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2. Application of Microchemical Research in Environmental Burdens Investigation

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Abstract: The presented work offers an overview of the microchemical applications of solid and non-cohesive, synthetic and natural materials realized by electron microanalysis. Microchemical study of materials for the purpose of research and monitoring of environmental burdens aims to identify potential contamination in the source area or its spread in the natural environment. In addition to the direct identification of the chemical elements of interest or mineral phases, the results of the electron probe micro-analysis analysis provide information on the physical and chemical stability conditions of the system under investigation. The work gradually presents solved examples selectively for various types of materials such as waste sludge, metallurgical waste, organic material, sands, ash, soils and river sediments. The analysed materials are in natural conditions in direct interaction with surface waters, atmosphere and biosphere and their interaction determines various variants of migration of pollutants in hypergenic environment. Migration is not always controlled by the active form of transport in the aquatic environment, as demonstrated by several examples. Migration of pollutants by mechanical or aeolian form of transport is frequent and may be unidentifiable by classical hydrochemical monitoring methods. The use of a microchemical study for the analysis of solid materials in a hypergenic environment utilizes their natural physical and chemical properties with respect to sorption capacity and their function as a natural geochemical barrier in the area of the migration route. The systematic analysis of the organic material of decaying plant tissues and the autogenous phases of FeOOH proves their effective usability as natural time-sensitive monitoring probes throughout their lifetime. Identifying elements of interest or pollutants on autogenous minerals directly identifies the distribution of contamination in the environment and their form of migration. The knowledge gained from the results of the microchemical EPMA study serves as a direct basis for the reconstruction of distribution, the form and extent of migration and the prognosis of the development of contamination in the environment.

Key words: microchemical investigation, EPMA analysis, environmental burdens

2.1 Introduction

Tackling the problem of environmental burdens “EB” or environmental damage “ED” is the forced response of society to the negative environmental impact of industrial and agricultural activity. The entry of contamination into the natural system can be simple, but its interaction with environmental components is virtually always complex. An example is the entry of contamination into groundwater and surface waters, which are in direct interaction with the rock environment, soils and with the inseparable part of the biota present everywhere. There is a set of direct links between environmental components that control the further chain of direct and feedback relations.

The basic methods for the investigation and monitoring of environmental burdens are chemical research based on full-surface analyses of the substrate in which contamination is assumed or identified along with groundwater and surface water analyses. The monitoring phase itself is based primarily on the analysis of the surface and groundwaters, as these are the main transport medium for the spread of contamination in the environment. The practice of the solution itself is pragmatic, but it does not cover the solution of the distribution of contamination in the contaminated environment and it cannot solve the physico-chemical stability of the contaminated source and its surroundings. An important aspect of the investigation and monitoring of the EBs is monitoring itself, which is intended to provide answers to the issues of contamination mobility and spread. The problem lies in the complexity of natural processes, since the movement of contamination does not have to take place only in the active form of transport of dissolved substances in water, but in a form as, for instance, mechanical transport.

The mechanically transported contamination can often be highly effective, but may not be identifiable by hydrochemistry.

Part of the above shortcomings of the research and monitoring of the EBs can be solved by targeted petrographic work and the application of electron microanalysis “EPMA” (Electron Probe Micro-Analyser).

The application of the EPMA microanalysis to solve the problem of environmental burdens enables microchemical study of rocks, soils, stream sediments, synthetic solid waste or even organic material. The aim of this paper is to provide an overview of the possibilities of applying the EMF study of solid materials on examples that were solved within the tasks focused on the EBs monitoring at the State Geological Institute of Dionýz Štúr (Kordík & Slaninka et al., 2015; Slaninka et al., running project).

2.2 Methods

Application of the EPMA analysis is oriented on chemical analysis of solid materials and is not intended for water or gas analysis. The EPMA microanalysis is designed for analysis of qualitative and quantitative content of chemical elements. The EPMA analysis fails to analyse light elements with an atomic number less than lithium, making it impossible to analyse crystal-chemically bound -OH/H_2O. Based on the analysed chemical composition of the solid phase, it is possible to identify a particular type of chemical phase or mineral and, in the case of a known crystallographic structure, to calculate the corresponding crystal-chemical formula.

Solid natural materials occur in several natural forms, such as solid compact rocks, minerals or glass. The solid phase is often present in the form of non-cohesive mixtures such as sludge, sands, dust aerosols or organic material.

The nature of the analysed material determines which preparation method is appropriate for the EPMA analysis. For compact materials, samples are treated directly into the form of a polished cut while bulk materials (soil, sludge) are cemented with epoxy resins to achieve compactness.

If needed, a 10 – 30 μm wide electron beam analysis can be used to address the distribution of chemical elements in the sample, resulting in an average analysis of some very fine objects. The use of a wide analytical beam is sometimes necessary due to the fineness of the analysed material.

The EPMA analysis is limited by electron beam parameters that can be focused on a circular space with a diameter of 1 μm. Analysed objects ranging in a nanoscale <1 μm can only be analysed as a mixture.

The samples were analysed at the SGIDŠ electron-optic methods workplace using BSE analysis of back-scattered electrons and EDXA energy dispersive X-ray spectroscopy microanalysis and chemical microanalysis using CAMECA SX100 electron microanalyser, hereinafter the EPMA "electron microprobe".

Analytical conditions of measurement of chemical composition of sulphides are following: accelerating voltage 25 keV with electron beam current of 10 nA. The following chemical standards were used: S, Fe, Cu / $CuFeS_2$, Pb / PbS, Zn / ZnS, As / GaS, Cd / Cd, Ag / Ag, Mn / Mn.

The analytical conditions for measuring the chemical composition of silicates and oxides were following: an accelerating voltage of 15 keV and electron beam current 20 nA.

The width of the analytical electron beam used was adapted to the analysed object, i.e. for phase analysis a beam with a diameter of 5 μm was used and for analysis of the area of fine-grained aggregates 15 – 30 μm.

The following chemical standards were used: F / LiF, Na / albite, Si, K / orthoclase, Al / Al_2O_3, Mg / forsterite, Cl / NaCl, Ca / wollastonite, Ti / TiO_2, Fe / fayalite, Mn / rhodonite, Cr / Cr, Ni / Ni, As / GaAs, S, Ba / baryte, Pb / $PbCO_3$, Cu / Cu, Zn / willemite, Sr / $SrTiO_3$, P / apatite.

2.3 Overview of applications of the EPMA analysis in research and monitoring of EBs

The application of the EPMA microanalysis in dealing with the environmental burdens must necessarily be based on the initial field research of the site and the nature of the assumed or identified contamination. In case of contamination with potentially toxic elements such as As, Pb, Zn, Cu, Sb, Co, Cr, Ni, Hg, it is important to target systematic sampling of suitable material, while the sampling itself must respect the concept of geochemistry of the landscape. The sample material should cover the source material of the contamination as well as the identified migration routes in and around the EB area. In the case of an unknown source of contamination or the location and extent of the contaminated area, sampling may be oriented as a survey.

A variety of natural or artificial synthetic materials can be encountered during sampling and subsequent EPMA studies. Each type of sample has its own specific pros and cons and can provide a variety of information about the distribution of contamination, migration or physico-chemical stability of the system. Therefore, the individual types of material are described separately systematically with a short overview obtained during our practice (Kordík & Slaninka et al., 2015; Demko, Šefčík & Luptáková, 2015; Šefčík & Demko, 2015; Demko, Luptáková & Šefčík, 2016; Demko & Šefčík, 2018; Šefčík & Demko, 2018; Šefčík & Demko, 2019).

SAMPLING for microchemical research to supplement full-mineral analysis of solid materials and waters must meet the principle of the geochemical relationships on the location or the concept of the landscape geochemistry (Darnley et al., 1995; Fortescue, 1992; Pereľman, 1975). In a practice, it is always important to respect the real conditions of the area of interest with regard to natural or artificial characteristics of the environment. The identification of the assumed or identified source is the sampling focused on the primary source material, such as waste sludge (Fig. 2.1-A), macroscopically visible mineral products, which are exotic in the area of interest, or strange (Fig. 2.1-D). Sampling should be directed to a material that is characterized by suitable properties and acts as a natural geochemical barrier in the landscape geochemistry (Fig. 2.1-C).

Sampling should be directed towards zones that are direct migration routes of the analysed pollutants or act as communication transport zones between different geochemical entities in the country (Fig. 2.1-B). The sample material that can be analysed by the EPMA analysis can be solid and compact, or not solidified with varying degrees of disintegration.

Samples that are significantly non-solidified or disintegrate can be cemented prior to preparation of the analytical specimen in a manner that preserves primary texture and structural relationships. For samples that are primarily non-cohesive, loose (sands) or primarily plastic (clays, sludges), the specimen can also be cemented with epoxy resins. As a sample material we used even organic material – plant tissues, at a variable stage of decomposition. If there is a suspension in the water samples, it is possible by means of evaporation and filtration to separate the suspension, which can be adjusted for the EPMA analysis similarly to loose and plastic materials.

Examples of various materials sampled in the EBs monitoring are shown in Fig. 2.1.

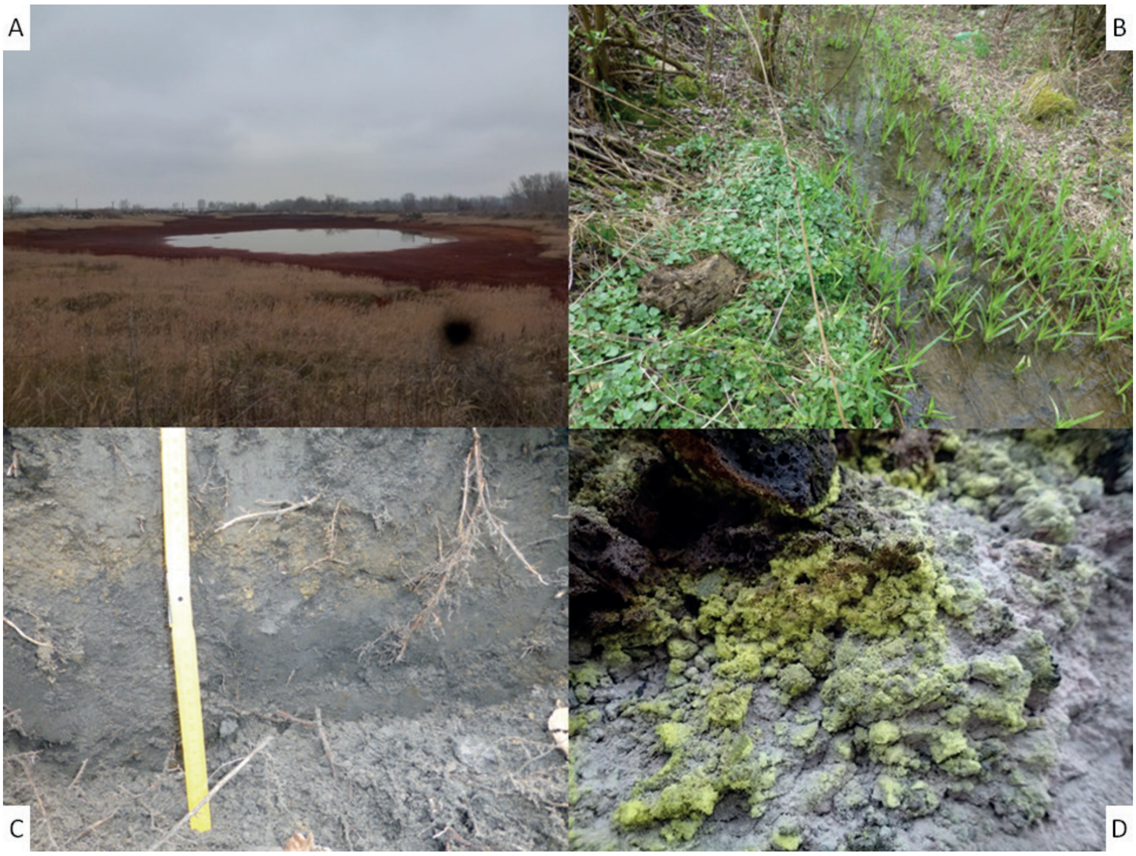
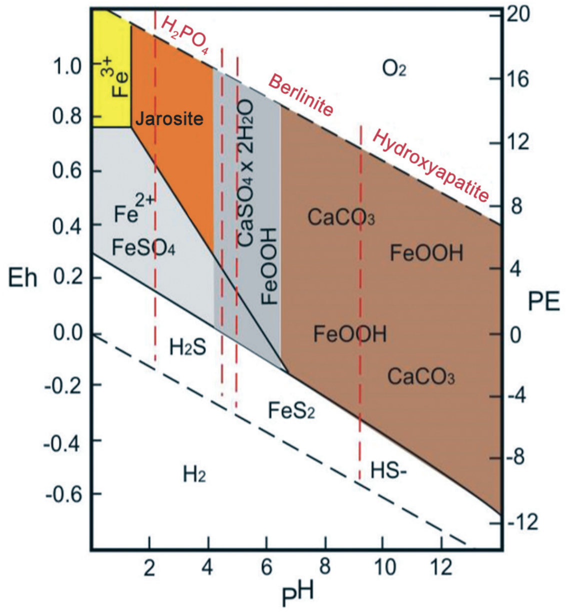


Fig. 2.1 Examples of various materials sampled within the EBs monitoring.
A) The Šulekovo tailings pond in Hlohovec as an example of the tailings pond for galvanic waste. The stored sludges containing Pb-Zn-Sn are in constant contact with atmospheric air and surface waters. The conditions in the tailings pond itself determine the physico-chemical properties of the environment influenced by surface water level fluctuations, sludge drying effect and wind erosion function. Fluctuations in pH/Eh properties of the environment directly determine the stability of the minerals that control the mobility of Pb-Zn-Sn within the vicinity of the tailings pond.
B) Artificial stream bed in close contact with the flotation ash dump in Trnové near Žilina. The brook line is the main migration path of leached arsenic from the landfill environment and ensures its contact with the final recipient of the Váh River. Stream sediment analysis can directly determine the potential migration and its intensity by the surface waters of the stream.
C) Detail of soil probe in landfill material of fly ash at the landfill in Trnové near Žilina. The soil probe shows the existence of a ferric horizon with the autogenous minerals FeOOH, which are good natural monitoring probes to identify the presence and migration of potentially toxic elements, e.g. such as As.
D) Efflorescence of chromium salts in the landfill of waste material after special metallurgical production in Istebné, Orava. The presence of chromium salts indicates an active reaction of the chromium-containing landfill material with the meteoric waters percolating through the landfill material. The reaction and migration of the metal is already identifiable during field inspections by means of strong colour contrast to the surrounding environment.

INDUSTRIAL WASTE SLUDGE is characterized by several principal properties.

- The sludge material is very fine by granularity. It consists of mineral and amorphous phases, which reach often the size limits of microchemical EPMA measurement, namely fineness and lack of cohesiveness. In the case of a limiting size of suitable material for microchemical analysis, it is appropriate to use a wide diameter analytical electron beam. The results obtained will correspond to the mean volume analyses for the analysed space determined by the parameters of the analytical beam.
- The absence of sludge cohesiveness is due to the presence of porous water and the small size of the sludge particles. For the preparation of analytical specimens it is necessary to dry up the sludge material and then cement it with epoxy resin. Impregnation with an epoxy resin results in the formation of a solid material suitable for the production of the analytical specimen (polished section), but on the other hand the impregnation itself may cause a fine resin overlap of the sample under study with a negative effect on the quantitative aspect of the analytical result.
- The sludge material itself is physically and chemically metastable, which is affected by H_2O saturation controlling O_2 activity. Water level fluctuations in sludge ponds or marshes can change the Eh conditions and hence the sludge system stability. A similar process is encountered in the treatment of the sludge material sample, where increasing the drying temperature and subsequent

dehydration alter the physical character of the sample. However, the controlled treatment is naturally conservative against changes in the mass of the elements analysed.



An example of sludge material analysis is the EPMA microanalysis of the sludge waste from electrochemical production (galvanization) of the Šulekovo sludge pond near Hlohovec (Fig. 2.1-A and Fig. 2.2). Systematic EPMA analysis identified amorphous phosphates, gypsum $CaSO_4x2H_2O$, and FeOOH more closely identified by Raman spectroscopy as goethite in the samples (Demko, Luptáková & Šefčík, 2015). Significant contents with average Pb(0.76)-Zn(1.2)-Cu(0.7) wt% were identified in the mixture. The average goethite contents analysed reached Pb(0.4)-Zn(1.0)-Cu(0.2) wt%. Microchemical study, in addition to contamination composition and distribution, made it possible to reconstruct the phase system Ca-Fe-SO_4-PO_4-CO_3, which corresponds to the dynamic evolution from acidic oxidation conditions Eh > 0.4 and pH < 4 towards conditions Eh < 0.4 and pH > 6.2 (carbonate precipitation), Fig. 2.2. Reconstruction

Fig. 2.2 Reconstructed physicochemical Eh-pH conditions of the Ca-Fe-SO_4-PO_4-CO_3 Fe-sludge phase system in the Šulekovo-Hlohovec tailings pond (Demko et al., 2016). EPMA identified Pb-Zn-Cu contamination is controlled by the stability of goethite FeOOH and amorphous phosphates.

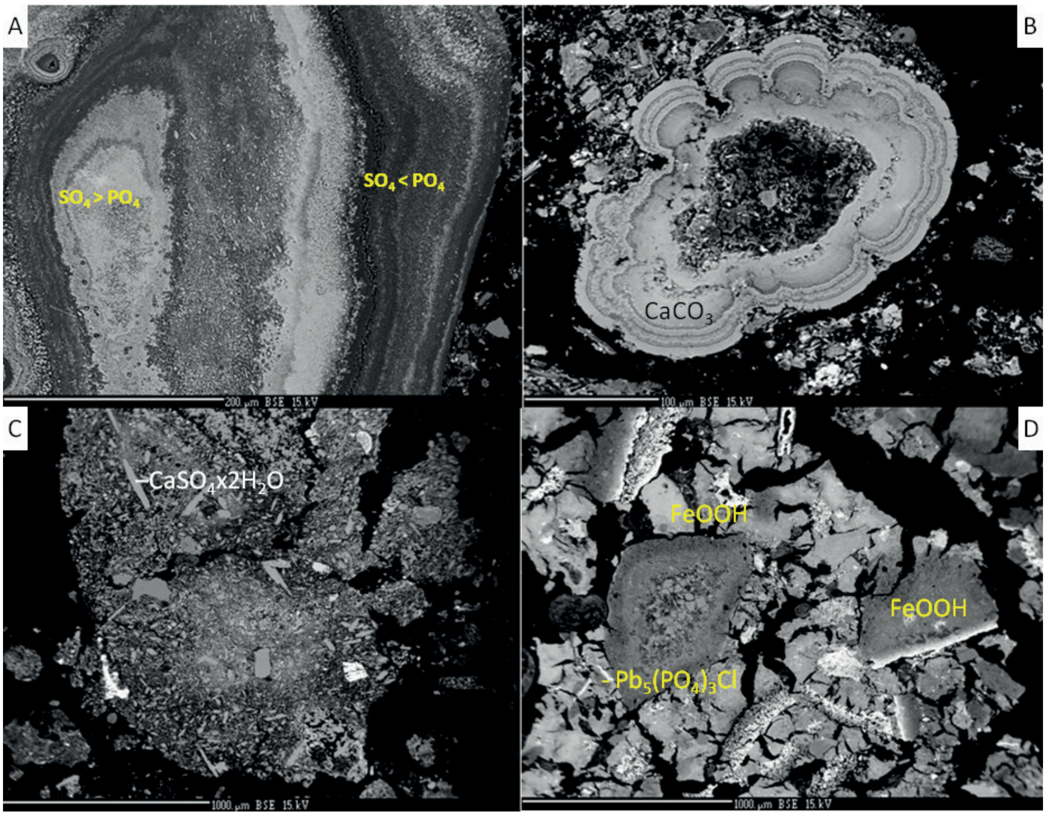


Fig. 2.3 BSE images of basic construction parts of sludge material from the sludge pond Šulekovo – Hlohovec (Demko et al., 2016). A) Oscillatory stratified concretion consisting of a mixture of amorphous phosphate (P = 13.14 – 11.02 wt%) and sulphate (S = 0.7 – 0.4 wt.%). Light stripes are richer in sulphates. EPMA analysed Pb contents < 0.09 wt%; Cu = 0.12 – 0.07 wt%; Zn = 0.17 – 0.13 wt%. B) Zonal geodes of autogenous $CaCO_3$, which are the product of the precipitation of carbonate from solutions percolating through the drainage system of the sludge material. $CaCO_3$ precipitation demonstrates the function of the dissolution – transport and $CaCO_3$ precipitation in the respective Eh-pH physical conditions of Ca-carbonate stability. C) A mixture of detritic quartz sand and feldspars that are cemented with a sludge mixture containing autogenous FeOOH and sulphates. Thin needle-like crystals form gypsum $CaSO_4x$-$2H_2O$ whose presence and morphology demonstrate physical Eh-pH conditions in the gypsum stability field. D) Goethite cementing mixture with $Pb_5(PO_4)_3Cl$ phosphomimetite pale rims. EPMA contents analysed for Pb (0.54 – 0.09), Cu (0.12 – 0.06) and Zn (1.2 – 0.12) wt% are representative Pb-Zn-Cu contents bound to the FeOOH phases. Phases of FeOOH, part of which is formed by goethite (identified by Raman spectroscopy), are the basic reservoir of Pb-Zn-Cu in sludge material in the tailings pond Šulekovo – Hlohovec. The identified fact shows that the stability of the source FeOOH is the basic factor determining the control of Pb-Zn-Cu migration in the tailings pond.

of natural physico-chemical conditions determines the simultaneous stabilization of sludge waste at the Šulekovo-Hlohovec tailings pond, which may be disrupted by external intervention into the system.

BSE images of the matrix parts of the sludge material from the Šulekovo – Hlohovec tailings pond are presented in Fig. 2.3 (Demko et al., 2016).

METALLURGY WASTE MATERIAL is surprisingly one of the most problematic wastes ever. Waste slag material is generally considered to be "clean" and "inert" and is therefore widely used as a "clean" and "inert" dump for roads or replacing building stone. It is likely and possible that most slag waste is "clean and inert", but this assumption applies only to the ideal metallurgical treatment and high efficiency of metal extraction from the ore being processed. Systematic research of the slag material, which was legally exported as a heap material to the old tailings ponds sites, or just as a random part of landfills without identified origin, showed that metallurgical slag waste often reaches concentrations of Pb, Zn, Cu, Ni, Cr, Sb close to the those of deposits. In addition to the identified Cr-Fe or Ni-Fe alloys, the sulphides of Pb-Zn-Cu-As or pure Sb, Cu, Sn are often identified. The slag material is loose-deposited in an environment where it interacts with meteoric waters. Hypergenic weathering of metastable synthetic material leads to the dissolution and release of potentially toxic elements into the natural ecosystem. The danger of metallurgical waste is compounded by the frequent presence of sulphides, which in the course of weathering produce H_2SO_4, which catalyses further dissolution. Under suitable conditions, an avalanche-like reaction can occur, which can result in extensive weathering and acidification of the environment. A few case-study examples are presented in Figs. 2.4-A, B, C, D.

ORGANIC PLANT MATERIAL is available in the natural environment virtually everywhere, where plants are available. Based on systematic EPMA research of soils, sludge material and stream sediments, in the scope of solving tasks related to organic monitoring, we developed an application based on EPMA analysis of decaying plant tissue. The plant tissues in soils or stream sediments are subject to natural decomposition. Decomposition of plant tissue leads to disruption of the plant's cell structure and degradation of highly organized carbon

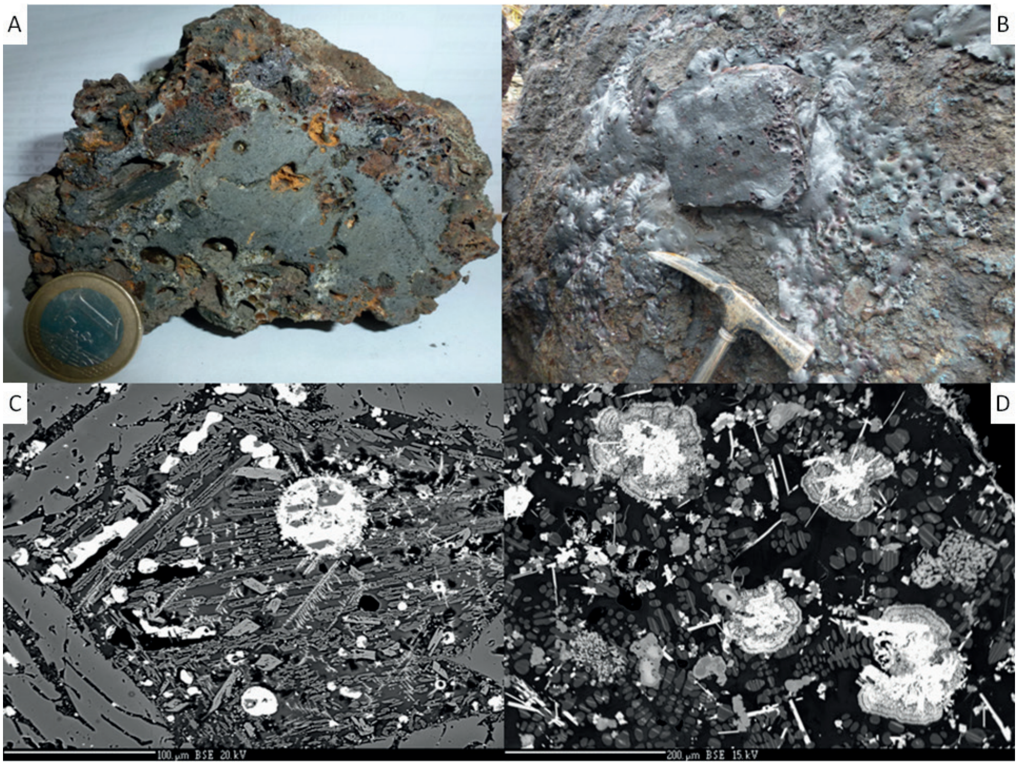


Fig. 2.4 Examples of investigated waste materials from metallurgy. A) Inside view of the split slag deposited in the Lintich tailings pond. Meteoric water, which infiltrated through the open pore space, caused the dissolution of Pb, Zn, Cu sulphides to form a solution of H_2SO_4, and consequently an overall alteration of the silicate slag. Decomposition of metastable silicate glass and sulphides releases Pb, Zn, Cu, As ions further into the environment (Demko et al., 2015). B) The metallurgical cast slag as a result of the sintering of molten waste material is a source of Cr, Ni, Pb, Zn, Cu, As, Sb released from the waste in hypergenic weathering processes. Kovohuty – Krompachy. C) The BSE image of the metallurgical slag as a detail of the oxidized material in Fig. 2.4-A. The metallurgical slag contains skeletal crystals (Zn-Fe-Mg)SiO_4, sulphosalts (Pb-Zn-Cu-Fe)S (white) and silicate interstitial glass (dark grey). EPMA identified levels in sulphosalts reach values of Pb (67 – 0.17) wt% and Zn (55.4 – 0.6) wt%. Interstitial silicate glass achieves Pb(6.0 – 3.9) wt% and Zn (4.7 – 3.4) wt%. Pb + Zn interstitial glass as well as Pb-Zn-Fe sulphosalts are both markedly unstable phases under conditions of hypergenous weathering. Interaction with meteoric waters dissolves silicate glass and oxidizes sulphides with the concomitant production of an aggressive acidic solution capable of triggering the domino effect of altering and releasing Pb, Zn, Cu into the surrounding environment. D) Light crystals $CuSO_4x5H_2O$ (chalcantite) with concentrically zonal rims as a product of dissolution of Pb-Zn-Cu sulphides in metallurgical slag in metal waste – Krompachy. The formation of secondary sulphates demonstrates the physico-chemical instability of metallurgical waste as a source of potentially toxic elements Cr, Ni, Pb, Zn, Cu, As, Sb (BSE image).

polymers containing naturally bound biogenic sulphur and phosphorus. The degradation of the organic system leads to an increase in active ion-exchange positions in the organic tissue. The release of phosphorus from the organic structure isolates the phosphate ions into separate amorphous phosphate aggregates. Degradation reactions of organic matter actively reduce the activity of O_2 in the environment, thereby catalysing the precipitation of FeS and FeOOH compounds. The increase in active ion exchange centres produced by the mixture of phosphates and FeOOH phases results in the formation of a highly effective organic sorbent. Examples of analysed plant tissue at different stages of degradation are shown in Figs. 2.5-A, B, C, D.

Due to its high sorption capacity and sorption affinity for a wide range of elements, the decomposing material of plant tissues is a natural monitoring probe. A basic condition for the functioning of the plant tissue as a "monitoring probe" is a contact with a percolating aqueous solution which can serve as a transport medium. In the case of the presence of actively migrating elements in aqueous solution, sorption to the decaying organic material occurs. Positive identification directly indicates environ with sorbed Pb, Zn, Cu, Cr, Ni, As, Sb as a migration path of contamination spreading or as an accumulation area.

The application of the EPMA analysis of plant tissues only works at the stage of tissue decomposition at a time when the primary structure of the tissue begins to lose its structure (Figs. 2.5-A, D). For freshly withered away plant tissues without signs of tissue morphology degradation, the analyses were not successful.

In case of negative identification of contamination on degraded plant tissue, the result is very successful as it shows that no water carrying contamination flows through the area with the analysed organic material. Decomposing plant tissues can be active in the natural environment as sorbent geochemical barriers for about 2 years. Negative analytical values may be interpreted in such a way that no contamination was present in the close vicinity, e.g. for 1 year back! The EPMA method for degraded plant tissues monitoring is very useful and very cheap compared to systematic sampling and water analysis. The absence of tissue contamination means no contamination, as opposed to zero analytical contamination values in waters, which can be interpreted as seasonal fluctuation in the style: "*contamination leaked out yesterday*".

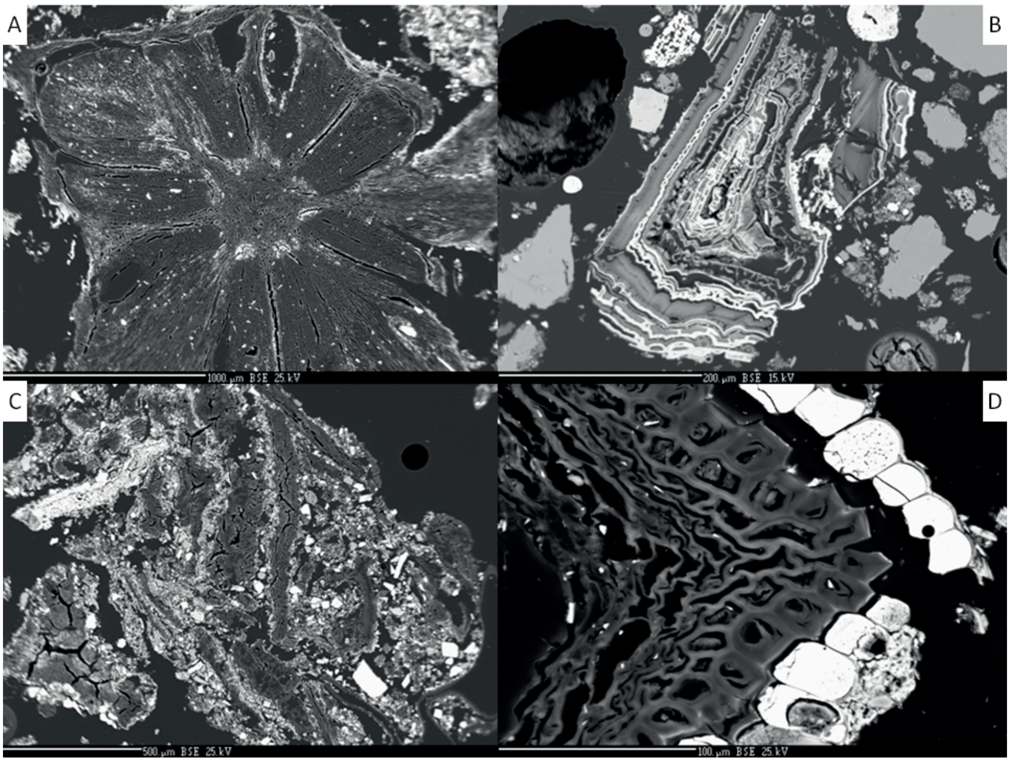


Fig. 2.5 Examples of analysed plant tissue at different stages of decomposition
A) Detail of flowering plant in middle stage of decomposition (decay). The surface of the plant tissue loses its morphology and the chemically identifiable organic material is transformed into complicated branched macromolecules with a large number of active ion centres suitable for bonding with the Pb, Zn, Cu, As, Co, Sb elements present in the environment. Originally organically bound sulphur and phosphorus form their own phases of the type -S-Fe-S-, -(PO_4)-, which contribute to the sorption potential of the decaying plant tissue (light streaks in the photograph). Location – Markušovský potok Brook, stream sediment, BSE image. B) Detail of decomposed plant tissue whose original structure is replicated by autogenously precipitated FeOOH or FeS (white bands). The organic material itself lost its original structure. Analysed contents of Cu (3.34 – 2.15), As (0.16 – 0.15), Sb (0.84 – 0.16) and Fe (43.1 – 14.6) wt%. Location Krompachy, BSE image. C) Rotten stems and tissues of decaying plants at an advanced stage of decay. The light flanges consist of the FeOOH and FeS phases, the precipitation of which was catalysed by the surface of the decaying plant tissue. Analytically identified contents of As (2.1 – 0.07), Cu (1.24 – 0.53), Sb (0.47 – 0.2), Fe (39.61 – 1.39) and S (3.0 – 0.23) wt% in organic material demonstrate effective sorption of migrating As, Cu, Sb on organic material and the role of decaying organic material as a temporary geochemical barrier. Location – Markušovce, BSE image (Demko & Šefčík, 2018). D) Detail of the plant tissue in the middle stage of decay, where the relict morphology of the cellular structure of the tissue structure still can be observed. The void cellular spaces at the edge of the decaying tissue (contact with the solutions) are filled with the autogenous phases FeOOH and FeS (white). The analysed contents are in the intervals of Fe (51.1 – 28.2), S (0.69 – 0.17), P (0.11 – 0.03), Co (0.05 – 0.04), As (0.66 – 0.44) and Sb (0.22 – 0.05) wt%. Location – Markušovce, BSE image.

SANDS

As sands we understand a non-cohesive aggregate of rock and mineral detritus with a size corresponding to < 2 mm. An important aspect is the absence of clay. Sand is a frequent natural sediment of stream sediments, or it can be produced as a product of geochemical heavy mineral prospecting with special targeted sediment sampling. Due to its non-cohesive and loose character, the EPMA analysis requires the preparation of a specimen that involves cementation with an epoxy resin. The chemical composition of the sand determines the modal representation of the detritic phases present. The EPMA analysis of sand is of fundamental importance when assessing the impact of mechanical migration of monitored elements or minerals when dealing with environmental geochemistry.

Despite the significant quantitative extent of mechanical transport and substance migration, systematic sampling of water for hydrochemical purposes is preferred in the EBs monitoring. It should be stressed that the absence of analysed elements in waters does not automatically mean a lack of element migration in the environment. The elements or their phases efficiently migrate also by mechanical transport and classical hydrochemistry is often blind to mechanical migration.

An example of the EPMA analysis for the needs of environmental burden survey is the analysis of wasted sand in the wider vicinity of a tailings pond in Markušovce, which is used for the storage of flotated waste after the treatment of sulphide ores. Images of the sand analysed are shown in Figs. 2.6-A, B, C, D. Qualitative and semi-quantitative composition of sand was evaluated by the EPMA analysis. The results showed that part of the stored flotation treated sand contained tetrahedrite, which served as a source mineral for mercury extraction. The tetrahedrite is unstable as a sulphide under hypergenous conditions and is subject to oxidation and dissolution. It is a paradox that large volumes of flotation-treated sand are discarded outside the tailings pond (systematically monitored by hydrochemistry) and are ready for construction as an inert raw material.

Another example of the use of the presented EPMA qualitative analysis of sands is the identification of scattered baryte and siderite in agriculturally used soils in the vicinity of the Markušovce tailings pond. The presence of the identified baryte and siderite in the soil suggests aeolian transport of the flotation-stored material from the tailings pond to the surroundings by wind action. The flotated material is exposed at the tailings pond, thereby subjected to the direct wind erosion.

FLY ASH

There are numerous ash dumps in Slovakia as a result of the massive use of fossil fuels in heating and power plants. Given the higher contents of sulphophilic elements in fossil fuels such as Pb, Zn, Cu, As, Cd, it is assumed that these increased concentrations are transformed into fly ash as residues.

In particular, carbon black and Si-Al glass beads, which are the product of melting the aluminosilicate minerals present in coal during high-temperature combustion, contribute to the ash composition (Figs. 2.7-A, B, C, D). The presence of sulphides, as primary minerals of fossil raw materials, is most unlikely because sulphides, like aluminosilicates, are incapable of existence during combustion. Systematic analysis of fly ashes from various fly ash dumps from Slovakia shows a negative answer:

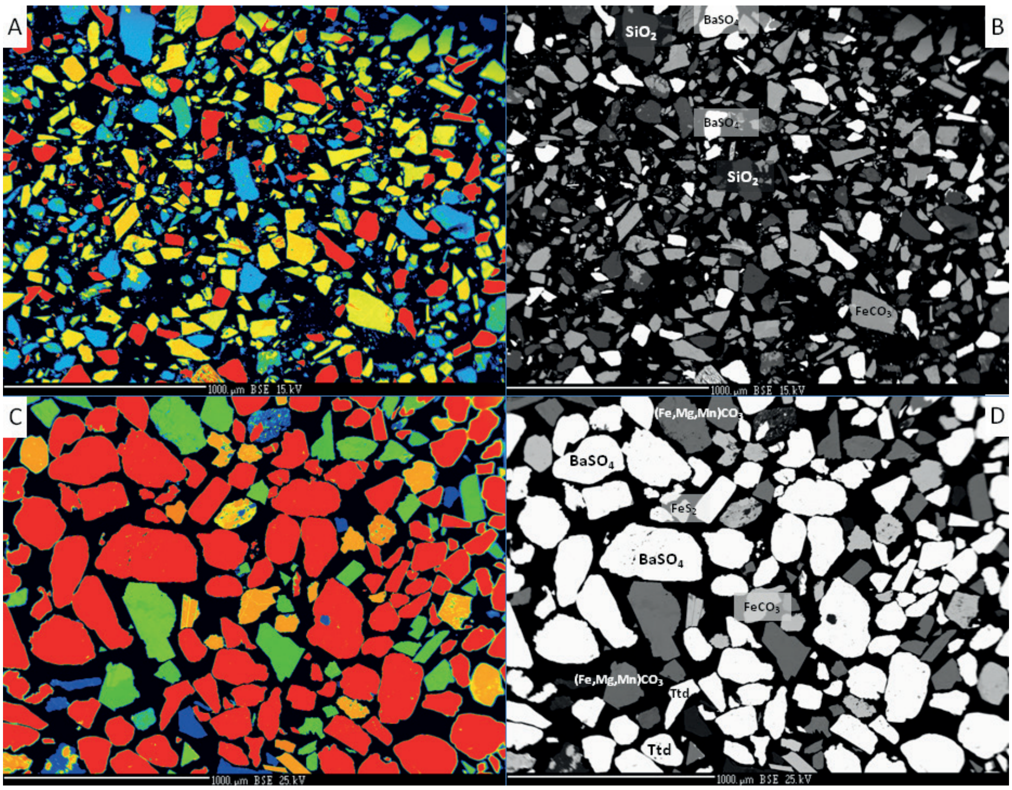


Fig. 2.6 BSE images of qualitatively analysed sand using EDXA analysis spectra interpretation (Demko & Šefčík, 2018). In the right part are the original BSE images and in the left part their artificially coloured equivalents.
A) $BaSO_4$ – red, SiO_2 quartz – light blue, $FeCO_3$ siderite – yellow. B) $BaSO_4$ + tetrahedrite $(Cu,Fe,Ag,Hg,Zn)(Sb,As)_4S_{13}$ – red, $FeCO_3$ siderite – yellow, $(Fe,Mn)CO_3$ – green, SiO_2 quartz – blue.

"In fly ashes the presence of presumed sulphophilic elements Pb, Zn, Cu, As, Cd is not identified by the EPMA analysis". There are several explanations, and they are not mutually contradicting. The ashes analysed are pure to the extent that the detection limit of microanalysis permits. At the same time, the identified status indicates that the fly ash is pure and the contents of Pb, Zn, Cu, As, and Cd are lower than is expected intuitively from the fly ash. On the other hand, there is a natural technical explanation why the concentrations analysed are so low. This is a controlled migration of flue gases out of the combustion system in the form of smoke into the landscape around the boilers neighbourhood. There are results that systematically identify contamination with sulphophilic elements in the direction of the prevailing chimney flow. The effect of exhalants on the chemical composition of soils and plants is discussed in Hronec, 1996; Hronec et al., 1992; Čurlík & Šefčík, 1999. The above interpretation of the deficit of chalcophilic elements in fly ash after fossil fuel combustion is reliable, but it is no longer applicable to fly ash, which is a product of combustion using efficient filtering equipment after 1990 – 1995. In the flue gas escaping Pb, Zn, Cu, As, Cd are filtered and concentrated back to the fly ash in a concentrated form!

Another complication that affects the composition of the fly ash is the type of material to be burned, since oil has been added to the coal fuel. The black oil itself, as a heavy residual fraction of oil processing, is enriched with contaminants such as chalcophilic elements. The ashes, which are a product of combustion of fuel enriched with black oil, should be enriched with chalcophilic contaminants.

Some metals such as Hg, Cd, Pb are principally concentrated into the fraction of airborne particles, while other non-volatile metals such as Fe, Cu, Cr and Ni are enriched in the heavy residual fly bottom ash fraction, which is typically present in high bulk spherical solids after melting aluminosilicates. The fractionation of elements such as As, Zn among the flying pollutants and the residual heavy fly ash fraction is intermediary. The results of Polc et al. (2016) show the preferential enrichment of Zn, Cu, Ba, Ni, Cr, As in the heavy residual ash fraction and the enrichment of Pb, Hg in the fly ash fraction as the product of "oily fuels" combustion. Examples of BSE images of the ashes are presented in Fig. 2.7.

SOILS are the product of the weathering of the rock substrate of the uppermost part of the continental crust in interaction with the hydrosphere, atmosphere and biosphere. The importance of soil's role in human nutrition and the existence of life itself is beyond question. Soils or pedosphere can be understood as a space where many processes of physico-chemical and biological nature take place. All processes taking place in soils have principally control over the distribution and mobility of the substance, including contamination by potentially toxic elements and their compounds.

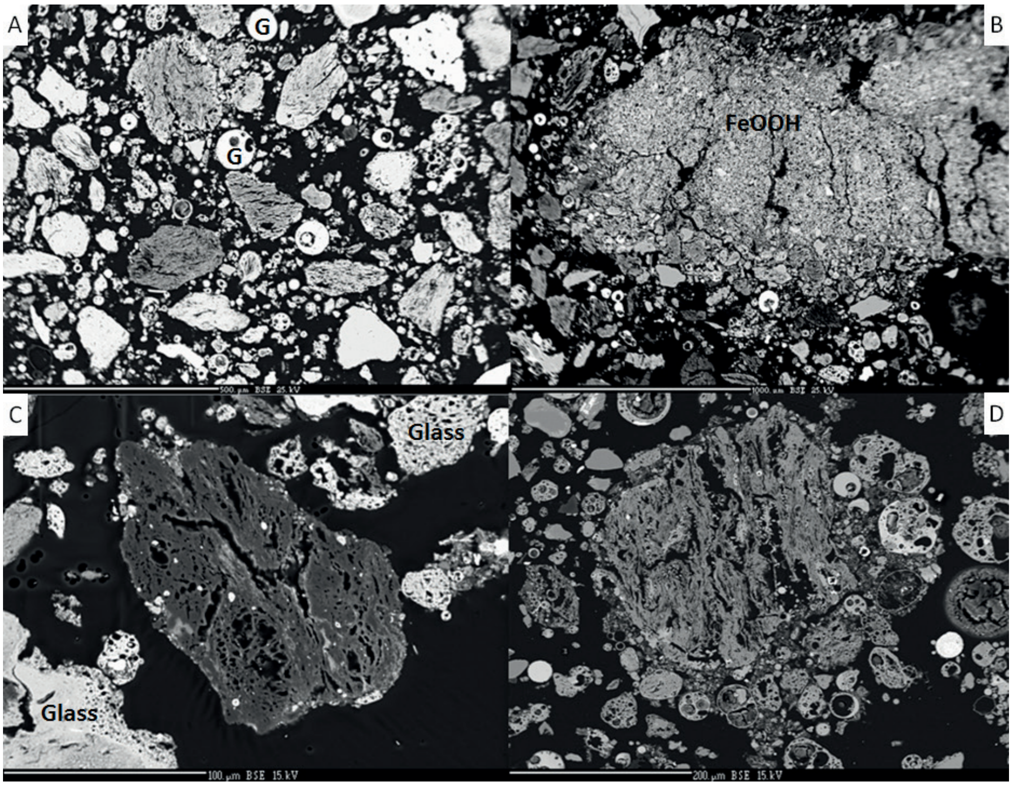


Fig. 2.7 Examples of BSE images of ashes. A) Fly ash composition view, BSE image. The spherical formations of silicate glass are mixed with the carbon blacks that form a porous organic carbon. Silicate glass spherical bodies are the product of aluminosilicate minerals melting in the original coal. B) A porous aggregate of autogenous FeOOH, which was formed by the dissolution and precipitation of migrating iron in a flotated fly ash dump in Trnové, near Žilina. Autogenous FeOOH serves as an effective geochemical barrier in the environment of active migration of As, Pb, Zn, Cu, Co, Sb. The analysed Fe contents are in the range (67.5 – 61.8) wt%. The identified As (0.15 – 0.09) wt% contents in porous FeOOH aggregates demonstrate the presence of arsenic in the environment of flotated waste and its secondary remobilized binding to FeOOH (BSE image). C) Detail of carbon black particles (graphite) between porous silicate glass bodies. Analysed contents of As + Pb + Cu + Zn + Cr + Ni < DT limit (BSE image). D) Detail of the soot particle surrounded by porous silicate glass beads of spherical morphology. Analysed contents of Cr + Ni + Zn < DT limit (BSE image).

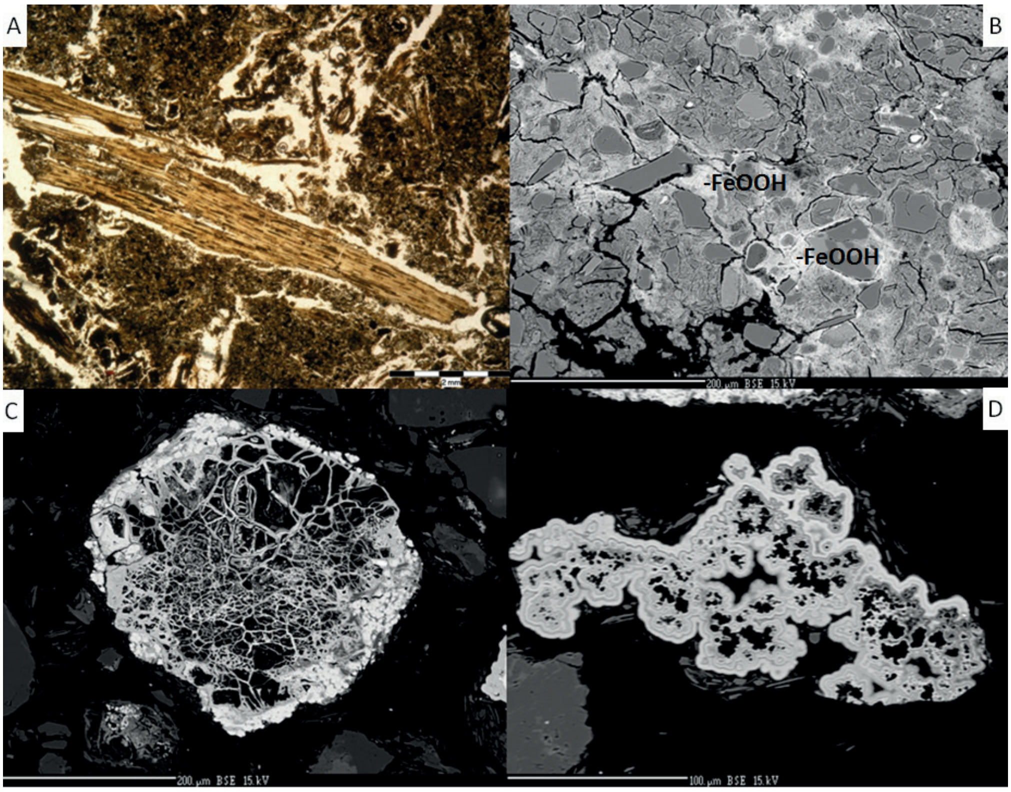


Fig. 2.8 Application of EPMA analysis for soils. A) The fragments of stalks and plant tissue in the sample of fluvisol from the Markušovský potok Brook. The presence of organic material in soils increases the sorption potential of the soil as an effective geochemical barrier in the landscape. Photo from a polarizing microscope. B) BSE image of soil containing detritic quartz, plagioclase and K-feldspar. The light zones in the white fraction represent the autogenous FeOOH phases with a high sorption potential for retarding and accumulating actively migrating metals in the environment. Analysed contents of Pb + Cu + Zn + Co + Cd + As + Ni + Cr < DT limit indicate the absence of accumulation of potentially toxic elements in the soil sample, as the FeOOH phases are effective sorbents and function as natural monitoring probes to assess active migration. Location Detva. C) Aggregate of autogenous FeOOH in the soil sample from Ľubietová. The FeOOH aggregate was formed by the precipitation of migrating iron from percolating solutions by the catalytic effect of the surface of the decaying plant root system. Analysed contents: Fe (53.12 – 31.8), S (11.99 – 0.25), As (3.63 – 0.76), Sb (4.6 – 0.18) and Cu (2.25 – 0.23) wt%. D) Zonal geode (nodule) of autogenous FeOOH in the soil sample from Ľubietová. Analyzed contents: Fe (49.58 – 48.02), S (1.87 – 1.8), As (0.76 – 0.64), Cu (0.32 – 0.21) wt%. BSE image.

Application of the EPMA analysis for soils results from soil composition: humus / organic substances, clay minerals, weathering rock substrate detritus, autogenous compounds (Mn-Fe)OOH, Figs. 2.8-A, B, C, D. An important role in dealing with migration and accumulation of elements in the soil complex is played by the analysis of organic material, especially the decaying residues of plant tissue. Another very successful objects for the identification of accumulation and migration flows are oxides and hydroxides of manganese and iron. All forms of (Mn,Fe)OOH are very potent and effective sorbents of the actively migrating elements Pb, Zn, Cu, Cr, Ni, As, Cd, Sb, Hg and can be successfully used as natural monitoring probes. For the EPMA analysis it is necessary to use cementation of the preparations with epoxy resins due to the non-cohesive decaying character of soil samples.

The use of the EPMA analysis of autogenous phases (Mn,Fe)OOH as natural monitoring probes is based on a simple logic. In the presence of free or actively migrating elements Pb, Zn, Cu, Cr, Ni, As, Cd, Sb, Hg, these elements are trapped on an effective sorption geochemical (Mn,Fe)OOH barrier. The identification of these elements by the EPMA analysis then shows that the area from which the (Mn,Fe)OOH sample was positively analysed is part of the migration contamination route or even belongs to the accumulation area. In the case of a negative result, we gain an important finding that during the existence of the analysed (Mn,Fe)OOH phase through the investigated soil complex there was no contamination! The EPMA-analyses are more effective in dealing with the migration of potentially toxic elements than overall soil analyses alone, as overall soil analyses provide an analytical result including non-mobile forms of the elements under investigation. The currently applied standards for permissible and limit concentrations of Pb, Zn, Cu, Cr, Ni, As, Cd, Sb, Hg in soils deal with passive understanding of element distribution in soils (Act No. 220/2004).

The application of the EPMA analysis for soils in Fig. 2.8.

STREAM SEDIMENTS are the deposits that are formed during sedimentation in watercourse troughs in places with decreasing entrainment energy of the stream. Dynamic development of the watercourse depends on the total flow (precipitation) or local configuration of the river bank morphology and the placement of mechanical barriers continuously modeling the river flow. Due to the dynamics of the water system, it is possible to differentiate between sedimentary phenomena that develop in a higher current regime and those characterized by calm sedimentation behind mechanical obstacles or in the low-energy environment of passive edges of banks. The facies of the sediments in the high-energy flow regime are coarser-grained and practically free of fine silt and clay fractions of sediment. Sediments formed in a quiet low-energy environment are finer-grained with a modal increase in silt and clay fractions.

The dynamics of stream sediment formation itself determines the potential of stream sediments as a tool for the investigation and monitoring of the spread of contamination in the aquatic environment. The coarse-grained sediments of the gravel to sand fraction are only useful for the identification of the mechanical form of migration. In addition to identifying mechanical migration of contamination, fine-grained sediments can also be used to assess the active transport of elements by an aqueous solution. It is important that the physical and chemical conditions allow precipitation of autogenous minerals such as (Mn,Fe)OOH or longer accumulation and decomposition of organic matter in the sediment. For fine-grained stream sediments the same possibilities of using the EPMA analysis apply to soils and sands.

Given the time and energy dynamic development of stream sediments, complications resulting from re-sedimentation of sediments must be taken into account.

The application of the EPMA analysis for stream sediments is in Fig. 2.9.

2.4. Conclusion

The application of the EPMA analysis in environmental geochemistry is widespread, but with a predominant focus on microchemical analysis as a complement to experimental research, e.g. Hiller et al. (2013; 2016), or as a solution to the stability of phases and their reactions under conditions of hypergenic weathering, e.g. Andráš et al. (2015), Radková et al. (2017), Majzlan et al. (2018).

The direct use of the EPMA analysis for the purposes of the environmental burdens monitoring stems from the fact that without knowledge of the primary distribution of potentially toxic elements in/around the source area, it is practically impossible to logically address the causes of the chemical elements migration in the landscape and to prognosticate the environmental emergencies.

The EPMA analysis provides the possibility of microchemical study of the elements to address the actual distribution of the elements among the phases or as the stability of the source phases under conditions of the hypergenic system, e.g. Fe-sludge at the tailings pond Šulekovo-Hlohovec, Fig. 2.3. The EPMA analysis is a direct tool for microchemistry of natural systems that cannot be replaced by whole-rock geochemistry of macro-samples. If a combination of classical geochemical analysis of rocks, soil, dust, ashes or stream sediments with microchemistry is possible, it is possible to reconstruct the geochemical dynamics of the system, such as in the case of various forms of As-Co and Hg-Sb-Cu migration (Fig. 2.10). Targeted application of a microchemical EPMA study for phase analysis such as (Mn,Fe)OH or decaying

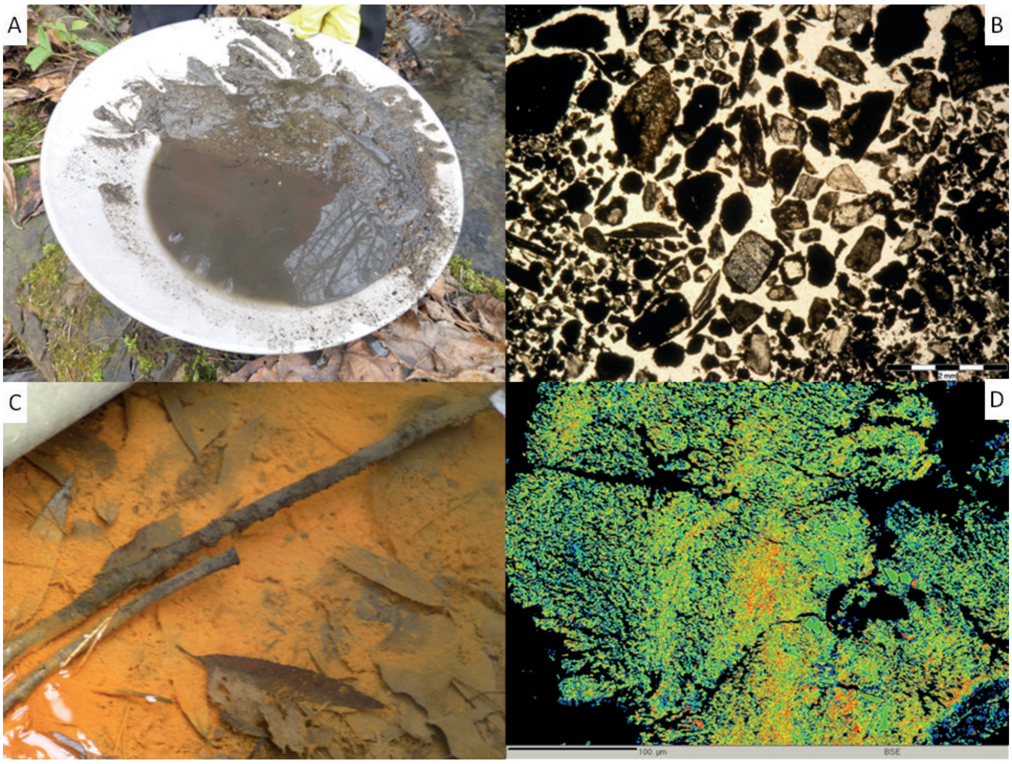


Fig. 2.9 Examples of application of microchemical survey for stream sediments. A) A pan serving as sampling tool for heavy fraction of stream sediments. B) A view of the heavy fraction sized in the Markušovský potok Brook below the dam of a large tailings pond. The presence of baryte, siderite, and quartz residue after the dissolution of sulphide ore in the stream sediments indicates a compromised sealing function of the Markušovce sludge dam and passive "mechanical" migration of waste material in the surface stream below the tailings pond! C) Coagulation of iron in standing marginal waters below the tailings pond in Markušovce. The resulting -Fe phases are an effective natural sorbent of actively migrating elements in the environment. Autogenous precipitates -Fe are natural monitoring probes to identify the migration of potentially toxic elements into the environment. D) Artificially stained BSE image of dendritic fractal texture of the SiFeOOH autogenous phase in a stream sediment sample. The high degree of branching determines the large active surface area of the strong sorbent with higher sorption efficiency. Analytically identified presence of Co 0.09 – 0.07% wt% and As 0.2 – 0.08 wt% demonstrates the function of active migration of Co + As in surface waters from the area of the Markušovce tailings pond (Demko & Šefčík, 2018).

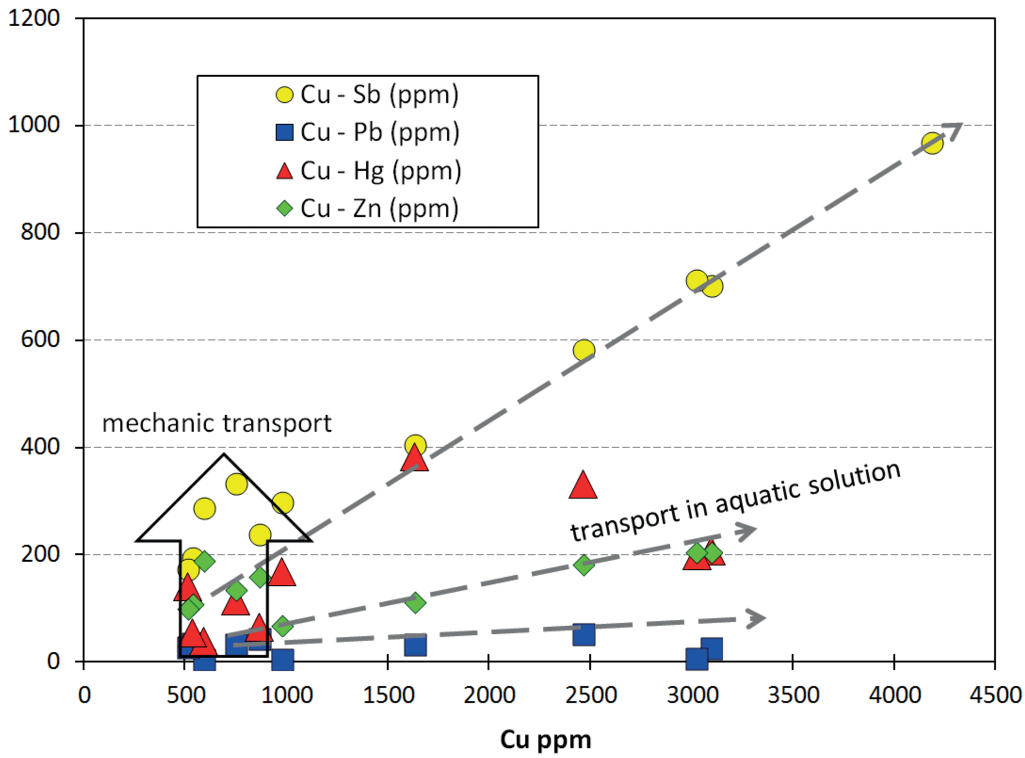


Fig. 2.10 Geochemical fractionation of Cu – Sb – Pb – Hg – Zn in samples of stream sediments of Markušovský potok Brook. Based on the application of EPMA microanalysis, which identified separate mechanical migration (transport of detritus) and independent active migration of Cu, Sb, Pb, Hg, Zn (sorption on plant tissues), it is possible to interpret movement and fractionation of contamination from tailings pond in Markušovce (Demko & Šefčík, 2018).

plant tissues uses the analysed objects as natural monitoring probes for their natural high sorption capacity. In the case of a positive microchemical identification of the elements of interest, it can be concluded that the analysed area is part of the source area or the pollutants migration route. In the case of a negative identification of the elements of interest by microchemical study of a natural monitoring probe, it is possible to draw an important conclusion that the studied area is not a source area or a migration route of the analysed pollutants. The advantage of application of the EPMA analysis is lower economic demands in comparison with classical hydrochemical monitoring. The cost of building a hydrogeological well is much higher than the production of an analytical preparation and EPMA analysis. A non-negligible factor in the use of natural materials as monitoring probes is that natural materials have been in direct long-term contact with water (transport medium), i.e. the analysed signal can be interpreted into the past of the existence of a natural probe. The analytical hydrochemical signal corresponds practically to the moment of sampling and is influenced by external climatic factors.

The presented overview of possible applications of the EPMA analysis as a research and monitoring method is not understood dogmatically as a solution for everything, but seeks to provide an idea and broader possibilities in the framework of the geochemical environmental research. It deserves special attention in the reconstruction of geochemical processes taking place on macrochemical and microchemical scales.

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