Quality of Groundwater, Proceedings of an International Symposium, Noordwijkerhout, 489
The Netherlands, 23—27 March 1981, W. van Duijvenbooden, P. Glasbergen and H. van Lelyveld (Eds.),
Studies in Environmental Science, Volume 17

SEM-EDXRA MEASUREMENTS ON THIN SECTIONS OF HEAVY METAL CONTAMINATED SOIL SAMPLES FROM COLUMN EXPERIMENTS

E.B.A.Bisdom[1], G.Heintzberger[1] and P.Lagas[2]

[1]Netherlands Soil Survey Institute, POB 98, 6700 AB Wageningen, The Netherlands

[2]National Institute for Water Supply, POB 150, 2260 AD Leidschendam, The Netherlands

ABSTRACT

Scanning electron microscope-energy dispersive X-ray analysis (SEM-EDXRA) were done on cutans around mineral grains. The cutans formed from leachates without fatty acids during column experiments. Various elements, amongst which heavy metals, were measured by SEM-EDXRA. Most of these were present in the original fluids used for percolation, but others originated in the column itself.

The hardening of the heavy metal contaminated soil samples took several months longer than normal. SEM-EDXRA measurements of the soil materials in the thin sections allowed <u>in situ</u> solid chemical analysis on a micro-scale. Trace elements and elements lighter than carbon, cannot be measured with this technique. These are therefore not represented in the given figures with X-ray images and point analyses. To quantify trace elements and to analyse all chemical elements in thin sections of soils, ion microscopy (SIMS) is necessary.

INTRODUCTION

Heavy metal contaminated soil samples, formed from leachates without fatty acids in column experiments, were hardened with polyester resin. The hardening of the polluted carbonate-containing dune sand took several months longer than normal and reimpregnation was necessary. Therefore, only the first samples were in a condition which allowed the preparation of thin sections at the time this paper was written. However, the results of these preliminary light microscopic observations and electron microscopic measurements were such that an introduction of this technical approach to the problem of contaminated soils seemed to be warranted.

The reason for making thin sections of polluted soil from model experiments, described by Loch et al.(in press), was the possibility of comparing in situ microchemical measurements on solid precipitates with those from wet chemistry and done on disturbed samples. This will be possible at a later stage when all the thin sections have been studied with light and electron microscopic techniques.

METHODS

When a thin section can be made from the polluted soil, light microscopy will reveal the nature of especially the larger components. Very fine soil constituents, amorphous materials and microcrystalline minerals are usually difficult to determine and submicroscopic techniques (electron- and ion microscopy, laser microprobe mass analysis, etc) can be used to obtain the required results.

A series of submicroscopic techniques which can be applied to thin sections of soils have been developed by the Netherlands Soil Survey Institute, the Technical and Physical Engineering Research Service of Wageningen and a number of technical research centers in the Netherlands and elsewhere. We started with SEM-EDXRA (scanning electron microscopy - energy dispersive X-ray analysis (Bisdom et al., 1975), followed by a comparison of this technique with EMA (electron microprobe analysis) (Bisdom et al., 1976). Such techniques, however, do not allow the study of trace elements, which can be done with ion microscopy (Bisdom et al., 1977) or laser analysis (Bisdom et al., in press).

Quantification of a micro-area with a diameter of 300 µm was done with the ion microscope type IMS 300 (Cameca) (Henstra et al., 1980) and at present in situ microchemical analysis of trace and major elements is possible in a micro-area with a diameter of 1.5 µm (Bisdom et al., in preparation). Consequently, submicroscopic techniques now allow the comparison of chemical studies from materials in thin sections with data from wet chemistry on disturbed samples from the natural and experimental environment.

LIGHT MICROSCOPIC and SEM-EDXRA ANALYSES

In the present study only the light microscope and SEM-EDXRA have been used. Light microscopy revealed that black and brown cutans could form around mineral grains and that these were more or less concentrated in separate microlayers with a variable thickness. The cutans or skins could completely surround the sand grains or just partly coat them. The cutans comprised crystalline, microcrystalline and amorphous materials. No larger and newly-formed minerals were found in the cutans with the light microscope. X-ray diffraction data (courtesy Dr.Breeuwsma, Netherlands Soil Survey Institute) demonstrated that FeS (mackinawite) and PbS (galena) were present in the clay fraction of a disturbed sample derived from the same part of the experimental column.

SEM-EDXRA measurements were done on black as well as on brown cutans. The black cutans (Fig.1) contained most of the chemical elements, including the heavy metallic elements Fe, Ni, Cu, Zn and Pb. Iron was the element that was most often present, possibly as FeS. The brown cutans usually contained less sulphur than the black ones and possibly combined with iron to form FeS. Ni was also found in the brown cutans but Cu, Zn and Pb were often not measurable. It was difficult to obtain SEM micrographs from the usually amorphous brown cutans. This may indicate a poor crystallinity of the material in the brown cutan, as was also found during examination with the light microscope. Other elements present were: Al, Si, Cl, K and Ca.

Elements like Al and Si in cutans were already in the soil and not part of the fluids used for these percolation experiments. These elements are present in the soil itself. If they form no part of the protrusion of the primary mineral underneath the surrounding cutan, the Al and Si could well be present in clay minerals, microcrystalline materials or amorphous materials.

CONCLUSIONS

Heavy metallic elements (Fe, Ni, Cu, Zn and Pb) from leachates in column experiments were usually concentrated in the black cutans. Only Fe and Ni were usually present in the brown cutans. Sulphur was found in larger quantities in the black rather than in the brown cutans. FeS (mackinawite) and PbS (galena) were represented according to XRD data. The present results are preliminary and given to demonstrate that in situ light and electron microscopic techniques can play a role in pollution studies. Minute compositional changes can be measured over very small distances in a thin section. Ion microscopy and laser analysis allow the study of trace elements. Submicroscopic techniques may help the interpretation of wet chemical data when these are compared with in situ microchemical data. Conversely, however, the chemistry of solids is greatly helped by the experimental data of wet chemistry. A combination of both disciplines will allow a practical and theoretical approach to a number of problems associated with soil pollution.

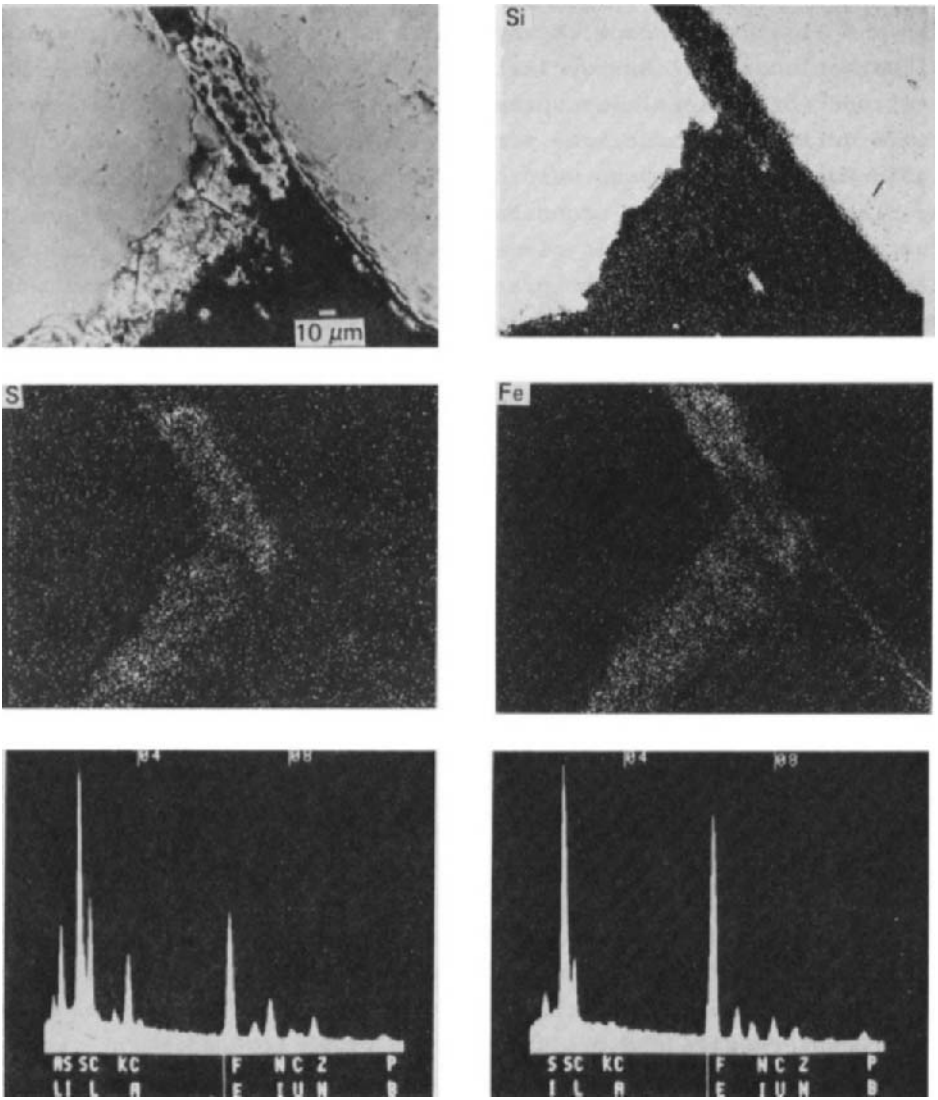

Fig.1. Backscattered electron scanning image of black heavy metal-contaminated precipitates (cutans) between two quartz grains. Larger concentrations of white in the three X-ray images give the distribution of Si, S and Fe. Two point analyses indicate compositional differences, including heavy metallic elements, in the cutans.

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