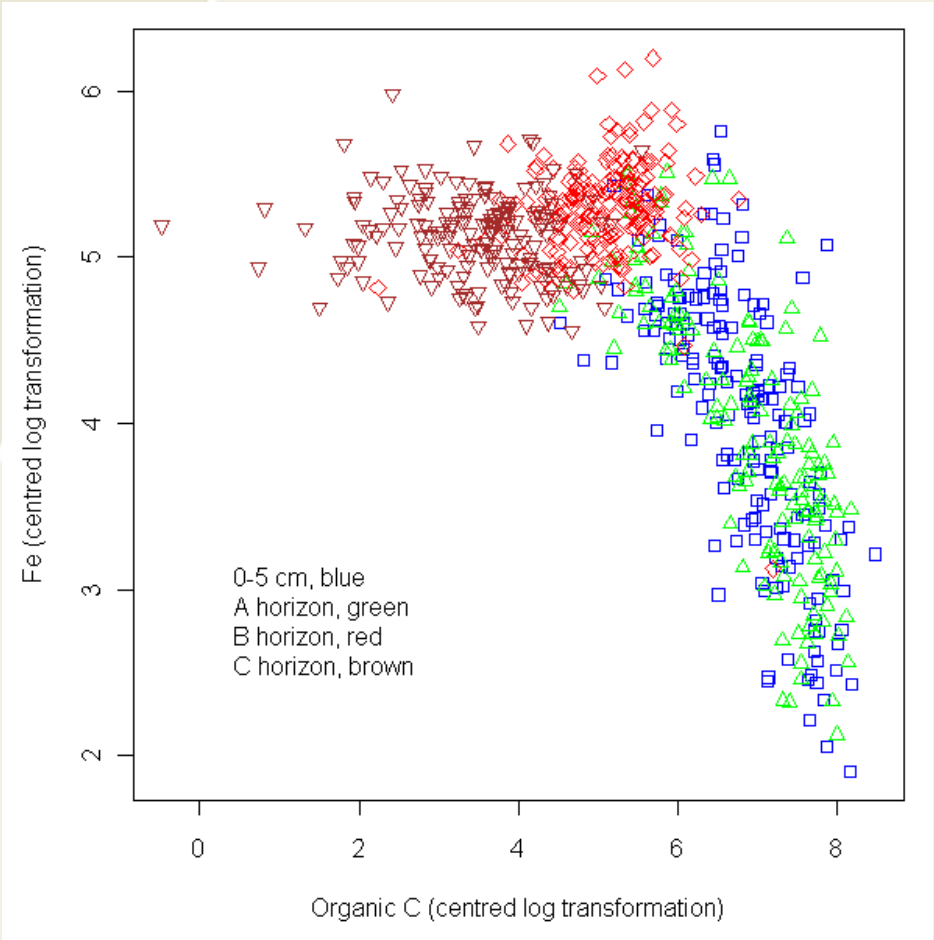
Earth Sciences Sector

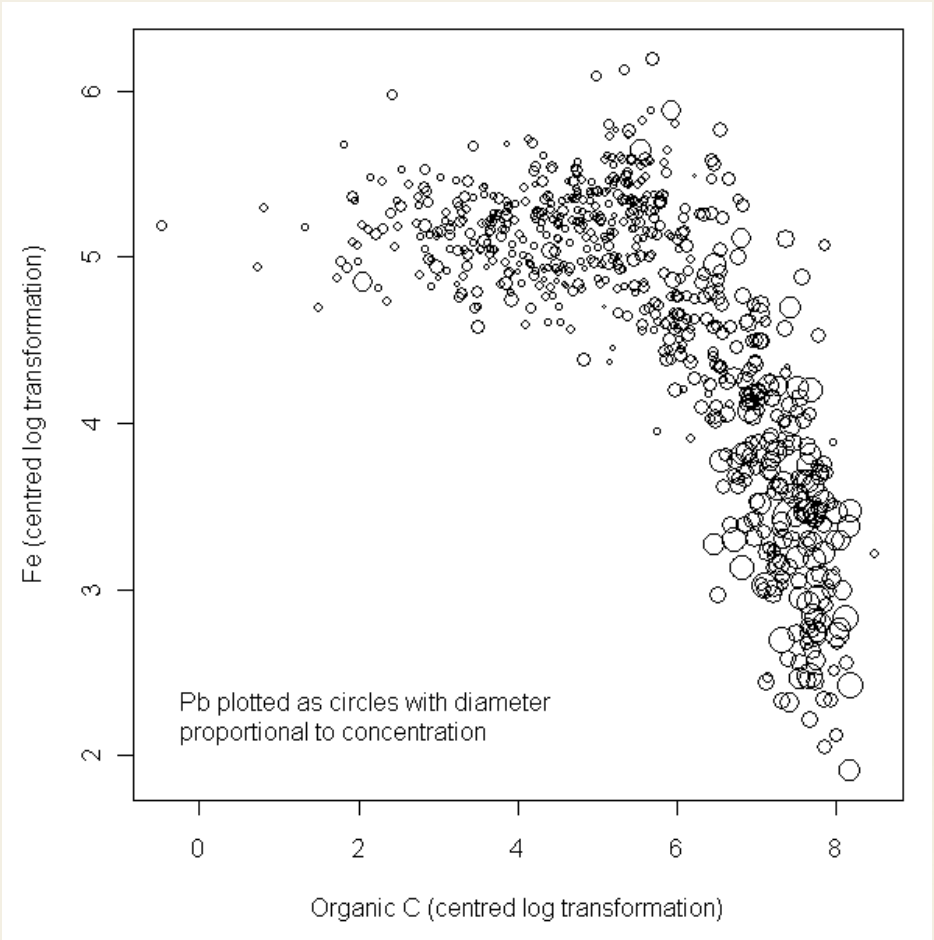




IRON, ORGANIC CARBON & Pb

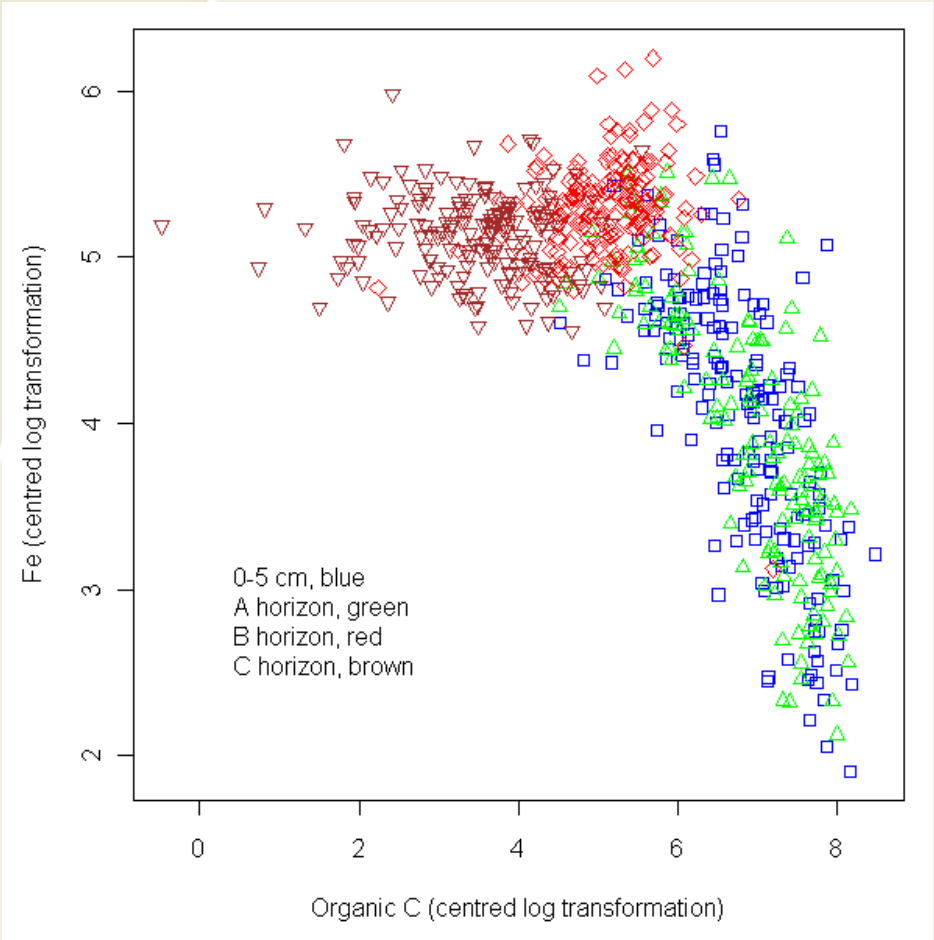
Earth Sciences Sector

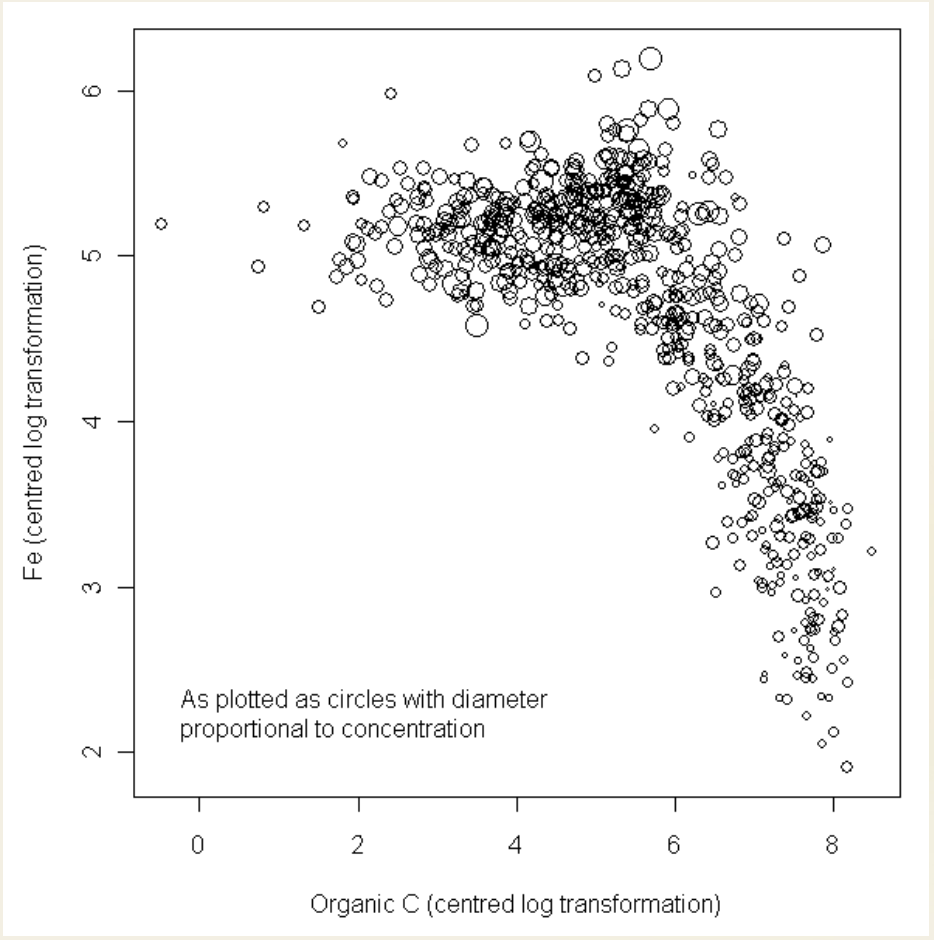




IRON, ORGANIC CARBON & As

Earth Sciences Sector





VARIATION EXPLAINED

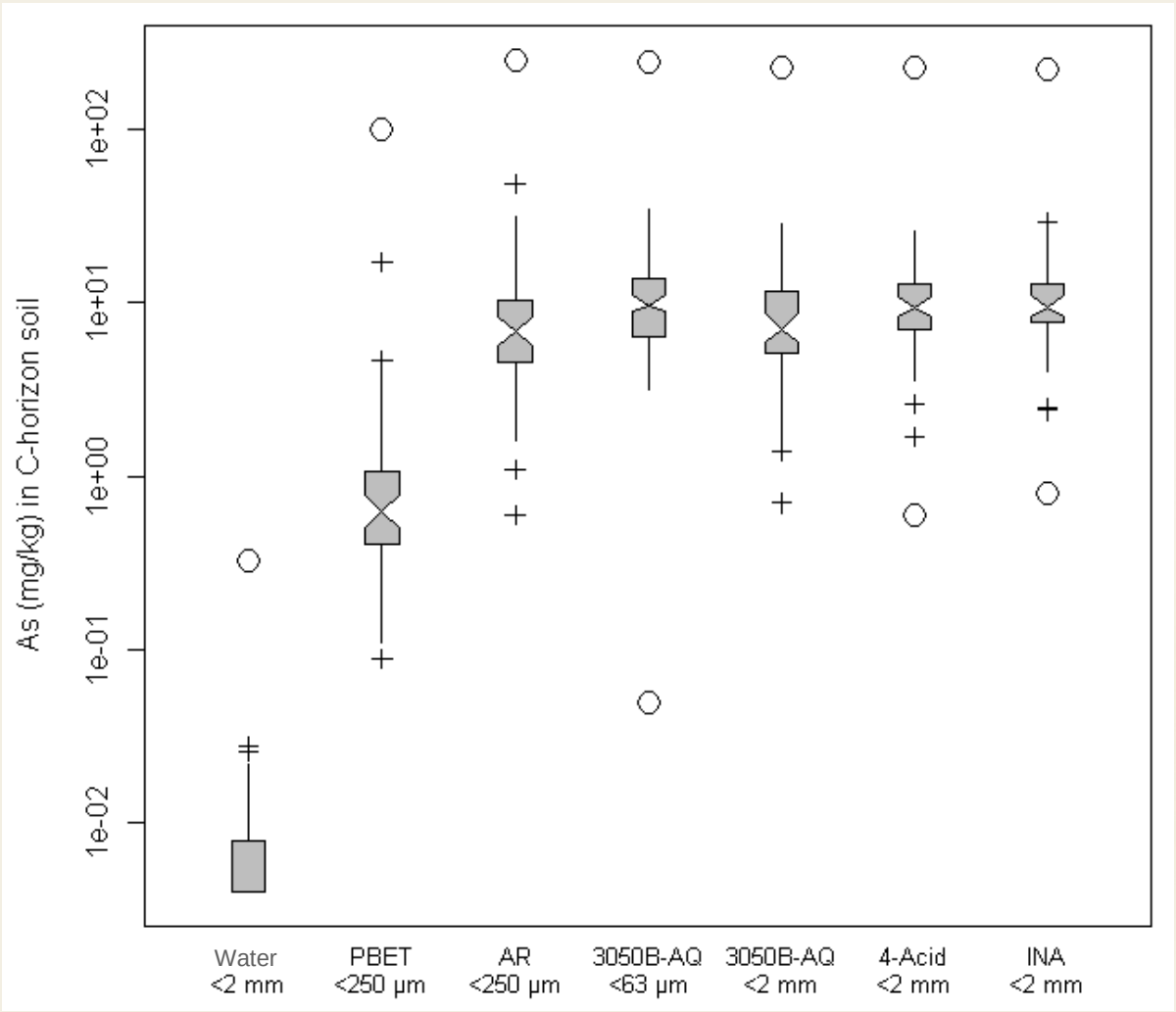
- Variations in trace element concentrations between soil horizons/intervals are due to their intimate relationship with the soils' major components;
- These, in turn, vary as a result of fundamental pedological processes of soil formation, such as:
  - The accumulation of organic matter in the uppermost horizons and B-horizon; &
  - The accumulation of Fe in the lowermost horizons.
- Which explains the similarities between the 0-5 cm interval and the B-horizon, and the 0-30 cm interval and the C-horizon in these data.

RELEVANCE TO RISK

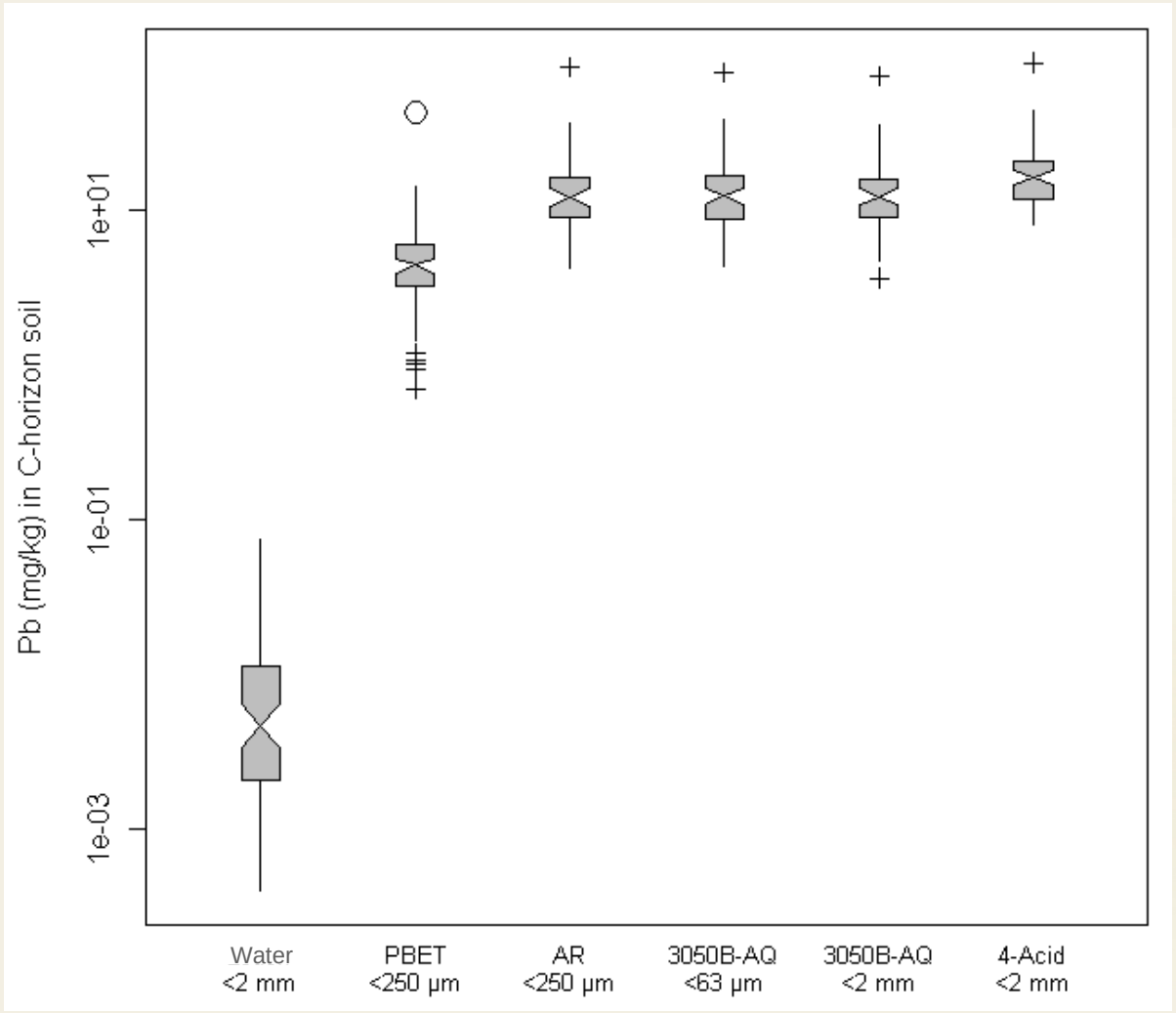
- Most methods of geochemical analysis employ strong acid mixtures, e.g., Aqua Regia, these release firmly mineral-bound elements and likely over-estimate the bioaccessible amounts of elements.
- Two alternative digestions have been investigated:
  - A Physiologically Based Extraction Technique (PBET) on the <250 µm fraction employing HCl at approximately pH 1 that emulates a gastric fluid; &
  - A water (H_2O) leach undertaken un-buffered at ambient soil pH that emulates what biota may be exposed to by contact.

METHODS OF ANALYSIS - As

Earth Sciences Sector

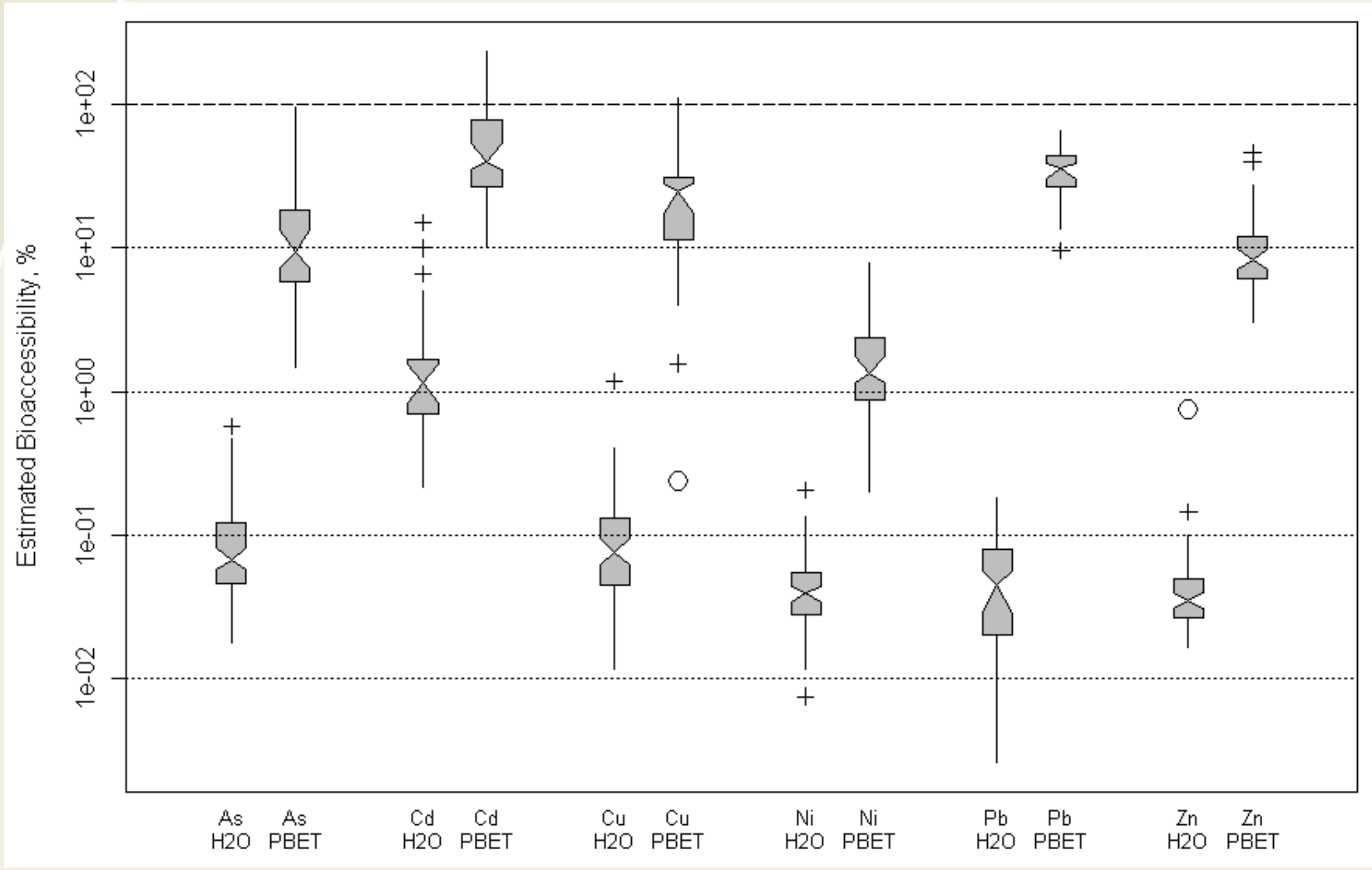


METHODS OF ANALYSIS - Pb



BIOACCESSIBILITY

Earth Sciences Sector



RELEVANCE TO RISK

- Near-total and total (Ni INA) methods yield similar levels in comparison to PBET and water leach data;
- Estimates of the median bioaccessible amounts for the six elements vary from 1.3% (Ni) to 40% (Cd) by the PBET procedure, and 0.04% (Ni) and 1.2% (Cd) by the water leach; and
- The high estimated bioaccessibility of Pb (median 36%) as measured by the PBET procedure in contrast to the water leach (0.05%) is notable, and likely related to the use of HCl in the digestion.

RECOMMENDATIONS - 1

- The US-EPA 3050B Aqua Regia variant (4:1 HCL-HNO_3) is an internationally acknowledged protocol;
- As there appear to be only small differences for most elements in results obtained by the various Aqua Regia-like protocols it is recommended that the US-EPA 3050B Aqua Regia variant be adopted for general use;
- Care needs to be taken comparing NOECs derived from ecotoxicological studies employing soluble salts and environmental levels derived from routine geochemical analyses.

RECOMMENDATIONS - 2

- Soil samples should be collected by horizon, data will be easier to interpret in terms of establishing the range of background variation and recognizing anthropogenic contamination as the confounding effects of soil major-component variability will be minimized;
- When, for operational reasons, interval sampling, e.g., 0-5 cm, or 0-30 cm, has to be undertaken, the intervals should be kept as narrow as possible in order to avoid confounding the resulting data with the effects of matrix variability;

RECOMMENDATIONS - 3

- Geochemical data will be most useful in supporting risk management decision making by their use in establishing the range of local natural background levels for use as remediation targets; and
- Care must be taken to ensure that in remediation decision making the methods of analysis and soil horizons/intervals are comparable between the remediation criteria and the available geochemical data.

- Thank you
- Questions?