SLOVAK GEOLOGICAL MAGAZINE

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Periodical of Geological Survey of Slovak Republic is a quarterly presenting the results of investigation and researches in a wide range of topics:

- regional geology and geological maps
- lithology and stratigraphy
- petrology and mineralogy
- paleontology
- geochemistry and isotope geology
- geophysics and deep structure

- geology of deposits and metallogeny
- tectonics and structural geology
- hydrogeology and geothermal energy
- environmental geochemistry
- engineering geology and geotechnology
- geological factors of the environment

The journal is focused on problems of the Alpine-Carpathian region.

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Matula M., 1969: Regional engineering geology of Czechoslovak Carpathians. 1. Ed. Maheľ, M., Bratislava, Vyd. Slov. Akad. Vied, 225 p.

Andrusov D., Bystrický J. & Fusán O., 1973: Outline of the Structure of the West Carpathians. Guide-book for geol. exc. X. Congr. CBGA, Geol. Úst. D. Štúra, Bratislava, 5 - 44.

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1. Editorial Board reserves the right to publish preferentially invited manuscript and to assemble thematic volumes,

2. Editorial Board sits four times a year and closing dates for individual volumes will be on every 15th day of March, June, September and December.

3. To refer to one Magazin please use the following abbreviations: Slovak Geol. Mag. No. .... D. Štúr Publ. Bratislava.

Scientific Editors: D. Bodiš and S. Rapant

Foreword

At present, there is no doubt that objective information about the environment of a country or state cannot be really objective without information about condition and degree of contamination of a geologic component of the environment. Contamination of waters, soils and sediments, stability disturbances of country, ecological drainage, values of natural radioactivity etc. are data needed to provide the conception of permanently tenable country development. A healthy and unpolluted environment and the elimination of negative human influences on the environment are dominant tasks in a strategy of permanently tenable utilisation of abiotic sources of the environment. Solution of these problems requires co-operation of all geological branches.

In latest decades, a significant role in balance between utilisation and protection of abiotic sources is played by new scientific discipline - environmental geochemistry that is studying distribution and interrelations of chemical elements in rocks, soils, waters, atmosphere and biote, and their impact on man.

In the provided monothematic issue there are published selected articles presented at a scientific seminar „Environmental geochemistry„, organised by Department of Geochemistry at Natural Faculty of Comenius University, Bratislava and Department of Environmental Geochemistry, Geological Service of Slovak Republic, Bratislava. The seminar was attended by more than 80 experts from the Slovak Republic, Czech Republic and Poland. Topics of delivered lectures and presented posters included a wide range of problems that are topics of current interest of geochemistry in Slovakia. For instance, methodical processes of environmental-geochemical ranking, environmental–geochemical mapping, medical geochemistry, environmental isotopes, utilization of analytical methods for the study of environmental samples, and the applications of environmental – geochemical evaluation (waste disposals, specific monitoring, geofactors and others).

The presented contributions shows a high skill level and wide range of problems, which are at present solved by environmental geochemistry.

The organisers of the conference would like to thank to all participants for their cooperation, their presented papers and posters.

BODIŠ & RAPANT

Environmental Geochemistry and Environmental - Geochemical Mapping of the Slovak Republic

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Abstract: Methodology and the results of the geochemical mapping of Slovak Republic territory (the Geochemical Atlases (scale 1 : 1 000 000) as well as environmental-geochemical maps (scale 1 : 50 000)) are presented in this article. Some theoretical problems of environmental-geochemical mapping are analysed, for instance environmentally important contents of elements and technique of their determination, principles and bases for creation of environmental-geochemical maps and others. Samples of individual parts of the Geo-chemical Atlases and environmental-geochemical maps are presented.

Key words: environmental geochemistry, geochemical maps, geochemical atlases, environment of Slovak Republic

Introduction

The distribution of elements in individual earth's zones is not random but controlled by the physical-chemical conditions and parameters, which were gradu-ally recognised by the progressively developing scientific discipline – geochemistry. Broadly speaking the purpose of the geochemistry is to study elements and their isotope distribution in atmosphere, hydrosphere, earth's crust, mantle and core. With respect to biota and human beings, the surface component of the environment with the domi-nant importance is the technosphere. This has become the subject of intensive investigation as a response to the population explosion as well as to the socio-economic, economic and technical development and related prob-lems with raw material processing and consequent envi-ronment contamination.

One of the most negative and probably the most dan-gerous impacts of human activities on geological compo-nents of the environment is the widespread contamination of natural waters, soils, recent sediments and rocks with inorganic and organic chemical compounds, that have a consequently negative impact on the character of a coun-try, biosphere and man. A large-scale contamination of the environment with a local, regional and even global character invoked the necessity to study changes in cycles of environmentally important elements and thus condi-tioned the birth and development of a new scientific dis-cipline – environmental geochemistry.

Definition and Role of the Environmental Geochemistry

The environmental geochemistry is the study of the distribution and mutual interactions of chemical elements in rocks, waters, soils, atmosphere and biosphere and their impact on man. Thus, it is dealing with a complex of interactions in the rock–soil–water–atmosphere-bio-sphere–life system, it investigates primary and secondary factors influencing sources, dispersion and distribution of elements in environment, as well as their role in food chain, including its key part – water and with water asso-ciated potential negative impact upon plants, animals and man. The so-called environmentally significant content (concentration) of an element is one of the key input data. This term means that such concentrations of elements, substances and components and in such forms, which in-dicates a pollution of the environment either by human or by geogenic origin and which can negatively influence the natural ecosystem. Their indicative values are given by environmental standards, norms, critical or maximal con-centrations defined for individual abiotic agents of the environment and also they are determined by experimen-tal studies (statistic analyses and modelling). Except for the monitoring of polluter concentrations in geologic en-vironment, the role of environmental geochemistry is also the investigation and identification of their origin (geogenic or anthropogenic), conditions and forms of mi-gration, forms of occurrences, toxicity levels, risk and conditions of their accumulation and the redistribution in various components of the geologic environment.

Rather than dealing with a broader spectrum of issues studied by other geosciences, environmental geochemistry closely cooperates with related and in some cases also with seemingly unrelated scientific disciplines. For exam-ple, concerning biological sciences, the interest of envi-ronmental geochemistry is not in organism and its associations, but in its living environment affected by natural and man-introduced processes.

The above mentioned concept suggests that environ-mental geochemistry is a multidisciplinary scientific branch expressly based upon national and international

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team co-operation of a wide range of specialists. Its current dynamic development and importance in practice can be documented by its development toward other disciplines such as medicine (geomedicine), hygiene (geohygiene), urban planning etc., it can be talked about applied environmental geochemistry.

The Environmentally Important Contents of Elements and Methods of their Determination

Concerning the distribution of elements, for various purposes geochemistry distinguishes positive and negative anomalies, prospective symptoms, criteria etc. One of the basic attributes of environmental geochemistry is to determine environmentally significant concentrations of elements/components as well as their background and critical values. In most cases there are determined maximal permissible concentrations that are obligatory and can be checked by legislative. On the other hand deficit environmental concentrations and criteria (various sums and ratios of elements) are important as well, for instance contents of the elements F, I, or that critical loads and their exceeding. In many cases these contents are very low, close to the detection limits of routinely used analytic techniques and methods. Analytical chemistry, development of analytical techniques and, last but not least, also a new approach to analytical procedures have considerably contributed to recognizing of forms of element occurrences, their biologically available concentrations (through sequential leachate and toxicity tests chiefly in soils, stream sediments, but also in other non-geological materials, such as emissions, sludges, waste of various kinds, etc.). All of the processes are preceded by the elaboration of specific sampling design and methods of sampling that are discussed, but often not respected in practice (for instance instructions for compilation of maps of geofactors of the environment etc.). It should be realized that mistakes done during sampling have usually greater influence on the total error than used analytic method.

With respect to determination of environmentally significant contents of elements/components for evaluation of pollution sources and their intensity, there are currently several approaches (or philosophies) in existence:

- legislative
- determination of a background pre-industrial (precivilisation) concentration
- application of statistic analysis
- combined
- geochemical

The **legislative** approach is based on comparison of observed concentrations of monitored parameters with limit values that are given in particular standards and defined for particular components of the geologic environment (for instance Slovak Technical Standard No. 75 7111, *Drinking water* – for underground waters, Resolution of Ministry of Agriculture of the Slovak Republic No. 581/94-540 – for soils etc.). The contents above (or below) limit levels are regarded as environ-

mentally significant. This approach is handicapped by the fact that the range of analytically monitored elements and components is often wider than the range in individual standards. Moreover, some standard values (mostly indirectly or experimentally derived from the daily dose per the average man's weight, lethal dose LD50, exposure time, or concentration causing death or deformations of plants and animals) are not always suitable for man-made pollution. The maximum permissible values of Zn (5 mg.l^{-1}) and chlorides (100 mg.l^{-1}) according to Slovak Technical Standard 75 7111, *Drinking Water* are good examples. Waters containing more than 5 mg.l^{-1} zinc can hardly be found in Slovakia, whereas chloride concentrations over 10 mg.l^{-1} always indicate secondary contamination except for waters circulating in Tertiary sediments at greater depths. It is worth mentioning that the legislative approach has more or less the character of a basic environmental information and does not deal with the biological availability of elements mentioned in the standards, which merits more detailed environmental geochemical research and evaluation.

The determination of *background* or *pre-industrial contents* of elements is an important step in environmental geochemical research as it provides a good basis for comparisons for follow-up investigations. These values can be identified by techniques that are summarised by Förstner – Wittman (1979) as follows:

- average composition of shales, applicable as a global standard value,
- fossil sediments laid down in a defined subaquatic environment, applying the conditions of autochthonous or allochthonous origin and regional-effect mechanisms,
- recent sediments from relatively uncontaminated regions,
- dated drillcores of sediments that provide a historical record of effects and changes in the investigated drainage basin and which left their imprints in the sediment.

Each of these four techniques has its advantages and disadvantages, and its application depends upon specific natural conditions of the investigated site and upon the research objectives. The resulting background values are often influenced by the predominance of a certain rock type, occurrence of ore and mineral assemblages, etc.

A number of *statistical analyses* are employed to determine background values (local or regional background) and also effect of natural environment on background concentration, i.e. partial distinguishing between geogenic and anthropogenic effects. The mathematical-statistical approach in modelling of environmental-geochemical significant contents and anomalies is similar to that applied in prospecting geochemistry. It determines the mean (modified mean) values and standard deviations. This approach is recommended mainly for elements and components which limits are not determined in standards (e.g. Sb in sediments and surface water) and for the evaluation of those components of the geological environment that are not dealt with in legislation (e.g. rocks, snow, etc.).

Statistical-analysis techniques most widely used to distinguish geogenic and man-made effects on background values are as follows:

- calculation of correlation coefficients, which indicates a common source of elements, e.g. if Zn, Pb, Cd and Hg display a correlation with organic carbon, they are probably of man-made origin. However, such correlation should be strictly reviewed, since, e.g. the above-mentioned correlation in black shales has a completely different meaning.
- cluster analysis,
- multivariant statistical methods, e.g. factor analysis, etc.

The **combined** approach is mostly based upon the legislative and statistical procedures that mathematically combine the limit values with the absolute concentrations of evaluated elements. One of these parameters is also a contamination index (Backman et al., 1997).

$$C_d = \sum_{f=1}^{n} C_{fi} \quad \text{where} \quad C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1$$

where C_d –level of sample contamination
C_{fi} – contamination factor for the i-th component
C_{Ai} – analytic value of the i-th component
C_{Ni} – normative value of the i-th component

The so-called geoaccumulation index represents another example of the combined approach that was implemented by Müller (1979) as the quantitative expression of the degree of contamination by heavy metals in stream sediments:

$$I_{geo} = \log_2 \frac{C_n}{1,5 \times B_n}$$

where C_n is an observed concentration of element n of argilliferous fraction of sediment (<2μm) and B_n is a value of geochemical background in argilliferous shale or observed background in argilliferous fraction of pre-civilisation sediments in evaluated region. Factor *1,5* is used because of possible background values variation due to lithogenetic effects. The values of geoaccumulation indexes are divided into 6 level scale of contamination by monitored heavy metals encountered in argilliferous fraction of the bottom stream sediments. In the case of combined approaches, we can already speak about the evaluation of the degree of contamination of the environment.

Another distinct method is the **geochemical approach**. This technique assesses environmentally significant concentrations of elements of the investigated component of geological environment (waters, soils, sediments, etc.). It determines whether the contents of elements are adequate to the given natural conditions of their formation, i.e. whether they correspond to the natural geological processes forming chemistry in local conditions. This approach requires a detail analysis of geochemical processes taking place in the respective components of the geological environment with assumed quantitative effect of geochemical processes. It is par-

ticularly suitable for distinguishing of proportion of man-introduced concentrations of contaminants and it enables evaluate proportion of man-made contamination of geological environment. This approach is mainly applicable when contaminant concentrations are below limits defined by the legislation, but obviously exceed concentrations that can be expected in the local geological environment. It is often applied to distinguish the degree of influence of man on natural water.

Main Principles of Creation of Environmental-Geochemical Maps

As in other geoscience disciplines, so also in environmental geochemistry are maps the most effective and the most often used approach for evaluation of condition of the environment, in term of visualisation of environmentally important element concentrations. Similarly, it is with interpretation of results that the dominant element is the summary distinction of the degree of contamination and negative impact on the ecosystem.

The simplest and the most frequently used method of expression of environmental-geochemical anomalies are maps with appropriate quantification that is graphically expressed. The important decisions regarding compilation of environmental-geochemical maps are:

- the aims of a map
- the group of users the map is trying to reach
- the character and relevance of input data
- map scale
- cartographic readability of the map

The main aim of environmental-geochemical maps is presentation of the spot or superficial model of distribution of the investigated parameters. This data group is commonly mathematically or logically combined with the character of the environment (geologic structure, hydrogeological conditions etc.) or with other groups of information, such as the demographic, geographic distribution of mortality, health reproduction, land use etc. The choice and mainly the form of expression of environmental-geochemical information must be designed to reach a group of users. For instance, for the administrative purposes it is highly recommended to use bold criteria expressed by the so-called semaphore coloured scale that simplify a communication between specialists (map authors) and state administrators. From the above mentioned it is obvious that environmental-geochemical maps are specifically created and can have different design from case to case.

Reproducible databases of input data in text, numeric and graphic form are considerable bases for map creation. Their verification is conditioned by character of the data and it has its own rules and prescriptions, for instance chemical analyses are internally and externally verified, other data groups are verified by statistical tools, etc. Basically, it can be said that environmental geochemistry operates with multimedia input data, and with regard to this there is a problem arising from their related interpretation: what form and what environment should the information be processed from the beginning to definite graphic form.

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One way is to process information with equal character separately and later transform them into integrated graphic form, for instance. That approach cannot be always accepted, in some cases the determining information is formulated in text as legislation, permissions, licences etc. Another way has become, for instance, hypermedia system called „Microcosm„ developed for the environment of MS Windows by Southampton University (Ashton – Simmons, 1994). This software is able to accept and transform multimedia data for subsequent mutual interpretation.

The information value of the map and its scale are conditioned by the number of information units – statistical density of the sampling grid. The number of units depends mainly upon complexity of natural conditions, map aims and sampled media. Map compilation and its scale plays an important role in solving of local, regional and global geochemical problems mainly in complicated interaction among society, hydrosphere, pedosphere and biosphere. At present maps are compiled with the help of a geographic information system (GIS). GIS in various forms represents a very useful tool for work with spatial data distribution, but in general it does not incorporate the fourth dimension – time, or evaluation of monitoring results, time anticipating models etc. This problem is being solved by a chronological succession of maps (principle of animation) or by the application of specially developed software.

As mentioned above for compilation of environment-geochemical maps it is necessary to maintain a simplicity of information expression, even if complicate simultaneously functioning factors are expressed, with respect to users and also with respect to cartographic readability of a map.

Environmental Geochemistry in the Slovak Republic

In the conditions of former Czechoslovakia and the present Slovakia the geochemistry was almost exclusively focused on activities regarding mineral deposits exploration e.g. prospective geochemistry and later on problems of hydrogeochemistry and groundwater protection.

Two main kinds of geochemical works mentioned above have given the methodological background of environmental geochemistry (design of sampling, sample adaptation, chemical analyses, and way of interpretation). The experts interested in environmental-geochemical problems were formed by the branches of geochemistry mentioned above. Geochemical-prospective works (mainly E. Mecháček, I. Čilík, J. Gubač, J. Václav and others) were the base for the delimitation of geochemical anomalies and the determination of occurrences of prospective and economically significant elements. Beside hydrogeochemical research (mainly Gazda) the main interaction processes were defined and classified (Gazda, 1974): water – rock, form of element transfer in liquid phase and conditions of phase equilibrium. Inasmuch as the water component of the environment is the most dynamic and at the same time the most vulnerable, it served as base for the elaboration of problems of environmental

protection against pollution (for instance Goldberg – Gazda, 1984).

Later on, especially during the beginning of nineties, when widespread geochemical mapping has begun (Vrana, 1991), the reproducible database of chemical composition of natural water, streams, rocks, soils, natural radioactivity and forest biomass were created. By this mean the concept of geochemical background and elements/components distribution in sampled media was formed at a certain level. Later on it was purposely updated in a set of maps of geofactors of the environment through supplementary data gathered by an identical methodical process. The activities mentioned above were accompanied by forming methodology for interpretation of results and mainly for the compilation of particular maps (Rapant – Bodiš, 1994; Marsina – Lexa 1995; Čurlík – Šefčík – Šurina, 1995). These were oriented especially on the summarisation of anomalies and the distinction of their geogene, geogenic–anthropogene and anthropogene origin.

The orientation of environmental geochemistry in Slovakia is also focused on one of its current trends – medical geochemistry, which includes retrieval viewpoint (Khun, 1996) and applied one, for instance in Žiar basin region (Khun et al., 1997). Recently there are ongoing projects focused on influences of the geochemical environment on state of health of inhabitants, for instance in Spiš-Gemer Rudohorie region (Rapant et al., 1998).

The development of applied environmental geochemistry proceeds also towards projects focused on critical loads evaluation and their exceeding (Bodiš et al. 1995), chemical time bombs (Rapant – Bodiš, 1995) and monitoring of geochemical parameters within the frame of monitoring of geological factors of the environment of the Slovak Republic (Klukanová, 1998) etc.

One of the new tasks of environmental geochemistry for a close future, currently elaborated abroad and in the Slovak Republic as well is for instance the monitoring of total concentrations and form of occurrences of „classic" environmentally responsible elements as As, Cd, Hg and Pb, because of their high toxicity and the processes leading to the creation of metal-organic compounds frequently relevant in a food chain. It will be inevitable to study biochemical processes that influence the cycle and distribution of elements in nature such as acid deposition, eutrophication of natural water etc.

As the beginning of modern and systematic environmental – geochemical mapping of Slovak Republic is considered the project *„Investigation of geological factors of environment of Slovak Republic"* (Vrana, 1991). Within the frame of this project the first Geochemical atlases of Slovak Republic were compiled and the methodical principles of evaluation and expression of particular components of environment in maps were set in the form of regional environmental-geochemical maps.

Environmental-geochemical mapping of Slovakia is especially focused on the detection of primary and secondary concentrations of elements and substances in rocks, soils, streams and waters (underground and surface). Beside inorganic components organic substances also are
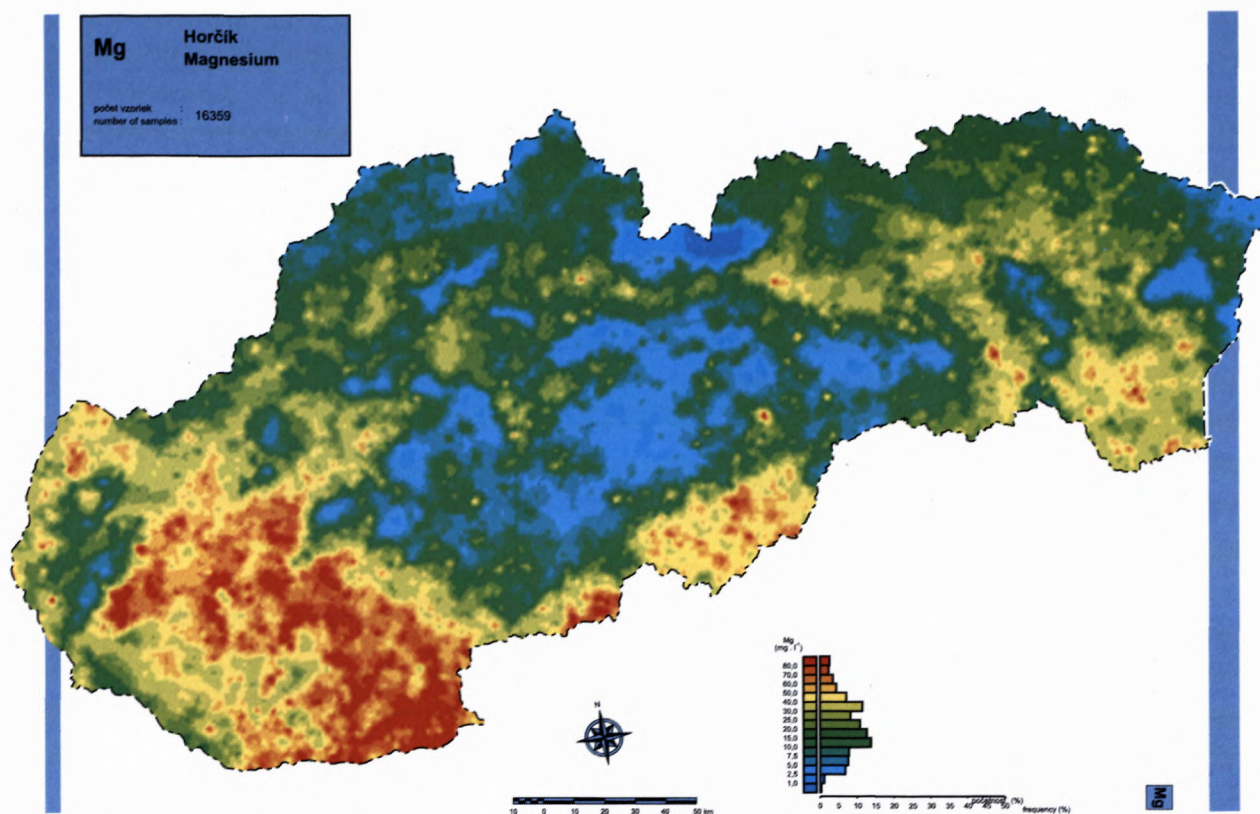
Fig. 1 Geochemical Atlas of Slovak Republic (1 : 1 000 000), Part I: Groundwater. Distribution of Magnesium.

monitored on a regional scale; however, in a smaller extent and as a group indicator of organic pollution.

From a regional viewpoint, the environmental-geochemical mapping of the Slovak Republic is done in two main levels. The first is represented by geochemical atlases of the Slovak Republic in a scale 1 : 1 000 000 and the second one by environment-geochemical maps of selected areas at a scale 1 : 50 000, or in case of urban areas a scale of 1 : 25 000.

Geochemical Atlases

The main aim of the Geochemical atlases was to compile one set of element maps at a scale of 1 : 1 000 000 showing a distribution of chemical elements and components in the groundwater (Fig. 1), soils, streams and forest biomass. The observed and derived components of natural radioactivity of rocks and water were similarly depicted in maps. Within the frame of the Geochemical atlas of rocks a Map of the litho-geochemical types at a scale of 1 : 500 000 was also compiled. The basic characteristics of individual Geochemical Atlases of the Slovak Republic is summarised on Tab.1. On Tab.2 there is an overview of the analysed elements and their limits of detection in particular volumes of Geochemical Atlases.

The elaboration of each part of the Geochemical Atlas of Slovakia is based on new sampling and new chemical analyses and measurements, except for the part „Rocks" where about 30% of archive analytic data were used (mainly in principal elements).

The first three volumes of the Geochemical Atlases of Slovakia were issued in 1996 as monographs in a bilingual Slovak-English version: „Groundwater" (Rapant et al., 1996), „Forest biomass" (Maňkovská, 1996) and „Natural radioactivity" (Daniel et al., 1996). In 1999 „Stream sediments" (Bodiš – Rapant, 1999) and „Rocks" (Marsina et al., 1999) were finished and issued as monographs. The volume of Atlas „Soils" was finished in 1999 and the monograph will be issued in 2000.

The compilation of maps, interpretation, sampling and analyses were done according to methods within the frame of International Geologic Programme IGCP No. 360, Baseline Geochemical Mapping (Darnley et al., 1995).

Within the frame of particular parts of the Geochemical Atlases of the Slovak Republic there were created a new state of interactive geochemical databases of the most important components of the environment. Moreover, an overview of the degree of environmental contamination of Slovakia was acquired. These results were fully used in subsequent environmental–geochemical mapping at more detail scales and following environmental-geochemical and ecological works.

Environmental-Geochemical Maps at a Scale of 1 : 50 000

Concerning the results of geochemical data obtained during the project of Geochemical atlases of the Slovak Republic, there is currently ongoing environmental-geo-

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Tab. 1 General characteristics of individual parts of the Geochemical Atlas of Slovak Republic

Sampling medium	Sampling density	Number of samples	Remark	Contractor
Groundwater	1 sample/3 km^2	16 359	springs, wells, drillholes, drainage	Geological Service of SR
Stream sediments	1 sample/2 km^2	24 422	Active stream sediments <0,125 mm	Geological Service of SR
Rocks	Irregular grid	3 839	„main rock type"	Geological Service of SR
Soils	1 profile/10 km^2	9 892	1 profile = 2 samples (A and C horizons)	Research Institute of Soil Fertility, Bratislava
Forest biomass	1 sample/16 km^2	3 063	Composite sample	Forest Research Institute, Zvolen
Radioactivity	1 point/10 km^2	4 900 (reference points)	− total natural radioactivity − individual components of natural radioactivity K, U, Th, Rn	URANPRES, ltd., Spišská Nová Ves

Tab. 2 Overview of analysed elements and their detection limits in individual parts of the Geochemical atlases

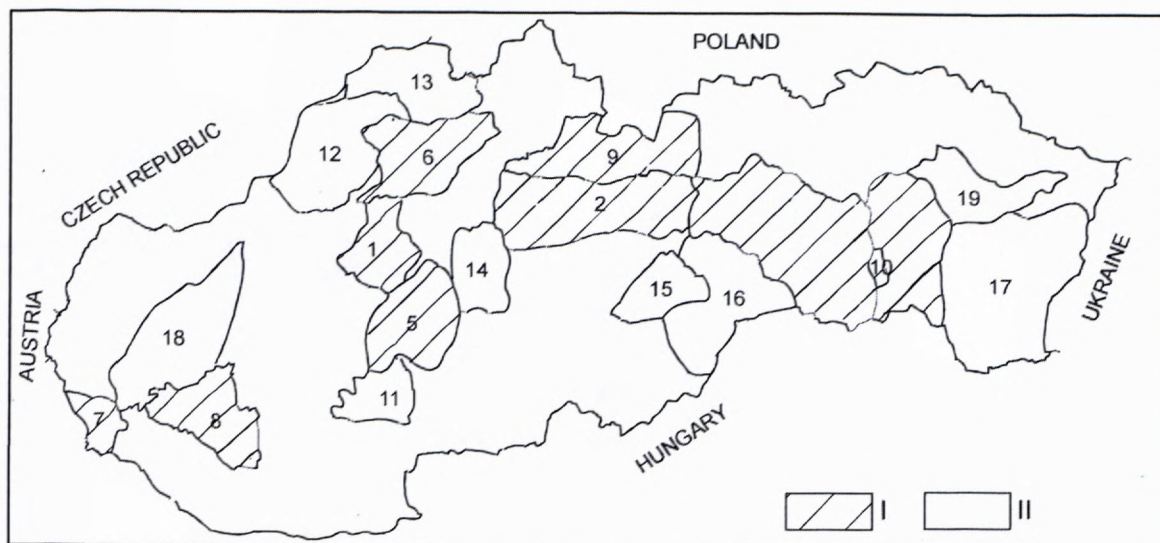| Groundwater		Stream sediments		Forest biomass		Rocks		Soils	
element	det. limit [mg.l^{-1}]	element	det. limit [mg.kg^{-1}]	element	det. limit [mg.kg^{-1}]	element	det. limit [mg.kg^{-1}]	element	det. limit [mg.kg^{-1}]
CO$_2$aggr.	2,2	Al	100	Al	4	Ag	0,04	Al	100
CO$_2$ free	2,2	As	0,1	As	0,01	Al	100	As	0,1
O$_2$	0,1	B	5,0	Ba	2	As	0,1	B	3
conduct.	1,0	Ba	30,0	Be	0,001	B	3	Ba	5
Al	0,01	Be	0,1	Ca	0,1	Ba	30	Be	0,2
As	0,001	Bi[b]	0,1	Cd	0,003	Be, Bi	0,1	Bi	0,1
Ba	0,01	Ca	100	Co	0,03	Ca, Ce	10	Ca	100
Ca	1	Cd	0,1	Cr	0,02	Cd	0,1	Ce	0,01
Cd	0,0005	Ce	10,0	Cu	0,1	Co	1	Cd	5
Cl	0,1	Co	1,0	F	2	Cr	5	Co	1
COD$_{Mn}$	0,08	Cr	5,0	Fe	0,3	Cu	1	Cr	5
Cr	0,0005	Cu	1,0	Hg	0,001	F	50	Cs	1
Cu	0,0005	Fe	100	K	0,05	Fe^{2+},Fe^{3+}	100	Cu	1
F	0,1	Ga	5,0 ·	Li	0,1	Ga	5	F	300
Fe	0,01	Hg	0,03	Mg	0,05	Hg	0,01	Fe	100
HCO$_3$	0,1	K	100	Mn	0,1	K	100	Ga	2
Hg	0,0002	Li	1,0	N	100	La, Li	1	Hg	0,01
K	0,1	Mg	100	Na	0,05	Mg	10	K	100
Li	0,002	Mn	10	Ni	0,3	Mn	10	La	1
Mg	1	Mo	0,2	Pb	0,07	Mo	0,2	Li	1
Mn	0,005	Na	100	Rb	0,8	Na	100	Mg	100
Na	0,1	Ni	1,0	S	50	Ni	1	Mn	10
NH$_4$	0,05	P	100	Se	0,01	P	100	Mo	0,2
NO$_3$	0,5	Pb	5,0	Sr	0,8	Pb	1	Na	100
Pb	0,001	Rb	5,0	V	0,07	Rb	5	Ni	1,0
PO$_4$	0,05	Sb	0,1	Zn	0,1	S	100	P	100
Sb	0,0002	Se	0,1			Sb	0,1	Pb	2
Se	0,001	Sn	1,0			Se	0,05	Rb	1
SiO$_2$	0,5	Sr	5,0			Si	100	Sb	0,1
SO$_4$	0,3	Ti	0,001			Sn	1	Se	0,1
Sr	0,01	Tl	0,2			Sr	5	Sn	1
Zn	0,001	V	5,0			Ti	10	Sr	1
		W	5,0			V, W	5	V	3
Data in mg.l^{-1}, except pH value and conductivity (µS.cm^{-1})		Zn	1,0			Y, Zn, Zr	1	W	1
		Zr	5,0			CO$_2$	100	Y	1
		Y	5,0			H$_2$O$^+$, 350 °C	100	Zn	1
		Data in mg.kg^{-1}.							

Fig. 2 Review of mapped regions (1 : 50 000): I = regions compiled 1991–1999: 1 = Horna Nitra, 2 = Nizke Tatry Mts., 3 = Hornádska kotlina basin and eastern part of Slovenské Rudohorie Mts., 4 = Košická kotlina basin and Slánske vrchy Mts., 5 = Žiarská kotlina basin and Banská Štiavnica area, 6 = Malá Fatra Mts. and some adjoining depressions, 7 = Veľká Bratislava urban area (1 : 25 000), 8 = Galanta district, 9 = Vysoké Tatry Mts. – Ružomberok – Liptovský Mikuláš, 10 = Košice urban area (1 : 25 000); II = regions under study: 11 = North-eastern part of Levice district, 12 = Central Považie, 13 = Kysuca drainage system, 14 = Banská Bystrica – Zvolen, 15 = Jelšava – Lubeník – Hnúšťa, 16 = Slaná drainage area, 17 = Tibreg, 18 = Trnavská pahorkatina, 19 = Vranov – Strážske –Humenné.
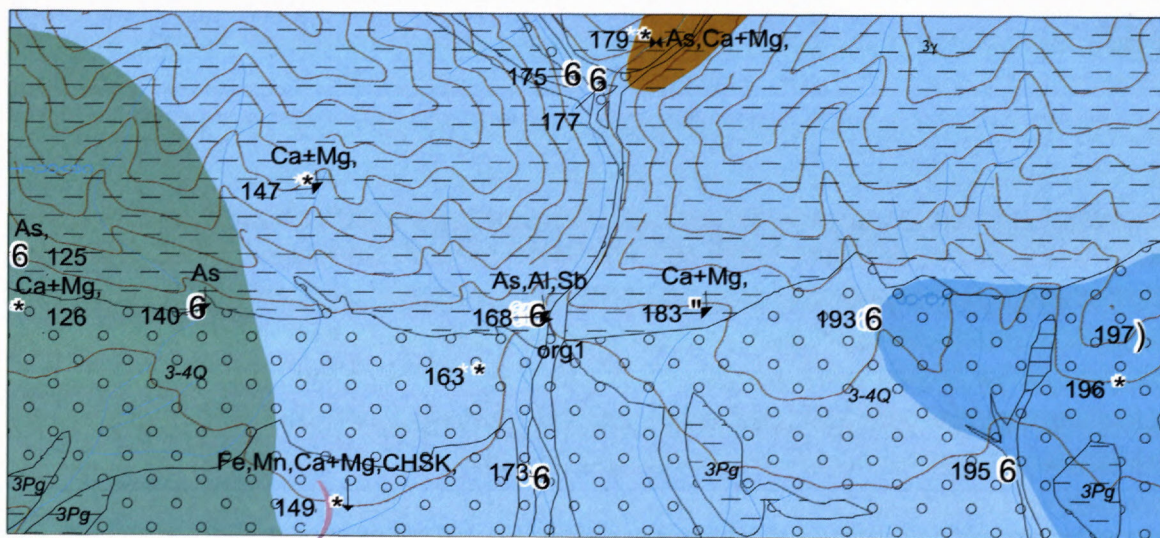
Fig. 3 Map of Natural Water Quality. A segment of the Vysoke Tatry Mts. Colours show qualitative properties of natural water. Traffic lights were used to show the water quality: blue represents the best water quality and red-most contaminated water. Raster represents the type of permeability. ?, □,? – type of sample collection sites with serial number, Al, As, Sb, ... – represent symbols of elements and components exceeding upper permissible limits.

chemical mapping of selected regions of Slovak Republic at a scale of 1 : 50 000 or a scale of 1 : 25 000 in urban areas (Fig. 2).

Environmental-geochemical maps, focused on sediments, soils, waters (ground, surface and meteoric) and rocks, represent a part of the basic set of maps of Geofactors of the environment. This set includes, except for geochemical maps also hydrogeological, engineering-geological, pedological maps, and maps of natural radioactivity. In order to unify and standardise the methodical process and compatibility of mapped regions there have

been issued method instructions for the compilation of individual maps, which are obligatory for all works financed by the Ministry of Environment of the Slovak Republic.

The following maps are standard for all regions: a map of natural water quality, a map of stream sediment geochemistry, a map of geochemical rock types and a map of pedogeochemistry.

Taking into account specifics of regions the following special geochemical maps were created: a map of snow geochemistry (in urban areas), a map of chemical time
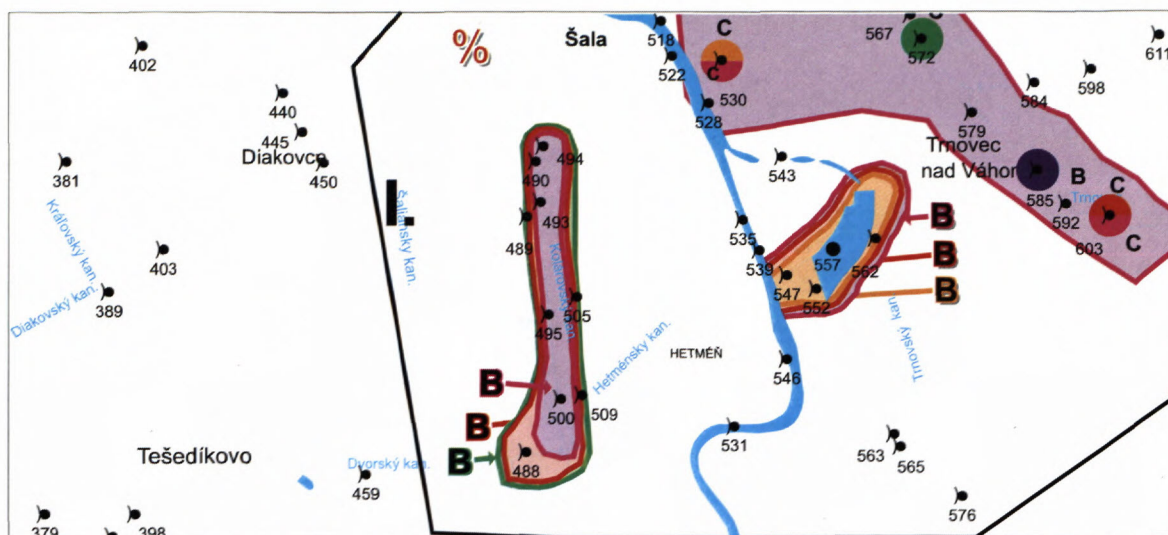
Fig. 4 Stream Sediments Geochemistry Map. A segment of the Galanta district. Multi-element map; colours – both surface and borders represent areas of exceeding contents of individual elements (green –Zn, violet – Hg, red – Cu, orange – As, ...). Circles represent the point anomalies. White represents non-contaminated areas. Points with serial number represent sampling collection sites. B, C – represent the level of exceeding values according to „Nederland letters". Contour borders with roman numbers allocate the areas recommended for detailed research.
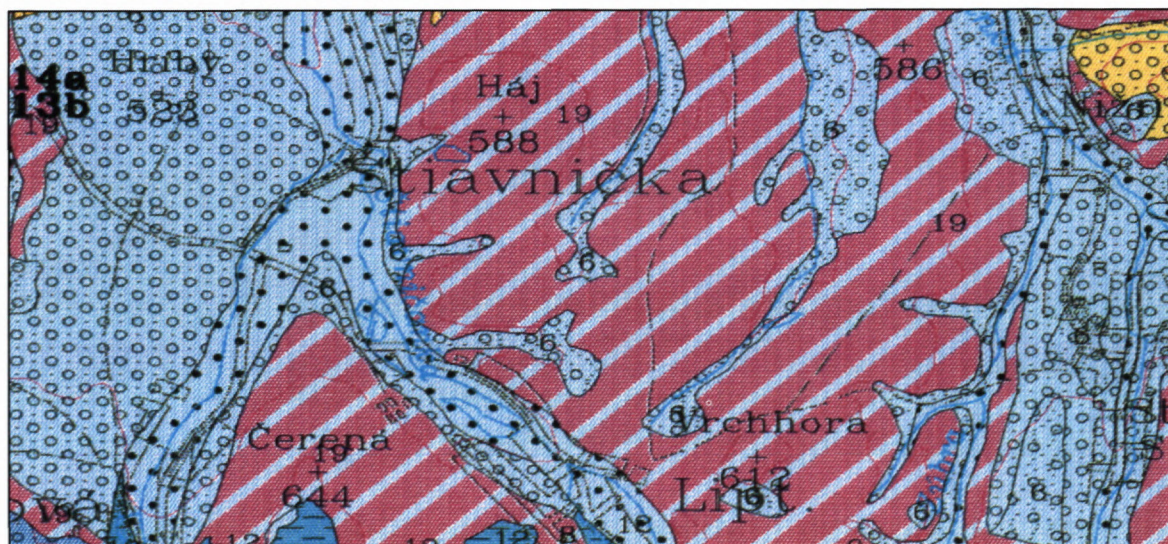
Fig. 5 Map of Geochemical Rock Types. A segment of Vysoke Tatry Mts. Colours represent geochemically defined rock types according to their reactivity. Geochemical reactivity decreases from high reactive carbonates (blue colour) trough basic rocks (e. g. basalts – green colour) and intermediate and rocks (e. g. andesites, rhyolites, granitoides – red colour) to non reactive siliceous rocks (e. g. quartzites – yellow colour). Semaphores were used to express reactivity of rock types. Blue represents the highest reactive rocks-carbonates and red one – non reactive-siliceous rocks. Raster shows genetic type (magnetic, metamorphic, etc.) and aggregate type (fine coarse-grained, breccias, etc.). Representation of two different altered rock types (e.g. claystones and sandstones) is shown as oblique bands.

bombs, a map of contamination degrees, a map of critical loads and their exceeding etc.

The analytic data and measurements gathered in the Geochemical atlases are used in the compilation of environmental-geochemical maps. The new sampling sites and new measurements are pointed predominantly in areas of geochemical anomalies found in the Geochemical Atlas, for the purpose of their verification and study in detail.

In environmental-geochemical maps the environmentally relevant anomalies (positive and negative) of ele-

ments/components that are of either human or geogenic origin are expressed in a synthetic way. As environmentally relevant elements and components we consider those that can negatively influence biota and man. The standard values (limit values from the Slovak Standards and standards valid for individual components of the environment) are the base for the determination of the environmentally important concentrations.

The number of monitored items for geochemical mapping usually ranges between 25–30 elements and compo-
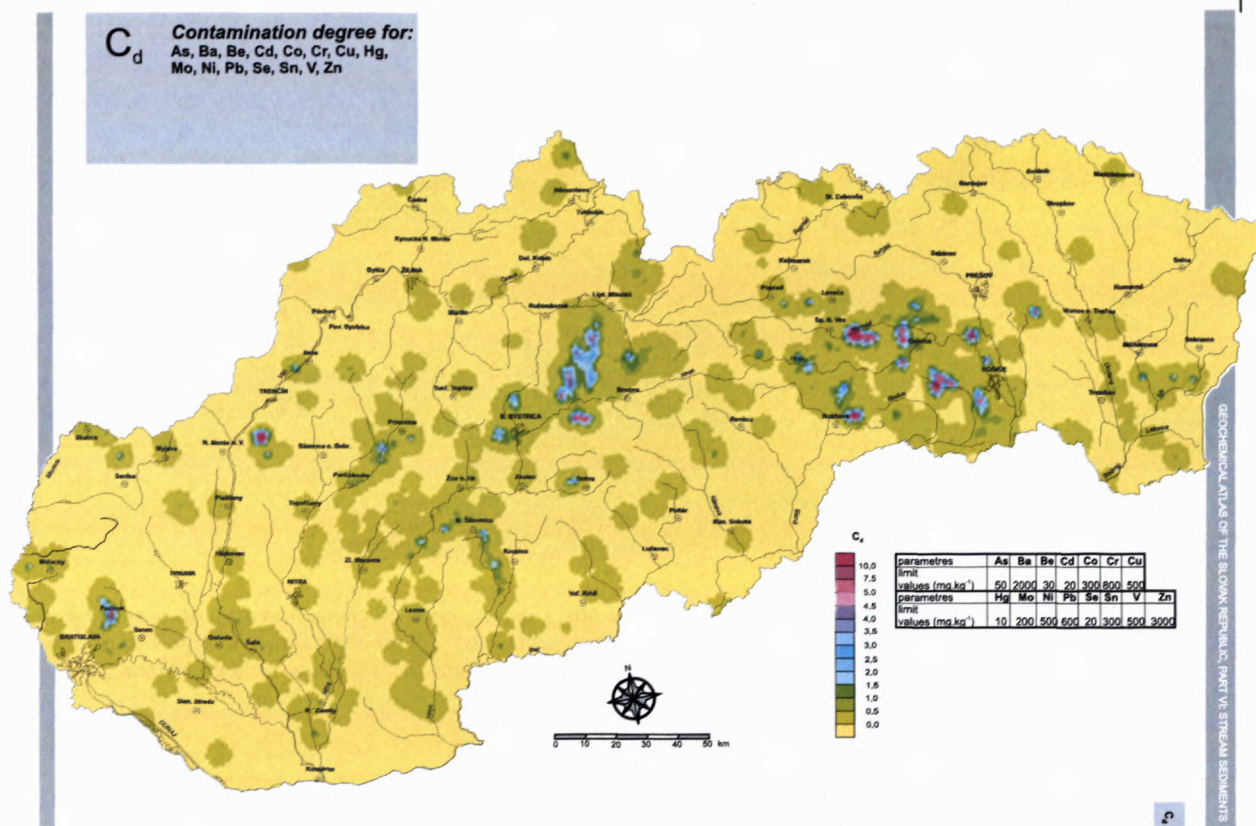
Fig. 6 Geochemical Atlas of Slovak Republic (1 : 1 000 000), Part VI: Stream Sediments. Map of Contamination Degree
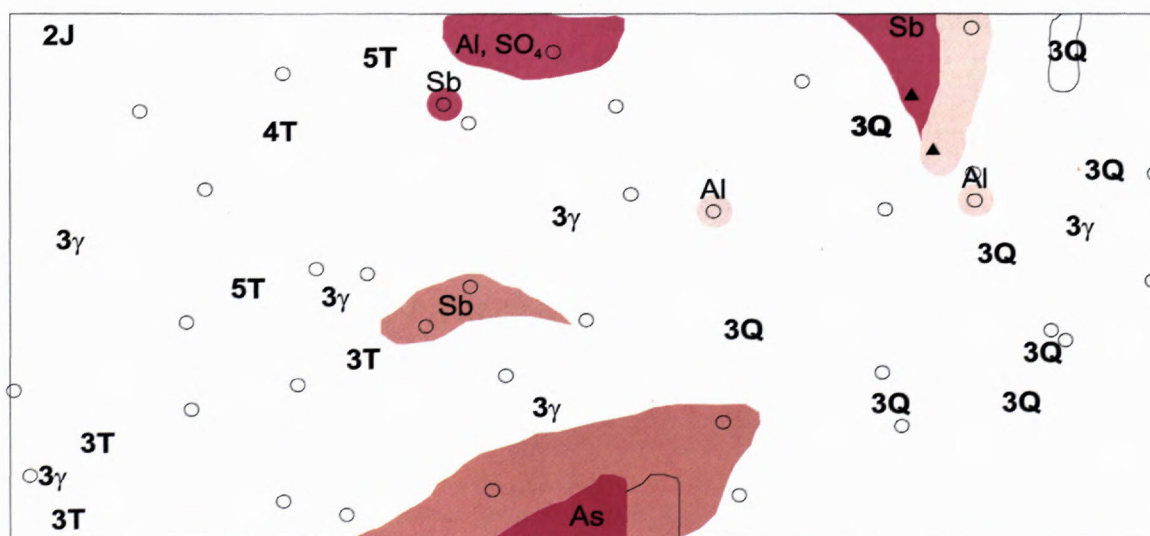
Fig. 7 Map of Areas with Contaminated Groundwater. A segment of the Nizke Tatry Mts. Al, Se ... symbols of elements exceeding limit values. Red colour, areas and point anomalies (local contamination) represent groundwater contamination. Red-most colour – higher contamination, white – represent non-contaminated areas. Geological age of aquifers is shown as a symbol (Pg – Paleogene, T – Triassic, ...). Raster represents type of aquifer permeability. Numbers show the degree of water bearings of aquifers (1-very high, 2-high .... 5 = area without aquifers).

nents (often even more). Modern computers enable to visualise the informative distribution of each monitored element in form of a model of monoelemental maps. However, the big set of maps hardly offers a full overview of the degree of contamination of the environment. On environmental-geochemical maps the monitored ele-

ments are joined into groups of elements according to their toxicity or their similar geochemical properties. In maps the determined groups of elements are plotted (Natural Water Quality Map – Fig. 3) or the anomaly concentrations are visualised with the use of method of intersection of subsets of monoelemental anomalies,
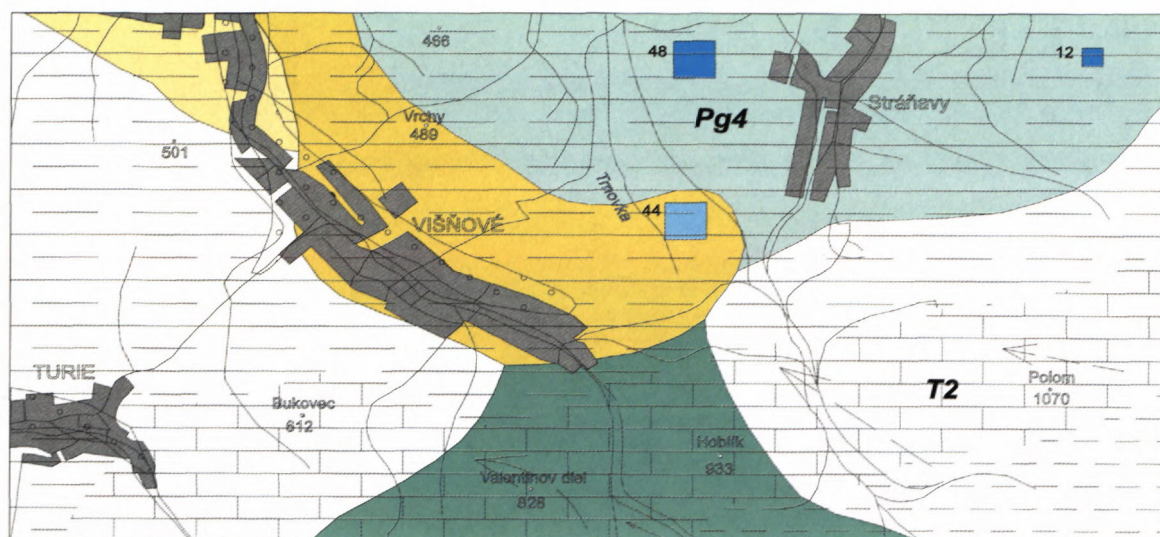
Fig. 8 Map of Chemical Time Bombs. A segment from the Mala Fatra Mts. Colours represent critical areas, plotted on the bases of potential CTB sources (contaminated groundwater, surface water, stream sediments). Square sizes show the degree of toxicity and intensity of blue colour shows the potentiality of spreading of CTB hot spots into the environment. Description of the rock environment as in Fig. 7.
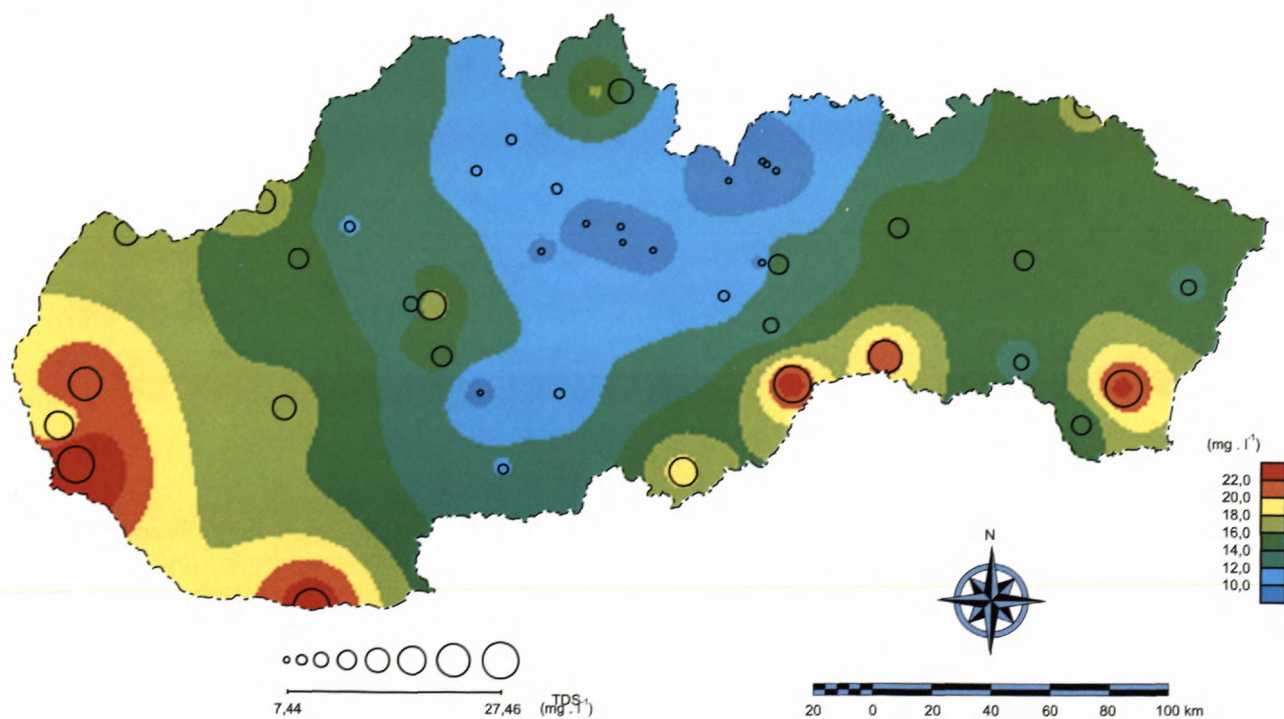
Fig. 9 Geochemical Atlas of the Slovak Republic, Part I: Groundwater. Distribution of TDS of snow-pack. Mean contains after 20 years of monitoring, 1997–1996.

which are expressed by colour of the first subset and in the intersection area by colour contour of the second subset (Stream Sediment Geochemistry Map - Fig. 4). In the case of the Map of Geochemical Rock types (Fig. 5), the distribution of chemical elements in rocks is expressed by mean concentrations of elements in rock bodies (complexes) that can be mapped in a field and outlined on a map. The complexes are outlined according to their geochemical (value of concentrations of monitored elements), as well as mineralogical (mineral content), and genetic criteria. A calculation of the contamination degree C_d that cumulates all excessive values of all monitored elements is another approach visualising and evaluating the analytic data from monitored analytic results.

The contamination level can be visualised in maps, the with help of mathematical interpolation, as well as with, the help of decorrugation (Fig. 6), or areas with equal degree of contamination can be joined into anomaly zones by the author of a map (Fig. 7). As an example of a map where various components of environment are evaluated, we can use the Map of Chemical Time Bombs (CTB – Fig. 8). In this map the anomalies in surface and underground waters and stream sediments are expressed together with point sources (waste disposals) (Rapant - Bodiš, 1995).

Mapping of critical loads/overloads was done in cooperation with the Norwegian Institute for Water Research (NIVA) according to the Henriksen et al. (1992) method. In the whole area of the Slovak Republic following receptors were monitored: surface and groundwater and forest soils (Bodiš et al. 1995, Babiaková et al. 1996).

A specific example of mapping of abiotic environmental component is mapping and monitoring of chemical composition of snow cover. This research was carried out since 1977 (Vrana et. al., 1989) a 44 selected sites around Slovakia (Fig. 9).

Conclusion

The applied geochemical research of environmental problems throughout the world dated since the end of fifties and intensively in sixties. In many countries there were established research teams that were focused on the application of geochemical background and its potential impact on agriculture, water management, land use, relation to biota and human health, etc. The first multi-disciplinary workshop has been organised in the USA at the beginning of 1972 (Thortnon, 1983) by the Sub-commission for Environmental Geochemistry in Relation to Health and Illnesses at National Academy of Science, and by the Association of Environmental Geochemistry.

The beginnings of environmental-geochemical research and survey of the Slovak Republic are dated since the second half of seventies. The task of protection of the environment and solving problems of the environment contamination has begun to be studied on the example of natural water because the water component of the environment is not only the most dynamic but also the most vulnerable.

The widespread geochemical mapping of Slovakia since the nineties is one of the bases for the geoscience disciplines for complex evaluation of the environment state of the Slovak Republic. The compiled geochemical databases and map outputs are integral part of the national environmental information system.

The methods used process for field and laboratory works, as well as the interpretations used in the Geochemical Atlases, were done with respect to well established methodology of similar foreign projects (IGCP 259, 360). The subsequent environmental-geochemical mapping with more detail scales has been done according to original methodical instructions that are based on the database and the results of the Geochemical Atlases and that respect the natural and socio-economic conditions in Slovak Republic.

On the one hand, the achieved results enable to evaluate and objectify environmental data of the Slovak Republic and determine the degree of its contamination, They form the base for the following environmental-geochemical works in regional and local scale and for study of rules of re-distribution and migration of elements in individual components of the environment and the mechanism of their influences and impacts on ecosystems and humans.

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Medical Geochemistry: A Brief Outline of the Problems and Practical Application in the Region of Žiarska kotlina Basin

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Abstract. Characteristics of the state of health of child population aged 0 - 14 in Žiarska kotlina Basin were studied to determine whether they were affected by geochemical agents in the environment. The potentially hazardous areas where the health of the population is endangered were outlined, according to data from State Health Institute in Žiar nad Hronom. In comparison to other areas we observed increased occurrences of malignancy, illnesses of endocrine glands, congenital defects and, up to 1989, also illnesses of the circulatory system. From the point of view of medical geochemistry the abundance of congenital defects and tumor illnesses of the monitored population can be related to increased natural radioactivity of the rocks and waters in the region and also by radon risk. The quality of the drinking water is related to the state of the health of the child population. In particular the concentration of nitrate in public water supplies, as well as in public and private wells is linked to health. The hazard for infants is great, especially in the settlements of Bzenica, Dolná Ždaňa, Piteľová and Lovča. These hazards resulting from the water and soil components of the environment of the Žiarska Kotlina Basin were detected and verified in direction of the river and creeks flats and their adjacent alluvium. From the monitored diseases and the contaminated areas we infer that a causal relationship exists between concentration of fluorine in the environment and the high rate of occurrences of tumors, blood illnesses, illnesses of endocrine glands and circulatory system. We consider these results and the interpretations presented herein as only a first step; the problem requires another more detail investigation.

Key words: medical geochemistry, Žiarska kotlina basin, child population

Introduction

Geographical factors of the distribution of some diseases are well known, practically since the medicine has become a science (Lag, 1992). A study of the history of medicine shows that Hippocrates and some of his fellows dealt with this problem more than two thousand years ago. Later, in the 4th century A.D., the ancient Chinese knew of the influence of environmental conditions on human health, especially regarding the occurrence of thyroiditis (Lag, 1992). Of course, these tracts from Middle Ages did not have any significant influence upon next evolution of this matter. It could be developed more progressively only after fundamental sciences like chemistry, physiology, microbiology and pathology achieved appropriate level.

Even though the medical science had known a long time ago that some diseases are typical for different parts of the world, the medical geography (some authors also use a term geographical medicine) (Armstrong, 1971; Khun, 1998) rose in to the level of a science only in the first decades of the 20th century. Of course, concerning the geographical aspects of the distribution of various

diseases they mainly searched for connections with climatic and/or topographic factors. Classical examples of such research includes, for instance, the well known relationship between specific climatic factors (temperature and rainfall) and the occurrences of malaria and yellow fever (Keller, 1988). An example from western Slovakian research is, a study of the distribution of tick encephalitis relative to selected geographical parameters (Krajčír, 1989). However, it is important to mention that a blend of geography and medicine cannot explain casual relations between large geographical differences and the distribution of some diseases. A responsible interpetation of such causality essentially needs geochemical knowledge (for instance, the distribution and forms of occurrences of chemical elements in the geochemical environment, their migration, etc.). This is opening a space for indipendent scientific field – *medical geochemistry*.

Problems of Terminology and the Role of Medical Geochemistry

The term "geomedicine" was used for the first time in Germany in 1931 (Lag, 1992). However, it was applied

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without a clear definition of its meaning only and with remark about its establishment it as an independent scientific field which problems would be addressed to scientists from various fields. The term „geomedicine„ had been used only rarely during the next decades. Moreover the term was not used consistently and in the same context. However, it is not easy to offer a good definition of this term. Geomedicine was defined as the study of the influence of normal environmental factors on the geographical distribution of health problems of human and animals (Lag, 1992). The definition excludes influence of so-called internal environmental factors (for instance, the working conditions) that are objects of research of industrial medicine. The term „industrial medicine„ was used mainly in regard to the international project "Man and the Biosphere", which was coordinated by Norway during 1960 - 1970 and in which a great emphasis was put upon the geomedicine research. Almost simultaneously, activities with similar objectives were started in Great Britain and the USA, where the expression "environmental geochemistry and health" came from (Khun, 1998). At present environmental geochemistry is viewed as a scientific field in which health is considered as an application of geochemistry and geochemical mapping of health condition of plants, animals and humans. Its basic researches were done in Canada, the former USSR, Great Britain, the USA and Scandinavia. For completeness, the term "geosanitation" is used in the former USSR (Lazarev, 1966). This field of study was considered to be a medical prophylactic science and was in close relationship with sciences like geography, geology, geochemistry etc. In the former Czechoslovakia, and now in Slovakia, the term used for research in this field (also as a study subject at the Faculty of Natural Sciences of Comenius University) is the one used in the title of this article. Its definition is as follows: *Medical geochemistry, as a part of geomedicine, is the science concerning the influence of chemical composition of natural and man effected geochemical environment on human and animal health, in the terms of external environmental factors (Khun, 1992).*

Geochemical Environment

The chemical composition of organisms reflects the external geochemical environment to a certain extent. The receiving of elements and substances from the environment depends not only upon the character of the organisms, but in many cases it dependes mainly upon the concentration of elements and on the overall character of the environment, i.e. on the conditions prevailing in the geochemical environment. This environment is not homogenous; trace elements as well as macroelements are distributed unevenly in its different areas. This environment depends upon the geological history of the area, the specific character of soil parent material, and the specific features of soil formation processes and chemical character of the waters. Then the results are, that areas differ from the "standard" by either an increased or decreased concentration of some element or elements. For humans and for all other organisms the range of concentrations of

element in the environment is very important; it is called the "protecting geochemical shadow" (Zýka, 1972). This means that organisms can live in health only within a certain range of chemical composition of the geochemical environment. However, the natural environment is to a great extent suppressed in many areas, and in some cases it is entirely suppressed. The last decades are characterized by the formation of a new artificial environment created by the intensive activities of mankind. Today the environment is typified by a general disturbance of the geochemical balance.

The relationship between humans and geochemical environment are closer than it is generally assumed. A sick state of health in humans makes itself felt whenever the balance between the human organism and the factors of external environment is disturbed. This state can be introduced by influence of endogenous factors (condition of human organism itself) as well as by the influence of exogenous factors (influence of the environment). Here then, is the focus of geomedicine research mainly. Unfortunately, the geochemical influence effects the human organism even before its birth. Much data published recently suggest that the character of the geochemical environment codetermines to a certain level the physical and psychical state of an adult person even before his/her birth.

Trace Elements in the Environment and Diseases

In many cases a dependence was observed between diseases and anomalous concentration of certain trace elements in the human organism. In some cases a direct relationship was also observed between the changes of certain trace elements concentrations in some organs, tissue or blood and the occurrence, seriousness, and duration of a sickly state. Although many scientists are skeptical about this matter, it certainly can be a step toward the discovering of any role that trace elements have in pathogenesis of given diseases, and some have, or certainly will also have, diagnostic or prognostic value (Zýka, 1972).

In his numerous publications V. Zýka has divided diseases with regard to the relationship between the concentration of trace elements in the geochemical environment and human health into two groups:

- Diseases induced by a simple deficit or abundance of a given element in the environment.
- Diseases induced by a complex disturbances of the balance of geochemical environment.

In developed countries the occurrence of diseases due to a primary and simple deficit of trace elements is very rare. This is so because the consumed food typically is derived from different parts of a country (even of a continent or among continents) and assures a sufficient supply of diverse elements. Of course, these problems are more frequent in neglected, poor countries where the inhabitants depend upon local supplies. In such cases, the dependence of the health of people upon the local geochemical environment is clear. For instance, miscellaneous deficiency diseases, include ones such as anemia or

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rachitide (Hopps, 1971). In some cases it is not a matter of a deficit of an element in the environment but of its unavailability for plants from soils caused by its fixation to the soil.

On the other hand, "geochemical" diseases are more frequent in environments enriched with various elements. For instance, a high concentration of Cu in the environment is the reason of various Cu-toxicities. An endemic gout a frequent phenomena in a environment rich in Mo. Exemas and eye illnesses are frequent phenomena in areas with a high clarke of Ni in soils and waters. Excess Mn in environment may be a reason of hypertension. In many cases it is not the matter of a simple effect of an increased concentration of single element but a complex effect of the environment, although the determining factor is an excess of a single element in the environment.

The second group of diseases is more complicated. Their constant increas and spreading is caused mainly, or to certain extent at least, by radical changes in the geochemical environment, i.e., disturbances in the balance of this environment. This group includes such serious diseases as disseminated sclerosis, congenital defects, cancer diseases, diseases of the blood circulation system. For instance, a study in England shows that in the areas with increased concentration of Pb in soils and waters have almost three times higher occurance of the disseminated sclerosis than in the areas with a normal concentration of Pb. On the base of comparison of the illness distribution and geological conditions of the areas (occurrences of galena) also Finnish authors have admitted that there can be direct correlation between frequency of the illness occurrences and increased concentration of Pb in the environment (Khun, 1992).

Some data collected during recent years indicates that some cases various intensity of geographical distribution of congenital defects are significantly effected by the geochemical environment. Distribution of these anomalies was studied in the USA with respect to radioactivity of the environment. An increased occurrenc of all types of congenital defects (except mongolism) was observed in northern New York State, an area in which rocks contain high concentrations of radioactive elements.

Probably the earliest papers treating medical-geochemical research were published in England. The first "geochemical" theory of cancer origin was published by Haviland in 2. half of the last century (collection of works from years 1868 - 1888, in Zýka, 1972; Zýka, 1975). Haviland recorded various level of mortality caused by cancer diseases (the number of deaths per 10 000 inhabitants during 1851 -1860 in 625 registered regions of England and Wales) on a geological map, and he studied the dependence of the distribution of these diseases on the overall character of the various geological - geographical areas. This revealed that the areas with high mortality were predominantly alluvial basins that were seasonally flooded (acid soils rich in organic matter). On the contrary, mountain areas were characterized by low cancer mortality. However, the most interesting discovery was the particulary low rate of mortality in limestone areas. For instance in Hampshire, the limestone area was char-

acteristzed by low cancer mortality. The situation is similar in river flat of Test and Itchen Rivers that come from limestone regions. There are many examples demonstrating the relationship between concentration of some chemical elements in the geochemical environment and cancer diseases distribution (for instance Augustin and Zejda, 1991, in the former CSFR; Piispanen, 1991; Yang and Hung, 1998) but their overall review is not scope of this article. However, if we analyze the results of individual authors concerning geographical distribution of cancer diseases and their relationship to geochemical environment, we can summarize that the areas with relatively low cancer mortality are characterized by well aired and drained soils poor in organic matter, rich in sources of fresh, hard and not chemically treated water and also with sufficient amounts of Ca, Mg, Na, Cu and Mn accessible in water. On the other hand, the areas with high cancer mortality are characterized by high content of organic matter in soils (acid soils), poorly aired and drained soils, soft waters (deficit of Ca, Mg, Na, Cu and Mn) or artificially treated surface water with increased content of some trace elements as, for instance, As, Co, Cr, Ni, Pb, Ra, V, Zn etc.

Cardiovascular illness was relatively infrequent at the beginning of the 20th century, while in present it is main cause of mortality in the industrial countries. Also some interesting recent studies indicate that the geographical differences in cancer mortality are linked to geographical differences of trace elements concentrations in soils and waters, respectively, with disturbances of balance in the geochemical environment (Bada et al., 1998). The geographical distribution of mortality due to circulatory illnesses was studied in many countries: Japan, USA, Great Britain, Ireland, Switzerland and others where a very interesting interrelationship between mortality and the character of geochemical environment was observed. Special interest was paid to the chemical composition of drinking water – i.e. hardness of drinking water (Zielhuis and Haring, 1981; Bernardi et al., 1995; Bada et al., 1998), but less research projects were focused on the possible relationship between mortality and chemical composition of soils and atmosphere.

After the Second World War the stroke (apoplexy) was the main reason of mortality in Japan. The mortality caused by this disease was also high in comparison with that one in the USA, Great Britain and Germany at this time. However, in Japan there are remarkable geographical differences in this mortality. In north-east (NE) Japan the river water carry more sulfate (waters with dominant of SO_4^{2-} ions or acid waters, characterized by the presence of a free sulfuric acid). This geographical distribution of river waters coincide with an increased rate of stroke mortality. The relationship between the geographical distribution of the high mortality and ratio of SO_4^{2-}/CO_3^{2-} in river waters is very significant. River waters of provinces distinctive for their high stroke mortality have the ratio greater than 1.8 (the NE provinces), while in provinces with lowest rate of mortality the ratio is less than 0.3 (western Japan provinces). Zýka (1972) summarized the results concerning the circulatory system illnesses obser-

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ved in various countries, regions and cities and he found that ilness occurrences and mortality caused by this illness increase with decreasing water hardness, with a decreasing concentration of Ca in the drinking water, respectlively.

Several of the above mentioned examples of the influence of the geochemical environment on human health point out the importance of this problem witch was neglected in the past. However, recently there has been increased interest in this field – the establishment of The Society for Environmental Geochemistry and Health (SEGH) in London, which is also publishing a journal "Environmental Geochemistry and Health".

Here we publish the preliminary study of the Žiarská Kotlina Basin as a demonstration of the knowledge of medical geochemistry. The conclusions reached in this study represent the results of the research project "Evolution of the carrying capacity of the Žiarska Kotlina Basin " in the topic of "Characteristics of health state of the child population in the Žiarská Kolina Basin". The project was sponsored by Ministry of the Environment of Slovak Republic, under the Division of Nature and Country Conservation, assessment of influences on the environment and interdivisional relations.

The Ecological and Veterinary Laboratories Ltd. of Spišská Nová Ves were the contractor of the project. Within the frame of the project, the health - sanitary loads of the population were analyzed with respect to geochemical assessment of individual environmental agents. The data about the health state of the child population of the studied region originated from annual reports of health care of treated children aged 0-14 years during 1987-1995 in the former Žiar nad Hronom district (according to administrative organisation of districts in Slovakia). The data from pediatric clinics of hospitals of the four tributary areas: Žiar nad Hronom (ZH), Nová Baňa (NB), Banská Štiavnica (BŠ) and Kremnica (KR) were available. Data from year 1991 were available only from ZH and BŠ and data from year 1987 were available only for infant children (0-6). With respect to „10th Revision of the International Classification of diseases MKCH-10,, following groups of diseases with their following numerical and descriptive identification were monitored:

I. Infectious and parasitary diseases (diagnoses A00-B99)

II. Tumors (diagnoses C00 - D48, for instance, malignances and carcinomas in situ, malignances of lymphatic, hematopoethic and related tissue)

III. Diseases of blood and hemopathic organs and some defects of the immune mechanism (diagnoses D50 - D89)

IV. Disease of the endocrine glands, nutrition and metamorphism (diagnoses E00 - E90)

V. Mental retardation and defects of behavior (diagnoses F01, F03-F99), for instance, mental retardation

VI. Diseases of the nerve system (diagnoses G00-G99), for instance infant brain illness

VII. Diseases of the circulation system (diagnoses I00 - I99), for instance hypertension and other diseases of the hearth, brain and veins

VIII. Diseases of the respiration system (diagnoses J00 - J99), for instance asthma

IX. Diseases of the digestion systems (diagnoses K00 - K93), for instance ulcerous illness of stomach

X. Diseases of the skin and subcutaneous tissue (diagnoses M00 - M99), for instance atopic dermatitis

I. Diseases of the muscular and skeletal systems and mesodermal tissue (diagnoses M00 - M99), for instance juvenile arthritis

II. Diseases of the urinal and genital systems (diagnoses N00 - N99), for instance inflammatory illness of the kidnies

III. Congenital defects, deformations and chromosome anomalies (diagnoses Q00 - Q99), for instance congenital defects of the circulatory system

A comparison of the percentage of the tributary areas of the former Žiar nad Hronom district result the facts, from which the following are the most significant:

a) A significantly increasing trend of tumor occurrences in the tributary ZH area (Fig. 1).

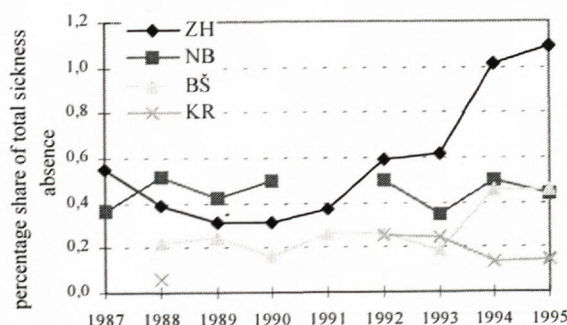b) An indication of increasing trend of blood diseases since 1993 (Fig. 2).
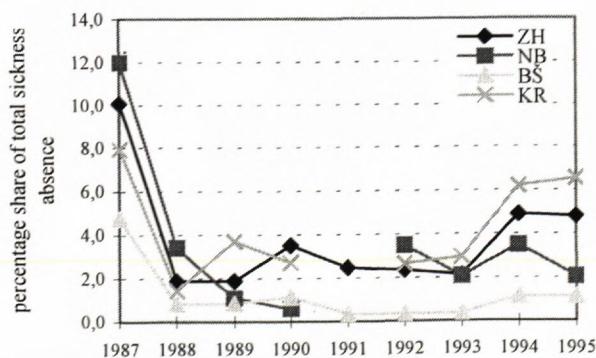

Fig. 1: Diseases II. - tumors

Fig. 2: Blood diseases - III.

c) The distribution of endocrine gland illnesses in the ZH is markedly greater than in the other tributary areas (Fig. 3). Thyroid tumors frequently occur in former ZH district in comparison with the Slovakian average (Khun et al., 1996).

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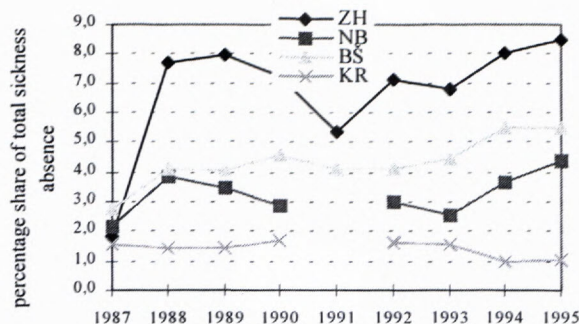
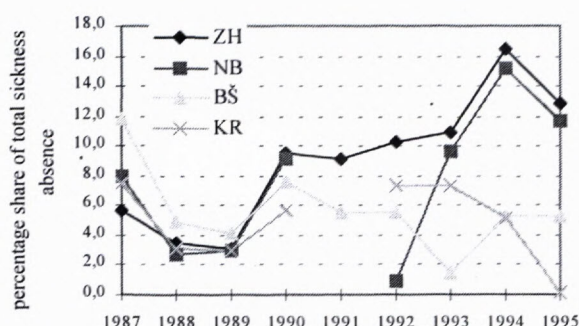21

Fig. 3: Diseases of endocrine glands - IV.

Fig. 4: Diseases XVII. - congenital defect

d) The rising trend of congenital defects since 1990 exceeds those in other districts (Fig. 4).

The result of the environmental-geochemical evaluation of the collected data is compiled on "The map of potential hazard in term of population health in Žiarská Kotlina Basin" at a scale 1:50 000 (adapted on Fig. 5) in which an assessment of various parts of Žiarska Kotlina Basin is given for the health of the child population. The influences of specific agents are summarized as follows: .

Rocks

From the stand point of possible influence of rock environment on health of monitored population the higher importance has a group of sedimentary rocks (in comparison to neovolcanoes) with wider range of toxic elements (As, Cd, Pb, Se, Sb) that have high potential ability to enter the environment (soils, water). In term of elements in food chain the fluvial sediments and deluvium - fluvial sediments (Holocene, Pleistocene) are characteristic by association of 4 toxic elements. They virtually reflect their geochemically anomalous distribution from 5 source areas (Méres et al., 1998): The northern part of the monitored area is characterized by the source areas of creeks Rudnica and Lutilský Potok. Water of Rudnica Creek springs in Kremnica ore field (anomalous contents of Zn (max. 1 107 mg.kg^{-1}), As (max. 47:3 mg.kg^{-1}) or Hg (max. 0.352 mg.kg^{-1})) and possible negative influence on settlements Stará Kremnička and Pitelová. Lutilský Potok Creek has anomalous concentrations of As (50.7 mg.kg^{-1}) and it threatens part

of village Lutila and town Žiar nad Hronom. The southern part of the monitored area is characterized by sources areas of Teplá Creek (land cadastres Sklenné Teplice, Lehôtka pod Brehmi, Hliník nad Hronom, Repište) and Vyhnianský Creek - the area with polymetallic mineralization (remarkable concentrations of Hg, max. 0.774 mg.kg^{-1}, As 43.2 mg.kg^{-1}).

The alluvial sediments of the Hron River flat contains already contaminated industrial material with anomalous concentrations of elements and determinate quality of another abiotic agent of the environment, that affect the settlements of Šášovské Podhradie, Ladomer, Dolná Ždaňa, Bukovinka, Revišťské Podzámčie, partially Lehôtka pod Brehmi and Bzenica.

Deficit in certain elements can also have a deliterious effect on the health of a population living in, or getting its food from the area of the deficit. The local rock types – quartzite, rhyolite, rhyodacite, slate and andesites - are low in Ca, Mg and P. These deficits can also have a negative effect on the health of a population. For example, the absence of Ca and Mg in the environment may by related to increased occurrences of malignancies. For instance, there is the "Magnesium theory" of increased incidence of malignancy or the "anticarcinogenic" influence of environments rich in Ca (Khun, 1992). Similarly, increased concentrations of As, Cd, Co, Cr, Pb in the environment are related to increased mortality due to cancer.

Soils

From the medical-geochemical aspect there are important sloppy fluvisoils of the Hron River and Lutilský Creek flats witch have a remarkably high content of organic matter that can have an influence on the occurrence of cancer. It is well known from the literature (Tromp and Diehl, 1955; Zýka, 1972) that areas with a high cancer mortality have characteristically high content of organic matter in soils (acid soils rich in organic matter), bad aeration and drainage (swampy). This relationship can be approximately illustrated by Figure 1. The graph on the figure indicates the highest occurrence of tumors in the child population, aged 0 – 14, right in the area of Žiar nad Hronom - in the monitored area. The soils in the Hron River flats are the most contaminated soils with heavy metals (contents reaching indication values B and C, Decision of Ministry of the Agriculture of the Slovak Republic No. 531/ 1994; Vozár, 1998). For instance, the contents of arsenic is within the range of C values (50 mg.kg^{-1}) in area of cadastres Lutila, Lovčica, Trubín, Stará Kremnička, Šášovské Podhradie, Ladomer, Vieska, Hliník nad Hronom and Repište. In the case of this element its carcinogenic, mutagenic and teratogenic effects are subjected to intensive medical research; however, in most cases it is the matter of professional exposure. For instance, increased occurrences of lung cancer among mines in the Schneeberg was caused by a high concentration of As - about 1% in mine dust (Khun, 1992). Its highest accumulation in human bodies is in hair

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Legend:

— border of the area of interest

— border of cadastres

⊞ high danger of hazard from soil and water component

▨ critical danger of hazard from soil and water component

▦ high danger of hazard from drinking water (nitrates) for infant population

▣ critical danger of hazard from drinking water (nitrates) for entire population

▨ high danger of hazard from air

■ critical hazard from air

— radon risk

Fig. 5 The map of potential hazard in term of population health in Žiarska kotlina Basin

and nails, doses of 5 - 50 mg per day (the toleration is different from human to human) are toxic, a lethal dose for a human is 100 - 300 mg per day (Bowen, 1979). From the environmental point of view, the physical properties of As compounds are very important. For instance, methyl arsenic (a very poisonous substance) comes into existence during regeneration of soils contaminated with As, however, it is quickly oxidized in the presence of sunshine. Receiving As from plants ("food chain") depends upon the concentration of soluble As in soils, soil type and plant sort. Data by Šalgovičová

et al. (1992) also revealed, that high concentrations of As were detected in the vicinity of Žiar nad Hronom in samples of animal origin.

Waters

The state of health of children (mainly infants) and the overall population is related to the quality of drinking water especialy concerning the nitrate concentrations of public water supplies, as well as in public or private wells (Fig. 6) (data from State Health Institute in Žiar nad Hronom, 1996). On the basis of nitrate concentrations

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Fig. 6: Scheme of nitrate occurrence in public and private wells according to results of laboratory tests of the State Health Institute in Žiar nad Hronom (y. 1996)
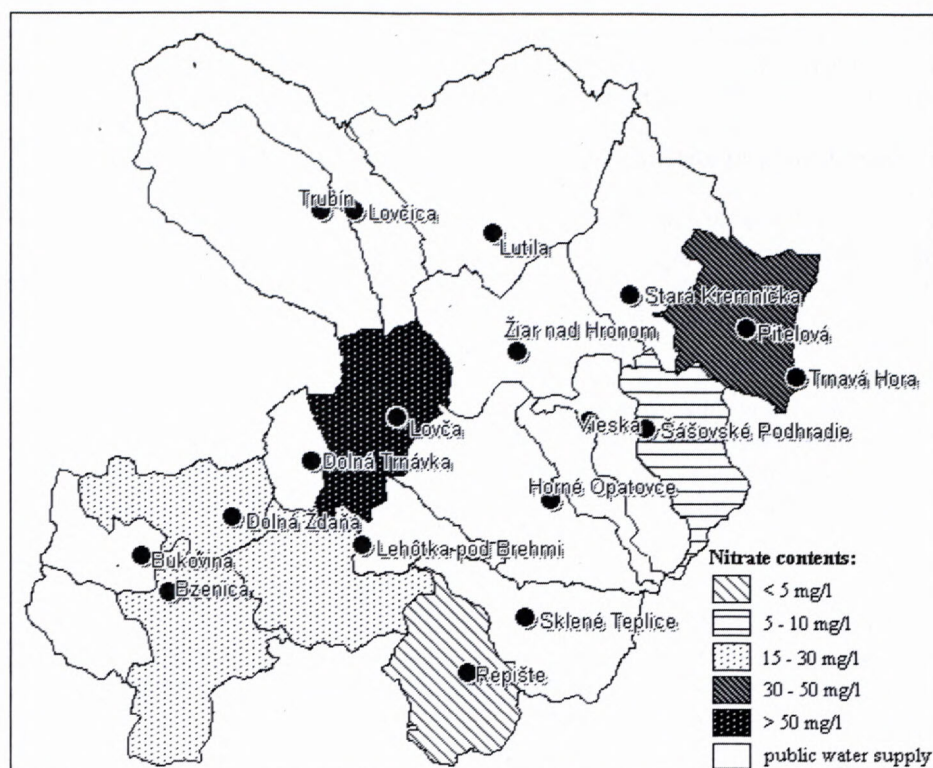
exceeding the allowed critical values, the potential negative influence and critical hazard can be predicted for cadastres and the wider surroundings of the Žiar nad Hronom. A great hazard for the infant population is from drinking water (15 - 50 mg.l^{-1} of nitrate, recommended value for infants is less than 15 mg.l^{-1}); it is also a critical hazard for the whole population where drinking water contains nitrate in excess of 50 mg.l^{-1}, such as was observed in the settlements of Bzenica, Dolná Ždaňa, Pitelová and Lovča (the critical hazard with respect to Slovak Technical Criteria for Drinking Water - STN 75 7111). It is important to mention that the average was counted from individual values, which means that in a given cadastres there are locally also values of NO_3^- even greater than 15 mg.l^{-1}. These facts are important mainly because the infant organism is 100 x more sensitive to NO_3^- than the adult organism. In the intestine flora nitrates (NO_3^-) are reduced to nitrites (NO_2^-) that is actively bonded to blood hemoglobin instead of the oxygen. As the result, there is insufficient oxidation in the infant organism and the occurrence of nitrate alimentary–methemoglobinemy (Sattelmacher, 1962; Shuval and Gruener, 1972). Nitrates also damage children liver. The accumulation of these residues and their further metabolism (mainly the origin of nithrosamine) contribute to the origin of cancer; a possible relationship in the tributary areas ZH (Fig. 1), blood diseases (Fig. 2), respectively. Noteworthy is also the fact, that in the case of adults the nitrates can be changed to nitrosamine and nitrosamide that are carcinogenous (Škárka and Ferenčík, 1992). There is a remarkably higher mortality rate due to tumor diseases of the inhabitants of the former Žiar nad Hronom district in comparison to the rest of Slovakia (Turčanová, 1994).

The danger from water and soil component was investigated and verified on the base of the negative influence of various components having a toxic effect, which migrate towards the river and creeks flats, and their adjacent alluvial plain in the area of Žiarska Kotlina Basin. The hazard is influenced by climatic changes, changes in structural - mechanical soil properties, land form, time etc. The high hazard is identical with the 2A category of the load of water components and critical hazard is identical with the 2B category of the load of water components, when water as a component of the environment, is strongly disturbed, contaminated and endangered as a natural water source. It is characterized by a high exceeding of limits set for elements and components important for sanitation and water management. There is exceeding of limits defined by standards and law regulations. In the studied area there are point and area sources of water contamination that have not been eliminated yet (Vrana, Kúšiková, 1998).

Radon

Radon is one of the important indicators of environmental assessment of the state of the environment (for instance in urban environment). The radon radiation from building walls, waters and rocks was studied in detail in Žiarska Kotlina Basin (Lučivjanský, 1995, Čížek, 1995, Daniel et al., 1997). Radon migrates in rocks along neotectonic zones by diffusion and convection and its distribution and the values of volume activities are influenced by climatic changes. The hazard from this element migrating from underground layers into residences depends on the value of its volume activity in the soil air and on the structural-mechanical properties of the

foundation ground, which are defined by standard (STN 73 1001 - Construction Foundation). The radio-active decay of radon causes an inner exposure which increases the danger of occurrences of malignancy and permanent damage of genetic information. The probably hazardous areas can be predicted within or near (especially within 5 m) of the vicinity of the tectonic zones (verified or inferred faults) i.e., zones containing young faults and places where these tectonic lineaments cross each other. In some buildings more than 11 % exceeding of the critical limit for concentration of radon in the environment (according to STN 73 1001 - Construction Foundation, in air of rooms assigned for human activities there must be equivalent volume activity of radon less than 200 Bq.m^{-3} per year on the average) was detected. Samples with increased values of volume activity of ^{222}Rn were taken from waters along tectonic lineaments trending NE - SW (the settlements Sklené Teplice, Stará Kremnička, Šášovské Podhradie, Buko-vinka, Pitelová, partially Lutila, cadastre of Repište). Since 1990 Žiarska Kotlina Basin has shown an increased share of sickness (congenital development defects of children, tumors) in comparison to overall Slovak average (Khun et al., 1996). Thus, increased attention must be paid to this problem with monitoring in apartments.

Fluorin and health problems

The enterprise for Al production „ZSNP„ in Žiar nad Hronom with its emissions does only not effect the near vicinity but the entire Žiarska Kotlina Basin. Here fluorine is the most dangerous pollutant. The highest pollution of fluorine in the factory vicinity occured in the 60^{ies}. The village of Horné Opatovce had to be moved. In the 70^{ies} when absorbers were introduced into the technology of Al production, the average annual emission of F dropped from 8 μg.m^{-3} in 1973 to 3 μg.m^{-3} in 1987, which was still three times greater than the acceptable limit. In the effected area deleterious influences were observed mainly on the soil cover, flora, fauna and, what is worse, on the child population. These effects were demonstrated by the more frequent problems with the respiratory systems, stains on teeth, changes in skeletal tissue and blood. The increased content of F in all moni-tored tissues was seen in the entire indigious population.

Aluminium was originally obtained from Al_2O_3, after adding the fluorosalts cryolite and aluminum fluoride. Enormous amounts of fluoride are released into the envi-ronment by this technology. Since the beginning of this operation of the factory in 1953 about 13 000 t of emissions were released annually into atmosphere, in which F was present in about 400 compounds. However, since the beginning of 70^{ies} the improvement of operation technology has decreased the pollution as follows (Kiss, 1992):

Time period	emission (t)
1970 - 1975	16 091
1975 - 1980	14 460
1980 - 1985	13 500
1985 - 1990	12 100

The situation has been changed by modernization of production operation after year 1990. In 1991 another decrease of released pollutants was reached - 10 871 t, from which 7.1% represents gas and solid fluids. New technology established in 1995 has reduced the concen-tration of fluoride in exhaust below the limit 1 μg.m^{-3} which is not harmful for the environment.

While fluorine is not an essential element for human well being, it is required for healthy development of young organism. The optimal daily intake of fluorine is considered to be 2 mg. Its lack causes increas of dental defectiveness - dental caries (Škárka and Ferenčík, 1992). An abundance of fluorine in the environment can cause serious defects in organisms. Acute poisoning cases are rare; they lead to irritation of the respiratory system leading to lung aedema (lung swelling), they are usually caused by professional exposure. Chronic poisoning – fluorosis - is caused by inhaling dust containing F. Problems with F in the environment are connected with demineralization (change of hydroxyapatite to fluoro-apatite) of bones and teeth (Turčanová, 1994). The most significant intake of F is orally, in comtaminated areas by aspiration of F-bearing dust. About 10 - 20% of the F is deposited in the organism, mainly in bones. In the case of increased intake osteosclerosis can occur, mainly in the spinal column. However, there are also defects of blood production, blood pressure, and disturbances of meta-bolism (Schwartz et al., 1997). Another negative affect of F there are changes of thyroid gland (Fig. 3); the rate of mortality due to malignant tumor of thyroid gland in this area is the highest one in Slovakia (Khun et al., 1996). Other deleterious effects of chronic exposure to increased doses of F were described on myocardium. A daily intake of 3 - 4 mg F over long time period can be poisonous dose for human. Beside antropogenic activities resulting in increased input of F into the environment (production of Al, freons, artificial fertilizers act.), the hazardous factors include increased consummation of mineral waters and tea (Turčanová, 1994, Schwartz et al., 1997), use of fluoride tooth pastes (in case of young children) and smoking (in case of teenagers).

Conclusion

The input data are about the population of children aged 0 – 14 that was collected from pediatric clinics of hospitals (ZH, NB, BŠ, KR) during 1987 – 1995. In almost the entire area of Žiar nad Hronom (ZH) our study demostrates an increase of malignant tumors, illnesses of endocrine glands, congenital defects, and since 1989, also diseases of circulatory system in comparison with NB, BŠ and KR.

Concerning medical - geochemical aspect, since 1990 the increase in the number of tumor illnesses and congenital defects of monitored child population in Žiarská kotlina Basin could be in causal relation with increased natural radioactivity of rocks and waters and with radon hazard as well. It is possible to predict a potential hazardous areas around tectonic faults in the

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studied area. In 1996 there was recorded 268.8 congenital development defects per 10 000 live born children, while in Slovakia in 1995 it was 236.3 (State Health Institute in Žiar nad Hronom, 1997).

The quality of drinking water has a relationship with health state of the child (and adult) population; of particular concern is the concentration of nitrates in public water supplies as well as in public and private wells. High danger of hazard was observed in settlements Bzenica, Dobrá Ždaňa, Pitelová a Lovča. The danger of hazard from water and soil components of the environment of the Žiarská kotlina Basin is verified by negative influence of various toxic components migrating towards the river and creeks flats and their adjacent alluvium.

With respect to concentrations of F in components of the environment from monitored groups of diseases of children population aged 0 - 14 in former Žiar nad Hronom district (considering tributary areas of 20 cadastres of Žiarska kotlina Basin) the following can be assumed:

⇒ High share of tumors (see, for instance, high incidence and mortality due to tumors of thyroid in adult population of former district Žiar nad Hronom in time period 1968 - 1984, or high rate of mortality due to not specified tumor diseases in time period 1983 - 1992 in comparison with overall Slovak average)

⇒ Blood diseases (for instance changes of hemoglobin values)

⇒ Diseases of endocrine glands, mainly changes of thyroid where displacement of iodine by fluorine as main element can be assumed

⇒ Diseases of circulatory system

It is important to realize that in mentioned components of the environment and in rocks as well, the most important factor is the form in which the element occure, i.e. its accessibility for living organisms. From this point of view the simple comparison of observed concentrations of chemical elements with limits given in particular standards (in the case of rocks with clarckes of earth crust) is more or less routine process, mainly for purposes of medical geochemistry. We have realized this and thus we consider the presented interpretations for the first approach only. This problem requires another more detail research, for instance, sequential analyses.

Acknowledgement

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Heavy Metal Fractionation in Soils of Different Genesis

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Abstract. McLaren and Crawford's method for fractionating soil Cu was used to fractionate Cd, Cu, Ni, and Pb in soil samples from three soil profiles. Study sites are located in the most environmentally stressed areas of Slovakia (Rudňany and Banská Štiavnica surroundings) and the investigated three soil types: Dystric Cambisol, Eutric Planosol, and Fluvi-eutric Gleysol, are pedogenetically very different. At the Dystric Cambisol site, Pb was predominantly bound by soil organic matter and Cu was distributed mainly between organically bound and residual fractions in topsoils. Ni can be related to the behaviour of Fe: it is redistributed from the surface to deeper horizons. The portion of Cd, Cu, and Pb associated with iron hydrous oxides was prevailing within the Fluvi-eutric Gleysol where co-precipitation from groundwater occurs. Positive correlations were found between oxalate extractable Fe and heavy metal fractions. Inside the Eutric Planosol, Cd, Cu, and Pb were mainly Fe-bound, but negative correlations occur between oxalate extractable fractions of heavy metals and iron hydrous oxides content.

Keywords: soils, heavy metals, sequential extraction, geostatistics

Introduction

The heavy metal content in the soil at any location has been influenced by many factors such as the soil's parent material, the pedogenesis, the plant cover, land use, and many anthropogenic activities, including the transboundary air-pollution. The impact of contributing factors vary from place to place and consequently caused the spatial variation of the heavy metal content. The observed value embodies this variation plus the fluctuations arising from the sampling and analytical procedures (Oliver & Webster, 1991). The resulting heavy metal contents of soils are highly variable and an objective assessment of the pollution state is strongly limited. For these reasons, geostatistical methods were used for the investigation of spatial dependence and territorial distribution of heavy metal content in soils of Slovakia.

The observed distribution and accumulation of heavy metals in soils depend on a number of factors, including soil properties (pH, soil organic matter, clay minerals, Eh-conditions), soil pedogenesis, soil-plant relationships as well as amounts, forms and origins of the heavy metals (Alloway, 1990). The analytical methods and procedures are a usefull tool to clear up these relationships.

The soil material varies greatly as size and chemical composition of the particles are concerned. Thus, the behaviour and fate of an element in the soil environment cannot often be reliably predicted, based on its total concentration. That is why a sequential extraction procedure was used to examine samples from several soil profiles. An overview of the use of extractants in soil studies, including accompanied uncertainties, was made by Beckett (1989).

In our research the calcium chloride, pyrophosphate, and acid oxalate extractants were used. Despite the possible imperfections, it is generally supposed, that forms of heavy metals - exchangeable, organically bound and occluded by free oxides, respectively, are extracted. In a more or less different way these extractants were used for soil heavy metal analysis by McLaren & Crawford (1973), McLaren et al. (1986), Bogacz (1993), and Asami et al. (1995).

Materials and Methods

Soils were sampled from three soil profiles at different locations (mentioned below) by using the genesis (horizon) principal. The samples were air-dried and ground to pass a 2mm sieve before analysis.

The determinations of pH, total organic carbon, CEC, base saturation, and clay content were made by standard methods (Kobza et al. 1999). The sequential extraction of Fe, Pb, Cu, and Ni followed the flow diagram in figure 1.

The total content and the concentration of metals in different extractants were determined by atomic spectrometry methods (ETAAS, ICP-AES). The reliability of the used digested and fractionation procedures was tested by CRM soil materials (SO-2 and SO-4, CCRMP, CANMET, Canada).

Geostatistical analysis of existing data was performed with a software from U.S. Environmental Protection Agency (Englund & Sparks, 1991; Yates & Yates, 1990).

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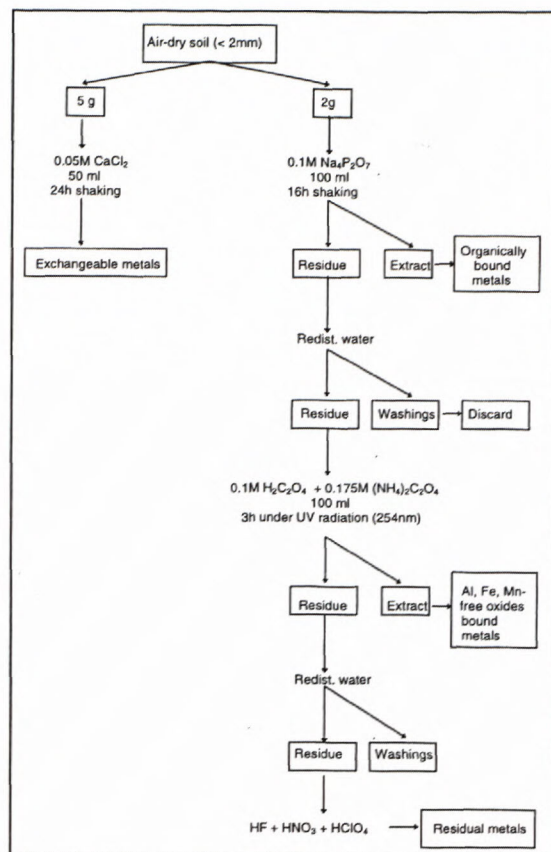
Figure 1: Sequential extraction scheme (modified version by McLaren and Crawford, 1973)

Geostatistical Investigation of Heavy Metals in the Soils of Slovakia

The data about heavy metal contents of topsoils were collected in the frame of the soil monitoring program (Linkeš et al., 1997) and supplemented by the data from a hygienical survey (collected by VUPOP Bratislava in 1990-1996). As a result, we have obtained irregularly placed sampling points, the topsoil of which has a known content of Cd (1148 sampling points), Pb (1301), and Hg (884). Their locations are shown in figure 2.

The distribution of all elements were strongly positively skewed. For subsequent geostatistical analysis the data were transformed by logarithmic or power transformations to stabilise variances. Isotropic variograms computed for the whole area could be described as the sums of nuggets plus exponential structures. Figure 3 shows the experimental values plotted as points and the model shown as the solid line.

Finally, we kriged the contents of Cd, Pb, and Hg over the 5 x 5 km blocks and mapped them (Fig.2). The nearest two sampling points within each octant around the estimated point were taken for calculation, making 16 in total. The metal contents show a regional pattern that seems to be linked with the spatial distribution of the soil associations, geology, mining and industrial activities, and emission effects as well.

The study sites were selected on the basis of these results (Fig:2). Experimental fields are located in the most

environmentally stressed areas in the Eastern (near Rudňany) and Central (near Banská Štiavnica) Slovakia. The studied soils belong to Dystric Cambisols, Eutric Planosols, and Fluvisols affected by gleyic processes (after FAO).

Properties of the Studied Soil Profiles

The study involved profiles of three soil types: Dystric Cambisol (DC), Eutric Planosol (EP), and Fluvi-eutric Gleysol (FG). The DC was much more acid (pH 2.9-4.1 in 1M KCl) than EP (pH 5.1-6.1) and FG (pH 5.0-6.6). The CEC of the DC, EP, and FG varied between 42-227, 126-184 and 198-476 mmol.kg^{-1}, respectively. The alkali plus alkaline earth cation saturation was <30% in the DC, but >70% in the two others. The total carbon content of the DC ranged between 4 and 15% in the A horizons and dropped to 0.3-2.9% in deeper horizons. In the EP and FG the carbon content varied between 0.4-2.9% and 0.2-1.0%. Free iron content (pyrophosphate plus oxalate extractable) ranged between 0.2-2.0 (DC), 0.9-1.7% (EP) and 0.9-1.3% (FG). The clay content varied between 9-19% (DC), 11-15% (EP) and 12-21% (FG). The mineral composition of the clay fraction was dominantly smectitic-illitic (DC and EP) and illitic-chloritic (FG).

The Study of Heavy Metal Behaviour in Soils through Sequential Extraction

Speciation of heavy metals in soils can be defined in many ways (Ure, 1990). First, it can be defined as the extraction and quantification of a soil phase, which is functionally designated in that its element content is, for example, the plant available content. Secondly, speciation can be defined operationally, i.e. by the extraction technique itself. The extraction will usually be designed to extract the element associated or bound to a particular soil phase. The use of selective extractants to quantify the element content in a particular phase is illuminated by the concept of "pools" of elements in soils, of different solubilities and mobilities, that can be selectively sampled by extractants of different strengths. By making use of a series of sequential extractions with reagents of increasing power, the individual phases can be isolated. Much work has been done on sequential extraction schemes for soils and sediments (Kersten & Forstner, 1989). The analysis of sequentially obtained fractions of heavy metals in studied soils leads to a better understanding of the influence of specific soil properties on the behaviour of heavy metals in soils.

Within the forest soil profile of Dystric Cambisol (DC) lead and copper were found to be concentrated in the surface horizons as a result of their adsorption by the soil organic matter (Fig.4) and due to the bioaccumulation and the emission origin as well. The topsoil contained lead mainly as organically bound (67-69%), Fe-bound and residual fractions contained 18-20 and 13%, respectively, of lead. Total copper was distributed mainly between organically bound (32-35%) and residual (56-59%) fractions, Fe-bound fraction contained 9% of Cu. In the
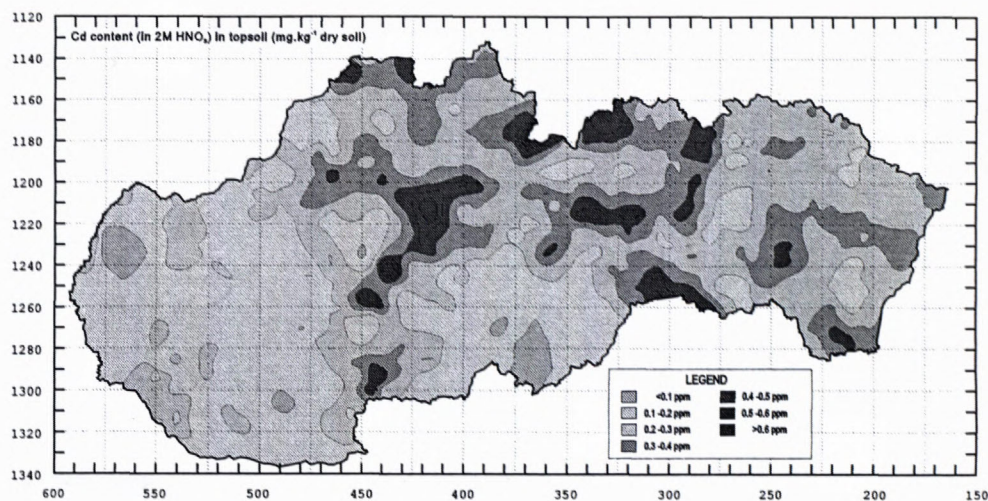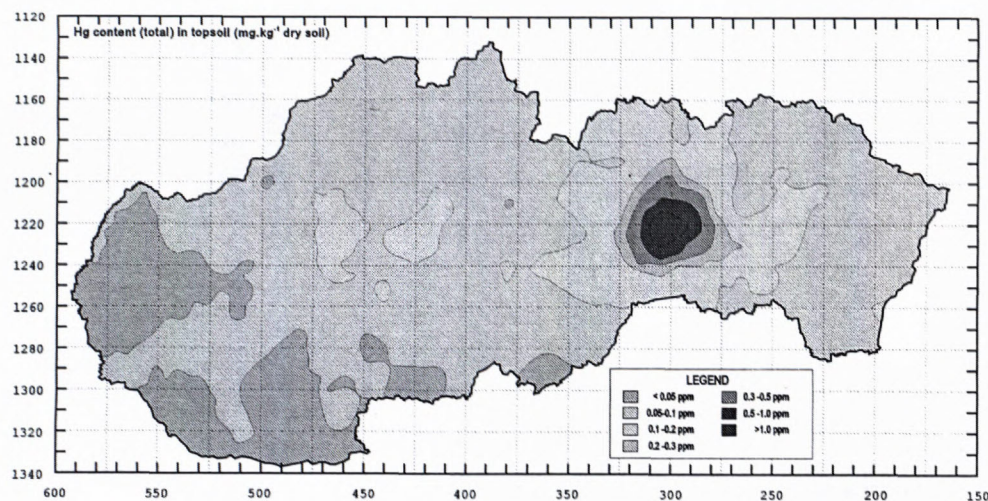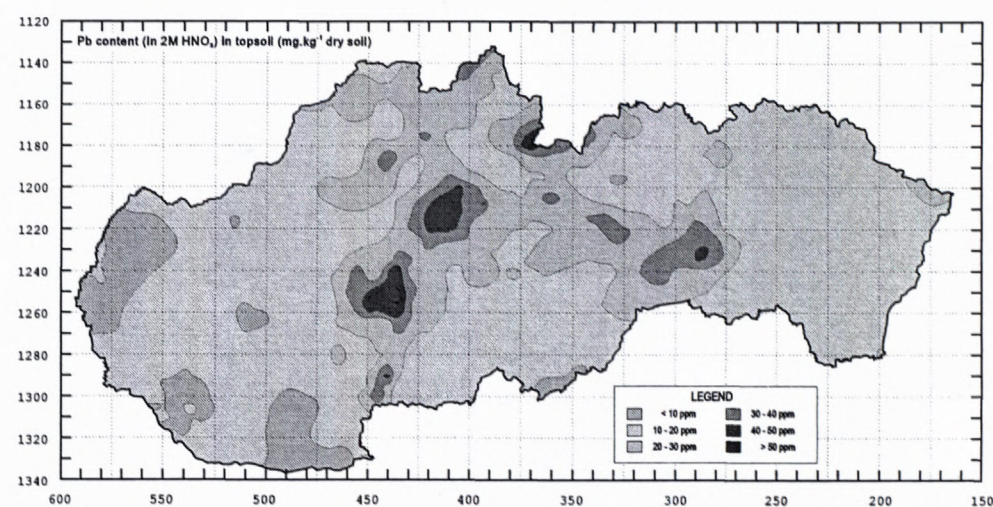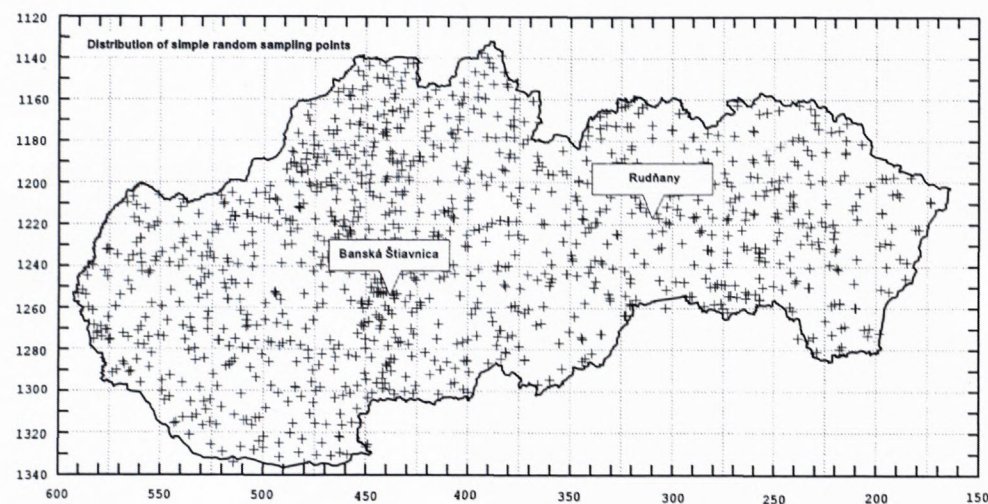
Figure 2: Study sites (Banská Štiavnica and Rudňany), locations of sampling points and isoline plots for selected heavy metals
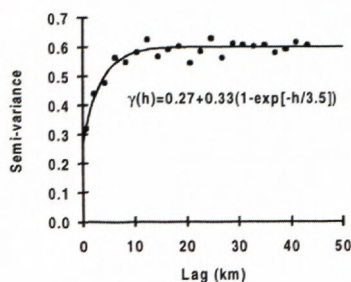
Figure 3: Example of experimental variogram for Cd [ln(ppm)]

subsoil horizons, a lower content of organically bound Pb (18-20%) and higher proportions of Fe-bound (38-49%) and residual (29-40%) lead were determined. Copper occurred predominantly in the residual fraction (78-91%) and much less as organically bound (4-18%) and Fe-bound (2-5%). A similar vertical distribution and relation to soil organic matter content has also been reported for heavy metals (i.e. Baker, 1990; Davies, 1990; Krosshavn et al., 1993).

The same conclusion for the forest soil profiles (DC) is obtained from diagrams in figure 5 where the determined content of pyrophosphate extractable Pb is directly proportional to organic carbon content. Atteia (1994) found a similar close relationship between the total Pb and the total organic matter content for Cambisol and Podzol in Switzerland. He explained the lower slope of the linear regression in Podzol as a result of a higher organic matter content in

Podzol for a similar Pb content. The similar dependence is valid for Cu, with the exception of the "Stara Voda" location influenced by mining activity in the past. In our case, the different slopes for Cu can reflect differences in the inputs into surveyed soil profiles.

Nickel shows a significantly different behaviour, even in the forest soil (DC) which is rich in organic matter content. Total nickel was distributed mainly in Fe-bound (21-48%) and residual (33-74%) fractions in the whole soil profile. The organically bound fraction contained only 2-18% of Ni. Correlation between the concentration of Ni bound to organic matter and the content of organic carbon in soil is insignificant (Fig.5). Nickel is concentrated in deeper horizons of the soil profiles and tends to be associated with accumulations of the Fe hydrous oxides, as follows from figure 5. The close dynamics of Ni and Fe in soils and the same vertical distribution pattern were found previously (i.e. McGrath & Smith, 1990; Atteia, 1994).

Since iron hydrous oxides are precipitated more extensively in soils affected by gleyic processes, they dominate the adsorption of the studied heavy metals inside both the Eutric Planosol (EP) and Fluvi-eutric Gleysol (FG) profiles (Fig.4). A tendency of the heavy metals to concentrate in this fraction is affected by the relative content of organic matter and iron hydrous oxides as well.

Within the Fluvi-eutric Gleysol (FG) profiles (with the exception of Gr horizon), total lead was distributed
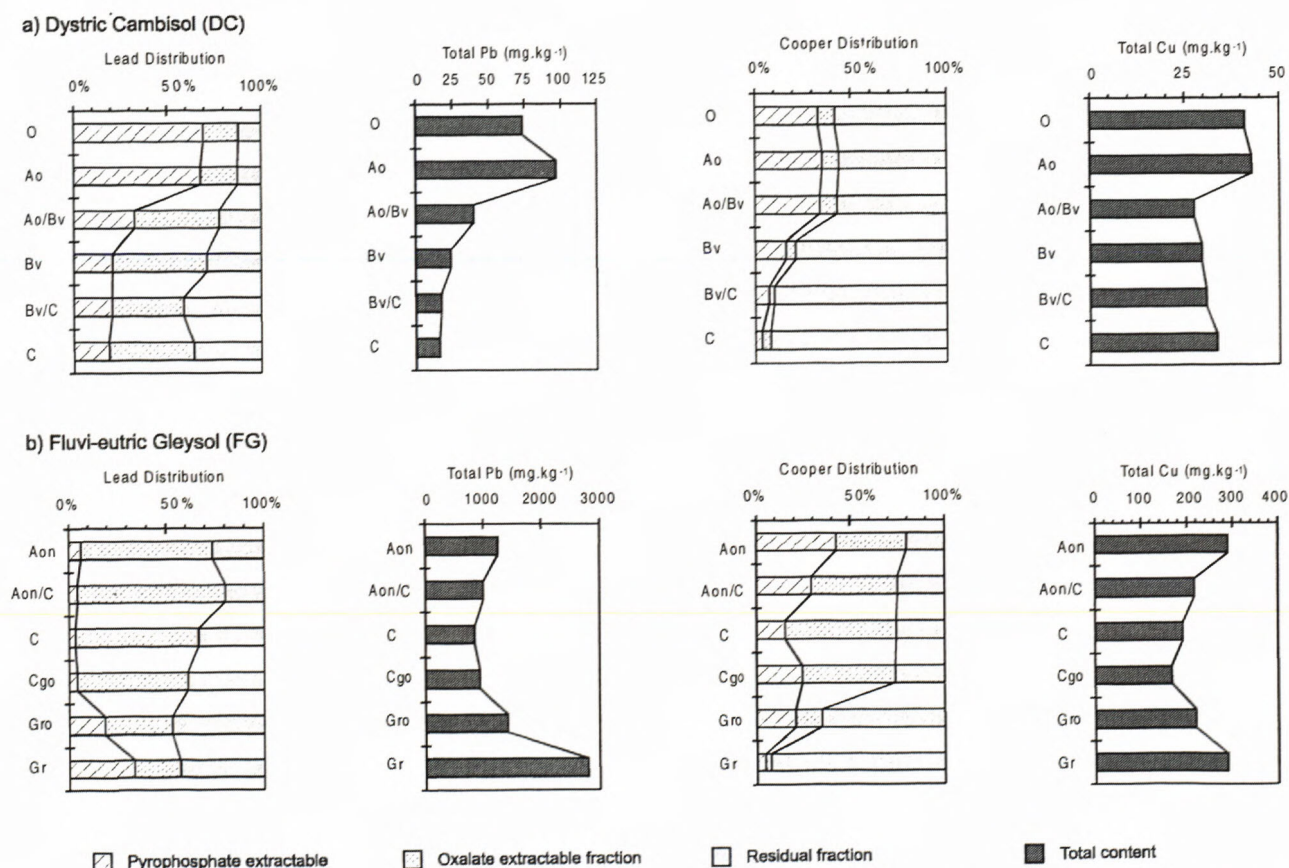
Figure 4: The distribution of organic (pyrophosphate), hydrous oxide (oxalate), and residual heavy metal fractions and their vertical distributions

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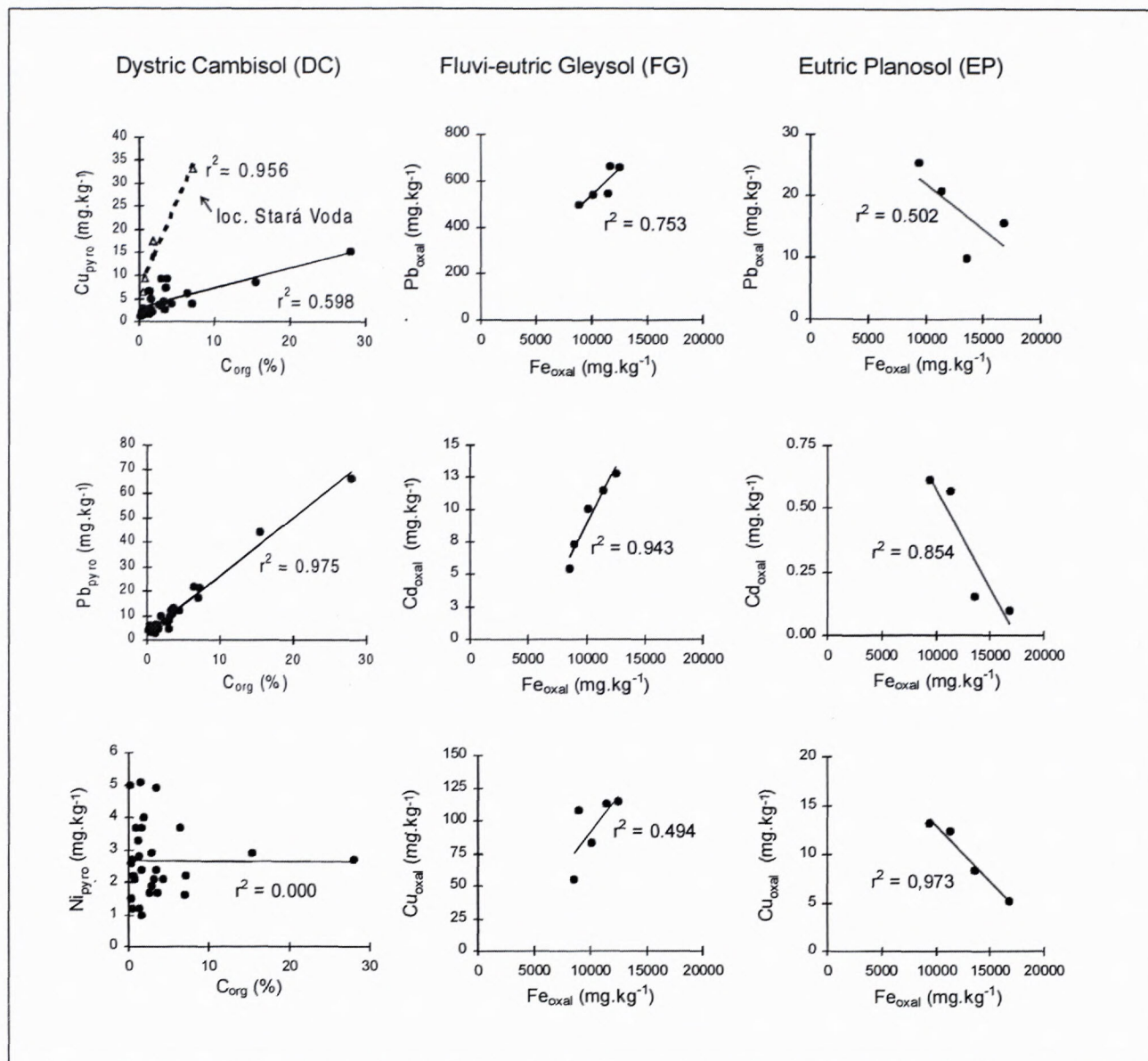
Figure 5: Relationships between heavy metal fractions and corresponding soil constituents

mainly as Fe-bound (57-75%) and residual (20-39%) fractions, only 2-7% of Pb was found as organically bound fraction (Fig. 4). Organically bound, Fe-bound, and residual fractions of copper contained 16-42, 38-60, and 20-26%, respectively, of copper. The oxalate extractable heavy metal contents are directly proportional to iron hydrous oxide contents (Fig. 5). This relationship results from the co-precipitation of heavy metals and iron hydrous oxides from the groundwater. That is why iron secondary oxides formation in the soil profile also leads to heavy metals accumulation in the same soil.

Inside the Eutric Planosol (EP) 55-78% of total Pb was found as Fe-bound, 19-44% in residual fraction and only 0.5-3% of organically bound Pb. These relationships among Pb, Cd, Cu, and iron hydrous oxide contents are indirect within the Eutric Planosol (Fig. 5). In Planosols, mobilization and precipitation of iron hydrous oxides

occur through oxidation and reduction following water-logging in the impermeable B horizon. Both iron concentration in deeper horizons and the emission origin of heavy metals cause the negative correlation in figure 5, at this location.

The calcium chloride extractable fraction accounted for only <1%, on average, of the total metal content and it was not subtracted from pyrophosphate extractable fraction either in the graphs or in the calculations.

Based on our results organic matter or iron hydrous oxides cannot be considered as selective sorbents for the individual element (Fig. 4). The amount of heavy metals adsorbed by organic matter or Fe hydrous oxides in soils depends greatly on the soil genesis and on the heavy metal origin. The different slopes in the above correlation graphs (Fig. 5) can reflect the differences in heavy metal loads or the different origins of heavy metal.

Conclusions

The obtained experimental results show the sequential extraction procedure as a source of valuable data on interactions between heavy metals and soil constituents, at selected locations. The above results suggest that pyrophosphate (organically bound) and oxalate extractable (Fe-bound) fractions represent the most important "pools" of heavy metals in the investigated soils. Within the forest soil profile of Dystric Cambisol (DC), lead and copper were found to be concentrated in the surface horizons. Pb was predominantly bound by soil organic matter and Cu was distributed mainly between organically bound and residual fractions. The total nickel was found mainly in Fe-bound and residual fractions in the whole soil profile. Iron hydrous oxides dominate the adsorption of studied heavy metals inside the both Eutric Planosol (EP) and Fluvi-eutric Gleysol (FG) profiles. Positive correlations were found between oxalate extractable Fe and heavy metal fractions within the Fluvi-eutric Gleysol where co-precipitation from groundwater occurs. Inside the Eutric Planosol, negative correlations occur between the oxalate extractable fraction of heavy metals and the iron hydrous oxides content. Based on our results, organic matter or iron hydrous oxides cannot be considered as selective sorbents for the individual element. The amount of heavy metals adsorbed by organic matter or Fe hydrous oxides in soils depends greatly on the soil genesis and on the heavy metal origin.

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Soil Contamination in a Flooded Area of Morava River Basin after the Flooding in 1997

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Abstract. During the flood of 1997 of parts of the Moravia River much sediment was redistributed as a sediment sheet several centimeters thick over an extensive area. Along with this redistribution of sediment there was also a redistribution of organic pollutants, trace elements and radioactive material.

Although at first the contamination level was feared to be high, it later turned out in most areas to be less critical. There were several local exceptions, howeover, where Ministry of Environment critical levels were exceeded On the whole, however, it appears that pollutats where scattered rather than concentrated.

In this study 111 near surface soil samples and 30 core samples of flood deposits were taken. Lab tests were run on 15 of trace elements, 34 of organic toxins and 4 of radioactive elements. The analytical results were treated statisticaly by corelations and evalutation of the spatial distribution trends.

Background concentrations were exeeded for following substances: TPH, PAHs, PCBs, chlorinated pesticides (DDT, DDE), trace elements (Cd, Co, Cr, Ni, Pb, Zn, Sb, Hg, Ba) and radioactive elements (Cs^{137}, U(Ra)).

Keywords. Environmental geochemistry, regional geology, floods in 1997 on the Morava River, organic contamination of sediments, contents of trace and radioactive elements in alluvial sediments.

Introduction

There was an extensive mass redistribution due to erosion in upper and middle part of Morava River basin during the flood et 1997. Eroded matter was deposited along the original riverbeds and river channels during flooding of alluvial areas. Huge areas were covered by an extensive sheet of sediments only several centimetres thick. The sediments in the flood plain area were composed dominantly of silt to sand size of particles, and sediments in and near riverbeds by sand to gravel size of particles. After the retreat of the flood waters the affected area became part of a gradually drying lagoon floored by very fine-grained and loamy deposits (Ottesen et al., 1989). The new alluvial sediments were separated from the riverbed by a natural levee or from dams with nearby natural depressions.

Along with minerals and soils from the source areas anthropogenic matter originating from technological facilities and landfills were also moved into the flooded area.

Many of the substances originating from this matter could have an immediate toxic effect. Others threaten organisms by their slow but gradually increasing concentration in tissues that could have a gradual toxic effect on humans. In the case of floods of long or short duration there is a real threat of contamination by flood sediments and soils having the trace elements (Hg, Pb, Cd, As), cyanides, oil substances composing in significant part of total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and also polychlorinated biphenyls (PCBs).

Further, there was erosion of radioactive elements derived from rock minerals coming from source areas and there also was a redistribution of radioactive fallout, material that was aftermath of the Chernobyl accident (Cs^{137}). This fallout material was "leached", together with other inorganic and organic substances originating from the upper part of soils of the entire Morava River basin. Because of the extensive migration of matter and toxicity of some of the substances to man and the environment, we have decided to map the distribution of selected pollutants in the present soil environment.

Sampling

All together 111 near-surface soil samples (up to 3 cm from the surface) and 30 core samples were taken to map the contamination of the Šumperk, Olomouc, Přerov, Kroměříž, Uherské Hradište, Hodonín and Břeclav Districts with radioactive elements. The distribution of sample sites is shown on the figure 1. Core samples were taken from the alluvial deposits by sampling probe to a 70 cm depth. Each 15 cm of the core samples was then sampled in a lab and each sample was individually analysed. An average value was then calculated for each core. The samples were also characterised visually and petrographically.

Analytical Methods

A wide variety of substances were analysed in the samples: organic compounds - (total organic carbon, TPH, PAHs, PCBs, OCPs), cyanides, trace elements (Ba,

Fig. 1 Localization of sampling sites

Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Zn, V, As, Sb, Hg, Sr) and radionuclides, (Th, U (Ra), K, Cs^{137}). The following analytical methods were used:

Total organic carbon (TOC). For analysis of carbon was used analyzer ELTRA METALYT CS 1000S (Germany). Total carbon was determined by the heating of 400 to 500 mg samples in an oxygen atmosphere at 1250°C. Generated carbon dioxide was measured by infrared detectors.. The content of inorganic carbon was determined after reaction of a sample with phosphoric acid. The content of TOC was detected by subtraction of inorganic carbon from total carbon.

The total extractable compounds (TEC) and nonpolar extractable compounds (or total petroleum hydrocarbons - TPH). Dried and homogenized samples were extracted with 1,1,2-trifluorotrichlorethane. To determine TPH, the co-extractive polar and semipolar compounds was removed from the extract with silica gel absorbent. The concentrations of TEC and TPH in extracts were measured by infrared (IR) absorption photometry (Perklin-Elmer 783).

Persistent organic pollutants (PAHs, PCBs, OCPs). The substances were extracted by a device Soxtec HT2 (Tecator, Sweden) with dichlormethane. To detect polycyclic aromatic hydrocarbons (PAHs), a portion of dichlormethane extract was fractionated (after the addition of internal standards and after partial drying) by column chromatography on silica gel by a gradual elution of n-pentane and dichlormethane and analysed by capillary gas chromatography with flame-ionization detector (GC/FID, Helwett-Packard HP6890). In the case of PCBs and chlorinated pesticides a portion of the dichlormethane extract was re-extracted with n-hexane after the addition of internal standards and drying (active copper was added in order to remove elementar sulphur). The detection was done by gas chromatograph with an electron-capture detector (GC/ECD, Helwett-Packard HP6890).

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Total and toxic cyanides. Total cyanides include free cyanides and bonded cyanides bounded in complexes, including organic substrates containing the cyanide group that creates HCN under conditions of analytical process. During the analysis the HCN was separated from the sample by distillation, with the help of diluted sulphuric acid and in the presence of magnesium salt and following the absorption of HCN in a solution of sodium hydroxide. Cyanide ions are then determined by photometry.

Toxic cyanides include free and also unstably bonded cyanides, which are released in a neutral pH, under temperature of 40°C in air bubbles. The freed cyanide is captured and determined by photometry.

Trace elements. Elements Be, Cd, Co. Cr, Cu, Mo, Ni, Pb, Zn, V, As and Sb were determined by AAS method, Ba and Sr by ICP method and Hg by cold vapor AAS method.

Radionuclides. Each sample core was divided into smaller samples 8 to 10 cm long (to provide sufficient sample with respect to sample composition). The divided sample cores and the A soil horizons were dried at temperatures to 105°C, homogenised, and then inserted into a measuring case, where they remained for two weeks in order to set the radioactive balance between Ra^{226} and DP Rn^{222}. A scintillation spectrometer PCAP (Nucleus USA) with detector NaI(Tl) 4 x 4" with a resolution 7.9% was used for measurements. A lead box with 9 cm walls was used to shield background radiation. The observed 512-channel spectrums were compared with observed spectrums of IAEA(The International Atomic Energy Agency) etalons (RG set: Th, U(Ra) a K). The observed values lower than above-mentioned detection limit is also entered onto the documentation charts, because they still have certain informative value. Under favourable conditions (if the large case is filled), the U content independent of Ra can be also determined, and thus the radioactive balance between U and Ra^{226} can be evaluated. However, the determination of U on the base of low-energy gamma radiation Th^{234} and the radiation of isotope U^{235} is effected by several times higher error than the determination of Ra^{226}, thus the real accuracy of direct determination of U is about 1.5 ppm.

Criteria of Environmental Risks Assessment

Concerning the hazard for the environment, the weight of observed concentrations of individual substances (organic matter and trace elements) were assessed according to the methods set by the Ministry of Environment of the Czech Republic (ME CR,1996):

Criteria A - are about the same as natural concentrations of analysed substances or the background. Anything in excess is taken as a contamination of examined area of environment, excluding areas with naturally increased concentrations. However, if the criteria B are not exceeded, the contamination is not considered critical enough to justify the starting of research or to start monitoring it.

Criteria B - are artificially set up criteria that are approximately equal to the arithmetical averages of criteria A and C. Excesses of the criteria B requires a preliminary analyses of the risk resulting from the observed contamination to identify the sources and reasons of contamination. According to the results decisions about any following research and monitoring are made.

Criteria C - was defined with respect to the physical, chemical, toxic, ecological and another properties of the substances. Different criteria are defined for different types of planned land use. (residential, recreational, industrial and general). Exceeding the criteria C means contamination that can be a real threat to human health and components of the living environment.

Because the criteria C are set up with respect to standard soil (25% of clay particles and 10% of organic matter), the adjustment for individual samples (only for organic matter) was made according to the following equation, given in the methodical directions:

$$I_c = I_{st} \text{ (\% organic matter / 10),}$$

Where I_{st} is the criterion of the C category for a standard soil type, and I_c is the calculated critical limit of the C category for a concrete portion of organic matter, which can be considered about the double of the C_{org} content value.

The Results of Analyses of Organic Geochemistry and Cyanides

The contents of organic and inorganic carbons and cyanides. The TOC (Fig. 2, localities are arranged from N to S in the flow direction of the Morava River) are in the range from 0.26% to 7.08%. Although the contents of organic matter can be, and certainly they are, the function of many factors (content, size and type of floating particles, particle size distribution, speed of the flow and its changes, and many others), the most probable general trend of organic matter (C_{org}), the concentrations seem to increase in the direction of the river flow (fining of the sedimentation, usually increased portions of organic matter in clays and claystones compared to silt (and siltstones) and sands (and sandstones)). With respect to the lack of relationship with other parameters of organic contamination analyses, which works with fractions extracted from rocks by organic solvents, a dominantly humic character of organic substances can be assumed (remains of higher plant parts, roots and fragments of herbs and farming crops, etc.) Some of these phytoclasts were visually observed during the sampling in the field.

The contents of inorganic carbons are usually very low which suggest a low content of carbonates in the mineral matrix after flooding of fine-grained sediments. The highest and highly extreme value 1.5% $C_{inorg.}$ (PCH17 - Hodonín district) corresponds to a maximum content 3.75% $CaCO_3$. The upper quarter of the values of C_{min} shows portions smaller than 0.48% $CaCO_3$ for more than l' of the samples.

The contents of all cyanides, mainly toxic cyanides are very low in all near surface samples. In the case of toxic cyanides, the highest observed value is 0.3 ppm for the sample from the Hodonin district, which is five times
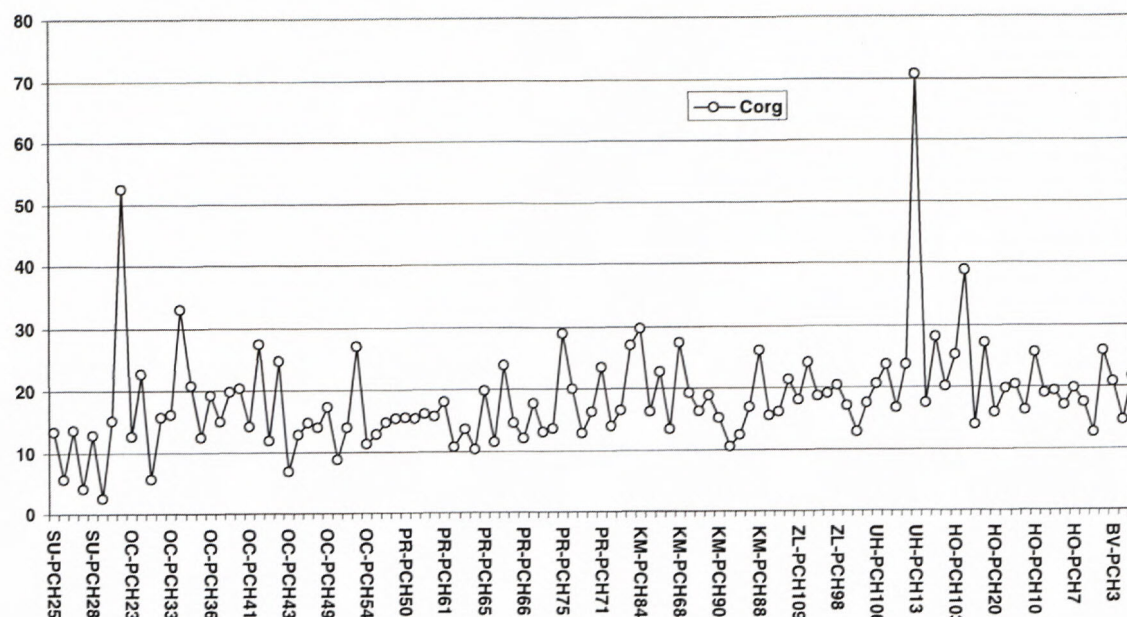
Fig. 2 The Content of total organic carbon in the samples (g/kg)
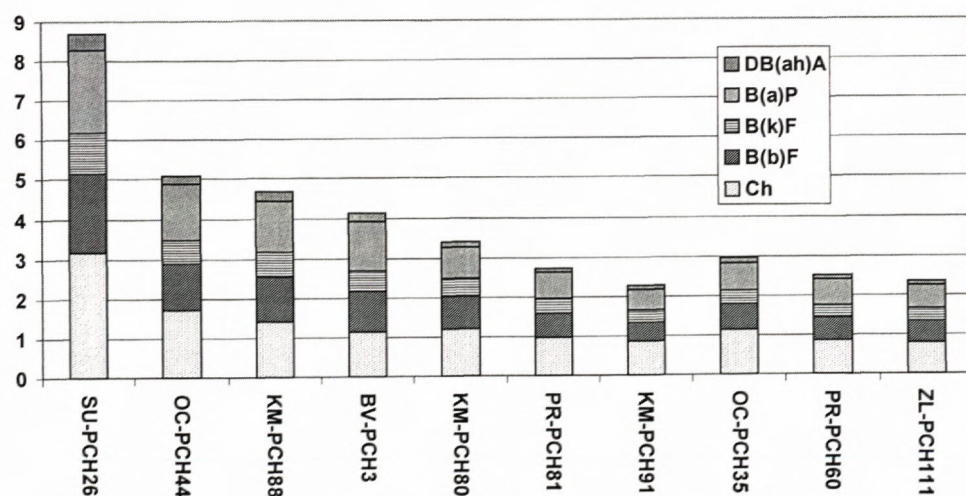

Fig. 3 Shares of some toxic and carcinogenic PAHs (ppm) for samples with highest total contents
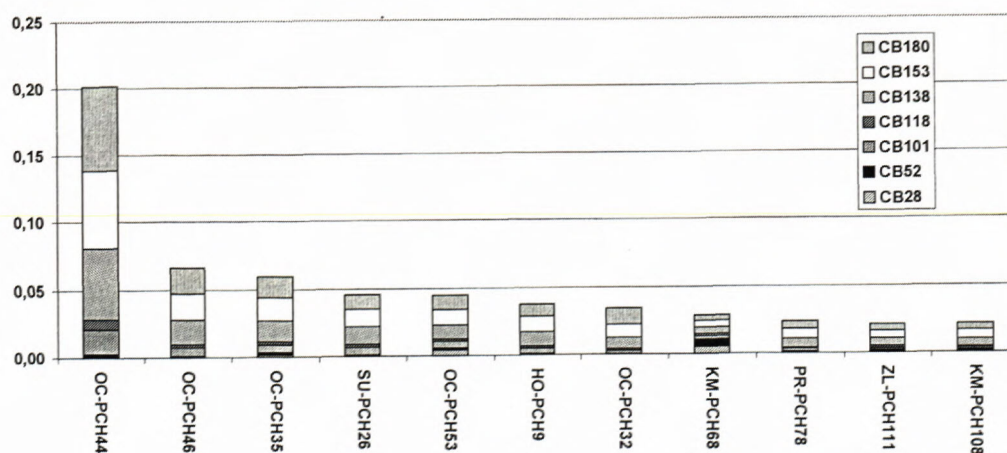

Fig. 4 Shares of individual congeneres on total content of PCBs for 11 samples with concentrations of PCBs greater than 0.02 ppp (criterion A)

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lower than the maximum acceptable critical value of the category A (1.5 ppm).

Contents of TEC and TPH. There is a close relationship between the total extracted portion (*TEC*) and nonpolar substances (*TPH*) with a correlation coefficient of 0.97. The prevailing majority of the extracted portions are composed of nonpolar substances (hydrocarbons).

The critical limit of category B for *TPH* (400 ppm) was not exceeded, which would otherwise call for additional detailed research. Even the highest observed concentration (150 ppm) is more than two-times smaller.

Polycyclic aromatic hydrocarbons. The following PAHs compounds were determined: acenaphtylen, acenaphthene, fluorene, benzo(j)fluoroanthen, dibenz (a,h) anthracene, anthracene, phenanthrene, fluoroanthen, pyrene, benzo(a)pyrene, chrysene, benzo(b)fluoranthen, benzo(k)fluoroanthen, benzo(a)anthracene, indene(1,2,3 cd)pyrene, benzo(ghi)perylene. The sum of PAHs, according to methodical directions, includes only benzo (a)anthracene, benzo(a)pyrene, benzo(ghi)perylene, benzo(k)fluoroanthen, fluoroanthen, phenanthrene, chrysene, indene(1,2,3 cd)pyrene and pyrene.

The contents of PAHs are statistically closely related to the contents of TEC, which suggests (with a significance level of 0.001 for a given amount of analyses) that the extracted portion is composed mostly of nonpolar hydrocarbons, of which the dominant group is PAHs. The PAHs concentration also has a significant correlation with the PCBs (coefficient 0.47).

The values of the observed PAHs concentrations are summarised in Table 1. The most contaminated samples are from the Šumperk district, where the criterion $C_{popul.}$ for benzo(a)pyrene was exceeded in one sample. Practically in all samples in which the increased concentrations of acenaphthene were detected, the increased concentrations of fluorene and phenanthrene are also observed. In three samples the values of total PAHs concentrations approximate the adjusted values of C criterions for general land use. The values concern the contents of organic matter. In the cases of samples from the Šumperk district, this adjusted value is significantly exceeded. The contents of the most common PAHs in the ten most contaminated samples are given in Figure 3.

Polychlorinated biphenyls. The increased contents of PCBs usually parallels the increased contents of PAHs, which supports an inference of a close structural, chemical and perhaps also in some cases genetical relationship of these substances, expressed by the coefficient 0.47, with a significance level of 0.001 for a given amount of observations (samples). In the samples where an increased amount of extractable matter was observed, there also commonly were increased concentrations of PCBs. A correlation coefficient also proves the relationship between the contents of PCBs and contents of TEC (coeff. 0.51) and TPH (coeff 0.46).

The critical concentration of PCBs 0.02 ppm for category A was exceeded in 11 cases. In the samples with the highest contents of PCBs, the highest portions of PCBs compounds are equally shared by hexachlorobiphenyls

CB138, CB153 and heptachlorobiphenyl CB180, which contain the highest amount of Cl and therefore are the most persistent against degradation. Usually they compose about 75% of the total PCBs content. The portions of individual substances of the most contaminated samples are given on Figure 4.

Organochlorine pesticides. These substances include DDT and its decay products - DDE and DDD which are also persistent in the environment. Hexachlorocyclohexane, lindane and heptachlor were also determined. However, their concentrations were very low, or under the detection limit. The critical limits for total chlorinated pesticides for soil for agricultural use (0.1 ppm) were exceeded in nine cases in the Hodonín, Kroměříž, Zlín and Přerov districts.

Results of Analyses of Trace Elements

The analyses concern not only the concentrations of individual elements but also their mutual relationship with respect to their space distribution (Table 2). A statistically significant relationship was determined especially between Pb and As, As and Sb, and also among the elements Cu, Ni, Zn and V. Concentrations of Be in samples were low, their values were in range of 1.5 - 4.4 ppm, which means that there were no values greater than the critical limit of the category A (5 ppm).

All 71 samples with a content of Cd greater than the detection limit (0.8 ppm), are considered to be contaminated soils in the category A, having a critical limit of 5 ppm. (according to existing Methodical Directions of ME CR, 1996). This result indicates a significant contamination of the study area in category A or, what is more probable, the critical value for the category A was set too low.

The Co concentration in the study samples have values of 6 - 50 ppm. The only observed maximum value of 50 ppm (a sample from Olomouc district) twice the critical limit (25 ppm) given for the category A. In the case of Cr the critical limit of category A (130 ppm) was exceeded in only one sample, (246 ppm) from the Zlín district.

In the cases of Cu, V, and As no samples exceeded the critical limit of category A (Cu – 70 ppm, V – 180 ppm, As – 30 ppm). The concentration of Mo in all but one case below was the detection limit (5 ppm). The concentration of the one case was at the detection limit.

The critical limit (60 ppm) accepted in A category for the concentration of Ni was exceeded in six samples. The content of Pb in many samples were approaching critical limit 80 ppm in A category. In one case, from the Hodonín district, the observed concentration of Pb was 4380 ppm what exceeded many times the critical limit of C category set up for general land use (300 ppm).

The concentration of Zn exceeded the critical limit (150 ppm) for contamination in the category A in seven cases. They are mainly from the Olomouc district (4 samples). In the case of Sb, only one sample from the Hodonín district, having a concentration of 39.08 ppm exceeded the 25 ppm the critical limit set for the category B. Another three

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Tab. 1 Concentrations PCBs and PAHs in soils

	substance unit	PCB	N	Aclen	Acten	Fluoren	Fen	A	F	P	B(a)A	Ch	B(b)F	B(j)F	B(k)F	B(a)P	I(123-cd)P	DB(ah)A	B(ghi)Pe	Suma PAU-A	Suma PAU-B
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
SU	PCH25	0,0016	<0,008	0,0101	0,0222	0,0244	0,1692	0,0272	0,7647	0,5821	0,2468	0,4044	0,2926	0,1232	0,1587	0,2860	0,2299	0,0582	0,2274	3,6271	3,0692
	PCH24	0,0019	0,0186	<0,008	0,0252	0,0203	0,1462	0,0398	0,4826	0,3703	0,1839	0,2714	0,1910	0,0801	0,1075	0,1933	0,1549	0,0478	0,1681	2,5010	2,0782
	PCH26	0,0454	0,0201	0,0707	0,3983	0,5283	2,9188	0,3318	7,2115	5,3325	2,1940	3,1663	1,9969	0,8443	1,0355	2,0725	1,4774	0,4083	1,3282	31,3354	26,7367
	PCH27	0,0016	0,0413	<0,008	0,0174	0,0203	0,0327	0,0121	0,1063	0,0874	0,0402	0,0697	0,0403	0,0177	0,0209	0,0482	0,0316	<0,008	0,0337	0,6198	0,4707
	PCH28	0,0019	0,0389	<0,008	0,0082	0,0142	0,0644	0,0153	0,2561	0,2020	0,0953	0,1428	0,1054	0,0464	0,0523	0,1179	0,0729	0,0196	0,0665	1,3182	1,0702
	PCH30	0,0030	-	<0,008	0,0190	<0,008	0,0180	0,0097	0,0521	0,0467	0,0205	0,0336	0,0275	0,0100	0,0211	0,0196	0,0177	0,0047	0,0193	0,3195	0,2486
	PCH29	0,0047	0,0092	0,0082	0,0441	0,0465	0,2799	0,0663	1,1376	0,8888	0,4376	0,6466	0,4679	0,2192	0,2303	0,5058	0,3548	0,0993	0,3208	5,7629	4,8022
	PCH31	0,0043	0,0134	<0,008	0,0116	0,0130	0,0736	0,0222	0,2890	0,2398	0,1193	0,2177	0,1439	0,0631	0,0748	0,1194	0,2079	0,0432	0,0813	1,7332	1,4228
OC	PCH23	0,0136	0,0120	<0,008	0,0181	0,0210	0,1455	0,0278	0,5215	0,4061	0,2073	0,3283	0,2500	0,1031	0,1273	0,2367	0,1967	0,0622	0,1665	2,8301	2,3359
	PCH22	0,0070	0,0116	<0,008	0,0096	0,0175	0,1190	0,0274	0,4640	0,3822	0,1972	0,3050	0,2328	0,0907	0,1236	0,2426	0,1738	0,0510	0,1514	2,5994	2,1588
	PCH21	0,0019	0,0120	<0,008	0,0094	0,0134	0,0978	0,0214	0,2665	0,2165	0,1221	0,1905	0,1248	0,0622	0,0740	0,1376	0,1106	0,0361	0,0965	1,5914	1,3121
	PCH32	0,0343	-	<0,008	<0,008	<0,008	0,0157	<0,008	0,0623	0,0469	0,0253	0,0466	0,0327	0,0151	0,0187	0,0297	0,0202	0,0079	0,0178	0,3389	0,2832
	PCH33	0,0034	-	<0,008	<0,008	0,0081	0,0288	<0,008	0,1164	0,0977	0,0542	0,0870	0,0615	0,0301	0,0363	0,0562	0,0449	0,0112	0,0323	0,6647	0,5538
	PCH35	0,0597	0,0142	0,0128	0,0460	0,0555	0,4640	0,0903	1,4070	1,1326	0,6161	1,1448	0,6467	0,3292	0,3265	0,7084	0,5036	0,1388	0,5094	8,1459	6,8124
	PCH34	0,0035	<0,008	<0,008	0,0116	0,0108	0,1146	0,0333	0,3912	0,2865	0,1783	0,2548	0,1833	0,0888	0,0939	0,1969	0,1373	0,0389	0,1275	2,1477	1,7810
	PCH37	0,0020	-	<0,008	<0,008	<0,008	0,0376	<0,008	0,1451	0,1190	0,0543	0,0913	0,0695	0,0289	0,0353	0,0691	0,0496	0,0164	0,0479	0,7640	0,6492
	PCH36	0,0035	<0,008	<0,008	<0,008	0,0114	0,0453	0,0082	0,1929	0,1581	0,0803	0,1363	0,1100	0,0535	0,0548	0,1111	0,0824	0,0211	0,0767	1,1421	0,9379
	PCH40	0,0020	-	<0,008	<0,008	<0,008	0,0143	<0,008	0,0542	0,0437	0,0204	0,0396	0,0301	0,0109	0,0162	0,0361	0,0248	<0,008	0,0253	0,3156	0,2746
	PCH39	0,0127	0,0124	0,0103	0,0369	0,0350	0,3757	0,0686	0,9656	0,7659	0,4098	0,6640	0,4203	0,2187	0,2164	0,5492	0,3159	0,0836	0,2976	5,4459	4,5601
	PCH38	0,0029	-	0,0094	<0,008	<0,008	0,0372	<0,008	0,0863	0,0688	0,0347	0,0708	0,0352	0,0157	0,0216	0,0420	0,0288	<0,008	0,0242	0,4747	0,4144
	PCH41	0,0019	-	<0,008	0,0090	0,0110	0,0613	0,0091	0,1443	0,1113	0,0587	0,0966	0,0673	0,0400	0,0282	0,0693	0,0431	0,0120	0,0436	0,8048	0,6564
	PCH42	0,0022	0,0128	<0,008	<0,008	<0,008	0,0469	0,0144	0,2401	0,1598	0,0805	0,1952	0,1054	0,0415	0,0540	0,0924	0,0751	0,0180	0,0549	1,1910	0,9989
	PCH46	0,0662	-	<0,008	<0,008	<0,008	0,0237	<0,008	0,0508	0,0434	0,0196	0,0415	0,0259	0,0144	0,0125	0,0235	0,0176	<0,008	0,0203	0,2932	0,2529
	PCH44	0,2019	0,0192	0,0162	0,0634	0,0811	1,0547	0,1977	3,0835	2,3584	1,1487	1,7289	1,1663	0,5520	0,5877	1,3832	0,7764	0,2160	0,7076	15,1410	12,8291
	PCH43	0,0026	-	<0,008	<0,008	<0,008	0,0606	0,0188	0,1694	0,1346	0,0699	0,1182	0,0828	0,0408	0,0427	0,0756	0,0576	0,0139	0,0475	0,9324	0,7761
	PCH45	0,0023	-	<0,008	<0,008	<0,008	0,0374	<0,008	0,1223	0,0930	0,0414	0,0753	0,0621	0,0262	0,0338	0,0531	0,0376	0,0127	0,0400	0,6423	0,5413
	PCH47	0,0062	0,0132	<0,008	<0,008	<0,008	0,0442	<0,008	0,1393	0,1104	0,0590	0,0925	0,0640	0,0314	0,0315	0,0640	0,0419	0,0128	0,0422	0,7464	0,6250
	PCH48	0,0024	0,0161	<0,008	0,0230	0,0201	0,0951	0,0209	0,3717	0,2707	0,1158	0,1716	0,1168	0,0571	0,0613	0,1169	0,0783	0,0301	0,0738	1,6393	1,3552
	PCH49	0,0025	0,0244	<0,008	0,0163	0,0179	0,2209	0,0443	0,8396	0,6180	0,2991	0,4951	0,3084	0,1373	0,1723	0,3004	0,1993	0,0628	0,1704	3,9265	3,3151
	PCH51	0,0018	<0,008	<0,008	<0,008	0,0094	0,0548	0,0117	0,1915	0,1539	0,0844	0,1398	0,0912	0,0465	0,0498	0,0919	0,0652	0,0162	0,0508	1,0571	0,8821
	PCH52	0,0033	0,0084	<0,008	<0,008	0,0085	0,0873	0,0177	0,4905	0,3795	0,2034	0,3264	0,2408	0,0955	0,1317	0,2556	0,1517	0,0423	0,1423	2,5816	2,1684
	PCH53	0,0450	0,0110	0,0132	0,0527	0,0676	0,5002	0,1301	1,3378	1,0420	0,5179	0,8677	0,5747	0,2459	0,3407	0,5363	0,4224	0,1185	0,3612	7,1399	5,9262
	PCH54	0,0019	0,0160	<0,008	0,0574	0,0778	0,2727	0,0533	1,0269	0,7960	0,3517	0,4689	0,2861	0,1424	0,1542	0,3417	0,1979	0,0571	0,2003	4,5004	3,8103
	PCH55	0,0016	<0,008	<0,008	<0,008	<0,008	0,0498	0,0105	0,3529	0,2533	0,1566	0,2359	0,1446	0,0674	0,0757	0,1199	0,0837	0,0212	0,0688	1,6403	1,3966
	PCH56	0,0029	0,0145	<0,008	<0,008	<0,008	0,0320	<0,008	0,1265	0,0962	0,0376	0,0681	0,0469	0,0224	0,0260	0,0527	0,0334	<0,008	0,0342	0,5905	0,5067
	PCH57	0,0020	-	<0,008	<0,008	<0,008	0,0151-	<0,008	0,0704	0,0549	0,0351	0,0626	0,0298	0,0156	0,0148	0,0312	0,0183	<0,008	0,0154	0,3632	0,3178
PR	PCH50	0,0044	0,0077	<0,008	<0,008	0,0098	0,0716	0,0175	0,1767	0,1371	0,0834	0,1335	0,0880	0,0398	0,0407	0,0806	0,0546	0,0170	0,0484	1,0064	0,8266
	PCH58	0,0029	0,0216	<0,008	<0,008	0,0111	0,0695	0,0097	0,2513	0,1982	0,0924	0,1578	0,0996	0,0468	0,0605	0,0994	0,0678	0,0178	0,0654	1,2689	1,0623
	PCH62	0,0058	0,0100	<0,008	<0,008	<0,008	0,0323	<0,008	0,1221	0,1058	0,0490	0,0836	0,0657	0,0288	0,0304	0,0540	0,0426	0,0077	0,0419	0,6739	0,5617
	PCH63	0,0075	0,0101	<0,008	0,0156	0,0234	0,1438	0,0389	0,4733	0,3824	0,2001	0,3035	0,2079	0,1068	0,0967	0,2105	0,1337	0,0351	0,1259	2,5077	2,0699
	PCH61	0,0115	0,0108	<0,008	0,0172	0,0160	0,1249	0,0217	0,5228	0,4343	0,2077	0,3540	0,2727	0,1109	0,1621	0,2523	0,1921	0,0517	0,1838	2,9350	2,4340
	PCH59	0,0021	-	<0,008	<0,008	<0,008	0,0169	<0,008	0,0561	0,0531	0,0202	0,0418	0,0328	0,0162	0,0154	0,0246	0,0165	0,0040	0,0169	0,3145	0,2615
	PCH60	0,0124	0,0110	0,0138	0,0650	0,0560	0,5337	0,1181	1,5238	1,2137	0,6137	0,8710	0,5753	0,2527	0,3123	0,6457	0,3883	0,0993	0,3563	7,6497	6,4585
	PCH79	0,0035	0,0142	0,0086	0,1266	0,1071	0,4708	0,0654	1,1967	0,9364	0,3914	0,5727	0,3985	0,1883	0,2037	0,4199	0,2760	0,0745	0,2619	5,7127	4,7295
	PCH65	0,0061	0,0334	<0,008	<0,008	<0,008	0,0576	0,0098	0,1945	0,1594	0,0787	0,1356	0,0986	0,0529	0,0466	0,0914	0,0764	0,0185	0,0609	1,1143	0,9011
	PCH64	0,0034	-	<0,008	0,0132	0,0275	0,2002	0,0369	0,3988	0,2963	0,1427	0,2181	0,1359	0,0610	0,0777	0,1394	0,0825	0,0261	0,0775	1,9338	1,6332
	PCH81	0,0035	0,0141	<0,008	0,0641	0,0650	0,7812	0,1429	1,9517	1,6009	0,7305	0,9483	0,6413	0,2629	0,3601	0,6456	0,4041	0,1018	0,3873	9,1018	7,8097
	PCH67	0,0028	0,0696	<0,008	0,0155	<0,008	0,0450	0,0126	0,2145	0,1873	0,1275	0,2000	0,1241	0,0629	0,0706	0,1666	0,0904	0,0236	0,0703	1,4805	1,1722
	PCH66	0,0059	0,0232	<0,008	0,0094	0,0125	0,2443	0,0628	0,5560	0,3862	0,2336	0,3106	0,2067	0,0978	0,1133	0,2154	0,1288	0,0404	0,1187	2,7597	2,3069
	PCH78	0,0237	0,0213	0,0120	0,0666	0,0686	0,5187	0,1126	1,3519	1,0684	0,5492	0,8031	0,5175	0,2616	0,2524	0,5869	0,3527	0,0857	0,3172	6,9464	5,8005
	PCH77	0,0033	-	0,0121	0,0149	0,0151	0,0661	0,0148	0,2610	0,2165	0,1127	0,1790	0,1193	0,0506	0,0725	0,1279	0,0768	0,0216	0,0782	1,4391	1,1907
	PCH76	0,0071	0,0185	<0,008	0,0168	0,0176	0,1894	0,0488	0,5477	0,4247	0,2327	0,3461	0,2359	0,1029	0,1292	0,2452	0,1545	0,0426	0,1472	2,8998	2,4167
	PCH75	0,0097	0,0196	0,0102	0,0328	0,0327	0,2035	0,0402	0,7875	0,6066	0,3122	0,4969	0,3687	0,1666	0,1777	0,3600	0,2732	0,0815	0,2260	4,1959	3,4436
	PCH74	0,0072	0,0207	0,0084	0,0182	0,0286	0,2068	0,0447	0,7724	0,6219	0,3337	0,5223	0,3708	0,1527	0,2011	0,3719	0,2447	0,0646	0,2347	4,2182	3,5095
	PCH73	0,0142	0,0134	<0,008	0,0566	0,0706	0,4828	0,1079	1,2644	0,9667	0,4975	0,6812	0,4520	0,1986	0,2487	0,5079	0,3140	0,0857	0,2869	6,2349	5,2501
	PCH72	0,0052	0,0634	0,0082	0,0134	0,0275	0,1198	0,0229	0,5913	0,4497	0,2170	0,3391	0,2534	0,1103	0,1326	0,2356	0,1684	0,0455	0,1576	2,9557	2,4111
	PCH71	0,0035	0,0100	<0,008	<0,008	<0,008	0,0494	<0,008	0,1870	0,1519	0,0730	0,1148	0,0860	0,0353	0,0404	0,0715	0,0699	0,0140	0,0533	0,9565	0,8112
KM	PCH80	0,0025	0,0234	0,0174	0,0450	0,0456	0,2860	0,0740	1,6071	1,4167	0,7425	1,1891	0,8524	0,3971	0,4232	0,7979	0,5708	0,1429	0,5536	9,1847	7,5869
	PCH82	0,0019	0,0138	<0,008	0,0092	0,0092	0,0531	0,0085	0,1722	0,1403	0,0647	0,1113	0,0708	0,0347	0,0380	0,0709	0,0469	0,0129	0,0425	0,8898	0,7399
	PCH83	0,0022	0,0200	<0,008	<0,008	0,0081	0,0327	<0,008	0,1029	0,0689	0,0409	0,0635	0,0492	0,0199	0,0231	0,0403	0,0729	0,0124	<0,008	0,5548	0,4452
	PCH84	0,0067	0,0160	0,0131	0,0193	0,0246	0,1411	0,0338	0,6700	0,5810	0,3211	0,5174	0,4006	0,1853	0,2049	0,3973	0,2954	0,0840	0,2733	4,1782	3,4015
	PCH85	0,0032	0,0104	<0,008	<0,008	0,0126	0,0456	<0,008	0,1520	0,1186	0,0585	0,1007	0,0721	0,0326	0,0367	0,0660	0,0478	0,0194	0,0374	0,8104	0,6633
	PCH70	0,0067	0,0197	<0,008	0,0090	0,0175	0,1288	0,0255	0,3901	0,3232	0,1482	0,2484	0,1837	0,0742	0,0951	0,1624	0,1289	0,0397	0,1211	2,1155	1,7462
	PCH69	0,0029	0,1117	0,0098	<0,008	0,0099	0,0711	0,0122	0,3137	0,2504	0,1250	0,1946	0,1404	0,0651	0,0785	0,1412	0,0895	0,0281	0,0847	1,7259	1,3487
	PCH68	0,0285	0,0169	0,0136	0,0131	0,0197	0,2015	0,0363	0,6923	0,5764	0,2731	0,4814	0,3771	0,1946	0,1971	0,3833	0,2495	0,0577	0,2537	4,0373	3,3083
	PCH93	0,0050	0,0156	<0,008	0,0144	0,0173	0,1360	0,0303	0,4359	0,3612	0,1765	0,2788	0,1869	0,0811	0,1128	0,2039	0,1188	0,0356	0,1068	2,3119	1,9307
	PCH94	0,0017	-	<0,008	<0,008	<0,008	0,0464	<0,008	0,1166	0,0849	0,0388	0,0695	0,0534	0,0337	0,0336	0,0607	0,0348	<0,008	0,0399	0,6123	0,5252
	PCH92	0,0022	0,0170	0,0141	0,0110	<0,008	0,0762	0,0167	0,2304	0,1834	0,0973	0,1554	0,1046	0,0486	0,0561	0,1038	0,0577	0,0113	0,0724	1,2560	1,0327
	PCH90	0,0026	0,0661	<0,008	0,0256	0,0438	0,4242	0,0987	1,0332	0,8335	0,4869	0,6319	0,4067	0,1817	0,2454	0,4387	0,2456	0,0659	0,2347	5,4626	4,5741
	PCH89	0,0018	0,0166	<0,008	<0,008	<0,008	0,0118	<0,008	0,0613	0,0559	0,0225	0,0445	0,0336	0,0192	0,0233	0,0322	0,0200	<0,008	0,0244	0,3653	0,2959
	PCH86	0,0113	0,0122	<0,008	<0,008	<0,008	0,0183	<0,008	0,0325	0,0226	0,0096	0,0236	0,0194	<0,008	0,0120	0,0117	<0,008	<0,008	<0,008	0,1619	0,1303
	PCH87	0,0024	0,0128	<0,008	<0,008	<0,008	0,0598	0,0100	0,1289	0,1132	0,0543	0,0812	0,0629	0,0307	0,0335	0,0589	0,0416	0,0100	0,0430	0,7408	0,6144
	PCH88	0,0095	0,0168	0,0142	0,1090	0,1100	0,7073	0,1420	2,3225	1,8958	0,9894	1,4217	1,1329	0,5019	0,6057	1,2819	0,8832	0,2349	0,7560	13,1252	10,8635
	PCH91	0,0049	0,0219	0,0093	0,1268	0,1401	0,9812	0,2601	1,8372	1,3815	0,6772	0,8479	0,4885	0,2294	0,2962	0,5409	0,3134	0,0895	0,2751	8,5162	7,1506
	PCH107	0,0027	0,0154	<0,008	<0,008	<0,008	0,0398	0,0097	0,0926	0,0777	0,0316	0,0635	0,0376	0,0235	0,0244	0,0348	0,0262	<0,008	0,0216	0,4984	0,4122
	PCH108	0,0213	0,0245	0,0153	0,0347	0,0381	0,3016	0,0718	1,0774	0,8620	0,4843	0,7524	0,5262	0,2356	0,2821	0,5471	0,3498	0,1079	0,3233	6,0341	4,9800
ZL	PCH109	0,0057	0,0177	<0,008	<0,008	0,0090	0,0517	0,0077	0,1454	0,1174	0,0559	0,0962	0,0704	0,0280	0,0371	0,0616	0,0418	0,0117	0,0395	0,7911	0,6466
	PCH110	0,0095	0,0308	<0,008	<0,008	0,0081	0,0668	0,0137	0,2216	0,2055	0,0925	0,1525	0,1131	0,0500	0,0572	0,1009	0,0749	0,0221	0,0610	1,2707	1,0329
	PCH111	0,0214	0,0461	0,0113	0,0470	0,0521	0,3860	0,6255	1,2319	0,9920	0,5394	0,7955	0,5601	0,2696	0,2925	0,5862	0,3920	0,1082	0,3440	7,2794	5,5595
	PCH99	0,0116	0,0326	0,0101	0,0229	0,0341	0,1978	0,2786	0,6983	0,5771	0,3135	0,4960	0,3560	0,1855	0,1774	0,3546	0,2376	0,0611	0,2298	4,2630	3,2821
	PCH98	0,0060	0,0273	0,0100	<0,008	0,0124	0,0747	0,0211	0,2462	0,1981	0,0934	0,2023	0,1010	0,0458	0,0505	0,0825	0,0592	0,0224	0,0532	1,3001	1,0601
	PCH97	0,0063	0,0204	<0,008	0,0104	0,0146	0,0965	0,0272	0,3138	0,2597	0,1464	0,2210	0,1540	0,0765	0,0811	0,1512	0,0908	0,0287	0,0802	1,7725	1,4407
	PCH95	0,0039	0,0187	<0,008	<0,008	0,0129	0,0566	0,0252	0,1811	0,1258	0,0659	0,1034	0,0638	0,0246	0,0304	0,0683	0,0408	0,0140	0,0337	0,8652	0,7060
	PCH96	0,0062	0,0358	<0,008	0,0095	0,0122	0,1055	0,1046	0,2510	0,1813	0,0751	0,1264	0,0882	0,0401	0,0432	0,0786	0,0558	0,0222	0,0476	1,2771	0,9645
UH	PCH106	0,0081	0,0246	<0,008	0,0168	0,0271	0,1536	0,1326	0,5088	0,4244	0,2079	0,3406	0,2484	0,1132	0,1287	0,2417	0,1653	0,0501	0,1498	2,9336	2,3208
	PCH14	0,0040	0,0345	<0,008	0,0149	0,0149	0,0756	0,0128	0,1778	0,1450	0,0751	0,1243	0,1076	0,0453	0,0592	0,0953	0,0846	0,0201	0,0781	1,1502	0,9150
	PCH15	0,0036	0,0720	<0,008	<0,008	0,0258	0,2058	0,0201	0,4044	0,2924	0,1750	0,3088	0,2438	0,0954	0,1445	0,2365	0,1980	0,0405	0,2004	2,6634	2,1658
	PCH12	0,0051	-	<0,008	<0,008	<0,008	0,0545	<0,008	0,0358	0,0380	<0,008	<0,008	<0,008	<0,008	<0,008	<0,008	<0,008	<0,008	<0,008	0,1283	0,1283
	PCH13	0,0121	0,0399	<0,008	<0,008	0,0110	0,0808	0,0098	0,1702	0,1551	0,0944	0,1653	0,1157	0,0513	0,0477	0,0934	0,1138	0,0361	0,0860	1,2705	1,0067
	PCH16	0,0142	0,0622	<0,008	<0,008	<0,008	0,0624	<0,008	0,1194	0,1015	0,0742	0,1640	0,1574	0,0649	0,0930	0,2309	0,0721	<0,008	0,1187	1,3207	1,0362
	PCH105	0,0035	0,0213	0,0079	0,0135	0,0119	0,0480	0,0115	0,1155	0,0808	0,0277	0,0527	0,0385	0,0223	0,0131	0,0292	0,0512	0,0359	0,0355	0,6165	0,4537

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Group	Sample	c1	c2	c3	c4	c5	c6	c7	c8	c9	c10	c11	c12	c13	c14	c15	c16	c17	c18	c19	c20
HO	PCH104	0,0036	0,0271	<0,008	<0,008	<0,008	0,0445	0,0085	0,1400	0,1203	0,0533	**0,0900**	0,0712	0,0356	0,0401	0,0655	0,0569	0,0107	**0,0516**	0,8153	0,6622
	PCH103	0,0036	0,0143	<0,008	0,0076	0,0099	0,0495	0,0094	0,1558	0,1205	0,0593	**0,1029**	0,0771	0,0274	0,0463	0,0656	0,0524	0,0196	0,0458	0,8634	0,6981
	PCH102	0,0034	0,0262	<0,008	<0,008	<0,008	0,0297	<0,008	0,0670	0,0597	0,0264	**0,0541**	0,0381	0,0145	0,0204	0,0339	0,0521	<0,008	0,0180	0,4401	0,3613
	PCH101	,0044	0,0149	<0,008	<0,008	<0,008	0,0263	<0,008	0,0856	0,0673	0,0423	**0,0597**	0,0468	0,0188	0,0290	0,0518	0,0236	<0,008	0,0320	0,4981	0,4176
	PCH100	0,0049	0,0313	<0,008	<0,008	<0,008	0,0244	<0,008	0,0271	0,0239	0,0147	0,0163	0,0254	0,0090	<0,008	0,0246	0,0397	0,0148	0,0323	0,2835	0,2030
	PCH20	0,0032	0,0248	<0,008	0,0086	<0,008	0,0638	<0,008	0,2372	0,1838	0,0764	**0,1477**	**0,1004**	0,0432	**0,0576**	0,0896	0,0735	0,0137	**0,0615**	1,1818	0,9911
	PCH19	0,0027	0,0290	<0,008	0,0124	0,0198	**0,1725**	0,0152	**0,6969**	**0,5362**	**0,2293**	**0,4478**	**0,3368**	0,1449	**0,1860**	**0,3042**	**0,2610**	0,0581	**0,2243**	3,6744	3,0582
	PCH18	0,0058	0,0249	<0,008	0,0121	0,0153	0,1028	0,0236	**0,3735**	**0,3141**	**0,1699**	**0,2845**	**0,2181**	0,0996	**0,1121**	**0,1960**	**0,1556**	0,0502	**0,1519**	2,3042	1,8604
	PCH17	0,0048	0,0297	<0,008	0,0135	0,0185	0,1045	0,0197	**0,3014**	**0,2464**	**0,1250**	**0,2036**	**0,1513**	0,0701	0,0800	**0,1430**	**0,1147**	0,0333	**0,1037**	1,7584	1,4223
	PCH10	0,0047	-	<0,008	<0,008	0,0228	0,0391	0,0167	0,0575	0,0479	0,0217	0,0440	0,0320	0,0147	0,0151	0,0291	0,0201	<0,008	0,0185	0,3792	0,2930
	PCH11	0,0043	0,0661	<0,008	<0,008	<0,008	0,0428	<0,008	0,0885	0,0626	0,0413	0,0499	0,0379	0,0163	0,0154	0,0402	0,0332	<0,008	0,0325	0,5267	0,4064
	PCH9	**0,0371**	0,0328	0,0106	0,0211	0,0209	**0,1602**	**0,1644**	**0,5528**	**0,4674**	**0,2561**	**0,4354**	**0,3521**	0,1507	**0,1822**	**0,3155**	**0,2682**	0,0775	**0,2668**	3,7347	**2,9046**
	PCH8	0,0034	**0,8536**	<0,008	<0,008	0,0209	0,0310	0,0106	0,0469	0,0353	0,0140	0,0290	0,0222	0,0114	0,0105	0,0195	0,0196	<0,008	0,0221	1,1466	0,2279
	PCH7	0,0095	0,0455	<0,008	<0,008	0,0141	0,0746	0,0389	0,2480	**0,2074**	**0,1107**	**0,1875**	**0,1255**	0,0609	**0,0639**	**0,1316**	0,0940	0,0431	**0,0652**	1,5109	**1,1829**
	PCH6	0,0058	0,0260	<0,008	0,0096	<0,008	0,0518	0,0289	0,1579	0,1341	0,0719	**0,1361**	0,0927	0,0401	0,0491	0,0719	0,0672	0,0246	**0,0538**	1,0157	0,7938
	PCH1	0,0026	-	<0,008	<0,008	<0,008	0,0397	<0,008	0,0921	0,0816	0,0393	**0,0789**	0,0488	0,0205	0,0298	0,0374	0,0262	<0,008	0,0318	0,5261	0,4568
	PCH2	0,0045	0,0242	<0,008	<0,008	0,0093	0,0373	<0,008	0,0573	0,0531	0,0264	0,0476	0,0399	0,0159	0,0194	0,0393	0,0309	<0,008	0,0226	0,4232	0,3339
BV	PCH3	0,0033	0,0148	0,0165	0,0280	0,0308	**0,3690**	0,0924	**1,0119**	**0,9113**	**0,7661**	**1,1506**	**1,0156**	0,5215	**0,5094**	**1,2350**	**0,8884**	0,2194	**0,8901**	9,6708	7,7318
	PCH4	0,0038	0,0285	<0,008	<0,008	<0,008	0,0448	<0,008	0,0668	0,0557	0,0246	**0,0513**	0,0333	0,0141	0,0207	0,0332	0,0344	0,0103	0,0256	0,4433	0,3571
	PCH5	0,0044	-	<0,008	<0,008	<0,008	0,0400	<0,008	0,1119	0,0819	0,0334	**0,0687**	0,0531	0,0270	0,0313	0,0414	0,0287	<0,008	0,0277	0,5451	0,4650
Values of criteries MD ME	A	0,02	0,05				0,15	0,1	0,3	0,2	0,1	0,05	0,1		0,05	0,1	0,1		0,05		1
	B	2,5	40				30	40	40	40	4	25	4		10	1,5	4		20		190
	C-gener.	1																			40

N	naphthalene	Ch	chrysene
Aclen	acenaphtylene	B(b)F	benzo(b)fluoranthene
Acten	acenaphthene	B(j)F	benzo(j)fluoranthene
Fluoren	fluorene	B(k)F	benzo(k)fluoranthene
Fen	phenanthrene	B(a)P	benzo(a)pyrene
A	anthracene	I(123-cd)P	indene(1,2,3cd)pyrene
F	fluoroanthene	DB(ah)A	dibenz(ah)anthracene
P	pyrene	B(ghi)Pe	benzo(ghi)perylene
B(a)A	benzo(a)anthracene		

Sum PAHs-A — sum of all listed PAHs
Sum PAHs-B — sum of PAHs responding to Methodical Direction of ME CR 1996

MD ME — Methodical Direction of Ministry of Environment of Czech Republic

[ ] substances for which there are no criteria in MD ME

Tab. 2 Correlation coeffitiens of elements

	Cd	Co	Cr	Cu	Ni	Zn	V	As	Sb	Hg	Sr	Ba
Be	0,39	0,28	0,63	0,69	0,68	0,59	0,69	0,35	0,10	0,09	-0,17	0,08
Cd		0,18	0,41	0,32	0,35	0,44	0,33	0,13	-0,10	-0,02	-0,35	-0,06
Co			0,28	0,34	0,47	0,22	0,29	0,22	-0,01	-0,03	0,01	0,08
Cr				0,61	0,61	0,50	0,65	0,37	0,03	0,06	-0,13	0,03
Cu					0,77	0,78	0,72	0,27	0,03	0,21	-0,03	0,03
Ni						0,57	0,74	0,21	0,06	0,06	-0,24	-0,01
						-0,01	-0,01	0,72	0,99	-0,03	-0,04	-0,03
Zn							0,55	0,32	0,00	0,20	-0,08	0,04
V								0,24	0,00	0,07	-0,07	0,05
As									0,73	0,07	-0,01	0,03
Sb										0,06	0,02	0,01
Hg											0,55	0,40
Sr												0,35

Note: At the significance level 0.001 and number of observations 111 the critical value of correlation coefficient is R=0.320.
The correlation of Cd with the other elements is preliminary only, about 1/3 of given Cd contents were under detection limit.

samples slightly exceeded the critical limit for A category (1 ppm). In the case of Hg, the critical limit A (0.4 ppm) was exceeded in two samples (0.96 and 2.15 ppm) from the Břeclav district. The level of contamination caused by Sr was not possible to judge, because no critical limits for individual categories were available either from the Methodical Directions of Ministry of Environment of the Czech Republic or in other guiding documents. The concentrations of Sr 78 - 265 ppm. The distribution of concentrations of Ba in samples of the analysed series was strange. Ten highest values exceeded the critical limit 625 ppm set for the category C for general land use. The critical limit C does not differ significantly from the critical limit A (600 ppm), below which the Ba concentrations were for the remaining samples. Inasmuch as no analytical value fell between 600 and 625, we assumed that the Ba concentration of most of the samples is the natural concentration or the background value.

Results of Measurement of Radionuclides

In the case of radionuclides, the studied parameters were the distribution of Th, U(Ra), K and Cs[137], and combinations of these elements with C_{org} and with some selected trace elements.

The Th content was 4 - 17 ppm and their distribution showed a slight increase southward. The U concentration decreased southward, although exceptions occurred. However no geographical variation was observed for U(Ra). The oscillating character of the U distribution curve was given mostly by higher error of analyses, mainly due to a higher weight of activities of Ra^{226} and Th^{232}. The value of U(Ra) was given mainly by activity of Ra^{226} that was more or less solid matter. The higher values of U again U(Ra) could be excepted mainly in places where, in a reducing environment, the U^{+6} (for example UO_2^{2+}) in solution was reduced to U^{4+} in the solid phase - the change of redox potential in basal sediments with organic impurities. There is no mutual correlation of weight activities or concentrations of U and U(Ra). The ratio of both values expresses the radioactive balance between U^{238} and Ra^{226}. The decreasing trend of U from N to S indicates transport of this element from upper parts of the river basin and also the gradual establishing of radioactive balance between U^{238} and Ra^{226}.

The K concentration increases slightly southward. The adsorption of K by clay minerals must be considered as it

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was for Th. If we overlay the curve of Cs^{137} with the exponential curve, then it indicates a southward decrease. Both analysed elements do not indicate any mutual relationship. It is important to mention here, that both compared elements have significant positive linear correlation with a probability of 95% at least, which confirms the facts known about the relationship of Cs^{137} with organic matter.

On the base of correlation analyses between radioactive and metal elements some significant relationship were observed between Th and some metal elements (Ba, Sr, Cu, Zn, Cr, Ni a V). Ba has a significant positive correlation with Th (correlation coefficient 0.3138 with a significance 0.05). Sr, which has a significant positive correlation with Ba, butdoes not have any relationship with Th. There are notable correlations between Th/Cu (coeff. 0.3091) and Th/Zn (coeff. 0.4262. with a significance of 0.01). The reasons for the associations may be that they had a in common source or they had a similar geochemical behaviour.

The correlation coefficients for the associatiation of Th with Cr and Ni are significantly positive with a probability of 98% at least. All these elements increase southward. Below the mouth of the tributary Dřevnice there is a notable increase in the contents of Cr and Ni of anthropogene origin after the flooding of Zlín, Otrokovice and Napajedla. The correlation coefficient of Th/V = 0.279.

The dependence of a connection of Cs^{137} to the content of organic matter in sediments was also observed in the sample cores. In one third of the samples there was observed an imbalance between U and U(RA) in the upper part of the profile (in flood water-laid deposits), which indicates a risk of a mobilisation of uranium by water. We have established certain critical limits for the judging of possible risks that results from the geochemical character of the studied elements, their migration abilities, and mainly from a proven long lasting negative influence on organisms. In the case of U(Ra) we consider as a critical value values equal or greater than 5 ppm, and at the same time values equal or greater than 3 in a ratio U/U(Ra). In the case of Cs^{137} we consider values equal or greater than 30 Bq/kg as critical values. We set up these limits considering radioactive background of the studied area, which we had obtained from geophysical data, and also considering known values of clark values of their content in rocks. From this point of view our critical limits are almost 2 times greater. Throughout the world, Cs^{137} is being monitored from the limit 30 Bq/kg. In the studied area this limit was exceeded in ten samples, mostly in the top part of core profiles. The limit of 5 ppm for U(Ra) was exceeded in two samples, also in top parts of the profile.

The distribution of radioactive elements in alluvial deposits, soils and soils of flooded areas of the Hornomoravský and Dolnomoravský Úval Depression could be effected by several factors. The depression area was provided with sediments, including Cs^{137}, from source areas with different geological environment. Also, there could have been erosion of material from chemical storage facilities, with some possibility thereby of enriching the radioactive elements.

The mountain catchment area is formed mainly by the crystalline areas of the Jeseníky and Rychlebské Hory Mts., in which underground mining was intensive in the past. In the case of the catastrophic flooding in July 1997, the radioactive elements, and also other minerals, could be moved from the mining area in the ion form (fixed to clay minerals, for example). They could be also fixed to eroded clastic particles, especially to heavy minerals of certain rock types. The rocks of the Orlicko-kladské crystalline complex should be considered as another natural rock sources. Mainly the west wing of the Sněžnická group represents a natural donation area, with increased contents of uranium. The transportation and accumulation of matter from flysch areas, mainly from Zlín, Vsetín and Kromněříž areas, and its geochemical character, are conditioned by the erosion of individual flysch sequences. It was proved by a geophysical study that some flysch sequences have increased natural contents of radioactive elements (for example belovážské sequences of magurka flysch and menilit sequences of inner flysch have increased the U content by tens ppm).

An important element, whose presence cannot be underestimated during cultivation of new farming soils, is Cs^{137}. As was mentioned above, the level of radioactivity in rocks is controlled by the contents of Th, U, K, and also Cs^{137} has some share. Each of these elements is controlled by the character of its migration.

Thorium (Th) belongs to elements having a low mobility; thus, during weathering processes, it passes into water solution in only a limited amount. In clastic particles Th is fixed to some heavy minerals (zircon for example), and it is also adsorbed by clay particles.

Uranium (U) occurs in rocks in two forms: with four charges (U^{4+}) and with six charges (U^{6+}). On the other hand U^{6+} is very mobile and the mobility of U^{4+} is also relatively small. During a reduction of U6+ to U4+ (for example in organic components) The U solidifies in a form of complexes and thus it can creates secondary accumulations.

Potassium (K) does not show anomalies, however, its concentration is characteristic for many lithotypes. It is fixed mainly to silicates with layer structures of tetrahedrons (micas and hydromicas); it is also adsorbed by kaolinite and montmorillonite and its carrier could also be K-feldspar of clastic origin.

Most of the caesium (Cs^{137}) is a residue of the Chernobyl accident. Cs^{137} is strongly tied in soil horizons, thanks to its large ion diameter. Plants (mainly mushrooms) accumulate and bring the radioactive caesium into the food chain. In the case of flooded areas, it is important to take in to consideration a great run off of Cs^{137} from forest plant cover and its accumulation in sedimentation areas, together with organic matter and another mechanical fractions.

Conclusion

In the Czech Republic this is the first attempt to evaluate the contamination of soil or rock environment by flood sediments on a regional scale. This attempt includes the application of methods of organic geochemistry, deter-

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mination of metal elements and also radionuclides in lithologically and genetically relatively related matter (near surface sampling of mostly fine-grained flood sediments).

It seems that the research of radioactive matter distribution can notably contribute not only in an evaluation of contamination of rock environment, but also in a search for source matter from source areas and in understanding the processes of redistribution in general.

The results show that the anthropogenic Cs^{137} that was deposited in our country after the Chernobyl accident will still contaminate the soil horizons on a regional scale, probably for a long time. The high content of this radionuclide (for example, in forest soils and also in plants, mainly in mushrooms, and subsequently in forest animals) were not, and still are not, evaluated with such support as they were in the developed countries. During the dynamic and long gradual processes of matter redistribution the radionuclides not only get into the soils and rock environment of flooded areas but also into alluvial and reservoir sediments. In the preserved samples from some reservoirs the layer enriched with Cs^{137} can be used for dating deposits as "before and after Chernobyl".

With regards to the vague evaluation of Cd and Ba contamination, it seems unavoidable to specify the critical limits for concentrations of trace elements, group organic substances and individual organic pollutants, and to set up new concentrations for the evaluation of radioactive risks.

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Utilization of Selective Extraction Techniques for Element Speciation in Soils and Sediments - Critical Evaluation of the Contemporary State

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Abstract. Requirements for environmental quality assessment and management have necessitated the development of selective chemical extraction procedures to evaluate trace metal mobility in soils and sediments, and uptake by biota. Although extraction procedures have been widely used on atmospheric particulates, dust and fly ash, street dust and roadside soils, sewage sludge, incinerated sludge ash, and soils and sediments, their status as useful analytical tools is controversial. This article reviews the major extraction techniques in use, and considers criticisms, and the suitability of these methods, in light of recent research findings. It concludes the review with recommendations for further developments to improve the validity of extraction techniques and understanding of the important biogeochemical phases and processes in soils and sediments.

Key words: speciation, soil, sediment, sequential extraction procedures

Introduction

Sequential chemical extraction techniques have been used to characterize chemical forms of elements in soils and sediments, which helps to predict elemental environmental availability, toxicity, and hazard to living organisms. Selective extraction procedures, consisting of subjecting a given sample to a series of increasingly strong reagents under specified conditions, have been extensively employed. They are based both theoretically and experimentally on more than 100 years of research (Jackson, 1985). These have been used to determine the „species" of particulate metals and radionuclides in soils and other natural particulate phases and to predict the extent to which contaminants may become mobilized should sediments be resuspended, and geochemical conditions change.

The metals in soils and sediments may be present in several geochemical phases that act as reservoirs or sinks of trace elements in the environment. Factors affecting the distribution of an element among different physicochemical forms include pH, ionic strength of the solution, the solid and solution components and their concentrations and affinities for an element, and time (Ritchie & Sposito, 1995). Elements may sorb to clays, metal hydrous oxides, silicates, carbonates, soil or sediment organic matter, or sulphides. In solution, elements may be in the solvated form (solvation complex) or complexed with organic and inorganic ligands. Speciation may also consider the type of bonding between an element and other solid components. For example, an element in ionic form may bind to clay minerals or organic matter by coulombic forces, whereas covalent bonds may be formed with surface ligands on hydrous oxide surfaces (Fendorf et al., 1994). Ligands can form inner or outer-sphere complexes with cations, either in solution or on an adsorbent (Ritchie & Sposito, 1995).

Total concentration was generally used to assess the potential effects of soil and sediment contamination. Tessier et al. (1979) stated that this implied that all forms of a given metal had an equal impact on the environment and pointed out that such an assumption was clearly untenable. Many methods have been employed to fractionate elements depending on the composition of the substrate and the portions of the substrate considered most important. Jones and Hao (1993) reviewed and evaluated 60 papers concerned with sequential extraction methods for natural systems and concluded that these methods have proven useful for metal speciation. The development of selective extraction procedures, as distinct form simple measurements of „total" metal in environmental samples, has been gradual.

The numerous reagents used and sequential schemes proposed in the literature, however, illustrate the difficulty in selecting the best method for the study of the different metal phases. The specificity and reproducibility of methods depend strongly upon the chemical properties of the element, the chemical composition of the samples, and various experimental factors. There is no general agreement in the literature on the solutions preferred for the various sediment and soil components to be extracted, due mostly to the „matrix effect" involved in the heterogeneous chemical processes. The most appropriate extractants are determined by the aim of the study, by the type of solid material (sediment or soil, sewage sludge, fly ash, dredged harbour mud, street dusts, manganese nodules, and so on), and by the element of interest. A vast literature exists on specific research areas, with appropriate extractant formulations for a selected problem. Reviews exist in such fields as geochemical prospecting, trace metal speciation in soils in general or more specifically in sewage sludge-amended soils, sediments, deep sea geochemistry, fly ash characterization, and solid

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waste (e.g. Pickering, 1986; Förstner et al., 1990; Förstner, 1986). These papers usually give many experimentals details as a basis of evaluation of the selectivity and effectiveness of reagents, such as solid to solution ratios, treatment times, specific extraction chemistry and matrix effects of many of the different reagents, and similar suggestions.

During the last decade, a great effort was devoted to the problems and to the further development of chemical analytical speciation techniques. Fractionation procedures and detection methods are being refined and new combinations of existing techniques were applied (Broekaert et al., 1990; Ure & Davidson, 1995).

The aim of this article is to evaluate the most recent extraction techniques in use, their suitability for most applications, the criticisms of these methods in light of the most recent research findings, and to recommend further developments for improvements of extraction techniques.

Definition of Speciation

There is no generally accepted definition of „speciation", and various meanings have been attributed to the term by different workers. Here, the broad definition evolved under the auspices of the Commission of the European Communities, Community Bureau of Reference, BCR (Ure et al., 1993a, b) is used. In this context, speciation may be defined as either (a) the process of identifying the different, defined species, forms or phases present in a material; or (b) the description of the amounts and kinds of these species, forms or phases present. Whichever approach is taken, the species, forms or phases are defined (a) functionally, (b) operationally, or (c) as specific chemical compounds or oxidation states.

Why the Need for Speciation in Soils ?

The existence of an element in different chemical forms in the gaseous, solid, or aqueous solution phases provides the conceptual basis for speciation in soils. More specifically a „ chemical species" in soil refers either to a specific molecular arrangement of the atoms of an element or, quite often, to the result of an operational process of detection and quantification aimed at elucidating the chemical forms. A comprehensive review of the species in soils can be found in the monograph by Schlesinger (1991).

The existence of an element in a soil is transitory, because the soil is only one „compartment" in the biogeochemical cycling of elements in an ecosystem. The residence time of an element, however, varies considerably, depending on the mobility of its predominant species and the rate of soil evolution (Sposito & Page, 1984). For example, aluminium, iron and silicon are the most abundant elements in soils, but < 1 % of their soil chemical species cycle in one year because most of their chemical forms are extremely immobile. This slow cycling is fortunate, considering the toxicity of Al to plants and animals, but unfortunate if iron nutrition is thereby limited. Thus,

slow cycling becomes a problem if it can lead to soils being deficient in elements that are required for plant growth (e.g. Fe, Cu and Zn).

The soil solution is the medium through which dissolved species are transported to a root surface and carried to groudwaters or surface waters. In addition, it acts as an important link between solid soil phases and other components of an ecosystem involved in biogeochemical cycling. The general behaviour and properties of the soil solution have been reviewed (Sposito,1986), as have the reactions of trace elements in soil solutions (Kabata-Pendias & Pendias, 1992). The total dissolved concentrations of trace elements vary quite widely depending on several factors, such as soil type and use and the proximity to potential pollution sources (Kabata-Pendias & Pendias, 1992). Ionic strength, pH and electron activity (pE) are the three major characteristics of the soil solution commonly recognized as affecting metal speciation. However, reaction kinetics and the relative concentrations and complexing affinities of cations and anions may be equally important (but are sometimes overlooked). The kinetics of reactions in solution are well documented from a theoretical pespective (Sparks, 1989). The kinetics of reactions between components in solution are considered to be so fast, if compared to solid-solid or solid-solution reactions, that it is justifiable to assume that solution equilibrium exists. In many cases, this is a reasonable assumption - for inorganic complexes in particular - but it may not be so for metal complexing by multidentate organic ligands, such as humic and fulvic acids, and some inorganic ligands (Sposito, 1986; Hering & Morel, 1990). For example, humate and fulvate ligands often have been treated in experimental study as monodentate ligands when considering their reactions with metal ions (e.g. Hering & Morel, 1990). In reality, this is unlikely to be the case and it is not possible to predict the net effect on reaction rates. Given the importance of metal-humate/fulvate reactions to plant uptake, it is an area that warrants further research to establish the importance, if any, of kinetics in the availability of metal cations to plants.

Metal cations may be soluble, readily exchangeable, complexed with organic matter or hydrous oxides, substituted in stoichiometric compounds, or occluded in mineral structures (see reviews by Beckett, 1989; Förstner, 1991). The chemical factors that affect the retention of a specific chemical form of a trace metal (e.g. effects of pH and ionic strength on „specific adsorption") are well documented (Alloway, 1990; Förstner, 1991). Increasing soil pH (or I) increases the number of sorption sites available on clay minerals, hydrous oxides, or organic matter, but will not necessarily increase the amount of a trace metal adsorbed by a soil component unless that specific component binds the metal most strongly and there are sufficient sites for adsorption. For example, increasing the pH of a soil that contains mainly hydrous oxides and kaolinite may only increase the fraction of total Cd („% Cd") bound to hydrous oxides (Mann & Ritchie, 1993). If sufficient Cd is added, however, the amount of total Cd that is in an exchangeable form can increase at lower pH values because of a lack of adsorption sites on hydrous

oxides. By contrast, raising the pH of a lateritic podzol (which contain mainly kaolinite) from 4 to 5 at both application rates of Cd increased % Cd in the exchangeable form because it was the major form present. The application rate did not affect % Cd in the exchangeable form, which indicated an excess of sites, even at pH 4. At higher pH values, exchangeable Cd decreased, possibly because Cd was adsorbed onto sites that were less accessible and could be displaced only by acid extraction, i.e. the residual form. In the same study, increasing the pH of a sandy soil increased exchangeable Cd at the expense of soluble Cd. The more Cd present, the smaller was the decrease in soluble Cd because of a lack of cation exchange sites.

The distribution of trace metals among soil components is important for assessing the potential of soil to supply sufficient micronutrients for plant growth or to contain toxic quantities of trace metals, and for determining amelioration procedures for soils at risk of causing the trace metal contamination of waterways.

Why the Speciation in Sediments ?

The tendency of an element to be accumulated by organism depends in particular upon the capacity of a sediment - water system to resupply trace elements removed from solution by biotic and abiotic processes. Solid components in sediments govern the dissolved levels of these elements via sorption- desorption and dissolution-precipitation reactions. Thus, particular trace metal species identification tends to be far more instructive than any total elemental concentrations. In order to asses the environmental impact of a given pollutant the following points must be addressed in contaminated sediment-water systems (Kersten & Förstner, 1995):

1.) What is the reactivity of the metals introduced with solid materials from anthropogenic activities (hazardous waste, sewage sludge, atmospheric deposits, etc.) by comparison with the natural components ?

2.) Are the interactions of critical metals between solution and solid phases comparable for natural and contaminated systems ?

3.) When the solid inputs or the solid-solution interactions lead to weaker bonding of certain metal species, are the factors and processes of remobilization effective in contaminated sediments, as compared with natural systems ?

While most direct physico-chemical speciation approaches are too insensitive for the trace amounts of environmentally relevant metals encountered in sediment, wet chemical extractions have been shown to provide a convenient means to determine the metals associated with the principal accumulative phases in sedimentary deposits and to elucidate the mechanisms of their diagenetic transformation. A general goal of all studies involving selective chemical extraction is the accurate determination of the partitioning of elements of environmental concern among different discrete phases of a sample. Mineralogical constituents of sediment considered important in controlling metal concentrations in sediment are hydrous

oxides of iron and manganese, organic matter, and clays. Fractionation is usually performed by a sequence of „selective" chemical extraction techniques which include the succesive removal or dissolution of these phases and their associated metals. Despite the clear advantages of a differentiated analysis over investigations of the bulk chemistry of sediments, verification studies conducted in recent years indicate that there are many problems associated with „operational" speciation by partial dissolution techniques. It is common for studies in wet chemical extraction to point out that the various extractants used are not as selective as expected. Van Valin & Morse (1982) concluded that „ the concept of an operationally defined element reactivity is generally used rather than attempts to characterize each phase individually". In recent years, some reviewers came to conclusions as pessimistic as „these techniques represent nothing but an operational tool and complementary approach until physical techniques are available with the new generation of microprobes and other sophisticated instruments". On the other hand, the results of the comparative study performed by Lion et al. (1982) suggest that „the role of sediment components may be evaluated from the perspective of competitive adsorption phenomena and that sediment adsorption characteristic and extractant-determined component-metal associations yield consistent information on the binding of metals".

A Review of the Most Frequently Used Sequential Extraction Techniques for Soils and Sediment Fractionation

The Tessier Method

In this landmark work, Tessier et al. (1979) proposed a five-step scheme consisting of selective extractants used in a sequence, to determine the forms in order of their decreasing solubility. The solids are extracted with $MgCl_2$ (Exchangeable metals), NaOAc (Carbonate-bound metals), $NH_2OH \cdot HCl$ in HOAc (Fe+Mn-oxide-bound metals), H_2O_2, HNO_3, followed by treatments with H_2O_2, NH_4OAc and HNO_3 (organically-bound metals), and finally $HF-HClO_4$ digestion (metals in the residue). Solids are rinsed with distilled water between extraction steps and the rinse water is discarded.

Exchangeable: In the Tessier scheme, the first or „exchangeable" fraction is obtained with a magnesium chloride solution (1 mol/L, pH=7.0) or a sodium acetate solution (1 mol/L, pH=8.2). According to Chapman (1965), the solubility of $CaCO_3$ in sodium acetate is low. The $CaCO_3$ fraction solubilized in relation to the total $CaCO_3$ content of the sample. A sodium acetate solution (1 mol/L) adjusted to pH=8.5 and a 0.5 g sample was chosen for the first fraction by Orsini and Bermond (1994) to minimize the loss of carbonates. Water soluble and exchangeable phases are regarded as mobile and readily bioavailable, whereas other forms are of minor importance for uptake (Chlopecka, 1993; Dudka & Chlopecka, 1990). The reagents found to give the best correlations to plant uptake in different studies include

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water, 1 M $MgCl_2$, 0.05 M $CaCl_2$, 1 M NH_4OAc, 0.1 M $NaNO_3$, 1 M KNO_3, 1 M NH_4NO_3, acidified $(NH_4)_2C_2O_4$, 0.1 N H_3PO_4, 0.1 N HCl and DTPA (diethylenetriaminepentaacetic acid), indicating that several alternate reagents to those of Tessier have proven useful.

Bound to carbonates: Tessier et al. (1979) used 8 mL of 1 M NaOAc adjusted to pH 5 with acetic acid. The complete dissolution of $CaCO_3$ can be limited by its solubility in the extract and by the dissolution kinetics. The dissolution time depends upon several parameters related to the sample: the grain size, the $CaCO_3$ content, the nature of the carbonates and the sample size. Orsini and Bermond (1994) found that a 1 M NaOAc solution adjusted to pH=5 with acetic acid completely dissolved the $CaCO_3$ while disolving little or none of the iron and manganese oxides after 5 h. Tack & Verloo (1995) determined that the conditions of the acid extractable step in the Tessier sequential fractionation scheme are not suited to dissolve selectively carbonates and associated metals if the sediment has a high carbonate content (>10 %). From thermodynamics, it is expected that large amounts of Fe would dissolve in these conditions. Experimentally, this solubilization of Fe does not occur, but the solubilization of carbonates is incomplete for kinetic reasons.

Metals associated with manganese and iron oxides: Tessier et al. (1979) extracted this fraction with 20 mL of either 0.3 M $Na_2S_2O_4$ plus 0.175 M Na-citrate plus 0.025 M H-citrate or 0.04 M NH_2OH . HCl in 25 % (v/v) HOAc at 96 ± 3 ^0C with occasional agitation for as long as required. A reducing solution of NH_2OH . HCl solubilizes iron (Fe^{3+} into Fe^{2+}) and manganese (Mn^{4+} into Mn^{2+}) oxides. Chao (1972) found 0.1 M NH_2OH . HCl was specific for Mn oxides. Others concur (Hickey & Kittrick, 1984; Gibson & Farmer, 1986), although Gupta and Chen (1975) found it did not dissolve all of the Mn oxide nodules. Some workers have discriminated between metals bound to amorphous Fe oxides and crystalline Fe oxides. Gupta and Chen (1975) used hydroxylamine to extract metals from amorphous Fe oxides, yet the same reagents, at a greater concentration, did not dissolve magnetite (Singh et al., 1988). Oxalate [$(NH_4)_2C_2O_4 + H_2C_2O_4$, in the dark] was used by Miller et al. (1986) for extracting metal from Fe oxides. Other reagents used to dissolve the crystalline iron oxides are sodium dithionite - citric acid and oxalate with ultraviolet irradiation (Gupta & Chen, 1975; Miller et al., 1986; Singh et al., 1988). Tessier et al. (1979) report that NH_2OH . HCl dissolves some silicates in sediments; however, silicate dissolution seems to be negligible in soil. Heron et al. (1994) have more recently suggested several extractants for Fe under different redox environments.

Organically bound metal: Tessier et al. (1979) add 3 mL of 0.02 M HNO_3 and 5 mL of 30 % H_2O_2 adjusted to pH 2 with HNO_3 to the soil or sediment and heat the mixture to 85 ± 2 ^0C for 2 h with occasional agitation. A second 3 mL aliquot of 30 % H_2O_2 (pH 2 with HNO_3) is

then added and the sample is heated again to 85 ^0C for 3 h with intermittent agitation. After cooling, 5 mL of 3.2 M NH_4OAc in 20 % (v/v) HNO_3 is added the sample diluted to 20 mL and agitated continuously for 30 min to prevent readsorption of heavy metals to the oxidized sediment. Hydrogen peroxide is the commonly used extractant for this fraction (Gupta & Chen, 1975; Gibson & Farmer, 1986) even though it dissolves Mn oxides (Keller & Védy, 1994) and does not dissolve all forms of organic matter. Hydrogen peroxide seems to be more efficient when used after the oxide extraction step. Orsini and Bermond (1994) found the kinetics of destruction of organic matter was slower than originally specified by Tessier and took 24 h.

Metals in the residues: Tessier et al. (1979) recommended the solubilization of the metals bound to the residue using a 5:1 mixture of HF and $HClO_4$ in a platinum crucible, however, many have successfully used polypropylene tubes. Orsini and Bermond (1994) show that a duration of 24 h is sufficient to achieve the complete solubilization of Cu. The method used by Miller et al. (1986) digests the residue with concentrated HNO_3 (65 %), but only $\approx$ 60 to 80 % of the metals dissolved under these conditions (FAC, 1989). Aqua regia dissolves all the metals in the residue except those in the silicates; the percentage extracted varies between 60 and 100 % depending on the metal (Keller & Védy, 1994). In general, aqua regia, HF and $HClO_4$ have been used in that order, though the order has been varied and the reagents combined. After HF treatment of the extraction residues, newly formed fluorides may be found (Hirner, 1992).

These and similar sequential extraction protocols have been applied to atmospheric particulates, dust and fly ash (Hirner, 1992), street dust and roadside soils (Gibson & Farmer, 1986), sewage sludge (Legret, 1993), incinerated sludge ash (Förstner, 1993), as well as soils and sediments (Gupta, 1989; Sheppard & Thibault, 1992). Other extraction schemes have been proposed (Salomons & Förstner, 1980; Towner, 1985) and multistep extractions involving various reagents have been described by many authors (McLaren & Crawford, 1973; Gupta & Chen, 1975; Chang et al., 1984; Miller et al., 1986; Singh et al., 1988; Oughton et al., 1992). Some authors have coupled this technique with physical fractionation (Keller & Védy, 1994).

The BCR Extraction

The BCR method (originating with the European Community Bureau of Reference, Quevauviller et al., 1994, 1998) consists of three sequential extraction steps using (1) acetic acid, (2) hydroxylammonium chloride, and (3) hydrogen peroxide/ammonium acetate. Between extracting reagents, the solids are rinsed with distilled water; rinses are discarded.

Results from the BCR extraction protocol, intended to harmonize and standardize selective extraction techniques (Lopez-Sanchez et al., 1993) were compared with results

of the Tessier extraction procedure on the same sediments. Although both methods gave reproducible results, substantial differences were found betwen the metals extracted by similar reagents. In particular, the BCR consistently extracted more metals (Cd, Cr, Cu, Ni, Pb and Zn), assumed to be associated with organic matter or sulphides, than did the Tessier procedure. Whalley and Grant (1994) used the BCR procedure to analyze mineral phasses previously equilibrated with metal-spiked (Cu, Ni, Zn) artificial seawater and found that the results were acceptably precise in comparison with real river sediments. In another study using the BCR procedure, Davidson et al. (1994) summed up the yields of metals in the three fractions to ensure they equalled the „total" metals as measured by acid digestion. The results of an initial study on the stability and reproducibility of metal „speciation" in a standard reference material, using the BCR extraction for Cd, Cr, Cu, Ni, Pb and Zn, showed generally stable distributions among the extraction fractions over a period of eight months (Fiedler et al., 1994). The results of an interlaboratory comparison study using another reference material, however, were less promising (Quevauviller et al., 1994). In this study, many contributing laboratories were unable to submit qualifying results.

Other Notable Selective Extraction Methods

Bendell-Young et al. (1992) proposed a method intended to reduce the complexity and robustness of selective extraction procedures, while maintaining comparability with the Tessier method. Another sediment method uses the Acid Volatile Sulphide (AVS) fraction, the solid phase sediment sulphide fraction that is soluble under cold acid conditions, to determine biological availability and toxicity. It has been proposed (Ankley et al., 1991) that this fraction is capable of binding an equimolar quantity of trace metals such as Cd and Ni, and that bioavailability and toxicity in sediments do not commence until the sediment metal : AVS ratio exceeds unity. Solubilization of organics using complexing reagents, such as pyrophosphate, EDTA (ethylenediaminetetraacetic acid) and DTPA (diethylenetriaminepentaacetic acid), that competitively desorb metal, or by oxidizing reagents (H_2O_2, $NaClO_4$) that destroy the binding sites in the organic matter, is also common (McLaren & Crawford, 1973; Miller et al., 1986; He & Singh, 1993).

Limitations of Selective Extraction Methods

The Tessier method has been extensively criticized since its inception (Accomaso et al., 1993; Förstner, 1993; Gupta & Chen, 1975; Heron et al., 1994; Kheboian & Bauer, 1987; Miller et al., 1986; Nirel & Morel, 1990; Orsini et al., 1994; Pickering, 1986; Riise et al., 1994), yet it remains a widely-used extraction procedure. Criticisms include: the extractions are not as selective as they were hoped to be, a problem recognized by Tessier et al. (1979); minor variations in analytical procedures have significant effects on the results; metals released by the

dissolution of one solid phase may be re-sorbed during the extraction process by remaining solid phases; metals may be mobilized and lost when distilled-water rinses are discarded; the overall procedure is imprecise and poorly reproducible; and labile phases may be transformed during the procedure, leading to an incorrect assessment of metal distribution in sediment (this point applies particularly to anoxic sediments). Lack of standardization and reference materials, lack of analytical sensitivity to detect metals in the extracted fractions, concern about background contamination in reagents and labware or during the many manipulation steps, and matrix interferences between some extraction reagents and trace metals being analyzed are also cited as problems.

We can discuss seven areas where sequential extraction procedures have been criticized. Many of these issues occur at the same time and confound the interpretation of the results. These include: 1) sample handling and preparation methods, 2) failure to sample pore water, 3) nonspecificity of the extractant for a particular contaminant of concern in a specific media, 4) readsorption and redistribution of the heavy metal of interest during the extraction, 5) insufficient procedure duration for the kinetics of the expected reaction, 6) surface occlusion causing inefficiency of the extractant, 7) quality assurance, analytical sensitivity, and matrix interferences.

Sample Handling, Preparation and Storage

The preparation and storage of samples for qualitative and quantitative determinations of species of one or several elements has always required special attention. The nature of this task differs from procedures adopted for total elemental analyses. However, it is essential to keep in mind that data on total elemental concentrations are often necessary in many investigations. Any procedure adopted for the preservation of samples between the time of collection in the field and the opportunity for analysis in the laboratory should not disturb the equilibria among the species. Contaminated solid materials are not necessarily stable (Whalley & Grant, 1994) and correct sample handling and storage prior to manipulation, extraction and analysis are critically important. Rubio and Ure (1993) discuss and compare approaches to sampling, sample pretreatments, contamination control, and consider the suitability of the extracting solution matrix for the analytical technique. Definitive protocols for sampling and sample pretreatment are required to prevent changes from reducing to oxidizing conditions, transformations of sulphides, pH shifts, light catalysed reactions, reactions with the sample container, time delays before analysis with biologically active samples, etc. Förstner (1993) reviewed concepts in sediment metal speciation and emphasized the sensitivity of sequential extraction techniques to artifactual changes in sediment geochemistry between sampling and analysis. A sequential extraction of sediments from Hamburg harbor, performed under oxygen-free conditions, indicated that essentially all of the Cd associated with anoxic mud was bound in a sulphidic fraction. In contrast, samples exposed to oxygen or dried before ex-

traction showed completely different distributions of Cd, a shift towards the reducible, carbonate-bound, and exchangeable phases. Maintaining strictly anaerobic conditions between the moment of sampling and analytical procedure can be a daunting challenge.

Sequential extraction of soils from the vicinity of a Polish copper smelter suggested a high proportion of Cu and Pb could be mobilized from the exchangeable and carbonate fractions of the soil (Rybicka et al., 1994), yet Scanning Electron Microscopy/Energy Disperzive X-ray (SEM/EDX), spectroscopy of soil particle size fractions indicated that both metals were mainly associated with sulphides and /or sulphates. The explanation put forward was that oxidation reactions during handling and / or extraction had converted much of heavy metal sulphides to soluble hydrous sulphates. However, SEM preparation is not benign and must also be considered as a manipulation of the sample.

Reliable and generally applicable methods for the preservations of the original distribution of the species in natural sediment and soil samples do not yet exist. Thus, it is important to be aware of the kinds and degrees of changes taking place in the soils or sediments while they are actually being studied. Whatever the extraction procedure chosen, the validity of selective extraction results will, however, be primarily dependent on the ways in which the samples are collected and preserved prior to analysis.

Failure to Sample Pore Water

Soluble contaminants in sediments may be transported to the water column with discharging groundwater, by diffusion, or through the pumping action of burrowing invertebrates. Although transport in the water column is rapid, transport in bulk sediments is typically dominated by molecular diffusion and concentration gradients. Thus, bioavailability, toxicity, and environmental mobility can be assessed from pore-water concentrations. However, sediment contaminant pore-water concentration gradients are rarely measured despite being technically feasible (either using „peepers" or by squeezing or centrifuging of core material). Sediment (soil) pore water concentrations also permit determination of the sediment (soil) - solid : pore-water partition coefficient, K_d. Stephenson et al., 1995 determined cadmium K_d values and they found that the highest K_d values are in the organic sediment cores from 8-9 m of water and the lowest are from a shallow (3 m) sandy core, which also had the highest sediment pore water Cd concentrations. The lower K_d values at depth in all cores imply that post-depositional mobility of free Cd is likely: the high K_d near the sediment-water interface suggest that natural enrichment of total Cd in surface organic sediment can be expected. These results show that sediment pore water contaminant concentrations can provide direct and relevant evidence for the assessment of biological impacts, and trace element fluxes and fate, in the environment.

Partition coefficients determined from soil pore water and solids, extracted from cores that were allowed to freeze in-situ in a long-term field study, are preferred to K_d values measured in the laboratory using batch K_d methods (Sheppard et al., 1993).

The use of pore water analysis for realistic K_d determination is important in soils where solid to solution ratios are normally large and anoxic pockets exist even in well-aerated profiles. This is especially important for very mobile elements such as I and As, and for elements such as Tc or U, that are strongly influenced by redox potential. Pore water measurements are certainly as important as chemical extraction results, yet the importance of pore water is ignored in all major extraction schemes.

Nonspecifity of the Extractants, Readsorption and Redistribution

Two major experimental problems with sequential procedures have been recognized: nonselectivity of extractants, and trace element redistribution among phases during extraction (Kheboian & Bauer, 1987; Nirel & Morel, 1990; Kim & Fergusson, 1991; Tessier & Campbell, 1991; Bermond & Eustache, 1993; Förstner, 1993; Xiao-Quan & Bin, 1993). Generally it is difficult to associate a given extractant reagent with a particular physicochemical phase. Instead, the specificity of an extractant is operationally defined according to what it extracts; e.g. acetate buffer extracts the „acetate-buffer-extractable „phase. Although it is often believed that this particular phase includes carbonate minerals, these minerals may not be uniquely attacked by this reagent. This is the nonselectivity problem. For the other problem - redistribution - trace elements liberated by one extractant have an opportunity to reassociate with remaining undissolved sediment (soil) components before recovery of the extract. Both processes scramble the true phase association of the trace elements thus complicating interpretations.

Lack of geochemical specificity was reported in experiments where Kheboian and Bauer (1987) studied metal spike recovery from mixed model phases. Kim and Fergusson (1991) studied the extent of Cd redistribution between phases by sequentially extracting and comparing a range of „synthetic" soils with a real soil. Shannon and White (1991) examined the selectivity of the Tessier method for FeOOH, FeS and FeS_2 minerals in sediment. Although the method worked reasonably well for amorphous FeOOH, sulphide minerals (particularly FeS) tended to be extracted prematurely. Tessier et al. (1990) reported a modification of the internal structure of ferrous smectites after a reduction treatment. Peroxide, in this case, seemed to act as a strong solubilizing reagent for the clay minerals (smectites and chlorite) that had become less resistant to this reagent by the action of hydroxylamine, used as a reducing agent, in the previous step. Jarvis (1984) showed that it was difficult to precisely define whether Cu or Cd was associated with either one or the other oxide in an Fe-Mn oxide mixture. Beckett (1989) presented the survey of the extractants most commonly used and listed the groups of compounds it is presumed that they extract. This survey also discusses the

efficiency of extractants at mobilizing iron, manganese, and aluminium, with the implication that an extractant that dissolves a particular category of iron oxide, etc., also mobilizes any trace metals that it contains.

The problems with nonspecifity of used extractants are also connected with the natural tendency of nonspecialists to adopt published extractant sequences as standard procedures, without appreciating the reservations of their proposers. For example, the effects of acid ammonium oxalate extractant have been shown to depend on the nature and degree of illumination of the reaction mixture (e.g., dark, daylight, or ultraviolet light), yet many publications do not specify which illumination was employed, and some workers at least appear to have worked under the undefined illumination of an open laboratory. Other workers have not recorded the pH, concentration of their extractants, reaction times or ratio of extractant to sample.

Bermond and Benzineb (1991) have studied readsorption and reagent selectivity. Their soil experiments showed a strong effect of acidity on the extraction of Cu and Zn. They suggested a high pH may reduce the extent of the readsorption or its kinetics.

Kheboian and Bauer (1987) observed significant redistribution of Cu, Pb and Zn between phases when using the sequential extraction scheme of Tessier et al. (1979). Others have reported redistributions of As, Cd, Ca, Cu, Pb and Se among various phases of soils and sediments (e.g. Qiang et al., 1994a). The extent of redistribution depends both on the affinity of the remaining undissolved phases for the metal ion involved, and the ability of the extractant used to inhibit the adsorption of the metal by those phases (Kheboian & Bauer,1987). Qiang et al. (1994b), concluded that the occurence and extent of redistribution is determined by both the soil composition and the chemistry of a given metal. Unfortunately, the extent of readsorption and /or redistribution is difficult to quantify for individual elements and for individual geochemical phases.

Speciation Based on Calculation Methods

In view of the errors that can be associated with sampling and sample preparation, and the limitations of many of the experimental procedures used in speciation, many investigators prefer to calculate the most likely species distribution pattern. Data inputs required include the total levels of cations, anions and ligand species present, and equilibrium constant values for all possible interactions between the various species. This approach is not new, e.g. a model for seawater was developed 38 years ago (Sillen, 1961).

In recent years with the proliferation of PCs several computer models have become widely available and are used for a variety of applications. Some of the commonly used models include GEOCHEM (Mattigod & Sposito, 1979) and its updated version SOILCHEM (Sposito & Coves, 1988); HYDRAQL (Papelis et al., 1988); ECOSAT (Keizer, 1991) and MINTEQA2 (Allison et al., 1991). These approaches involve solution of multiple simultaneous equations, some describing the competing chemical equilibria and other defining mass balance relationships. Perfect agreement between analytical and predicted speciation is an unrealistic expectation. Discrepancies may arise due to limitations of both the analytical approach and the modelling approach. From computational side, limitations include the uncertainty about the most appropriate equilibrium constants and the measured input data, and the fact reaction kinetics are not considered. In spite of this, because chemical speciation will remain time consuming and expensive, computer programmes are of great help.

Role of Organic Matter for Metal Behaviour

Speciation clearly evidenced the role of organic complexes in metal mobilization in soils (Frimmel & Christman, 1988). Ziang et al. (1994) showed that the reduction of manganese oxides and amorphous iron oxides by $NH_2OH \cdot HCl$ can be hindered by a covering or occlusion of organic matter. These components can behave as a combined phase rather than as discrete phases, making selective dissolution of these entities in soils impossible. Robbins et al. (1984) showed that the failure to remove organic matter prior to reduction of ferromanganese oxyhydroxides caused the organic fraction value to be artificially high, and oxyhydroxide values to be low. Removal of carbonates and organic matter „clean up" oxyhydroxide coatings, and facilitate the retrieval of any metal ions associated with this fraction. Occlusion, however, is very dependent on soil or sediment type and chemistry.

Quality Assurance, Analytical Sensitivity, Accuracy and Matrix Interferences

The need for quality control in speciation studies is important not only for the „absolute" reasons of scientific precision and accuracy but also to assist in achieving analytical methodologies that are robust enough to be used in different laboratories with comparable results. Universally applicable, validated methodologies make it possible for results from different scientists and different laboratories to be compared and provide the basis for the establishment of international databases on the occurence and distribution of elemental species in the environment. However, the lack of uniformity in the different procedures and only few suitable certified reference materials (CRMs) do not permit the results to be compared worldwide nor the procedures to be validated. With a view to improving and ensuring a good quality control of speciation analysis, the Community Bureau of Reference BCR (now The Measurements and Testing Programme) of the European Commission has organized a series of interlaboratory projects over the last decade, as well as the production of CRMs (Quevauviller et al.,1994,1996; Ure et al., 1993). The preparation of reference materials certified for the contents of element species is, however, a difficult task. This is because, firstly, the fractionation of the total content of an element in a material into its different species means that the species concentrations are low,

with all the consequent requirements for higher analytical sensitivity and greater care in avoiding contamination. Secondly, the species concentrations in the reference material must be preserved in such a way that they remain constant over the several year´s life of a reference material. The informations about the preparation, homogeneity and stability studies of commercially available soils, and sewage sludges CRMs, certified for species defined operationally are included e.g. in Quevauviller et al. (1997, 1998).

Conclusions and Recommendations

The differentiation of total contents in solid matrices remains largely operationally defined. Problems in published studies using sequential extraction include lenghty delays between coring, sectioning and analysis, failure to obtain pore water composition, failure to maintain anoxic samples under inert atmosphere during processing, excessive sample drying, failure to use N_2-purged reagent solutions for anoxic samples, insufficient analytical sensitivity, and lack of quality assurance. Neverthless, sequential extraction has proven its value in the field of geochemistry. When combined with other data, sequential extraction results can help in supporting hypotheses. The information however is too uncertain to provide hard evidence and always must be interpreted with extreme care and in the context of other observations. Chemical extractions can help to elucidate the long-term stability of contaminants in soils and sediments under changing environmental conditions.

Recommendations for further developments to improve the validity of selective chemical extractions are:
- design extraction sequences with improved selectivity for a particular soil or sediment sample
- use rigorous procedures for sampling, storage and manipulation
- readsorption effects can be reduced significantly when substituting the conventional static extraction system by a dynamic extraction process in a flow cell
- because of mutual inclusion effects between inorganic and organic phases, it may be necessary for certain samples to repeat the extraction steps several times
- washing solutions between adjacent extraction steps should be analysed, and not discarded
- use analyte spikes, standard reference materials, thermodynamic modelling and surface analysis to assess and confirm the specificity of metal release from substrates
- use corroborative evidence from sediment and soil pore water sampled under appropriate natural conditions.
- use the methods that require the minimum number of steps in sample preparation, or the minimum amounts of chemicals

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Iron (Fe^{2+}, Fe^{3+}) in Systems with Organic Substances

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Abstract. Relationships in systems of Fe^{2+} and Fe^{3+} - selected organic substances (humic and fulvic acids; amino acids - alanine, cysteine and glycine; saccharides and polysaccharides - D-glucose, cellulose, saccharose and starch; carbon acids - citric, acetic, oxalic and tartaric) were subjected to experimental research. The research investigated conditions under which soluble Fe complexes are formed, the conditions for Fe migration, and the conditions for the formation of insoluble complexes causing deposition of iron. The research showed that these relationship are very complex, depending upon the degree of oxidation of Fe, the pH values of the environment, the intensity of light and, in case of humic and fulvic acids, also upon the locality or origin of matter that the substances were extracted from.

Keywords: Fe^{2+}, Fe^{3+}, organic substances, soluble and insoluble complexes

Introduction

The role of organic substances (OS) in processes of migration of chemical elements has been accepted in geochemical theories for more than three-quarters of the 20th century. This research was stimulated through simple experiments by Harrar (1929), in which he an observed increased solubility of iron in environment where acetic acid is present. These observation and data about the natural presence of acetic acids in the environment were base for his theory about the influence of acetic acid on iron migration. It is important to mention that in chemical-analytical practice acetic acid has been used since a long time ago as an agent suppressing the formation of insoluble Fe^{3+} hydroxides and Al^{3+} hydroxides; however, in geochemical processes it had not been taken into account.

Looking at the influence of humic acids on Fe and Al migration has a very interesting history. We have not succeeded in finding the original or indirect references of who the author was of the often mentioned assumption because this phenomenon was proved for the first time by experiments only in in the 1970-ies. We assume that earlier mentioned of it was only based on empirical observation, supported mainly by experiences and the wide spread presence of humic acids in various sediments, soils etc.

In the frame of systematic experimental research of the relationship between OS and the chemical elements we have also paid attention to compounds of Fe^{2+} and Fe^{3+}. We found that the relationships among these systems are significantly more complex than was originally assumed. We proved that besides the migration, OS under certain condition also cause the accumulation of Fe and that in such case degree of oxidation of Fe is also important. The results of our experimental research of the relationships of Fe^{2+} and Fe^{3+} with selected OS are subject of this paper.

Brief Overview of Literature Research

Despite the fact that in chemical-analytical practice, the relationships of several Fe-OS systems are well known now for several decades, the research in their geochemistry and related scientific branches only started only in the 1960-ies and mainly in the 1970-ies. For example, Schnitzer and Khan (1972) have proved the generation of soluable Fe^{+3} complexes by humic acids (HA) and fulvic acid (FA) in the environment with pH 3 and 5. Fox (1984) observed that insoluble Fe^{3+} compounds do not precipitate even in strongly alkaline solution when HA is present. These observations were also confirmed by our introductory experiments (Babčan and Ševc, 1989). It is noteworthy that we have not proved the formation of soluable Al complexes with HA and FA.

The experimental research of relations between Fe and OS has become very wide spread in seventies. Hermann and Gerke (1992) proved the formation of Fe^{3+} complexes in the presence of humic substances in a wider range of pH values (2.5 - 6.4). Pandeya (1993) reported about the formation of soluable Fe^{3+} complexes in presence of FA and citric acid in solution with pH value of 5 and 8.5. Geetha et al. (1995) described saccharide Fe^{3+} complexes with glucose, sorbose, fructose, mannose, galactose, lactose and maltose. Tomasik et al. (1995) reported about the formation of easily hydrolyzable starch - Fe(O)(OH) complex.

Jersak et al. (1992) assign a good leakage of Fe from forest soils to oxalates. Gerke (1992) observed a strong time dependence (he reached a maximum of the release of Fe after 90 days) during leaching of Fe from soils by citric acid. Knocke et al. (1992) leached Fe from soils by humic and fulvic acids and then by tannic and oxalic acids. These acids have strong complex-making effects on Fe^{2+}, and the newly formed complexes prevent its oxidation.

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Ochs et al. (1993) compared the Fe leaching from rock decomposition and from soils, and stated that the most effective Fe leaching from soil-root system is reached at a pH of 3-4. Izeferis and Agatzinileonaardou (1994) investigated the release of Fe from laterite. From all investigated OS the most effective acid was oxalic acid, (except for Ni it was citric acid). Methoxyacetic, formic, acetic and salicylic acids were ineffective. The effect of oxalic acid was also confirmed by Cajuste et al. (1996).

At present many authors pay attention in their researches to redox reactions of Fe in systems with OS. Deng and Stumm (1993) investigated the kinetics of the reduction of Fe^{3+} by fulvic acids (optimum should be at pH 7.5). On the other hand, Liang et al. (1993) observed that, beside glutamate, FA also accelerates the oxidation of Fe^{2+}. Carter (1995) includes among strong Fe reducing agents glutamate, ascorbite and tocopherate. Karlsson et al. (1995) reported that in near-surface layers (with access to light) of waters of northern lakes the Fe^{3+} photo-reduction is running optimally at pH 4. Fe^{3+}. It is not being reduced in deeper layers but, due to an alkaline environment, the iron is segregated in the form of hydroxides. Volker and Sulzberger (1996) reported that fulvic complexes of Fe^{2+} are oxidized faster by hydrogen peroxide than by aqua-complexes. Pehkonen et al. (1993) investigated photo-reduction of Fe oxides and hydroxides in the presence of formaldehyde, formic salts, acetate, oxalate and butyrate. They observed that the pH of the environment and the wave length of light used are important factors of photo-reduction (a maximum of reduction accrued at a wave length of 330 - 405 nm.

Method of the Research

The primary goal of the experimental research was to investigate the influences of individual OS on soluable Fe compounds ($FeCl_2$, $FeCl_3$); and particularly to figure out what are the conditions when soluable, insoluble and transient Fe compounds are formed in pH ranging from 1 to 12. Further more, we investigated the redox effects of used OS on both Fe oxidation degrees. The systems with Fe^{2+} were investigated in the internal environment and excluding light.

The basic substances used in the research were natural (humic and fulvic) acids and artificial substances i.e. factory products with purity p.a. (amino acids - alanine, cysteine and glycine, saccharides - D-glucose and cellulose, acids - citric, acetic, oxalic and tartaric - all products of the factory Lachema, Brno, the starch from factory in Boleráze, saccharose from a factory in Sereď). Humic and fulvic acids were extracted from peat from the localities of Cérová and Hroboňovo. A detail description is given in the report by Babčan and Ševc (1989). The operating procedure itself consists of several operations, which repeatability was verified by two series of experiments. Accurate setting of required pH values of solutions (the so called starting pH values) in range from 1 to 12 occurred as a specific problem. On the basis of preliminary experiments, we adopted the following technique.

Given amount of OS (100 mg) was added into approximately 80 ml of distilled water (in case of experiments with Fe^{2+}, CO_2 and another gasses were removed by boiling) and the required pH was set by adding HCl or HaOH. 1 millimole (mmol) of $FeCl_2$ or $FeCl_3$ solution was added into the prepared solution, then the pH of the solution environment was re-adjusted and the volume of the solution was filled up to 100 ml. The samples were stored and occasionally stirred for 24 hours, then the coagulum that formed was removed by centrifuge. Finally, the Fe content was measured in a proportional part of the solution. Fe^{3+} was determined by complex-metric titration according to Přibil (1997), Fe^{2+} was determined from the difference after prevailing oxidation of Fe^{2+} to Fe^{3+}. The content of Fe in insoluble compounds corresponds to the difference between the initial Fe content in solutions and the Fe content in the final respective solutions. In the attached graphs the Fe contents in solutions (after recalculation to volume 1000 ml) represents soluable Fe form of the given oxidation degree and at given pH conditions.

In case of experiments with Fe^{2+}, the tests were done in internal atmosphere of Ar or N_2, with and without access to light (Erlenmeyer flasks were wrapped in foil and inserted into closed cabinet). The repeatability of setup of initial as well as final pH values of solutions and repeatability of determination of individual Fe oxidation degrees in the systems with tartaric acid in solutions with two different pH values are shown on the graphs given in figures 1 and 2. Statistical data of mentioned tests are summarized in table 1. The test on reproducability of setup of pH values 5 and 7 showed that the value of standard deviation was 0.6 to 0.8%.

Result Overview and Discussion

The observed experimental values from the research of the systems Fe^{2+}, Fe^{3+} - organic substances are given on figures 3 to 33. The graphs show the relationships between soluble and insoluble forms of Fe^{2+} and Fe^{3+} compounds in solutions containing given organic substances and at given pH conditions. More Fe in solution means a more soluble system; values close to the X axis refer to insoluble or lightly soluble systems (bonds) of iron.

1. Fe Systems Without Organic Substances

A study of the so called "solely water" Fe systems, i.e. systems without OS, served as the standard for judgment of Fe compounds behavior in given a environment. In the case of Fe^{3+} compounds the data for water only systems are given in figures 5, 6 and 22. Data for Fe^{2+} are on figures 3 and 4. Data regarding water only Fe^{3+} systems usually approximate values published in analytical reference books. Data from Fe^{2+} systems are original, with the observation that in strongly acid medium only small portion of Fe^{2+} is oxidized and also with the observation that the forming of insoluble Fe^{2+} compounds is shifted toward higher pH values when light is absent.

Table 1 Statistical data from tests on repeatability of setup and changes of pH values in solution environment, and determination of Fe forms in systems Fe²⁺ - tartaric acid.

Designed setup of pH	Number of tests	Set values of pH	Reached pH of solution	Sum of Fe (mmol) after test	Content of Fe²⁺ (mmol)
5.0	5	5.03 ± 0.03	4.23 ± 0.09	10.04 ± 0.54	8.80 ± 0.46
7.0	7	7.20 ± 0.06	6.17 ± 0.24	8.80 ± 0.30	7.00 ± 0.42
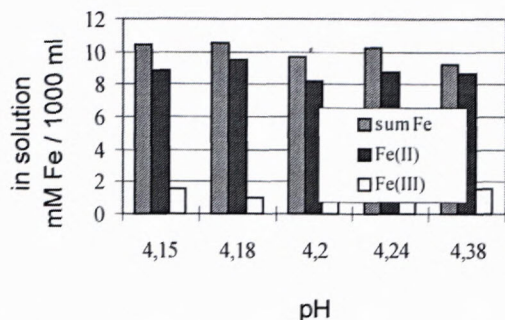
Fig. 1 Repeatability of setups of pH values, and determination of Fe in systems Fe²⁺ - tartaric acid (designed setup pH = 5, without access of light)
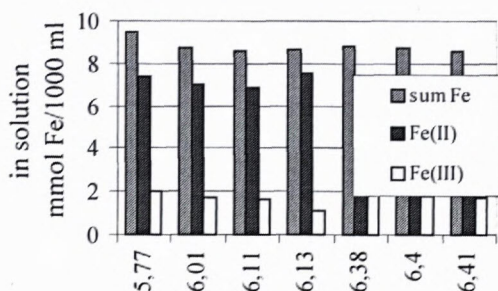
Fig. 2 Repeatability of setups of pH values and determination of Fe in systems Fe²⁺ - tartaric acid (designed setup pH = 7, without access of light)
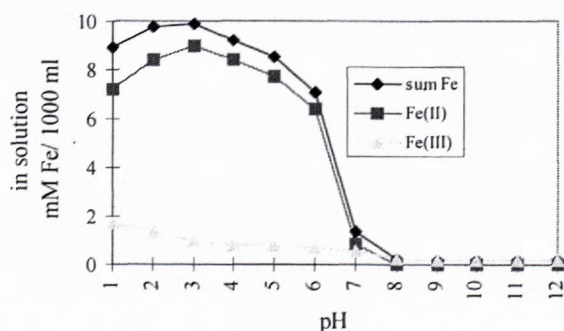
Fig. 3 Systems Fe²⁺ – water (with access of light)

Fig. 4 Systems Fe²⁺ – water (without access of light)

2. Systems with Humic and Fulvic Acid

Figures 5 and 6 show the relationships in the systems Fe³⁺ - humic and fulvic acids. Results of the study of HA and FA from two localities are significantly different, which supports the opinion that the effect of these substances is dependent upon their origin. At the same time this observed phenomena can be the reason for the differences in the conclusions about mentioned systems reported by various authors. The differences are probably caused by structural singularities of HA and FA from given localities. It is obvious that HA and FA from the Cérova locality have a different function groups as from Hroboňové.
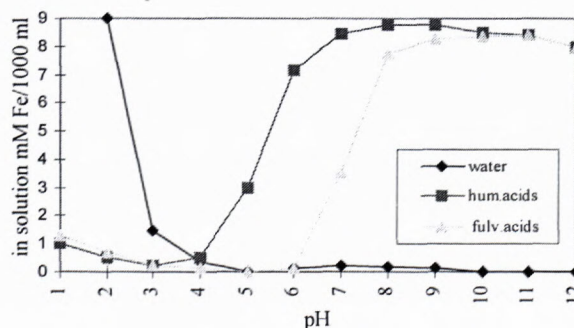
Fig. 5 Systems Fe³⁺ – water - humic and fulvic acids

According to summary values of Fe content in solutions, the systems Fe²⁺ - HA (with access of light) and Fe²⁺ - FA (without access of light) are alike. However in the case of systems with HA and access of light, the participation of Fe oxidation forms is different. In the systems without access of light some oxidation of Fe²⁺ could took place during the mechanical manipulation (centrifuge, pipette, etc.) that we could not avoid.

3. Systems with Amino Acid

Out of three investigated amino acids (alanine, cysteine, glycine) cysteine had the most significant influence on systems with Fe³⁺ (Figs. 9 and 10). Probably due to sulfur present in cysteine molecule, there was an outstanding reduction of Fe³⁺ (with access of light), as show by the results presented in figure 9. The effects of the
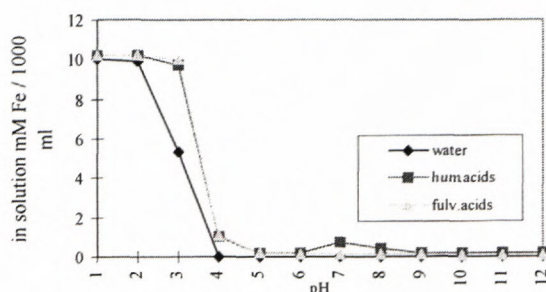
Fig. 6 Systems Fe³⁻ – water - humic(HA) and fulvic acids (FC), (Hroboňovo)
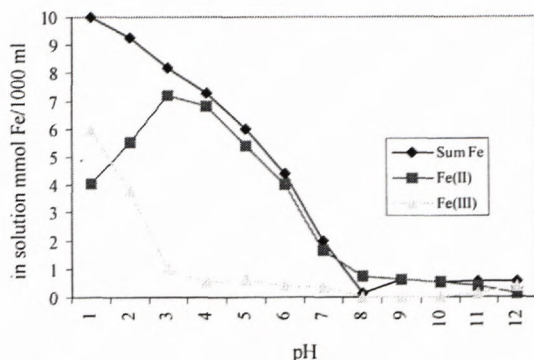
Fig. 7 Systems Fe²⁻ – humic acids (with access of light)
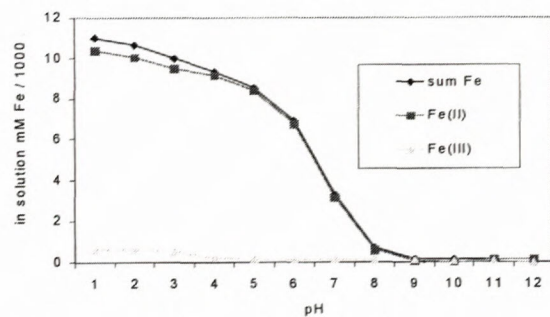

Fig. 8 Systems Fe²⁻ – fulvic acids (without access of light)
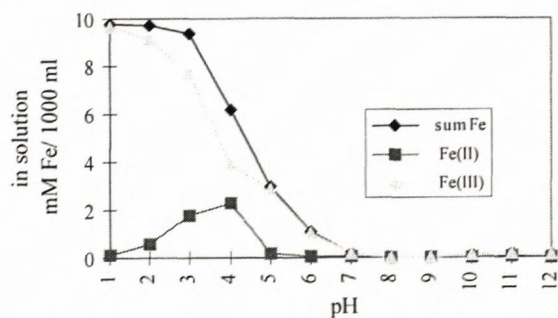
Fig. 9 Systems Fe³⁻ – cysteine (with access of light)
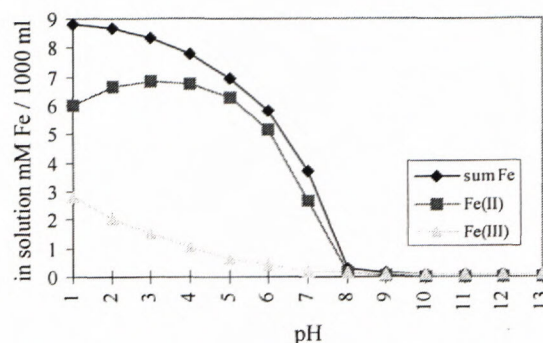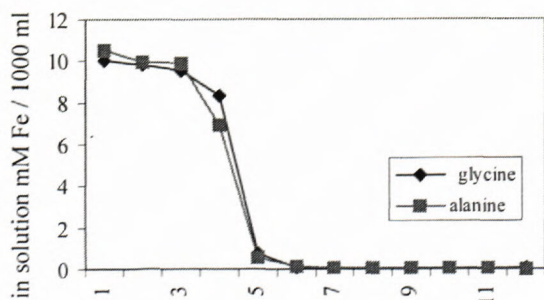
Fig. 11 Systems Fe² – glycine (with access of light)
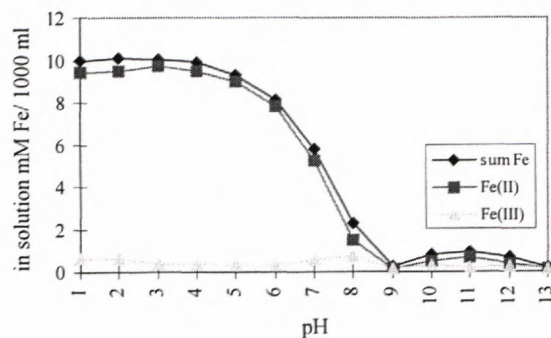
Fig. 12 Systems Fe³⁻ – glycine (without access of light)
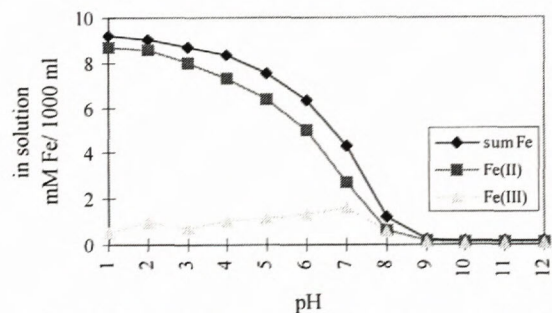
Fig. 13 Systems Fe³⁻ – alanine (with access of light)
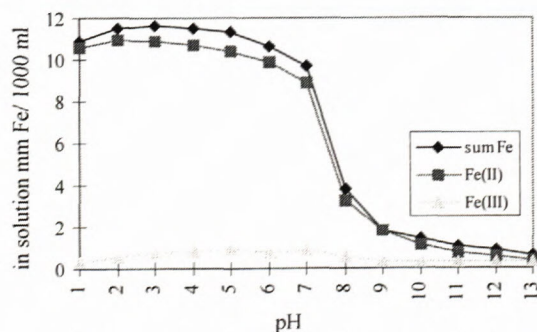
Fig.14 Systems Fe³⁻ – cysteine (with access of light)

Fig .10 Systems Fe³ – alanine and glycine (with access of light)
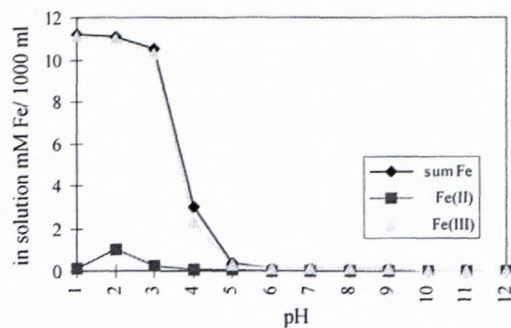
Fig. 15 Systems Fe³⁺ – cellulose (with access of light)
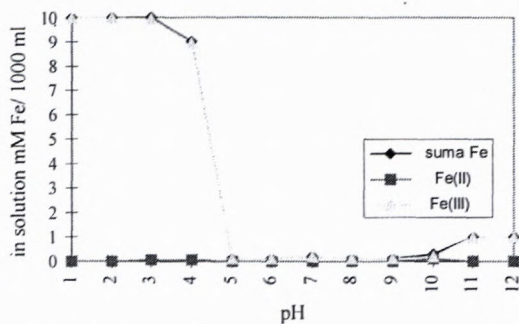
Fig. 16 Systems Fe³⁺ – D-glucose (with access of light)
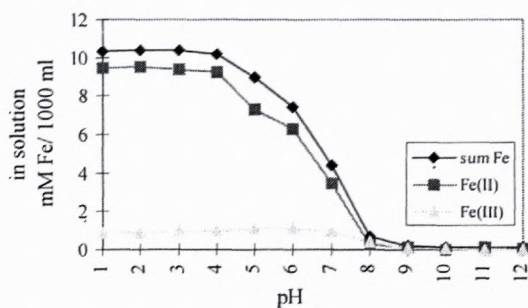
Fig. 17 Systems Fe²⁺ – cellulose (with access of light)
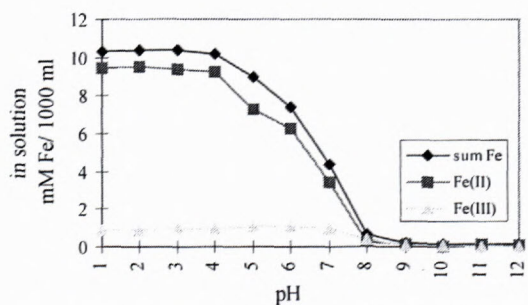
Fig .18 Systems Fe²⁺ – cellulose (without access of light)
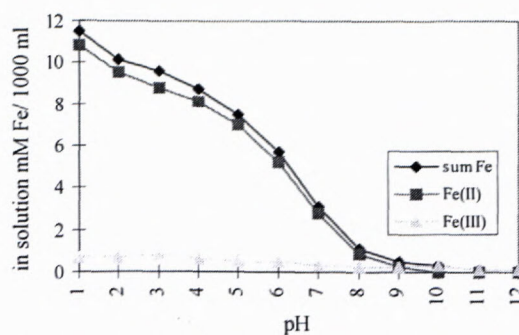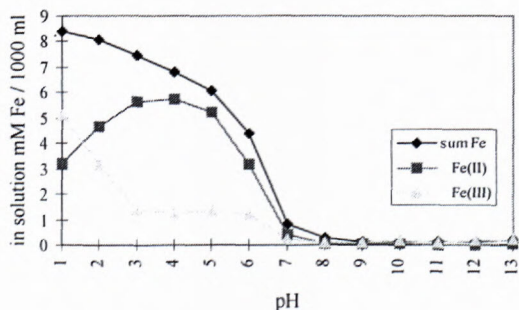
Fig. 20 Systems Fe²⁺ – D-glucose (without access of light)
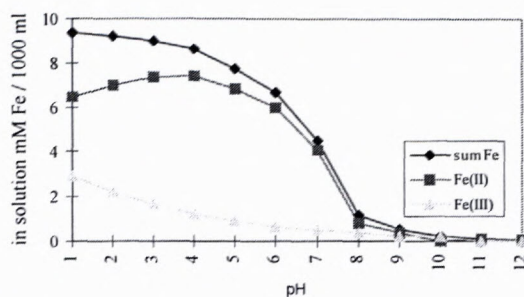
Fig. 21 Systems Fe²⁺ – starch (with access of light)
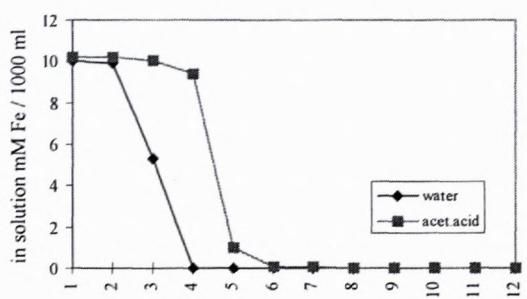
Fig. 22 Systems Fe³⁺ – water and acetic acid (with access of light)
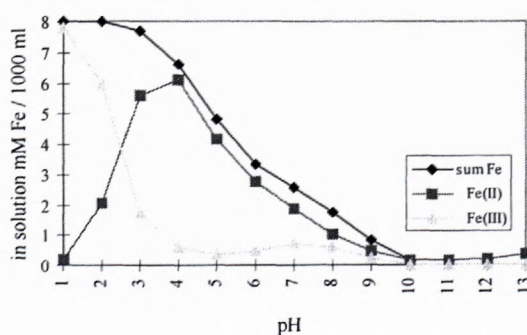
Fig. 23 Systems Fe²⁺ – acetic acid (with access of light)

Fig. 19 Systems Fe²⁺ – D-glucose (with access of light)

other two acids differ from solely water systems only by shifting of pH values when formation of insoluble compounds occurs (Fig. 10).

Glycine in the systems with Fe^{2+} behaves differently when light is present or absent. In an acid medium (Fig. 11) stronger oxidation of Fe^{2+} occurs; however, if light is blocked out (Fig. 12) this effect is markedly suppressed. The light influences the oxidation of Fe^{2+} also when alanine is present (Fig. 13), whereas in case of cysteine the oxidation of Fe^{2+} is suppressed.

4. Saccharides and Polysaccharides

Fe^{3+} in systems with various saccharides and polysaccharides behaves very similarly, except for a few cases. A little reduction occurs only in the environment with cellulose (Fig. 15), when formation of insoluble compounds is shifted toward higher pH values. The shift of formation of insoluble bonds was also observed in a case of glucose. Interesting is also the reduction of Fe^{3+} in a strongly alkaline medium.

Fe^{2+} systems are markedly oxidized in the presence of glucose and light (Fig. 19). Fe^{2+} systems with starch behave a little less markedly in this way (Fig. 21).

5. Carbonic Acids

Each of the investigated carbonic acids (or their salts) behaves in a specific way in relation to the Fe^{3+} and Fe^{2+} systems. Although much is known of these domains from analytical chemistry, many of our observations are new; these will be useful in explaining of the geochemical, pedological biological and other phenomena.

Acetic acid in systems with Fe^{3+} significantly shifts the formation of insoluble iron compounds to the alkaline zone (Fig. 22). In the case of acetic acid systems with Fe^{2+}, the almost quantitative oxidation of Fe in a strongly acid medium with access of light (Fig. 23) is significantly different from the solely water systems (Figs. 3 and 4). The difference is also rather significant without access of light to the system (Fig. 24).

Dicarbonic oxalic acid slightly reduces Fe^{3+} (Fig. 25) and, in comparison to the solely water systems, it shifts the formation of insoluble Fe^{3+} compounds to the alkaline zone more moderately than does acetic acid, for instance. The acetic acid invokes significant changes in systems with Fe^{2+}. When light is present (Fig. 26) there is significant oxidation of Fe^{2+} and so there is also formation of soluble Fe compounds (Fig. 25). When light is blocked out (Fig. 27), the oxidation of Fe^{2+} is minimal, however the solubility of Fe^{2+} compounds is significantly decreased due to formation of insoluble iron oxalate.

Another dicarbonic acid, but with two hydroxyl groups in a structure, is tartaric acid. It has unusual influence on both Fe forms. It reduces Fe^{3+} compounds when air is present (Fig. 28), namely in two maxima - in the pH range of 4 to 5 - and a little bit more intensively in the pH range of 9 to 10. A second significant influence is a shift of the insoluble Fe^{3+} compounds formation to the strongly alkaline zone (Fig. 28).
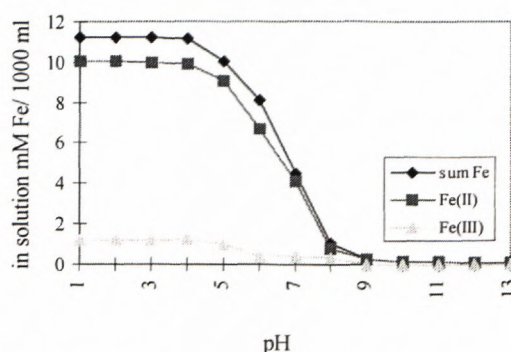

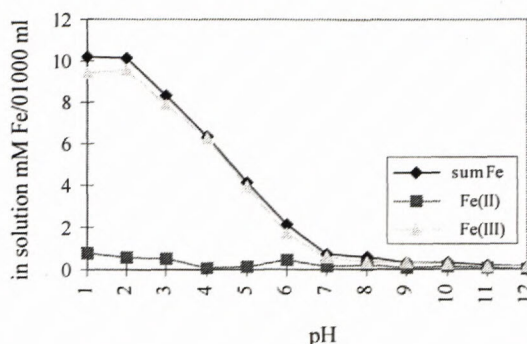Fig. 24 Systems Fe^{2+} – acetic acid (without access of light)

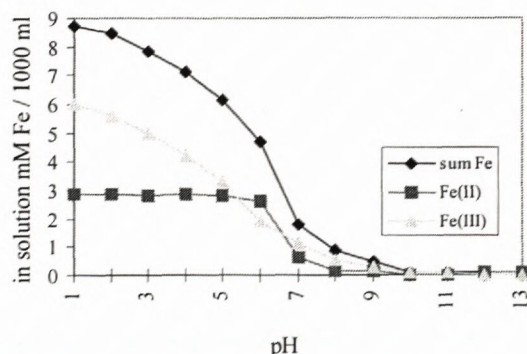Fig. 25 Systems Fe^{3+} – oxalic acid (with access of light)

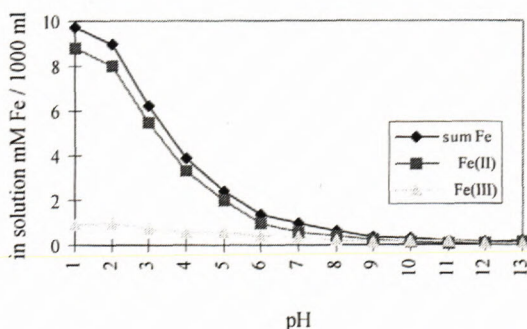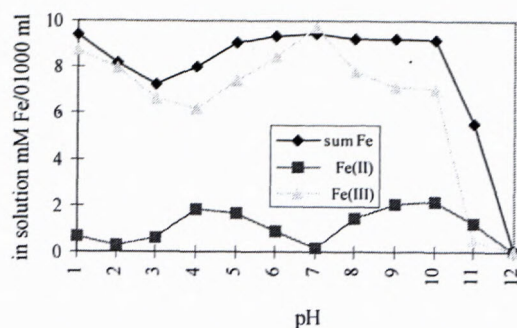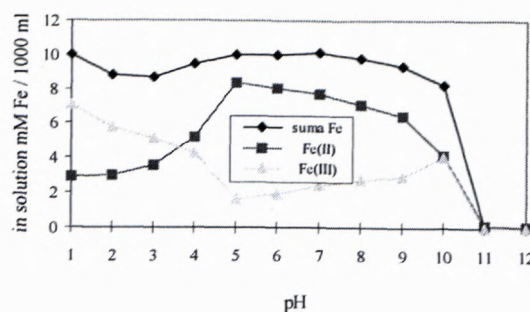Fig. 26 Systems Fe^{2+} – oxalic acid (with access of light)
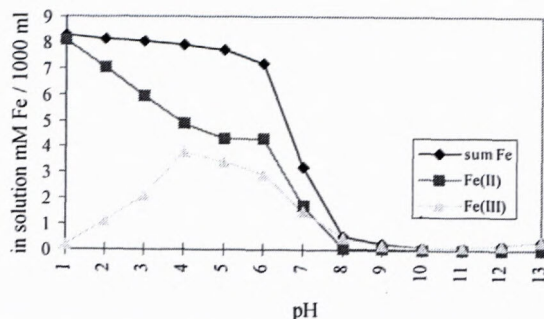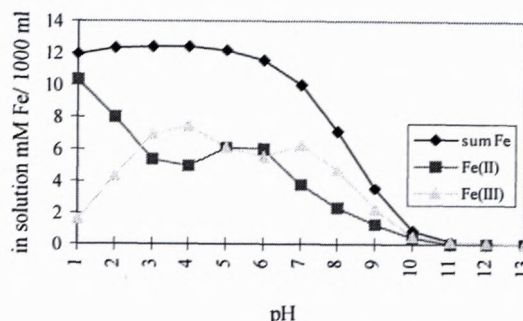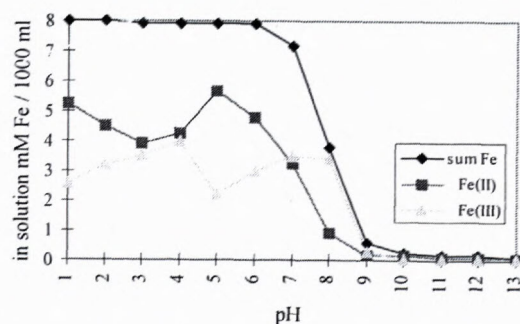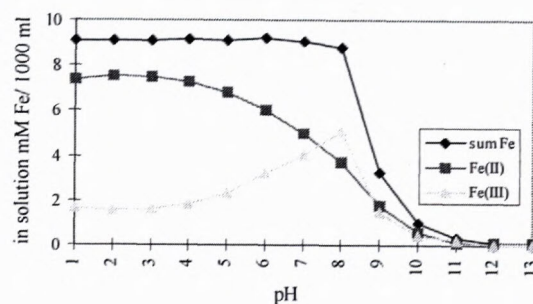

Fig. 27 Systems Fe^{2+} – oxalic acid (without access of light)

In the presence of tartaric acid the oxidation of Fe^{2+} compounds respond whether the system is in the light or dark (Figs. 29 and 30). Soluble compounds formation is shifted toward alkaline zones in these systems; however, a little bit less than in systems with Fe^{3+}.

Fig. 28 Systems Fe²⁺ –tartaricacid (with access of light)

Fig. 31 Systems Fe²⁺ – citric acid (with access of light)

Fig. 29 Systems Fe²⁺ – tartaric acid (with access of light)

Fig. 32 Systems Fe²⁺ – citric acid (with access of light)

Fig. 30 Systems Fe²⁺ – tartaric acid (without access of light)

Fig. 33 Systems Fe²⁺ – citric acid (without access of light)

Tricarbonic citric acid in presence of light very strongly reduces Fe^{3+} compounds, with a maximum in the slightly acid to the alkaline zone (Fig. 31). The shift of formation of insoluble iron compounds is striking, up to strongly alkaline zone. The formation of insoluble compounds in the presence of citric acid is also shifted towards the alkaline zone in systems with Fe^{2+}(Figs. 32 and 33). Oxidation of Fe^{2+} interestingly occurs with or without light.

Conclusions

The experiments confirmed that the relationships in systems of Fe^{2+} and Fe^{3+} and organic substances (OS) are very complex. It was revealed that the formation of soluble and insoluble Fe and OS complexes as a condition of migration or accumulation of iron depends upon the degree of oxidation of Fe, the pH values of the environment, access to light and, in case of humic and fulvic acids (HA,

FA), also upon the origin of the matter from which these acids were extracted. Even small change in the conditions may lead toward changes in the character of Fe - OS systems.

1. Significant by different results were obtained in the case of HA and FA extracted from peat obtained from two localities. When light was present, neither HA nor FA prevents the oxidation of Fe^{2+}.

2. Neither amino acid alanine and glycine suppresses oxidation of Fe^{2+} when light is present; however, under these conditions cysteine reduces Fe^{3+}.

3. Cellulose reduces Fe^{3+} in an acid environment, with access to light. D-glucose and starch do not prevent oxidation of Fe^{2+} when light is present. All these substances form with soluble complexes Fe^{2+} and Fe^{3+} and shift formation of insoluble Fe compounds toward higher pH values.

4. Carbonic acids have various influences on Fe compounds. In the systems with Fe^{3+} they shift the formation

of insoluble complexes towards the strongly alkaline zone, tartaric and citric acids also reduce Fe^{3+} in presence of light, and at the same time they do not suppress the oxidation of Fe^{2+}, neither in either light or in dark conditions (acetic, tartaric, citric acids). Oxalic acid prevents the oxidation of Fe^{2+} when light is blocked out and it forms insoluble oxalate $Fe(COOO)_2$ even in acid environment.

The information gathered from these study of systems Fe^{2+}, Fe^{3+} - selected OS may explain many problems of iron migration in the geochemical, pedological, biological and others processes.

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Mineralogical and Environmental Evaluation of the Settling Ponds at the Deposit Dúbrava in Nízke Tatry Mts.

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Abstract: In this study, a complex mineralogical and environmental evaluation of the settling pond material has been performed and processes, that occur in these wastes, have been modeled. The settling pond material consist predominantly of the granularity fraction over 50 microns, having a neutral to weak alkaline pH. Gangue minerals largely prevail over sulphide ore minerals. The evaluation of natural barriers against the dispersion of toxic elements, from the settling ponds into water-bearing horizons, has determined that this role is pursued by Fe-oxyhydroxides created in the wastes due to oxidation of Fe-bearing minerals. Also, the importance of carbonates as a natural neutralization component of the wastes was confirmed. Experimental leaching of the waste materials in various conditions (temperature, pH, humic acids) showed sudden pH changes, induced by the presence of carbonates, extensive decomposition of stibnite (the influence of temperature and pH is minimal), the slow ability to leach out Fe and As from pyrite and the arsenopyrite, and minimum influence of humic acids on the amount of leached elements.

Keywords: stibnite, experimental leaching, Nízke Tatry Mts., settling pond, oxidation

Introduction

The Dúbrava deposit, located in the Ďumbier part of the Nízke Tatry Mts used to belong to the largest stibnite deposit in Central Europe. In 1992, after the mine become inactive, it was necessary to deal with the problem of the solid waste, laid down at the settling pond. This could be a source of toxic materials that might pollute the geological environment and the surface and subsurface waters. At the Dúbrava deposit, the possible contamination is of special concern because this area is protected as part of the Nízke Tatry National Park (NAPANT).

A dileterious effect of the mining on the environment has already been observed. Stolečnan (1984) and Stuchliková (1991) studied the influence of the waste on the quality of groundwater. Letko (1992), Arvensis et al. (1994), and Arvensis (1988) examined details of the character of the flotation waste accumulated in the settling ponds and its influence on the environment.

At other Slovak localities similar problems were studied by several additional authors (Šucha et al, 1998). Šucha et al. (1997) and Lišková et al. (1999) studied the acidificationaround Banská Štiavnica (Štiavnické Vrchy Mts.). Trtíková (1997, 1999) examined the oxidation of sulphides in the wastes after mining activities in the area of Malé Karpaty Mts. Šotník and Rojkovič (1998) studied the weathering of mining and technological wastes in the district of Slovinky and Rudňany. Lintnerová (1996) studied the mineralogy of Fe-ochres originating in acid mining waters at the Smolník deposit.

A complex mineralogical evaluation of a solid flotation waste, the understanding of processes occurring during weathering of the settling ppond material, a study of the mechanism of toxic elements migration into the environment and the modeling of processes occurring at the settling pponds are the main aims of this study.

Geological Characteristic, Mineralisation and Setting Pits at the Dúbrava Deposit

The Dúbrava mining district is located on the northern slopes of the western part of the Nízke Tatry Mts., in the central zone of the Ďumbier anticlinorium. The deposit is underlain by Ďumbier crystalline basement. North of it Mesozoic cover occurs, predominantly formed by dolomites. The crystalline basement is represented by a huge complex of granitoides and extensively metamorphosed crystalline schists. The petrographic research of the surrounding rocks determined the presence of highly prevailing granitoide rocks, less common aplites and pegmatites, gneisses, migmatites, dioritic rocks and basanites (Michálek and Chovan, 1998).

At the Dúbrava deposit quartz-sulphide veins are the prevailing form of ore occurrences, which originated by the filling of fissures. Disseminated and stockwork ores are more rare, and are present mainly near veins in fault zones. Over a length of 5 km Sb ore mineralisation has the character of extensive stockwork in granitoides and migmatites of the Ďumbier crystalline basement. Ore mineralisation is related to the mylonite zones, which
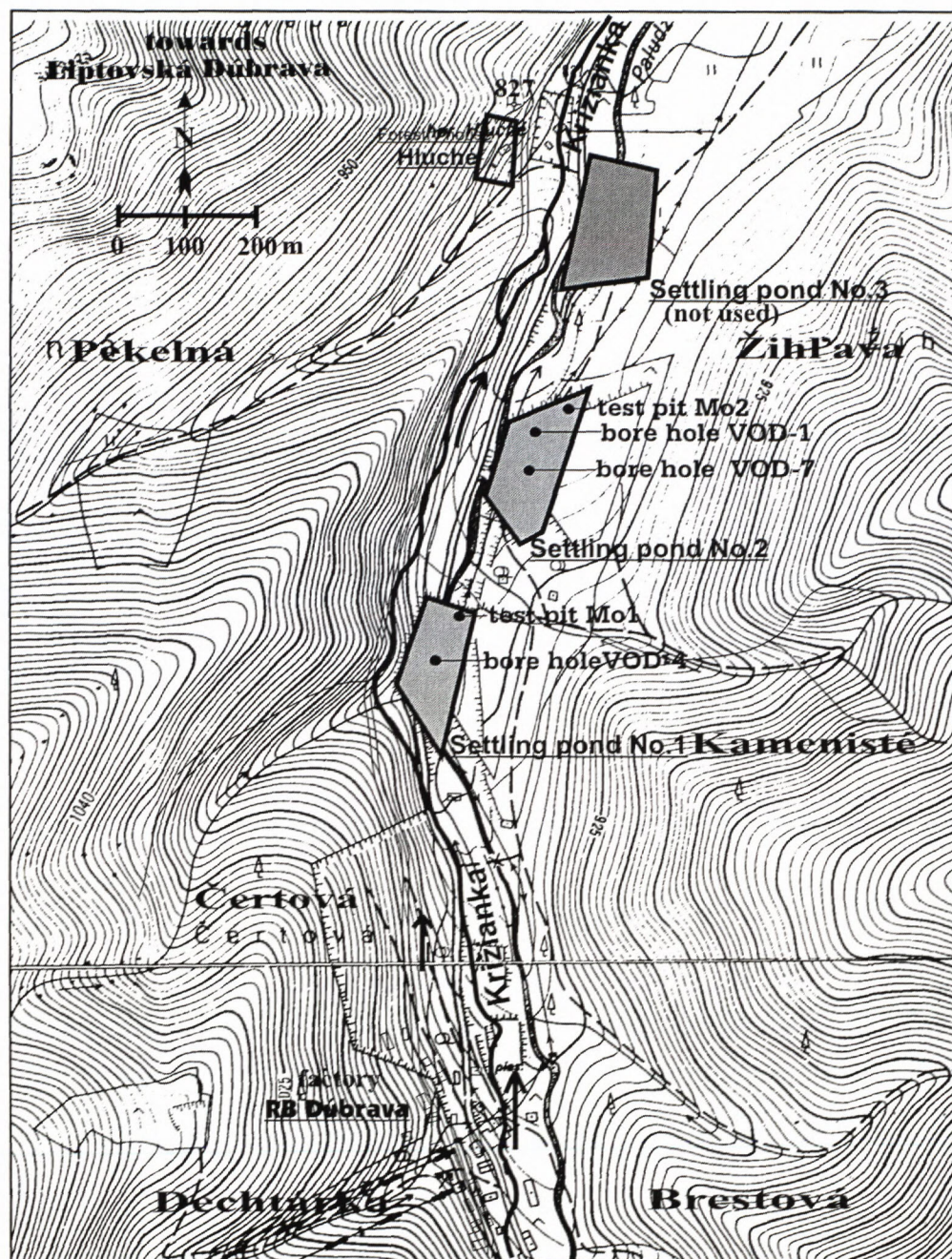
Figure 1: Map of the vicinity of the stibnite Dúbrava deposit with marked locations of sample sites at the settling ponds no. 1 and no. 2.

have discrete veins and veinlets of variable thickness, quality and systematically changing (Michálek and Chovan, 1998).

Due to hydrothermal processed nearly all rocks in the area of the deposit are altered. According to the intensity, the alteration process near quartz-sulphide veins is possible to divide into 3 zones (from the weakest to the strongest): 1.-chloritisation, 2.- muskovitisation, 3.-illitisation and carbonatisation. In the mylonite zones, reactivated during the Alpine orogeny, mainly the presence of illite and traces of smectite and kaolinite were detected by RTG-diffraction analyze (Orvošová et al., 1998).

At the Dúbrava deposit the following minerals were identified (Michálek and Chovan, 1998):

main: stibnite, pyrite,

associated: scheelite, molybdenite, bismuthinite, tetradymite, marcasite, pyrhotite, Ni-sulphide (?), argentite, gold, arseno-

pyrite, sphalerite, zincenite, plagionite, robinsonite, heteromorphite, semseyite, jamesonite (?), boulangerite, galena, antimony, senarmontite, tetraedrite, bournonite, chalcostibite, „horobetsuite", Bi-Pb-Sb sulphosalts, hematite, magnetite, rutile,

vein: quartz, Fe-dolomite, baryte, strontianite, calcite, aragonite, siderite, monazite, illite, kaolinite, montmorilonite, smectite,

secondary: romeite, stibioconite, valentinite, bindheimite, cervantite, Sb-ochres, malachite, limonite

For the ore processing three settling ponds were necessary to establish at the deposit (Fig. 1), that are located at the right side of the stream Križianka (Arvensis et al., 1994; Arvensis, 1998): The settling pond no. 1 is situated uppermost in the Križianka valley (875 - 885 m above sea level), just below former factory Rudné bane Dúbrava, at the area of 24 000 m². The settling pond no. 2 is located

below the settling pond no. 1 in the height 855 - 875 m above sea level and covers an area of 27 500 m². It is estimated (according to the archives of Rudné bane Dúbrava), that during 1947-1989 1 223 216 tons of flotation slimes were deposited at the settling ponds no.1 and 2. In 1992, during the restoration works both settling ponds were covered by a layer of a loamy material. Settling pond no. 3 is the youngest one; it was prepared for the mining predominantly of low grade disseminated ores in 1989. It is situated below the settling pond no. 2. Because of the end of mining activity this area has not been used. The settling pond material contains wastes after flotation treatment of Sb-ores - flotation slimes, that have similar grain size to a loamy sand (Letko, 1992). The character of the flotation waste at the settling ponds is given by mechanical properties of the processed ore material (Arvensis et al., 1994; Arvensis, 1998). The waste components distributed to the settling pond contained increased concentrations of some heavy elements, mainly Sb, As, Cd, Mn and Fe. However, the resulting concentrations in surface and groundwaters (after their mixing with the waste water) did not exceed the indicators of the allowed degree of pollution (Letko, 1992). Analyses of solid phases in the wastes, deposited at the settling pond and in the surrounding of the settling pond, proved the presence of several elements in extremely high concentrations, while the highest concentrations (over 1000 mg.kg^{-1}) were reached by Sb, Sr, Mn and B (Letko, 1992). Before their restoration the settling ponds were free of vegetation and they had apparently a decreased evaporation and surface discharge. The percolation of meteoric waters (pH 4.3 - 4.5) from the settling ponds is nearly over 70 000 m³. The leaching of the settling pond material proved the Sb-content in the leaching solution 1.0 to 32 mg.l^{-1} while HSbO$_2$ was the prevailing form of Sb in the leaching solution. According to the norm for drinking water in the EU countries (Sb = 0.001 ppm) the leaching solution from the settling ponds should be diluted at least 100 to 3000 times (Arvensis et al., 1994; Arvensis, 1998). According to the results of the modeling of the transport of the residual Sb from the settling ponds into a solution Jorgensen and Pedersen (1992) in Arvensis et al. (1994) suppose that after 700 - 900 years the Sb-concentration in the leaching solution from the settling pond will be 2-3 mg.l^{-1}.

In the year 1992 the company Geologický prieskum Spišská Nová Ves (GP SNV) bored three drill holes at the settling ponds no. 1 and no. 2, that aimed to determine the sediment composition and hydrogeological and hydrogeochemical relationships in the body of the settling ponds. In the water from the drill holes six microelements had the highest composition: Sb, Ba, Pb, Cu, Zn and As. In the water from the drill hole VOD-1 at the settling pond no. 2 only three of the elements were present, Sb, Ba, Cu, and in the drill hole VOD-7 Pb was present as well (Arvensis et al., 1994; Arvensis, 1998).

Methods

A grain size analysis was performed using the following methods of the settling pond material placed in a graduated cylinder filled by distilled water using a 0.1M solution of sodium hexametaphosphate and 15 % solution of HCl. The following fractions were obtained: <2, 2-20, 20-50 and >50 micrometers. In the granulometrically separated fraction <2 micrometers we analysed the sorption capacity of clay minerals using the saturation by the vapour.

First, the samples for the measurements were dried at 60°C. After desiccation, from each sample 10g portions were weighted; to the one 25 ml of distilled water was added, and to the other 25 ml of a 1M solution of HCl. The acidity (pH) was measured by the instrument IONOMETER-M931.

All samples from the settling pond material, selected for microscopic observation, weighed exactly 1 kg. They contained a substantial proportion of fine fraction, which was removed by mud discharging and by classic panning. The samples treated by panning were dried and than the ferromagnetic fraction was removed by a permanent magnet. Later, the scheelite content was determined by an ultraviolet light. The separation into the light and heavy fractions was the next phase of sample treatment, for which CHBr$_3$ has been used, a liquid with a maximum density of 2.88 g/cm³. The heavy fraction was further split into diamagnetic and paramagnetic fractions using an electromagnetic separator. All separated fractions were weighted out on an analytical scale in order to determine their percentage proportions in the initial 1 kg of the original settling pond sample.

Microscopic observations of quantitative and qualitative appearance of minerals and effects, related to their destruction in various fractions, were performed under a binocular microscope and in the reflected, polarised, light on a Jenapol microscope. We used the method of number of grains in a given area for semiquantitative evaluation, while this evaluation was recalculated to 100%. In every separated sample 800 grains were evaluated. RTG-powdery diffraction analysis was performed on the instrument Philips 1710 in the laboratory of the Geological Institute SAV Bratislava, the scanning electron microscopy (SEM) was performed at the instrument JEOL-840 in CLEOM PriFUK and the optical emission spectroscopy was performed on the spectrograph PGS-2 at the Geological Institute PriFUK Bratislava.

From the samples of flotation waste taken from the settling pond no. 2 we prepared leaching solutions using the method of Mehr and Jackson (1960), that is based on dissolution of Fe-oxyhydroxides using the C$_6$H$_5$O$_7$Na$_3$ .2H$_2$O regulator and Na$_2$S$_2$O$_4$ and, according to the determined content of toxic elements, which these oxides have captured. In the obtained leaching solutions we determined the amounts of Fe, Zn, Cu, As and Sb using the atomic absorptive spectroscopy with flame atomisation at the instrument Perkin-Elmer 1100 in the laboratory of the Geological Institute of the PriFUK.

The simulation of the processes that occur in the mining wastes under laboratory conditions was included in this study. We used three different types of samples shown on table 1.

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Table 1: Description of samples used for the simulation of processes occuring in the mining wastes in laboratory conditions.

Sample	Number and amount of samples	Characteristics of the origin of samples
1.a, 1.b, 1.c, 1.d	4 samples (100 g each)	Vein stibnite broken in fraction < 0.8 mm
2.a, 2.b, 2.c, 2.d, 2.e, 2.f	6 samples (500 g each)	Original settling pond material
3.a, 3.b, 3.c, 3.d, 3.e, 3.f	6 samples (500 g each)	Original settling pond material enriched in 1 g of vein antimonite broken in fraction < 0.8 mm

To these samples, after their emplacement into graduated flasks, were added a solution of distilled water with a pH adjusted to 3.2 using HCl and to 7.4 using NaOH and then they were placed into environments with temperatures at +5°C, +30°C and 20°C, respectively. Into 6 samples we added 1 g of humic acids each, in order to evaluate the ability of these organic matters to sorb toxic elementsbrought into the solution during the oxidation of sulphide minerals. The exact parameters of the experimental leaching conditions of various samples is shown on table 2. During the whole progress of the experiment we measured the pH using the instrument Elteca 110 and we observed the changes occurring at the surface of the material in the graduated flasks.

Table 2: The analysed As, Sb and Fe concentrations in the leaching solutions from the samples of vein stibnite and of settling pond material with characteristics of the leaching conditons for individual samples.

Designation and characteristics of samples	As [µg/l]	Sb [mg/l]	Fe [mg/l]
1.a (pH 3.21, +5°C)	-	21.36	-
1.b (pH 3.21, +30°C)	-	30.64	-
1.c (pH 7.43, +5°C)	-	31.72	-
1.d (pH 7.43, +30°C)	-	30.24	-
2.a (pH 3.21, +5°C)	5.46	2.92	<0.05
2.b (pH 3.21, +30°C)	10.52	3.28	<0.05
2.c (pH 7.43, +5°C)	4.36	3.36	<0.05
2.d (pH 7.43, +30°C)	10.4	4.04	<0.05
2.e (pH 3.21, +20°C, HA)	5.76	3	<0.05
2.f (pH 7.43, +20°C, HA)	11.88	3.2	<0.05
3.a (pH 3.21, +5°C)	10	6.48	<0.05
3.b (pH 3.21, +30°C)	12.44	4.84	0.07
3.c (pH 7.43, +5°C)	7.36	6.68	<0.05
3.d (pH 7.43, +30°C)	14.2	4.2	<0.05
3.e (pH 3.21, +20°C, HA)	13.2	4.76	<0.05
3.f (pH 7.43, +20°C, HA)	15.48	5.24	<0.05

HA – humic acids

After two months of leaching of stibnite samples and samples of settling pond material we frequently partially evaluated the obtained leaching solutions by analysing the amount of Sb, As and Fe, in solution using atomic absorptive spectroscopy on the Perkin-Elmer 1000 instrument in the laboratory of Geological Institute of the PriFUK.

Results

Sediments of the Settling Ponds

Samples from test the pits MO1 (settling pond no. 1) and MO2 (settling pond no. 2) were used for the study of sediments from the settling ponds. The test pit MO1 was 290 cm deep and the test pit MO2 310 cm deep. Altogether 44 samples were taken. The test pits were dug during the field work in 1997. Also, we used the samples from drill holes VOD-1, VOD-4 and VOD-7 (depth interval 0.2 m - 3.5 m) that were drilled at the settling ponds no. 1 and no. 2 by GP SNV in 1992 (Arvensis et al., 1994; Arvensis, 1998) and samples taken from the outlet of the drainage system of the settling pond no. 2.

The pH values of the flotation wastes, analysed in the samples from the settling ponds MO1 and MO2, are 7.9 - 8.1. These values prove, that pH of the wastes is neutral to weakly alkaline, without determination of any substantial changes in relationship to the depth or to the place of sampling at the settling ponds.

Minerals of the Settling Ponds Identified by Optical Methods and by RTG-powdery Diffraction Analysis

Using the mud discharges and panning of all the settling pond material samples (1 kg per sample), by the separation in heavy liquid ($CHBr_3$) into light and heavy fractions, by the exact determination of weight and the calculation of qualified estimate of mineral proportions of heavy and light factions in the total volume of the settling ponds it was determined that the light fraction forms about 99.9 % of the total amount of the settling pond material. This fraction is formed by a greater proportion of the sandy fraction and by a smaller proportion of the fine-grained clayey material (about 20 - 40 %), that was removed during mud discharging. Quartz and feldspars are the main gangue minerals that are present in the light fraction, identified by optical methods, as well as by RTG-powder diffraction analysis. Only illite was identified by the RTG-diffraction analysis of the samples of granulometrically separated clayey fraction of <2 micrometers.

The heavy fraction of the settling pond material, which represents about 0.1 % of the total is formed of gangue and ore minerals. The main gangue minerals of the heavy fraction are carbonates. They occur as either a form of hydiomorphic grains of a white colour probably calcite, or as a form of hypidiomorphic and allotriomorphic grains of a creamy colour, that are affected by partial oxidation,

probably the Fe dolomite, ankerite, (determined by RTG-diffraction analysis of the heavy fraction).

Using a qualified estimate we calculated that carbonates form nearly half (about 45 %) of the total proportion of the heavy fraction from the settling pond material. Using the optical methods and RTG-diffraction analysis some other gangue minerals present in the heavy fraction were identified: abundant apatite, less common biotite and zircon and accessory chlorite, muscovite (white mica), epidote, garnet, amphibole and titanite. In nearly all of the samples anthropogenous material was identified in accessory amounts.

Ore minerals form about 30 % of the total amount of the heavy fraction from the settling pond material. Pyrite (about 17 %), arsenopyrite (about 6 %) and stibnite (about 1 %) are the main ore minerals, identified using optical methods and RTG-powder diffraction analysis. In addition the heavy fraction has sparce rutile and accessory Sb-sulphosalts, Fe-oxyhydroxides, Sb-ochres, marcasite, sphalerite, ilmenite and hematite.

Using the optical methods, we focused on the study of qualitative and semiquantitative proportions of minerals at the settling ponds and at the evaluation of the differences in the intensity of the sulphide minerals oxidation in the samples from the test pits MO1 and MO2 and in the samples from the drill holes VOD-1, VOD-4 and VOD-7. Qualitative and semiquantitative proportions of minerals from the both types of samples was nearly identical. Smaller differences in the quantitative proportions and in the intensity of the oxidation were determined on pyrite, arsenopyrite and stibnite, as described below. The comparison of semiquantitative proportion of minerals is shown in figure 2.
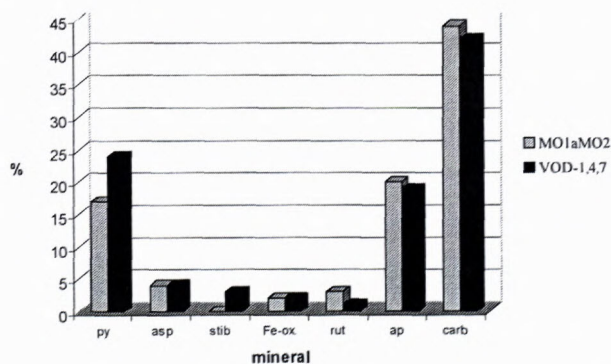

Figure 2: Comparison of the semiquantitative proportions of some heavy fraction minerals from the settling ponds of the Dúbrava deposit in samples from the test pits MO1 and MO2 and in the samples from drill holes VOD-1, 4 and 7, determined by optical observations.

Pyrite - is the dominant ore mineral in all samples.
At the settling pond two generations of pyrite are present:
a) pyrite (I.) - hypidiomorphic to allotriomorphic grains in size from 20mm to 2 mm. All grains show traces of mechanical treatment and marginal oxidation. During the study of pyrite in reflected light we determined that, besides the corrosion of margins predominantly in the larger grains, the overprinting of pyrite by secondary

minerals occurs on small cleavages. However, the degree of oxidation of individual pyrite grains varies and weakly oxidised grains prevail, representing their initial stage of destruction. During the observation of the surface of the separated grains using the scanning electron microscopy (SEM), the crusts of secondary minerals are clearly seen, probably represented by Fe-oxyhydroxides. The oxidation processes did not much changed the original morphology of the grains.

In the samples from the drill holes VOD-1, VOD-4 and VOD-7 pyrite grains of the fractions smaller than 0.2 mm prevail, but the intensity of their oxidation is less distinct and many non-oxidised grains prevail.
b) pyrite (II.) - forms very tiny (the size of grains is less than 10 mm), idiomorphic and hypidiomorphic crystals included in quartz. The oxidation of pyrite (II.) was not observed and the grains are unfractured.

Arsenopyrite - is an abundant ore mineral. It occurs in the form of idiomorphic to hypidiomorphic crystals, that are partially fractured by mechanical treatment. Rarely, it appears in the form of hypidiomorphic grains in quartz. The oxidation of arsenopyrite grains from the test pits MO1 and MO2 is clearly visible in reflected light, as well as by SEM. It affects mainly the margins of grains. On some of the grains reddish coating and crusts of oxidation products about 10 mm thick are present. These coatings and crusts are not continuously evolved, but they are limited to definite flakes that are separated from the grains at some places. An apparent destruction of the centres of the arsenopyrite grains was not observed however, at places with fissures after mechanical treatment, thin veinlets of secondary minerals, proceeding inside the crystals, are visible. Arsenopyrite crystals from the samples from the drill holes VOD-1, VOD-4 and VOD-7 show almost no oxidation alterations and their internal structure is not affected, excluding the rare fissures caused by the mechanical treatment.

Stibnite - is the ore mineral, which showed the largest differences in quantitative proportions, as well as in the oxidation intensity, between the samples from the test pits MO1 and MO2 and the samples from the drill holes VOD-1, VOD-4 and VOD-7. Stibnite in samples from the test pits MO1 and MO2 is less abundant. Stibnite occurs in the form of allotriomorphic, oval aggregates with tracks after mechanical treatment. We discovered an important fact, that in individual samples stibnite occurs in the large form of grains only (over 0.2 mm), while its appearance in the under-sized fraction (less than 0.2 mm) is negligible. The destruction is most visible on these aggregates, proceeding from the margins inside their central part . The grains include several tiny veinlets, fissures and cavities, but they are not filled by any products of oxidation. This supports the assumption that in stibnite grains the destruction occurs by sequential decomposition (dissolution). Rarely, aggregates of stibnite, including allotriomorphic quartz grains, are present.

In samples from the drill holes VOD-1, VOD-4 and VOD-7 stibnite is an abundant mineral. Hypidiomorphic and allotriomorphic aggregates occur in intermediate-sized, as well as in under-sized fractions, where they

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prevail. The grains are locally fractured, mechanically treated and they are not affected by substantial oxidation.

Toxic Elements in Effluxes from the Settling Pond no. 2

The presence and content of toxic elements in the effluxes from the settling pond no. 2 were determined by analysing the leaching solutions from the sample of flotation waste on the outflow of the drainage system (sample no. 1). Due to comparison also sample from the flotation waste from depth 150 cm from this settling pond was analysed, too (sample no. 2). The amounts the Zn, Cu, As and Sb were determined, which were captured on Fe-oxyhydroxides (FeOOH). Fe, which was liberated by dissolution of these Fe-oxyhydroxides in leaching solutions, was determined, too (table 3).

Table 3: The concentrations of toxic elements in the samples of settling pond material no.1 and no. 2 determined by atomic absorbtive spectroscopy

	Fe (g/kg)	Zn (g/kg)	Cu (g/kg)	As (g/kg)	Sb (g/kg)
Sample No.1	12.83	0.032	0.0019	0.004	1.221
Sample No.2	2.685	0.01275	0.00535	0.00285	0.31575

The Fe contents were recalculated for the amount of Fe-oxyhydroxides and we ascertained that in the sample no.1 20.39 g/kg and in sample no.2 4.27 kg of Fe-oxyhydroxides are present. Consequently, the relatively large differences in toxic element contents between the samples no.1 and no.2 are related to the amount of Fe-oxyhydroxides and to the general character of these samples. The sample no.1 was taken from the surface drainage of the settling pond, therefore it was in considerable amount exposed to the climatic effects and to the subsequent oxidation of Fe-sulphides, more than sample no. 2. As shown in table 3, the contents of analysed elements (Zn, Cu, As), excluding the Sb-content (where it was calculated that 1 kg of Fe-oxyhydroxides at the settling ponds would be able to capture up to 60 g of Sb), are rather low in sample no.1. These values suggest that at the settling pond at given conditions a slow oxidation of sulphide minerals is in progress.

Oxidation of Sulphide Minerals from the Settling Ponds of the Deposit Dúbrava under Laboratory Conditions

During two months of observation of the experiment progress an distinct change in pH of the leaching solution was determined in the first week. This change was predominantly related to the samples poured by the solution with a pH of 3.21. Here the pH prevailingly reached the value of 7-8. In the samples receiving the solution with pH 7.43 such a significant changes of pH values were not determined.
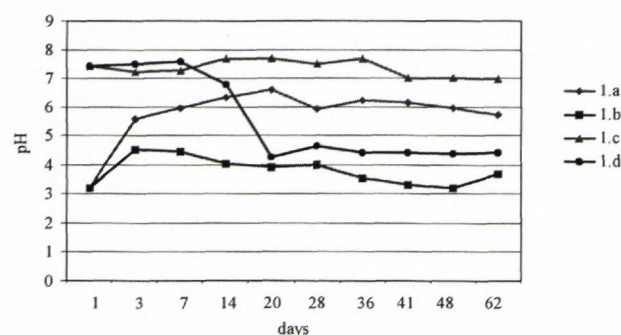

Figure 3: Diagram of pH change of experimentally leached samples of stibnite 1.a-1.d.

At the graphic illustration of the changes in pH values in the samples 1.a -1.d (leached stibnite), (Fig. 3) two different trends of evolution are possible to infer, depending predominantly on the temperature of the environment. The pH value of the sample 1.d, receiving the leaching solution with a pH of 7.43 at the temperature 30°C, progressively decreased to the value 4.4 and the pH value of the sample 1.a, receiving the solution with a pH of 3.21 at the temperature +5°C, increased to the value 6.6.

In the samples 2.a - 2.f (leached settling pond material) and 3.a - 3.f (leached settling pond material enriched in stibnite) (Figs. 4 and 5) an immediate change in pH occurred in all samples receiving the acid solution towards neutral to weak alkaline pH. This pH did not change substantially during the whole time of the experiment. The pH value in the samples receiving alkaline solution slightly increased to 8. Neither temperature, the pH of the leaching solutions, nor the humic acids affected the pH evolution, but probably it was influenced by the mineral composition of the settling pond material.

The next change that was determined during the progress of the experiment, was the origin of the grey spots in the samples of the leached settling pond material, enriched in stibnite (3.a-3.f). In the samples not enriched in stibnite (2.a-2.f) these changes either did not occur or they occurred only rarely. Based on more detailed observations, it was discovered that we are dealing with the process of oxidation and the destruction of stibnite grains in the settling pond material respectively.

The results of atomic absorptive spectroscopy analyses of these leaching solutions are shown on table 2. The determined As-contents are very low, but some dependence of the amount of leached As on the environment, in which the sample was leached (temperature, pH), was possible to observe. As shown on table 2, the highest amounts of As are present in the samples of the settling pond material, emplaced at the temperature +20°C and +30°C. Neither pH nor humic acids substantially influenced the amount of leached As.

Using the analysise of the leaching solutions, a relatively high antimony content was determined in all samples (table 2). The highest amount of Sb was leached
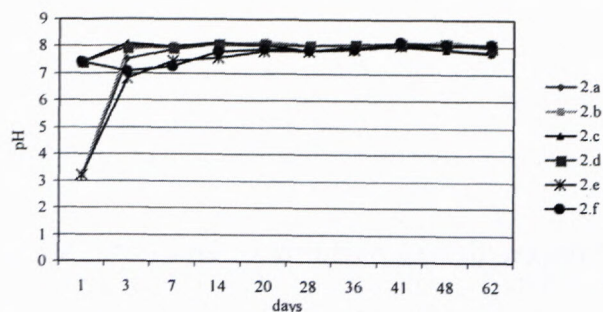
Figure 4: Diagram of pH change of experimentally leached samples of settling pond material 2.a-2.f.
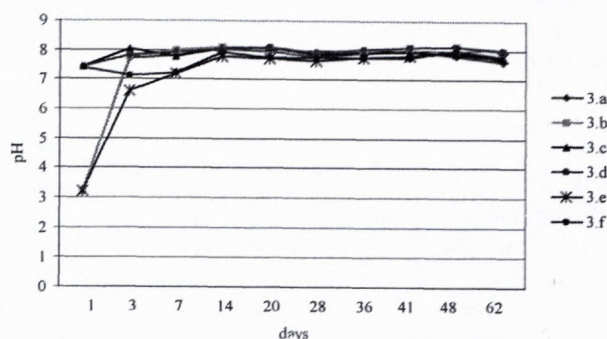

Figure 5: Diagram of pH change of experimentally leached samples of settling pond material enriched by stibnite 3.a-3.f.

from samples of vein stibnite. We did not observe any dependence of the amount of leached Sb on the temperature, pH and humic acids. However, some differences were detected among individual samples of settling pond material, as in all samples 3.a-3.f, enriched in stibnite, higher Sb·contents were analysed than in the samples 2.a-2.f, not enriched in stibnite. Consequently, the Sb content in the leaching solution depends on the amount of stibnite, that was present in the leached material.

Discussion

The results of granulometric analysis, used for describing the settling pond material, are in agreement with the results of previous studies, but with some minor differences, that are related predominantly to the proportions of the aleurite and psammite components in this material. While Arvensis et al. (1994) describes these wastes as psammite to aleurite sands of a creamy colour with brownish tint and with predominance of the aleurite component, our results determined the predominance of the psammite component, with its concentration in all analysed samples to 60 - 90 %, while the proportion of the aleurite component was maximum 40 %. Using the grain size analysis we also determined the presence of the pelite (clayey) fraction, with the concentration in samples reaching a maximum of 1 %. However, such amounts can not be generalised for the total grain-size composition of the deposited wastes, if considering the different character

of the material distributed to the settling ponds and the location of the test pits, from which the samples were taken. By the RTG-diffraction analyse of the pelite fraction only illite was unambiguously identified, but its presence was further determined by RTG-diffraction analysis of the samples not granulometrically separated. The presumed presence of other clayey minerals, described by Orvošová et al. (1998) from the underground workings - kaolinite and mainly smectite, was not detected either by using the saturation of the clayey material or by the ethyleneglycol method. However, their presence at the primary occurrences was only rare.

The total quantitative and semiquantitative proportions of minerals could be characterised by a significant predominance of gangue minerals over ore minerals, which form an accessory component of the wastes. Especially the carbonate content (the neutralisation potential of the settling ponds), determined by a qualified estimate, is nearly two times larger than the pyrite and arsenopyrite content. Quartz, plagioclases, K-feldspars, carbonates (Fe-dolomite, calcite) and apatite are the main gangue minerals of the settling ponds. Biotite, muscovite, chlorite, zircon, rutile, garnet, amphibole, epidote and titanite were identified as minor or accessory minerals. The presence of these minerals is in agreement with their average content in the rocks of the Dúbrava deposit. Pyrite, arsenopyrite and stibnite are the primary ore minerals. In accessory amounts unidentified Sb-sulphosalts, Fe-oxyhydroxides, Sb-ochres, marcasite, ilmenite, hematite and sphalerite were detected.

By comparison of the samples from the test pits MO1 and MO2 from 1997 with the samples from the drill holes VOD 1, 4 and 7 from the year 1992 it was determined that the quantitative and qualitative proportions of the minerals of the light and heavy fraction in both types of samples were nearly identical. Pyrite and arsenopyrite had some small differences in the intensity of their oxidation, because in the samples from the test pits MO1 and MO2 weakly oxidised grains of pyrite and arsenopyrite prevail. However, any other significant oxidation alterations were not observed and we suppose that today they are not being oxidised in larger quantity, inasmuch as the carbonates present in the settling ponds hamper the oxidation processes of these sulphides. A neutral to weakly acid character of the deposited wastes is also supported by the results of the pH measurements - the obtained values are 7-8.

Larger differences in the quantitative proportions and in the intensity of the oxidation in both types of samples were detected in one of the sulphide components of the settling pond material - in stibnite. While in the samples from the drill holes VOD-1, 4 and 7 stibnite was present in larger quantities to 5 % without any oxidation alterations that is also supported by the results of Arvensis et al. (1994). The stibnite contents in the samples from the test pits MO1 and MO2 mostly reached accessory amounts only. Stibnite in these samples was much strongly oxidised and fractured, but without the presence of secondary minerals that were not determined in any sample.

The assessment of the increased Sb-content (1221 mg/kg) in the sample taken below the outlet of the drainage system that was absorbed by Fe-oxyhydroxides confirms the assumption, that stibnite is neutral to weakly alkaline pH of the wastes, in the environment without the access of oxygen from the air, it decomposes into unidentified Sb-compounds that penetrate into the settling pond waters and migrate. Fe-oxyhydroxides present in this sample in the amount of 20.39 g/kg (2.04%) replace the absenting clay minerals (smectite) and at the settling ponds they play the role of a natural sorption barrier. These secondary minerals of Fe are generally important due to their ability to transport and capture various elements, that change their composition in the waters (Trtíková, 1997). We calculated, that 1 kg of Fe-oxyhydroxides at the settling ponds of the deposit Dúbrava would be able to capture up to 60 g of Sb.

Based on the results of the microscopic study and on the analysed amounts of Sb, Cu, Zn and As in the sample taken below the outlet of the drainage system, we suppose that at the settling ponds a very quick oxidation of stibnite, its decomposition and subsequent migration of Sb into the environment occurs in the first years of depositing of the wastes at the settling ponds. At the present time, the detected low concentrations of Cu, Zn and As prove the slow oxidation of the sulphide minerals, in which these elements are present, and their small influence on the toxic pollution of the vicinity of the settling ponds.

Two months of experimental observations of the oxidation processes, occurring in the settling pond material and in the samples of leached vein stibnite, gave us valuable results, that could be theoretically applied to the real processes occurring at the settling ponds.

At first it was thought that the relatively high Sb-content in the leaching solutions during the short period of leaching suggested a quick decomposition of stibnite in the aqueous environment without access of oxygen from the air. Using this information it is possible to explain the decreasing Sb-contents in waters from the drill holes VOD-1, 4 and 7 during the two years of monitoring (1992-94), described by Arvensis et al. (1994) and Arvensis (1998). Similarly, we can explain the small amount of stibnite in samples from our test pits MO1 and MO2 from 1997.

The process of leaching and the Sb-content in the leaching solutions in various samples was not affected either by the temperature or by the pH of the environment. Based on this information we inferred that Sb belongs to those elements (Cu, Ni, Cr, Pb), for which according to Letko (1992), no sound relationship have been observed between the solubility and the pH value. Jorgensen and Pedersen (1992) in Arvensis et al. (1994) experimentally proved a very little influence change of the pH of the environment on the ability to leach out Sb.

The determined low Fe and As concentrations prove the show ability to leach out these elements from the settling pond minerals. The result is in agreement with the determination of the relatively low oxidation of pyrite and arsenopyrite, using the optical observation as well as with the results of analyses of the leaching solutions from the sample taken below the outlet of the drainage system of the settling pond no. 2. The finding of the dependence of the amount of leached As on the temperature, that illustrates the higher concentrations of this element occur in warmer environments, is also a very interesting result.

The experimental modelling of the leaching of elements from the settling pond material was followed also by the presence of humic acids, one of the substantial components of the natural organic matters. These matters, together with fulvous acids, belong to the group of specific natural organic matters that are of relatively high molecular nature, typically with high sorption abilities. They have a dominant position in the processes of interaction with chemical elements, together with other mineral components in soils, waters, sediments (oxides and hydrous Fe and Mn oxides, clay minerals, natural carbonates).

We can evaluate the interaction of chemical elements with components of natural systems from several points of view. The relationship between the form of the binding of a chemical element and its mobility represents one of the views. Today, great interest is devoted to the problems of migration of chemical elements, predominantly toxic metals, in ecosystems. However, data from the literature are still inconsistent, due to the very complicated nature of the related problems. We will mention only some of the complex studies: Alloway et al. (1992), Cibuľka et al. (1991). Babčan and Ševc (1994, 1996, 1997) studied the experimental modelling of the relations among Ag, Be, Cd, Hg, Pb, Zn and organic matters at various pH conditions.

In summary, the bindings among the chemical elements and the components of the natural systems are influenced by many factors (pH values, concentrations of organic matters, their structure etc.). The binding of chemical elements for instance with organic matters in natural systems should not be regarded as stable inasmuch as we are dealing with heterogeneous and very dynamic systems. As the result of various biogenetic and abiogenetic processes, several changes in the bindings of chemical elements occur. In the model experiments, the comparison of the results liberation of Sb and As from the settling pond material and from stibnite showed that in the systems with humic acids no binding of these chemical elements on humic acids occur.

Conclusions

Mineralogical and environmental evaluation of the settling pond material using the experimental modelling of the processes occurring in the flotation waste enabled us to find out that today, from the viewpoint of the influence on the environment, the settling ponds are not dangerous for the following reasons:

1. The settling ponds at the Dúbrava deposit are relatively young and they contain a sufficient amount of carbonates that neutralise the environment at the settling

ponds and in this way they decrease the intensity of the oxidation processes and the migration of As, Fe and other elements.

2. At the settling ponds relatively quick decomposition of stibnite and consequently the depletion of Sb-content at the flotation waste occur. Sb, in the form of unspecified compounds, goes into the water solution at the settling ponds and migrates.

3. A part of the Sb-compounds that originated during the oxidation of stibnite without any marked dependence on the pH of the environment is captured by Fe oxyhydroxides at the settling ponds and they do not migrate in substantial amounts into the vicinity of the settling ponds.

The oxidation of stibnite at the settling ponds is relatively quick, but in the flotation sediments still a relatively large amount of pyrite and arsenopyrite remain. Their extensive oxidation, related to the liberation of As and Fe into the surrounded environment of the settling ponds, depends on the neutralisation potential of carbonates, on the amount of infiltrating water and on its properties (pH, temperature).

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Certification of Reference Material - Zeolite 1

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Abstract. Certified reference material named "Zeolite 1 " has been prepared in Geo-analytical Laboratories of Geological Survey of Slovak Republic, accredited testing laboratories in Spišská Nová Ves within the project "Programme of Metrology Development in Slovak Republic" and research projects "Reference Laboratory of Ministry of Environment of Slovak Republic for Geology and Analyses of Geological Material and Rock Environment". The project includes a description of the sampling sites of candidate reference material, sample preparation, testing of homogeneity, inter-laboratory comparative tests and determination of certified values. 21 foreign and 6 Slovak laboratories took part in the certification of chemical composition of zeolite. 27 certified values for the main and trace elements were determined from the recorded values.

Key words: zeolite, reference material, inter-laboratory test

Introduction

The main target of preparation of the certified reference material "**Zeolite 1**" [1], [2], [3] was to prepare and widen the selection of reference materials by a new type, which is on the base of natural geologic material with aluminosilicate matrix, and which provides quality control of analytic data, precision and accuracy of analytical processes and validity of methods that are used in laboratories.

Characteristics of Deposit and Zeolite Composition

From several occurrences and deposits of zeolite tuffs the deposit of Majerovce [4] was selected for the preparation of certified reference material. The zeolite of deposit Majerovce represents the part of zeolite-rhyodacite tuffs of Earlier Badenian, which occurs on the surface from the northwestern border of Vranov nad Topľou to Pusté Čemerné (Fig.1).

The natural zeolite tuffs are composed of large group of minerals. The information about structure and thermic analyses are very important before beginning the certifying chemical analyses of the composition. The mineralogical composition of zeolite tuff sample from the Majerovce deposit was determined by X-ray diffraction analyses with the use of $CuK_{\acute{a}}$ radiation (Hricová 1999) [5]. The mineral clinoptilolite that composed a substantial part of the tuff was identified from a X-ray record (Fig.1). This mineral is accompanied by cristobalite (C), quartz (Q) and carbonate (D). The reflections of feldspar were filtered out from the X-ray record. The values of measured inter-planar distances are presented in 10^{-10} m and they are compared with table values of card register JCPDS [6].

The curve of differential thermic analyses of clinoptilolite does not show strong thermic effects in temperature range 40 – 1000°C. A gradual loss of molecular water is characteristic for zeolite minerals, which course is recorded by thermo-gravimetric curve (Diagram 2) [5].

Preparation of Zeolite Sample as Reference Material

A zeolite sample with weight about 100 kg was taken from the open pit mine at the Majerovce deposit and delivered for subsequent processing to Geo-analytical Laboratories of Geological Survey of Slovak Republic in Spišská Nová Ves. The preparation of candidate reference material consisted of the following steps: sample adaptation, check of granularity, homogeneity test, stability test, inter-laboratory comparative tests, statistic evaluation of recorded data and determination of certified values.

Sample Treatment

The whole 100 kg sample was dried at a temperature of 40°C, crushed in a jaw crusher in two steps to granularity of 2 and 0.5 cm. The sample was reduced to two 50 kg samples by quartation. Both parts of the sample were then milled in a cylindrical mill to samples with granularity less than 0.1 cm. The sample was then reduced to 25 kg weight by quartation in rotary quartering equipment and then homogenised in an abrasionless agate mill to an analytical fineness with a grain size under 0.09 mm. The whole agated sample underwent grain size control by dry screening through a screen with holes 0.09 mm.

Homogenisation of Analytic Sample

For the purpose of ensuring of perfect homogeneity, the sample was homogenised for 24 hours in 50 litres PE container with sealed glass ampoule of technetium solution with activity 3.7 Gbq. The technetium solution caused ionisation of the container´s content to prevent the
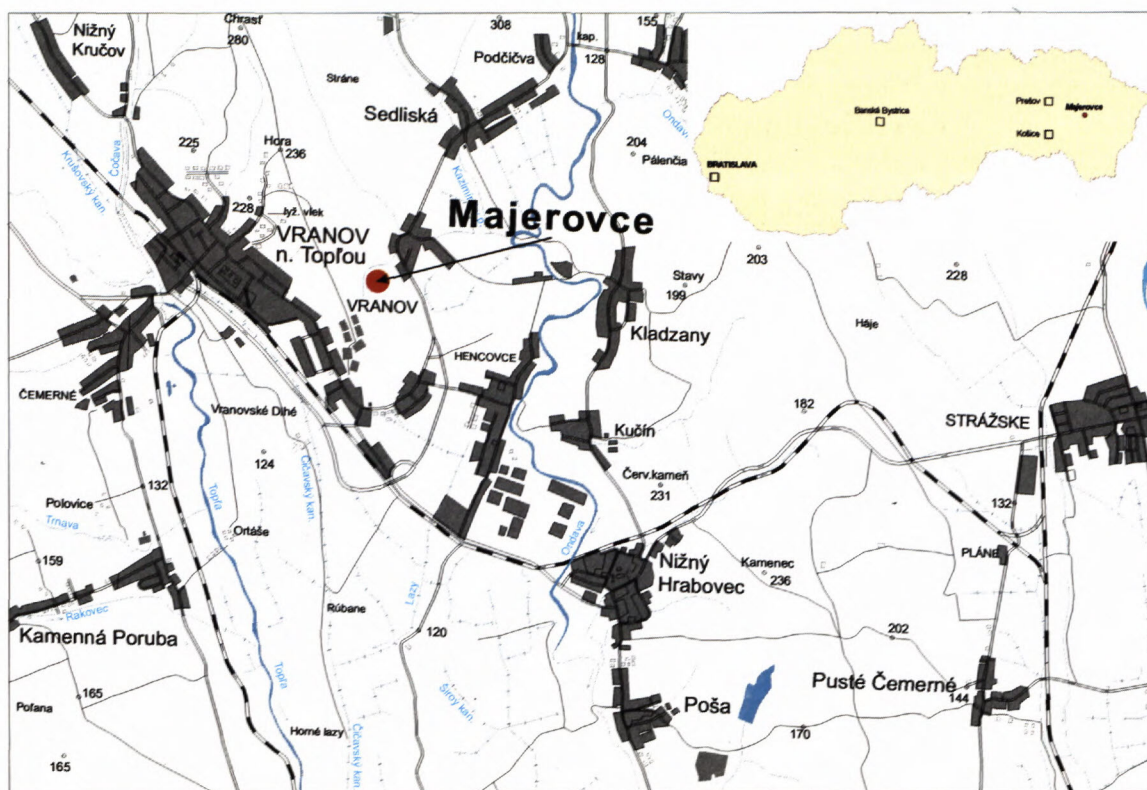
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Figure 1 Map of the sample site at the Majerovce deposit

forming of an electrostatic charge and sample clustering during mixing. Immediately after homogenisation the sample was weighted by 50 g and 100 g into 100 and 200 ml PE vessels with a screwing seal, labelled and stored in a dark and dry chamber.

Homogeneity Control

Twenty vessels from the whole set of 500 vessels were selected by random sampling. The samples were then tested on variance of concentrations of selected elements, so-called tracers of inhomogeneity (macro elements Fe, K, Ti, and trace elements Ba, Pb, Sr, Zn), the variances were tested within a sample and among the samples. The concentrations represent also various concentration levels. The homogeneity control was made by quantitative analyses of the above-mentioned elements in energo-dispersion X-ray fluorescence spectrometer SPECTRO X – LAB 2000, (Mackových 1999) [7].

The evaluation of homogeneity was done in accordance with Slovak Technical Standard (STN) No. 01 2841 [8] and ISO Guide 35 [9]. Because the tests confirmed the suitable homogeneity of all monitored components, the inter-laboratory comparative testes could be performed.

Analytic Data Evaluation and Statistical Analyses

21 foreign and 6 Slovak laboratories took part in certification of reference material (Tab.1).

The analysed sample was from 4 separate charges. Delivered analytical data were statistically evaluated by programme for inter-laboratory test - ISO 5725 [10] and according to following standards: STN 01 2841 [8] and ISO Guide 35 [9]. Statistical analyses and expertise were used to identify the statistically outlying values, which were excluded from the data set used in the following evaluation process. The prepared analytical data were evaluated according to ISO Guide 35 criteria for preparation of RM and they were divided into certified and uncertified values (Tab. 2) (Lučivjanský, Mackových 1999) [11].

The following criteria were chosen for determination of certified values:

- data, entering certification process of one element, must be obtained minimally from two independent analytical methods,
- the set of processed data must be from 6 laboratories at least,
- the uncertainty of measurement must be smaller than:

  6 % from base value of element for concentration range $0.1 – 100$ %

  12 % from base value of element for concentration range $1 – 999$ µg/g

  18 % from base value of element for concentration range $1 – 999$ ng/g

The components of which the recorded data set has not fulfilled these criteria have been included among informative, uncertified values.

Tab.1. Names of participating laboratories

No.	Organisation	City	Country
1.	British Geological Survey	Nottingham	Great Britain
2.	CEVA, s.r.o.	Trencín	Slovakia
3.	Czech Geological Survey, Analytical Laboratory	Prague	Czech Republic
4.	ECOCHEM-stredisko ICP,	Prague	Czech Republic
5.	Ekologické laboratória, s. r. o.	Spišská Nová Ves	Slovakia
6.	Federal Institute for Geosciences and Natural Resources	Hannover	Germany
7.	Geoekologické laboratóriá š.p.	Turcianske Teplice	Slovakia
8.	Geological Institute of Hungary, Laboratory	Budapest	Hungary
9.	Geological Institute of Romania, Environmental Geochemistry Department	Bucharest	Romania
10.	Geological Survey of Austria	Wien	Austria
11.	Geological Survey of Estonia	Tallinn	Estonia
12.	Geological Survey of Finland , Chemical Laboratory	Espoo	Finland
13.	Geological Survey of Norway, Laboratory Section	Trondheim	Norway
14.	Geologická služba SR, Geoanalytické laboratóriá	Spišská Nová Ves	Slovakia
15.	Geologický ústav SAV	Bratislava	Slovakia
16.	Institute of Geology of Lithuania, Spectroscopy Laboratory	Vilnius	Lithuania
17.	Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Wroclaw University of Technology	Wroclaw	Poland
18.	Katedra chemie, Zemědělská fakulta	Ceske Budejovice	Czech Republic
19.	Netherlands Inst. of Applied Geoscience TNO – National Geological Survey, Section of Geochem. Lab.	Haarlem	The Netherland
20.	Okregowa Stacja Chemiczno-Rolnicza w Warszawie	Warszawa	Poland
21.	Polish Geological Institute, Central Chemical Laboratory	Warsawa	Poland
22.	U.S.Geological Survey, Colorado	Denver	U.S.A.
23.	University of Pavia, Laboratorio Energia Nucleare Applicata	Pavia	Italy
24.	University of Ljublana, Dep. of Chemistry, National Institute of Chemistry	Ljublana	Slovenija
25.	Vernadsky Institute of Geochemistry and Anal. Chemistry RSA	Moscow	Russia
26.	VSEGEI HIMLAB	St.- Petersburg	Russia
27.	VSŽ LABORTEST s.r.o	Košice	Slovakia

Table 2 Certified Values:

Component	Al_2O_3	CaO	Fe_2O_3 Total	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	TiO_2	As	Ba	Be	Ce	Cs
Unit	%	%	%	%	%	%	%	%	%	%	µg/g	µg/g	µg/g	µg/g	µg/g
Certified value	12.21	4.51	1.75	2.19	1.41	0.045	0.612	0.055	67.11	0.190	1.96	779	1.96	52.3	3.88
Uncertainty U_c	0.16	0.08	0.03	0.04	0.02	0.001	0.011	0.003	0.31	0.003	0.09	13	0.08	2.6	0.13
np	70	79	79	68	75	18	63	54	58	63	38	60	26	21	18

Component	Cu	Ga	Hg	La	Pb	Rb	Sb	Sr	V	Y	Zn	Zr
Unit	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Certified value	5.12	13.9	0.329	32.6	20.8	95.7	0.379	617	12.6	21.8	38.2	158
Uncertainty U_c	0.25	0.2	0.008	1.2	0.4	1.9	0.025	6	0.4	0.7	1.2	3
np	58	31	30	16	67	44	22	48	51	48	87	24

np – number of accepted laboratory measurements

Uncertified Values:

Component	LOI	Ag	Bi	Cd	Co	Cr	Dy	Er	Eu	Gd	Ge	Hf	Ho	In
Unit	%	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Uncertified value	9.49	0.040	0.198	0.065	2.26	4.33	3.72	2.51	0.565	3.31	1.62	4.05	0.693	0.026
Uncertainty U_c	0.36	*	*	0.011	0.21	0.52	*	*	0.059	*	*	0.63	*	*

Component	Li	Lu	Mo	Nb	Nd	Ni	Pr	Sc	Se	Sm	Sn	Ta	Tb
Unit	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Uncertified value	14.1	0.337	1.57	11.9	22.0	2.86	6.54	5.13	0.260	3.66	3.05	0.94	0.570
Uncertainty U_c	2.5	*	*	1.8	0.9	0.29	*	0.36	*	0.12	0.23	*	*

Component	Th	Tl	Tm	U	W	Yb
Unit	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Uncertified value	10.40	0.467	0.420	4.51	2.60	2.69
Uncertainty U_c	0.72	0.109	*	0.43	*	0.33

* number of accepted laboratory means < 2

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Evaluation of Used Analytical Methods

The most frequently used analytical method for determination of certified values of the main elements (10 elements) was atomic emission spectrometry with inductively coupled plasma (AES-ICP) – 69 times, X-ray fluorescence spectrometry (RFS) – 66 times and atomic absorption spectrometry (AAS) - 24 times. Except of these methods, the methods as gravimetry and photometry were used – 25 times. Some of the used analytical methods do not have the same level of precision or reproducibility of repeated measurements. The assessment of the standard deviation values for repeatability and reproducibility of the measurements found as the most suitable methods: atomic emission spectrometry with inductively coupled plasma and X-ray fluorescence spectroetry methods (Figure 2).
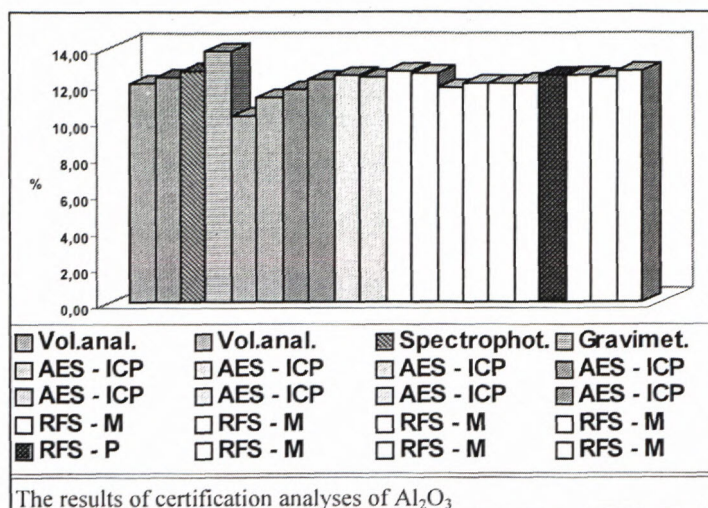

The results of certification analyses of Al_2O_3

Figure 2. Comparison of analytic methods for determination of aluminium gained from 20 laboratories
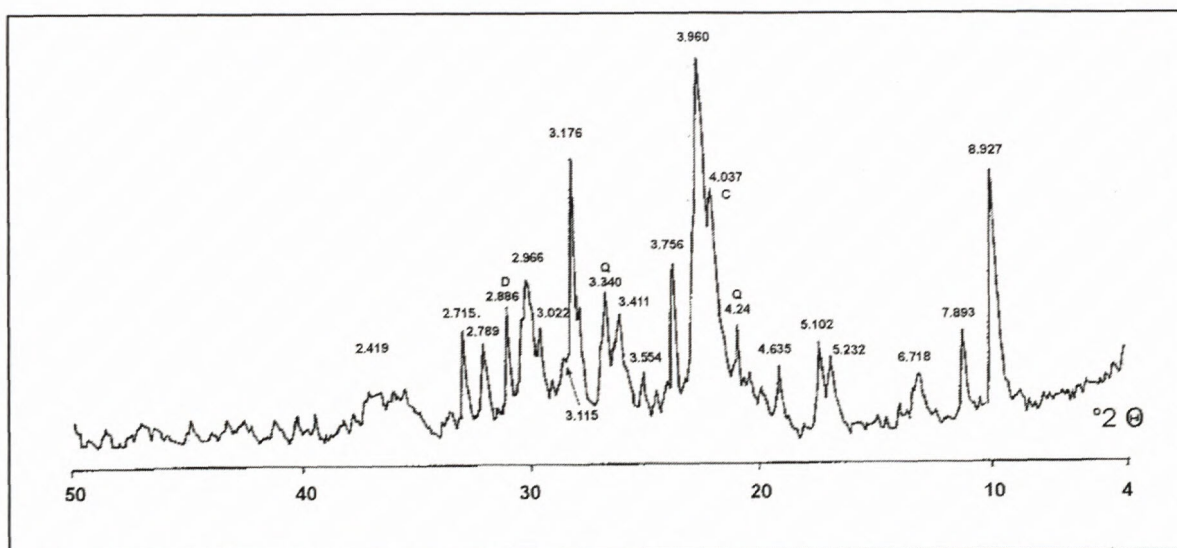

Diagram 1 – X-ray record of zeolite tuff from the Majerovce deposit

Certified values of trace elements (17 elements) were most frequently determined by X-ray fluorescence spectrometry method – 62 times and atomic emission spectrometry with mass detection (AES-ICP/MS) – 62 times. The other used methods were: atomic absorption spectrometry with added techniques – 41 times, atomic emission spectrometry with inductively coupled plasma – 22 times, optic emission spectrometry and neutron activation analyses – 13 times.

The determination of the main and trace elements by AES-ICP and AAS methods were done after absolute decay of sample in mineral acid mixture or after alkaline melting of the sample. In AES-ICP/MS method only decay in mineral acids including HF was used. In RFS method two kinds of sample preparation were used. The main elements were determined from melted borate pearls (RFS-M), and trace elements were analysed from pressed tablets (RFS-P).

Conclusion

The selection of geologic reference materials with aluminosilicate matrix was widened by preparation of the certified reference material "Zeolite 1".

The process of preparation and certification was performed under the patronage of the Slovak Metrology Institute, Bratislava, in accordance with international standards ISO Guide 34 [12] and ISO Guide 35 [9]. 6 Slovak and 21 foreign laboratories took part in the certification.

10 certified values for the major matrix elements, 17 certified and 33 uncertified values for trace elements have widened the spectrum of possibilities of analysts in providing of reliability verification of analytic data, precision and accuracy of analytic processes and evaluation of methods used in testing laboratories.
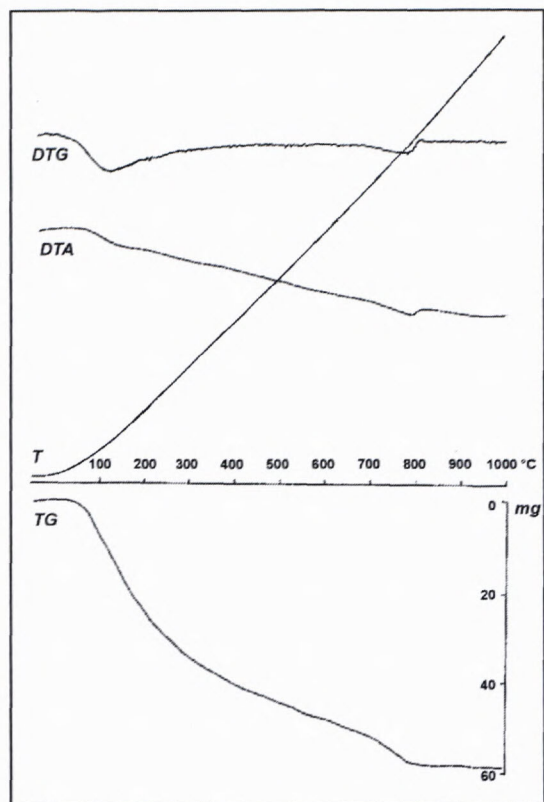
Diagram 2 – Thermic analysis record of zeolite tuff from the Majerovce deposit

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