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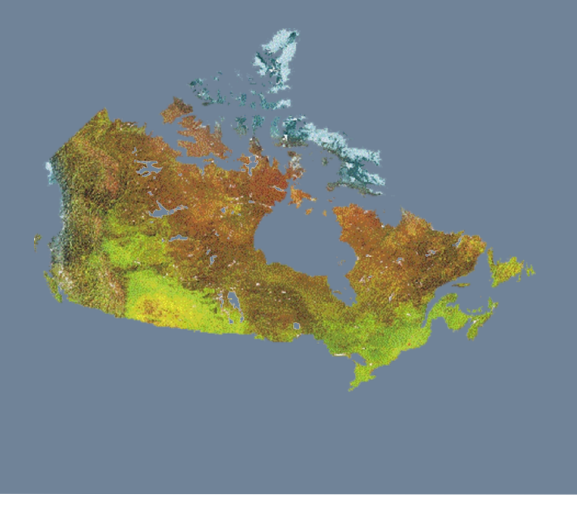
SAMPLE "INTEGRITY" - AN EVALUATION OF SAMPLE VARIABILITY FOR SOILS AROUND ROUYN-NORANDA, QUEBEC

R.D. Knight[1], and P.J. Henderson[1]



Sample "Integrity" - an evaluation of sample variability for soils around, Rouyn-Noranda, Quebec

Metals In The Environment
Geological Survey of Canada

Abstract

A detailed soil sample collection grid was established 3 km southwest of the Horne smelter at Rouyn - Noranda, Quebec. The work supports interpretation of a regional geochemical survey of humus and soil within 100 km radius of the smelter and was designed to determine geochemical variability at a site affected by smelter particulate deposition. Soils in the grid are luvisols formed on glacial lake silts and clays and overlie pillowed volcanic bedrock. Vegetation comprises small poplars and alders, with a fern ground cover; carbonized stumps and a thin layer of charcoal beneath humus indicate the site has been subject to forest fire. Litterfall, humus, and B-horizon soil samples were collected at 10, 20, and 30 m from the intersection of two perpendicular transects and at a point halfway between the 30 m sample locations. Three samples of each were collected at the point of intersection. C-horizon soil was collected at the intersection, the 30m sites, and halfway between the 30m sample locations. In preparation for ICP-AES geochemical analyses, litterfall and humus samples were macerated, and all samples sieved to <2mm. The litterfall samples were digested using perchloric acid, and all other samples using aqua-regia. The B- and C-horizon soil samples were analysed in duplicate. A total of 48 analyses were carried out.

Geochemical variation among litterfall, B-horizon, and C-horizon samples lies within the range of analytical variation, and trace metal concentrations (Cu, Pb, Zn, Ni, Cr) are within 10s to 100s ppm. For non-smelter-related elements, such as Ni, humus concentrations are equivalent to those of C-horizon soil. For Cr, humus values are lower than those of C-horizon soil. In contrast, smelter-related elements, Cu, Pb, and Zn, have humus concentrations that are 1000's of ppm, and range within a variability of several 1000 ppm across the site.

Humus geochemistry reflects non-uniform distribution of metal-rich smelter particulate, and indicates that site variability is an important factor in mapping the distribution of smelter particulate and in modeling deposition.

Introduction

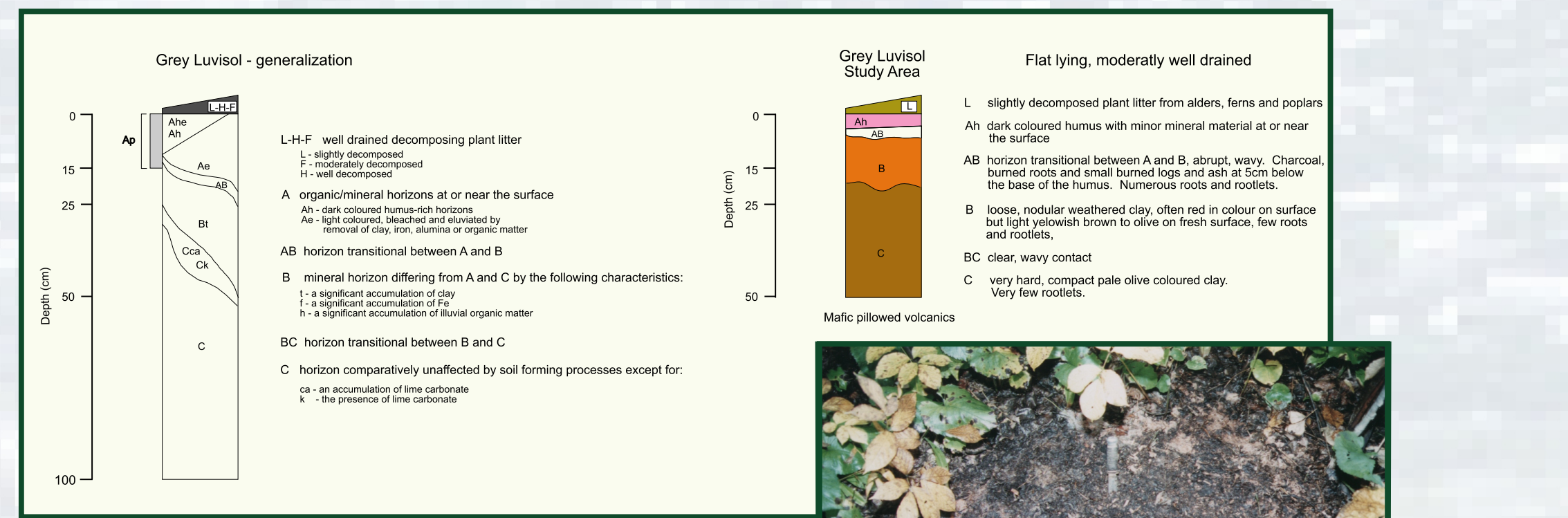
The objective of this study is to investigate the variation in distribution of elements in litterfall, humus and soil over a small geographic area close to an anthropogenic source to demonstrate if high input from the source

1) masks local variation with an evenly distributed high value
or
2) results in large variations between high and low values

Choosing the Site

In order to minimize the potential of geochemical variation based on factors other than the anthropgenic point source (Horne Smelter) a site was chosen close to the smelter that fulfilled the following criteria:

1) Flat lying - few depressions where water can pool, equal humus thickness
2) Similar vegetation with open canopy - small poplar, alders, shrubs and ferns
3) Similar bedrock - mafic pillowed volcanic rock
4) Similar homogenous soil parent material - homogeneous glacial lacustrine clay and silt
5) Limited human activity - old cut lines, no walking paths no ATV or snowmobile trails
6) Close to and downwind from the smelter - about 3 km SE of the Horne smelter stack

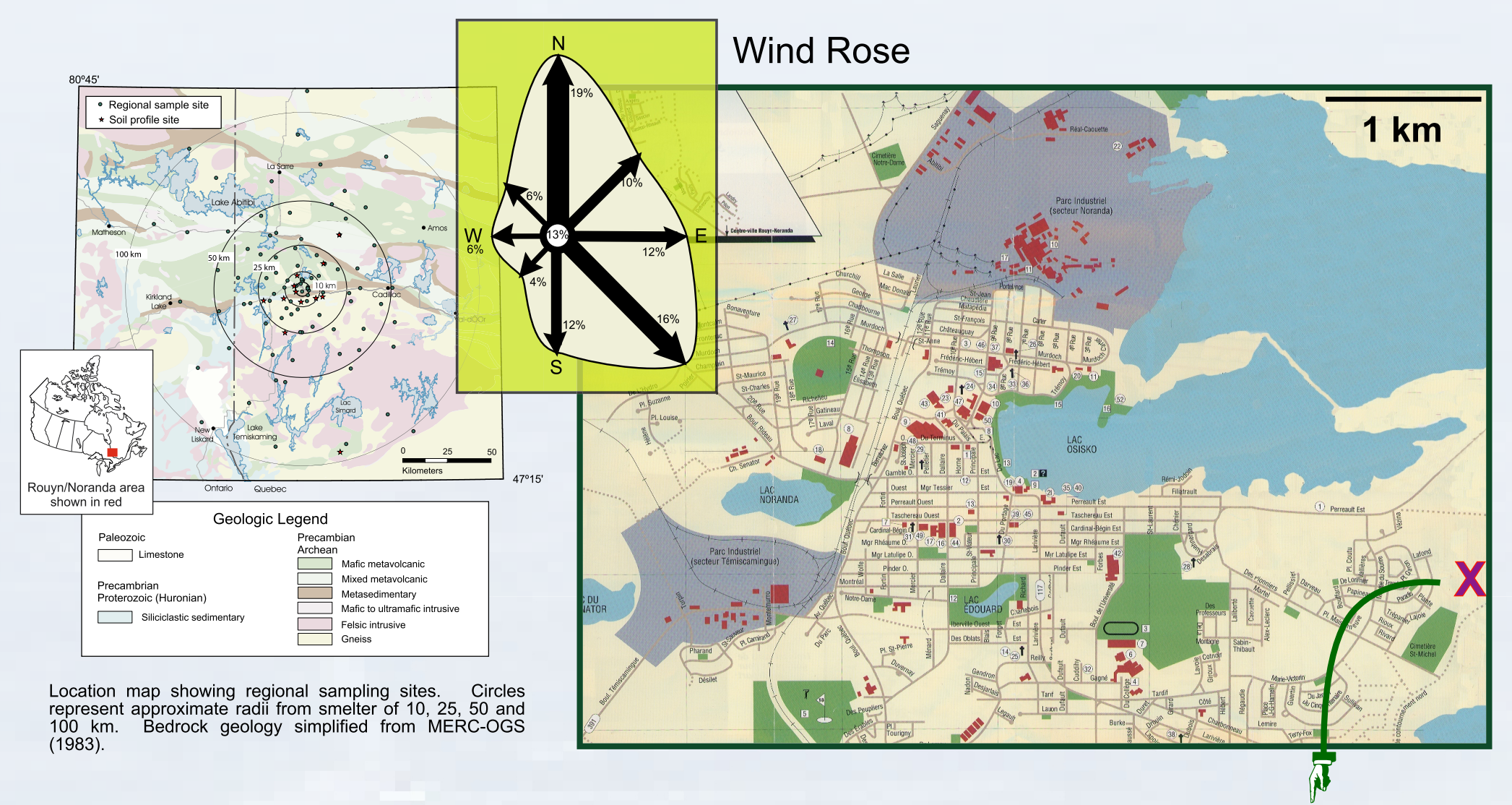


Characteristics of Luvisol developed in the Rouyn-Noranda area (revised from Agriculture Canada Expert Committee on Soil Survey, 1987).

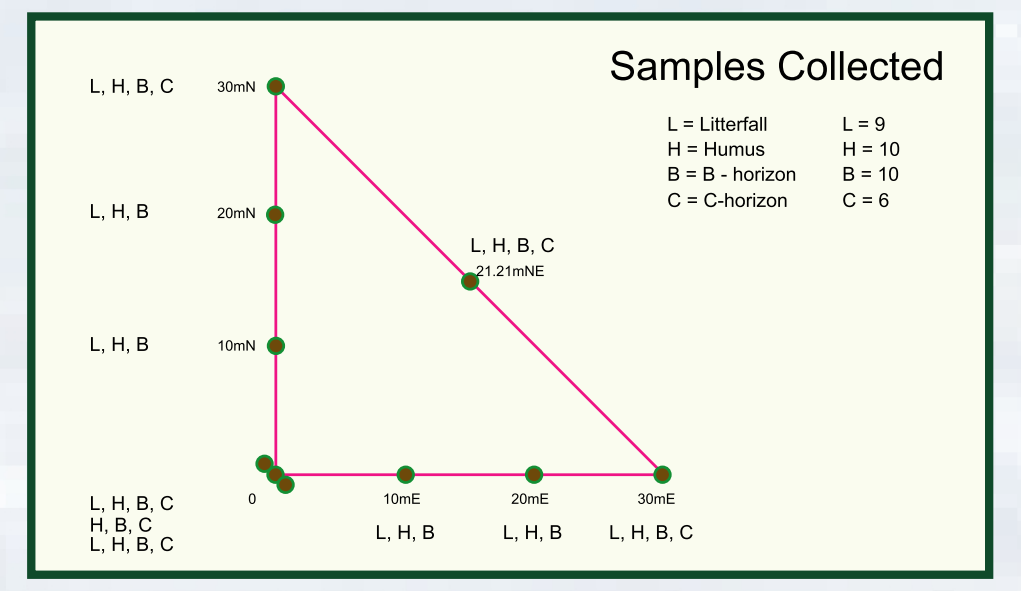
Hole dug after litterfall and humus has been removed. Note the undecomposed leaves and the abundance of roots in the humus. Few roots penetrate the B-horizon clay.

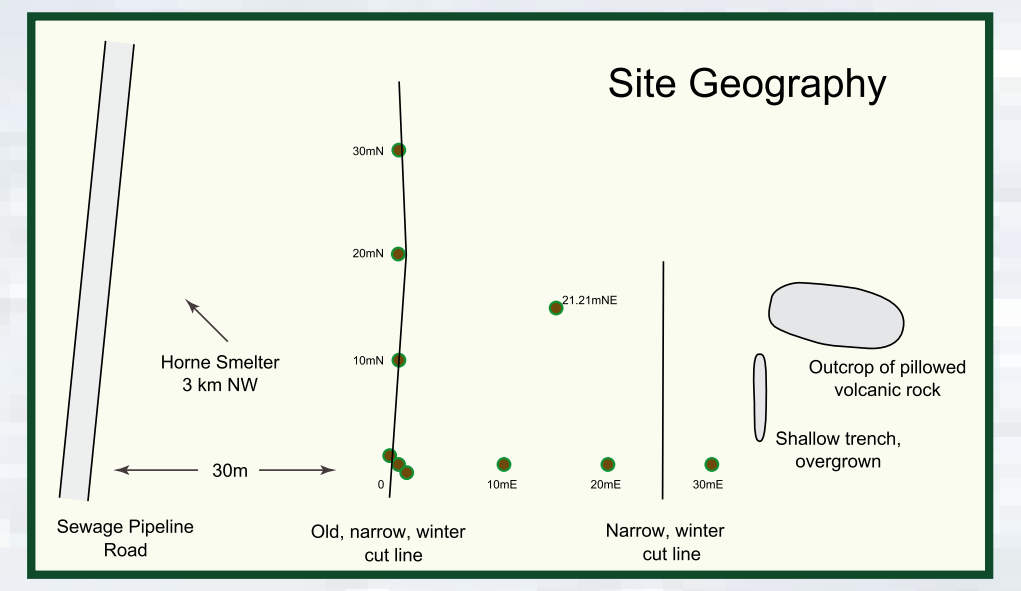
Humus surface after litterfall has been removed. Note that some clay is exposed indicating an uneven and thin humus. Knife for scale.

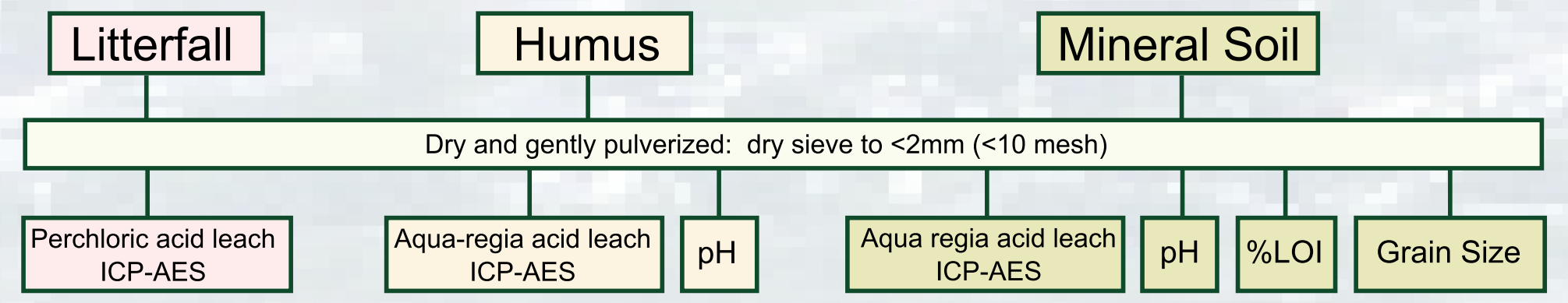
Three augered holes used to collect pale olive, C-horizon, clay.



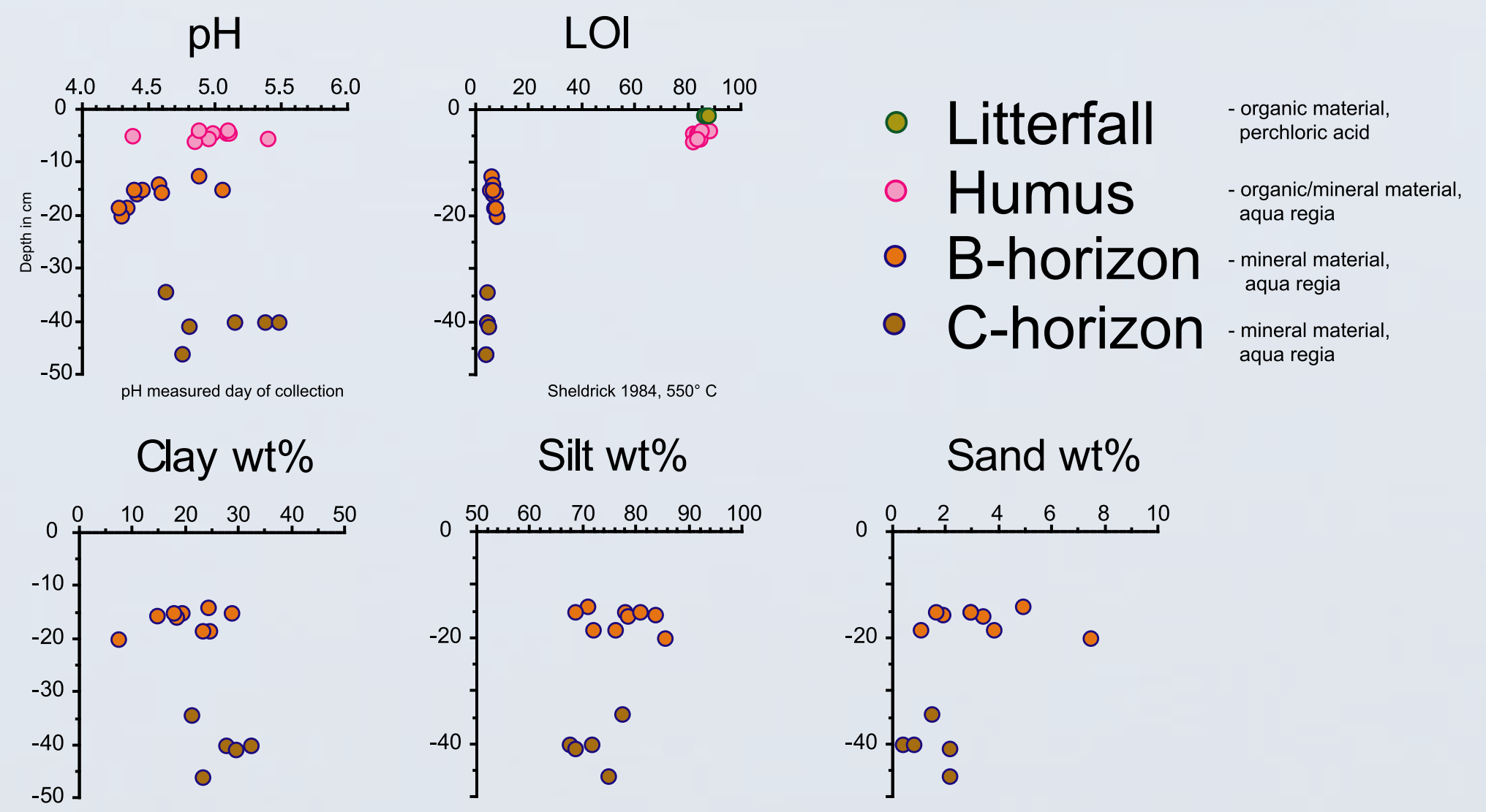
Location map showing regional sampling sites. Circles represent approximate radii from smelter of 10, 25, 50 and 100 km. Bedrock geology simplified from MERC-OGS (1983).



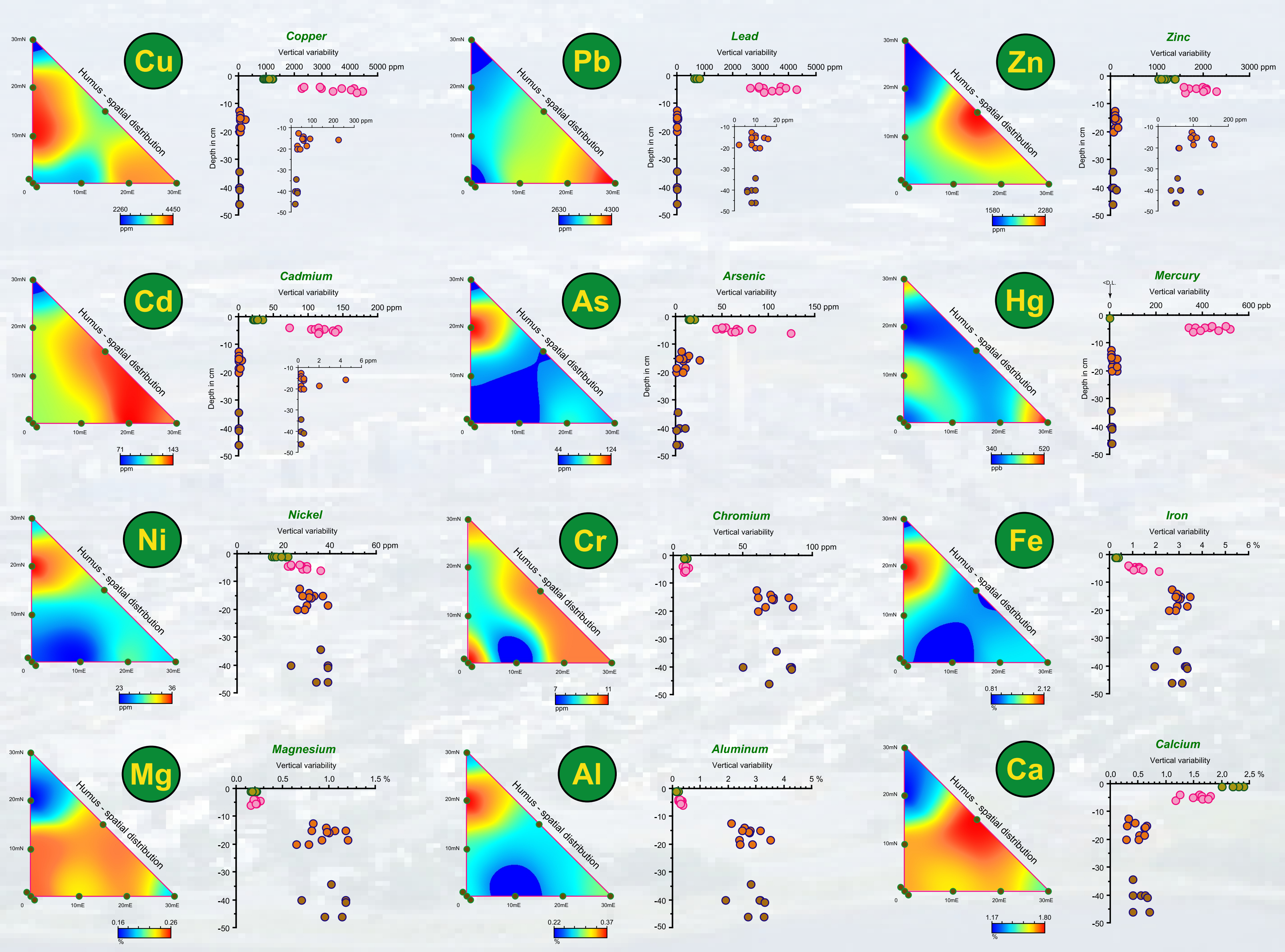




Litterfall
Humus
Mineral Soil
Dry and gently pulverized: dry sieve to <2mm (<10 mesh)
Perchloric acid leach ICP-AES
Aqua-regia acid leach ICP-AES
pH
Aqua regia acid leach ICP-AES
pH
%LOI
Grain Size

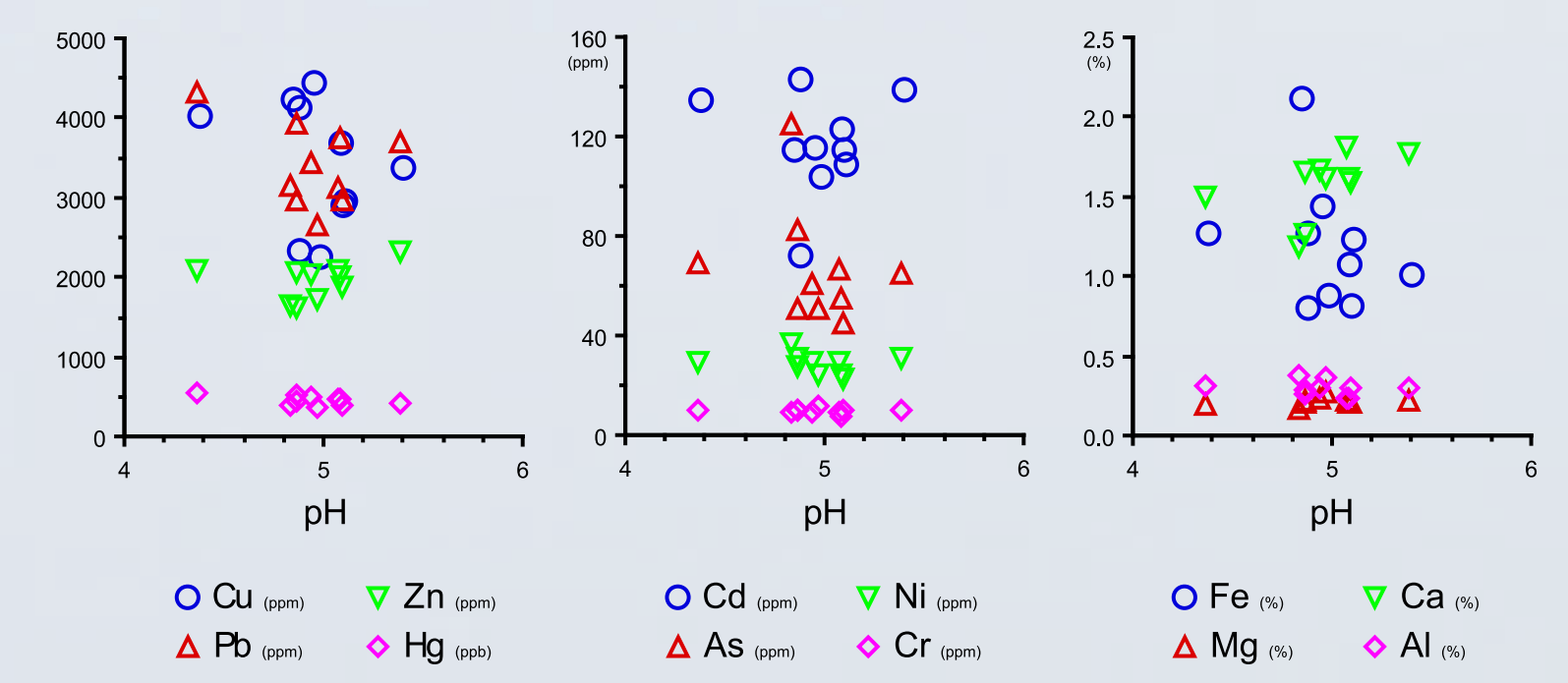


Spatial Distribution in Humus & Vertical Variability L,H,B,C horizons

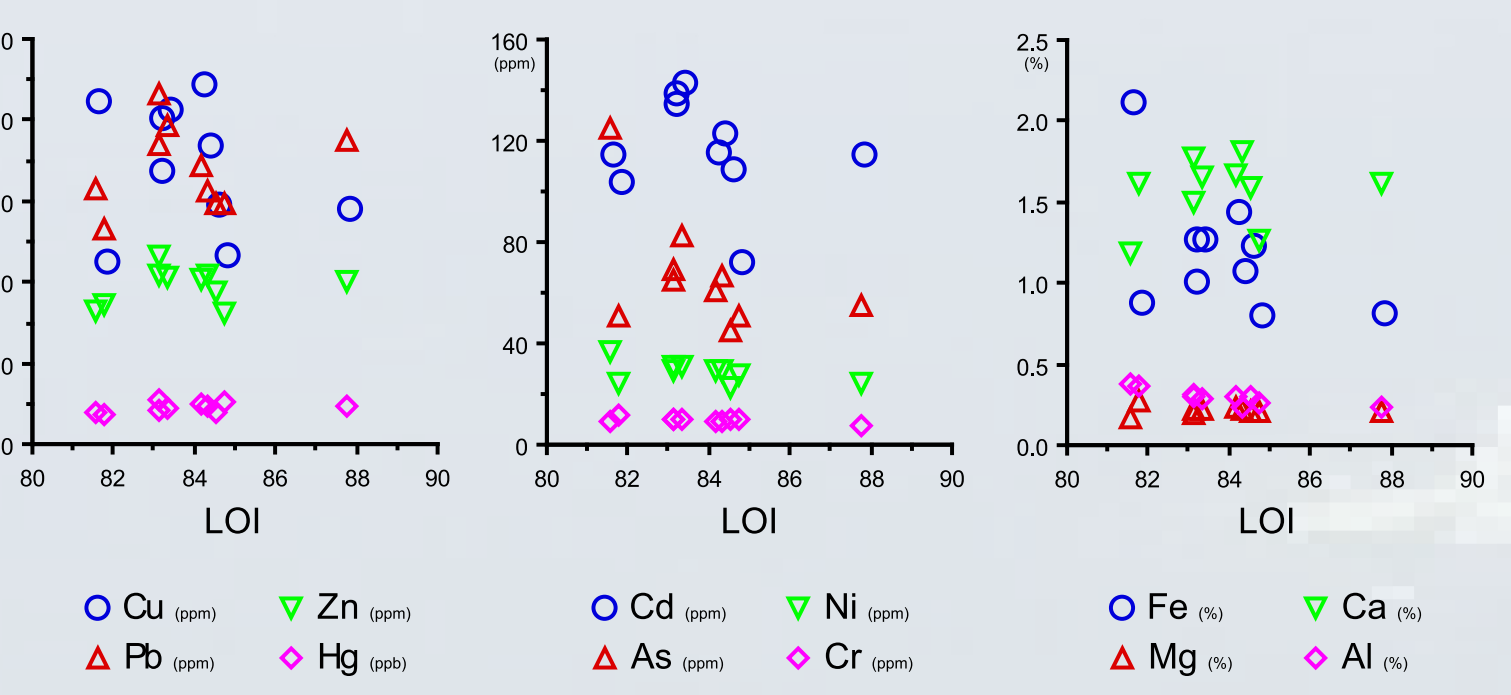


Surfaces generated using Natural Neighbour Interpolation within MapInfo and Vertical Mapper

pH vs Element Concentration in Humus



LOI vs Element Concentration in Humus



What are the Factors Controlling Trace Metal Variation

As discussed in "Choosing the Site" variations in vegetation, forest canopy, humus thickness, drainage, bedrock type, parent material, and human activity, other than the smelter operation, are minimal across the study site. A comparision of trace metal concentration to pH or LOI for humus indicate no relationships. The controlling factor for the trace metal signature is most likely smelter emissions in the form of dust particulate. What form do smelter dust in humus have and are they still the primary metal residence site?

Smelter Dust

Smelter emissions, in the form of aerosols and dust fall on trees, plants, and the ground surrounding the smelter. Through settling and/or biochemical recycling, some of the dust is retained in soil/humus, where it is subject to weathering and soil-forming processes. As part of the GSC-MITE (Metals In The Environment) initiative, the distribution of smelter dust in humus was examined to provide physical evidence for the interpretation of the anthropogenic component of geochemical maps. Smelter dust in humus was examined using a scanning electron microscope linked to an energy dispersive X-ray spectroscopy beam (SEM-EDS). Humus samples were air-dried (~30°C) and sieved to <0.425 mm. Because of surface charging, organic matter was removed by hydrogen peroxide treatment prior to microbeam analysis. This involved treating the samples with 30% hydrogen peroxide until CO^2 generation ceased. SEM microbeam images and X-ray spot detection chemistry were generated using a Cambridge S-360 SEM interfaced to an Oxford-Link eXLII EDS with mapping capabilities. Digital 748 x 568 pixel TIFF images were captured at varying magnifications with an operating voltage of 20 keV, a specimen current of 1nA, and a working distance of 25 mm.

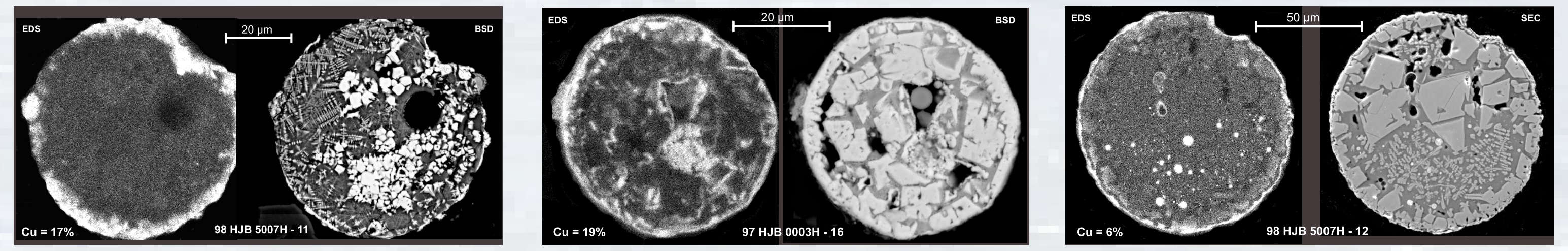
SEM Results

The anthropogenic dust displays excellent preservation indicating that weathering and soil forming process have not been significant. Dust diameters ranged from 0.5 to 427 µm suggesting that some of the material was released to the environment before the installation of electrostatic precipitators. Secondary and backscattered electron (BSE) images indicate two distinct morphotypes corresponding to angular to subrounded dust and to spherical dust. For the spherical dust five broad classes and element associations are described;

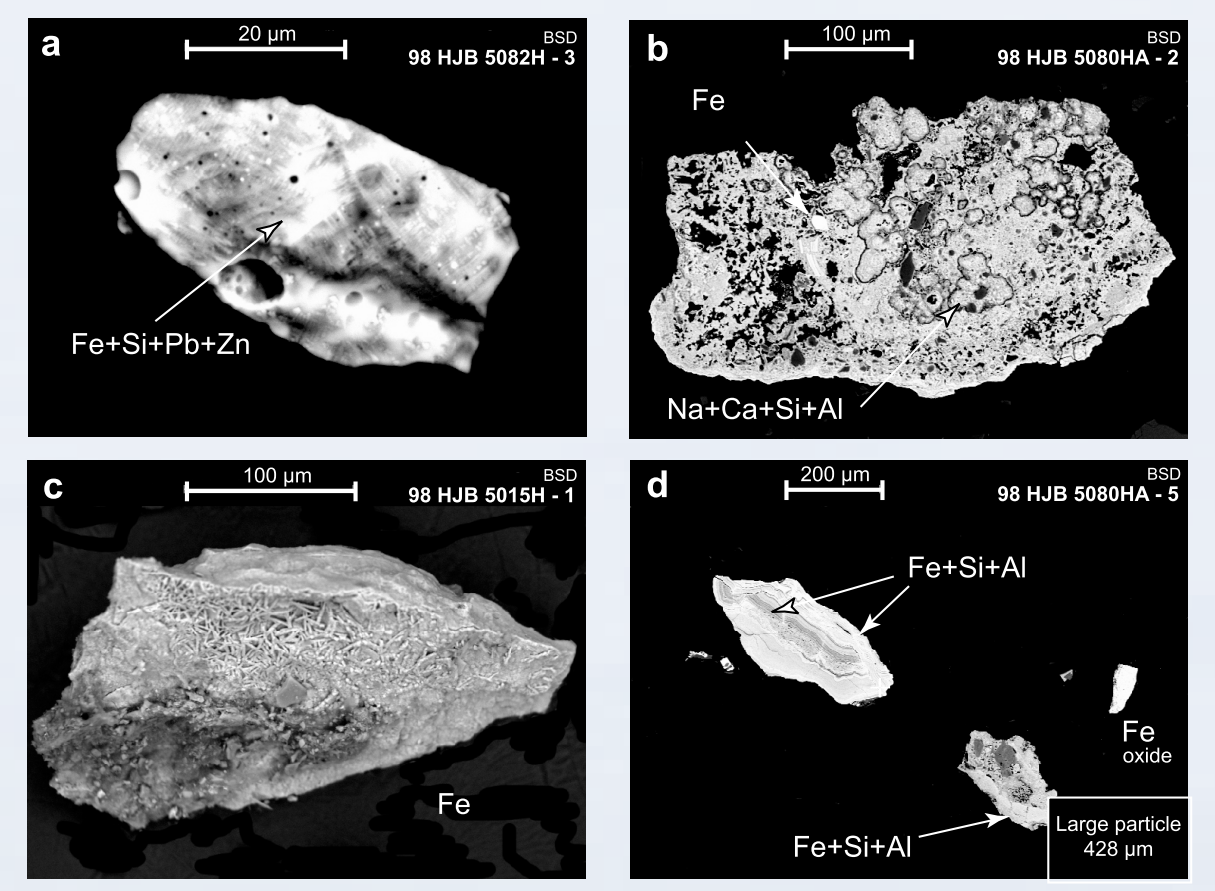
1) Plated, Fe and Fe+Si,
2) Tubular, Fe and Fe+Si+Al
3) Etched, Fe, S+Cu+Fe a matrix of Si+Al+Fe,
4) Granular to smooth, crystalline Fe with a Si+Al+Mg matrix
5) Lunar, gas bubble craters, Si+Al+Na with minor Fe

EDS Results

EDS examination of particles belonging to each class was carried out in order to determine the location and area percent of trace metal in the spherical dusts. Reults of 3 samples categorized as Class 1 - Granular are presented. Bright areas on the EDS images correspond to Cu. Bright areas on the SEM backscatter images (BSD correspond to Fe.

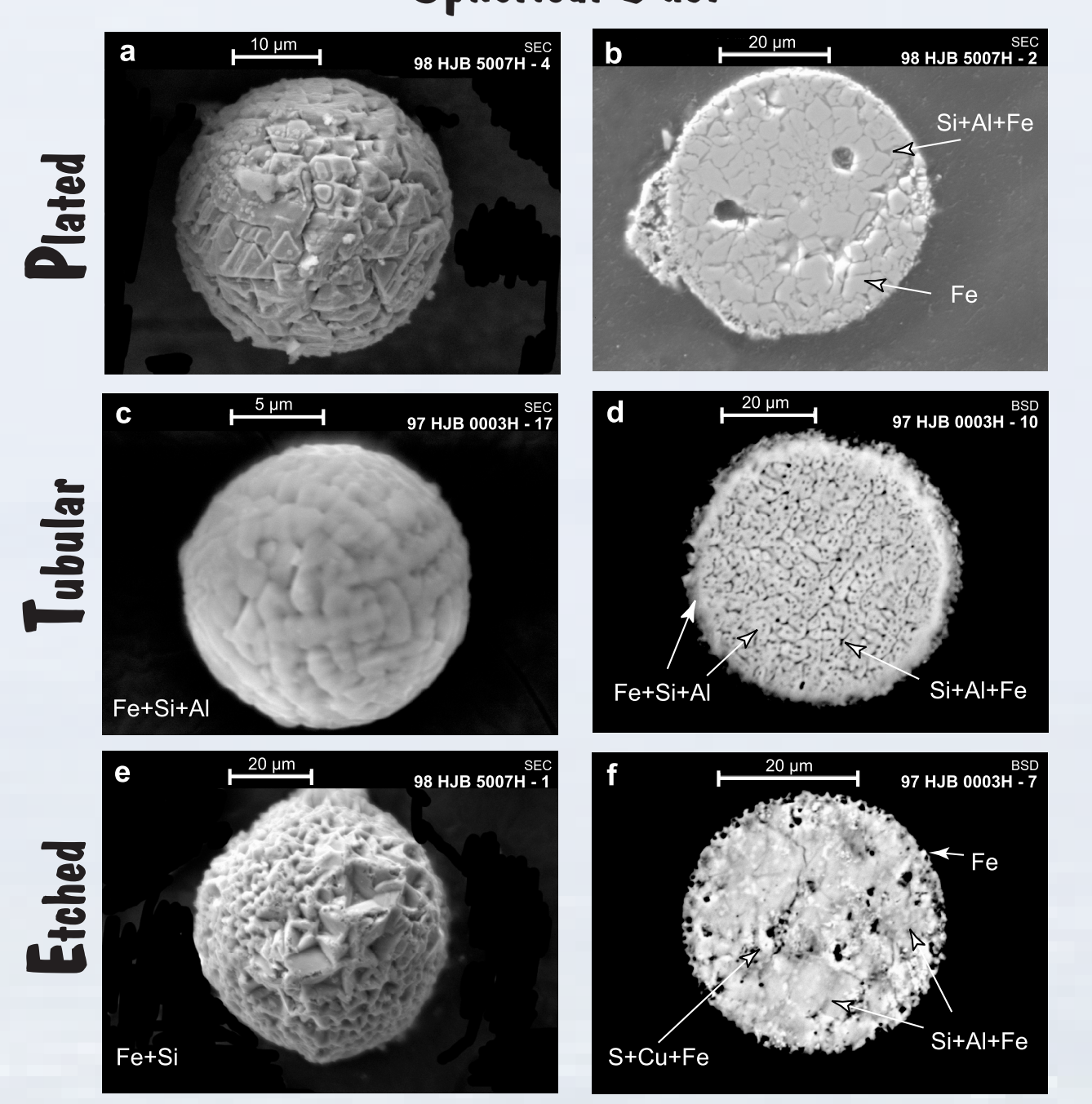


Angular to Subrounded Dust

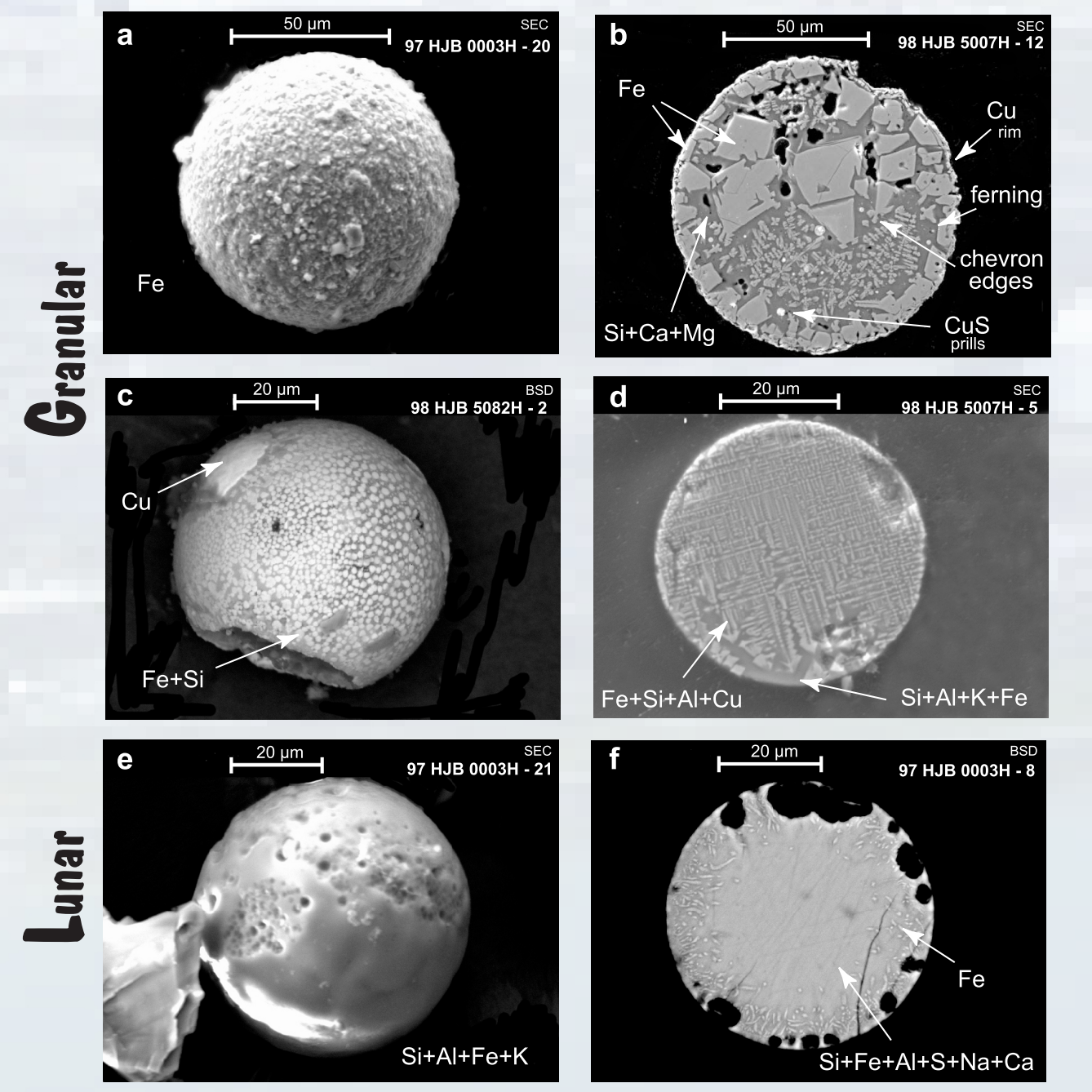


a) smooth surfaced dusts with visible gas release bubbles or craters,
b) botryoidal slag,
c) corroded surface of a angular dust,
d) multiple layered accumulation of stack release gases.

Spherical Dust



a) raised platelets on the external surface,
b) possible internal texture of agglomerated and partially melted dust,
c) dust surface is covered with short elongated tubes,
d) internal texture displays partial melting of original agglomerated dust
e) surface of dust is covered with molds of varying depths,
f) internal textures are not evident although the irregular surface mould are evident at the dust edges.



a) intact rough external surface,
b) corresponding internal textures contain 2 phases of Fe occurring as angular to subrounded particles and dendritic texture, in a glass matrix
c) intact smooth external surface with a Cu cap,
d) trellis texture in a glass matrix,
e) class 5 dust displaying spheres partly smooth and partly cratered,
f) glass matrix with Fe zones enriched towards the corroded sphere edges.

Does the Copper Add Up?
A preliminary mass balance approach

SEM examination of smelter derived dust indicates that most of the Cu determined by spot x-ray examination occurs in the spherical morphotype. A preliminary mass balance was estimated by determining the following parameters.

- Size of the particles
- Abundance of the particles
- Volume of a smelter particle
- Number of Cu-bearing particles
- Amount of Cu in a Cu-bearing particle
- Volume of Cu in a Cu-bearing particle
- Weight of Cu in a Cu-bearing particle
- Amount of Cu/ gm of sample

- How many particles are there?

During the regional soil and humus study an investigation of size and abundance of smelter-derived dust was carried out at sites varying in distance downwind from the point source. For a site located 3 km from the smelter 111 particles were found in 0.04 g of sample. Their mean radius is 5×10^{-4} cm.

- How many contain Cu?

Of 63 spherical smelter particles, Cu was detected in approximatly 50% .

- How many Cu-bearing particles are there per gram?

The number of Cu-bearing particles per gram of sample equals:
(number of particles / weight of sample examined) x 50%
111 / 0.04 g x 50% = 1388 Cu-bearing particles/g

- How much Cu is in a Cu-bearing particle?

EDS examination and image processing of 3 spherical particles from the "granular" class indicate Cu-rich areas compose 5 - 20% of the particle. Hence, in a Cu-bearing particle, the volume of Cu is estimated as 20% the volume of the particle. The volume of a particle is $4/3\Pi r^3$ $r = 5 \times 10^{-4}$ cm Volume $= 5 \times 10^{-10}$ cc:

$$V_{Cu} = 0.2 \times 5 \times 10^{-10} \text{ cc} = 1 \times 10^{-10} \text{ cc}$$

- What is the Weight of Cu in a one particle?

EDS examination indicates that Cu is often not associated with Fe, Zn, Pb, or S. For this preliminary mass balance Cu-rich areas are assumed to be Cu (s.g .8.2).
Weight of Cu in one particle (Wt_{Cu}) = s.g. x V_{Cu}

$$(Wt_{Cu}) = 8.2 \times 1 \times 10^{-10} \text{ cc} = 8.2 \times 10^{-10} \text{g}$$

How much Cu comes from Cu-bearing particles?

Weight of Cu per gram of sample =
number of Cu-bearing particles per gram of sample x weight of Cu / particles

$$Wt_{Cu/g\ sample} = 1375 \text{ Cu particle/g} \times 8.2 \times 10^{-10} \text{gm}$$

$$Wt_{Cu/gm\ sample} = 1.14 \times 10^{-6}$$

~ 1 ppm

The mass balance using smelter particles does not reflect the geochemical analyses.
Most of the Copper in humus is not currently residing in the smelter-derived dust particles.

Trace Metal Variability

The following factors ***do not*** account for trace metal variability at a site near an anthopogenic source.

- variations in vegetation,
- forest canopy,
- humus thickness,
- drainage,
- bedrock type,
- parent material,
- human activity (other than the smelter operation),
- pH
- LOI
- smelter dust particulate (as observed today).

Although emission of smelter particles is likely the primary mechanism for delivery of metal to humus, the dust particles are not the current primary resident site. Many of the particles in humus may represent slag phase (resistant) emissions.

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[1] Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario

For more information, please contact R.D. Knight (ross.knight@canada.ca)

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