Complex geochemical investigations of soils on holocene sediments of flood plain and lowland areas

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The process of evolution of the earth resulted in the formation of a unity of life and geochemical environment, which finds its expression in form of most different coherences and interactions. Thus the chemical composition of the different components of lithosphere, atmosphere and hydrosphere exerts a substantial influence on all parts of the biosphere. The contents of major elements and trace elements trace inside the biosphere via the food chain towards the human organism in a system of most complicated interactions (KOVALSKIJ, 1977).

Because of their unique position at the boundary between geosphere and biosphere, like no other geological material suited to characterize the geochemical behaviour distribution of elements in a region under most different aspects of environmental geochemistry. Soils on holocene sediments of flood plain and lowland areas show a special geochemistry among the other constituents of the pedosphere, which is different from that of other soils from other regions and depends on their specific genesis. On account of their geographical position they are especially predestined for a superposition of the characteristics by secondary, anthropogenic geochemical accumulations of elements, which have developed in consequence of the steadily growing industrialisation. Several authors reported about extreme enrichments of elements like heavy metals of environmental importance in river sediments and flood plain soils as a result of an intensified intake from the considerably loaded rivers (ARGE ELBE, 1980; MULLER et. al., 1981; CLAUSSEN, 1983; SALOMONS et. al., 1984).

The aim of the present investigations consists in the preparation of a survey about the geochemical proportions of the different soil types on flood plain and lowland areas on the basis of the examination of selected, characteristic vertical soil profiles representative of a greater area, which allows to derive scientifically well-founded statements both for the assessment of potential load limits and for the estimation of the actual level of loads from the knowledge of the primary geochemistry. Furthermore, presuppositions necessary for a geochemical mapping of the country on the basis of pedogeochemical data were to be made.

# investigation programme

Altogether 20 vertical soil profiles were selected for sampling corresponding to the areal distribution of the soils on flood plain and lowland regions and to the registration of the most important rivers under special consideration of the southern part of the G.D.R. (Table 1).

Table 1: List of the sampling points of the vertical soil profiles selected

| river        | number<br>of profile | soil type                        | sampling point •<br>locality/district |  |
|--------------|----------------------|----------------------------------|---------------------------------------|--|
|              |                      |                                  |                                       |  |
| Elbe         | D 36                 | vega                             | Posta/Pirna/Dresden                   |  |
|              | D 37                 | vega                             | Scharfenberg/Meißen/Dresde            |  |
|              | L 32                 | vega                             | Köllitsch/Torgau/Leipzig              |  |
|              | H 28                 | colluvial gley }                 | Brambach/Roßlau/                      |  |
|              | H 29                 | colluvial gley }                 | Halle                                 |  |
|              | M 34                 | strongly perio-<br>dically rede- | Buch/Tangerhütte/Magdeburg            |  |
|              |                      | posited flood                    |                                       |  |
|              | B 33                 | gley                             | Hinsdorf/Wittenberge/<br>Schwerin     |  |
| Werra        | S 22                 | vega-gley                        | Eisfeld/Hildburghausen/Suhl           |  |
|              | S 23                 | gley-vega                        | Barchfeld/Bad Salzungen/<br>Suhl      |  |
| I 1 m        | S 24                 | ground gley                      | Gräfinau-Angstedt/Ilmenau/<br>Suhl    |  |
| Sormitz      | G 20                 | vega                             | Rauschengesees/Leutenberg/            |  |
| (>Saale)     | 6 21                 | raw flood plain                  | Gera                                  |  |
| Saale        | н 30                 | vega-gley                        | Zickeritz/Hettstedt/Halle             |  |
| Weiße Elster | G 17                 | vega-gley                        | Neumühle/Greiz/Gera                   |  |
|              | G 18                 | gley-vega                        | Wiederau/Borna/Leipzig                |  |
| Pleiße       | L 19                 | vega                             | Zeschwitz-Kotteritz/                  |  |
|              |                      |                                  | Altenburg/Leipzig                     |  |
| Wiltsch      | K 16                 | vega                             | Wiltschmühle/Eibenstock/              |  |
| (->Zwickauer |                      |                                  | Karl-Marx-Stadt                       |  |
| Mulde)       |                      |                                  |                                       |  |
| Zwickauer    | K 15                 | gley-vega                        | Silberstraße/Zwickau-Land/            |  |
| Mulde        |                      |                                  | Karl-Marx-Stadt                       |  |
| Spree        | D 25                 | gley-Vega                        | Kirschau/Bautzen/Dresden              |  |
| Warnow       | B 27                 | low-moor peat soil               | Rühn/Bützow/Schwerin                  |  |

A detailed description of the processes of sampling and sample preparation is given by VOLAND et. al. (1987).

# analytics

The determined major elements and trace elements and the methods of determination used are shown in Table 2.

| Table 2: List of the elements determination used                       | determined and methods of  |
|--|--|
| element  | method of determination  |
| majorelements  |  |
| Si, Ti, Al, Fe, Mn, Ca, K  | X-ray fluorescence analysis  |
| Mg, Na   | atomic absorption spectrometry -flame (HF/HNO <sub>3</sub> -digestion)                             |
| trace elements   |  |
| Ag, B, Ba, Be, Co, Cr, Cu,<br>Ga, Mn, Mo, Nb, Ni, Pb, Sn,<br>Ti, V, Zr | atomic emission spectrometry -electric arc   |
| Li, Rb, Cs   | atomic absorption spectrometry -flame (HF/HNO <sub>3</sub> -digestion)                             |
| Se .   | atomic absorption spectrometry<br>hydride process<br>(MOHR et. al., 1983; VOLAND<br>et. al., 1987) |
| trace elements - boiling 1.5   | N HNOs-extractable fraction  |
| Cd, Cr, Cu, Mn, Ni, Pb, Zn   | atomic absorption spectrometry -graphite tube (MACHELETT et. al., 1986)                            |

# pedological parameters

pH-value glass electrode

#### evalution and results

The classification of the vertical soil profiles with regard to their geochemistry was carried out on the basis of the calculation of the Clarke concentration value by means of division by the respective Clarke value for soils.

In addition, a comparison between the element concentrations and the limiting values of the concentration admissible in arable soils after KLOKE et. al. (1984) was made.

Table 3: Range of the determined concentrations for the trace elements investigated /ppm/, Clarke values for soil after LEVINSON (1974) (THORNTON, 1983) and VINOGRADOV (1954), Kloke values after Kloke et. al. (1984) and number of samples n

| concentration /ppm/ |      |    |        | Clarke value<br>for soils | Kloke value | number<br>of samples |
|---------------------|------|----|--------|---------------------------|-------------|----------------------|
| element             | Min. | _  | Max.   |                           |             | n                    |
| <br>Ag              | 0,1  |    | 17     | 0,1                       |             | 138                  |
| В                   | 28   | -  | 881    | 10                        | 25          | 138                  |
| Ba                  | 137  | _  | 12000  | 500                       |             | 138                  |
| Be                  | 2    | -  | 17     | 6                         | 10          | 138                  |
| Cd+                 | 0,1  | -  | 12,1   | 0,5                       | 3           | 55                   |
| Co                  | 5    | -  | 157    | 8                         | 50          | 138                  |
| Cr                  | 28   | -  | 457    | 200                       | 100         | 138                  |
| Cs                  | 13   | -  | 28     | 6                         |             | 42                   |
| Cu                  | 6    | -  | 514    | 20                        | 100         | 138                  |
| Ga                  | 3    | -  | 105    | 15                        | 10          | 138                  |
| _i                  | 29   | -  | 88     | 30                        |             | 60                   |
| Mn                  | 107  | -  | 9364   | 850                       |             | 138                  |
| Mo                  | 1    | -  | 16     | 3                         | 5           | 138                  |
| Nb                  | 10   | -  | 56     | NB                        |             | 138                  |
| Ni -                | 10   | -  | 208    | 40                        | 50          | 138                  |
| РЬ                  | 13   | -  | 1469   | 10                        | 100         | 138                  |
| Rb                  | 90   | -  | 160    | 60                        |             | 60                   |
| Se                  | 0,1  | 2- | 5,1    | 0 0,2                     | 10          | 75                   |
| Sn                  | 1    |    | 1097   | 10                        | 50          | 138                  |
| Ti                  | 1514 | -  | 10486  | 4600                      | 5000        | 138                  |
| V                   | 22   | -  | 259    | 100                       | 50          | 138                  |
| Zn+                 | 31,2 | -  | 1933,8 | 50                        | 300         | 55                   |
| Zr                  | 115  |    | 1141   | 300                       | 300         | 138                  |

<sup>+</sup> boiling 1,5 N HNOz-extractable fraction

Table 3 shows the ranges of concentration determined for the particular trace elements, the appropriating Clarke values for soils and the Kloke values.

The behaviour of the elements concerning their vertical distribution in dependence on the specific pedological parameters was studied separately for every soil profile.

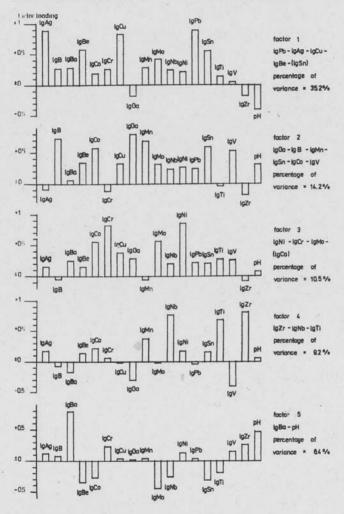


Fig. 1: results of the factor analysis

As a part of the statistical treatment of the results a factor analysis and a hierarchical cluster analysis were carried out for the complete data of all vertical soil profiles investigated for the decadic logarithms of 17 selected trace elements and the pH-value as a pedological parameter in the SPSS/PC-system. The method of average linkage between groups and the cluster measure of the squared Euklidean distance were applied to the hierarchical cluster analysis. The results of the factor analysis are shown in Fig. 1.

#### discussion

The several soil types among the soils on holocene sediments of flood plain and lowland areas provide extraordinarily heterogeneous patterns of distribution for the elements investigated. Both the position of the profile along the rivercourse (distance from the source) and the lateral distance from the bank of the river exert a substantial influence on the distribution of the elements.

The geochemical relations in flood plain soils of the headwaters of a river are principally determined by the primary intake from geogenic sources, appearing in form characteristic associations of elements. Thus typical parageneses of elements originating from deposits or occurrences located in the drainage area of the river and mined in former times or being still in exploitation were detected as accumulations in the flood soil. Enrichments of elements originating from pneumatolytic and hydrothermal mineralization parageneses Sn-Mo-W and Bi-Co-Ni-Ag-U (BAUMANN et. al., 1982) occurred in the upper and medium course of the Zwickauer Mulde river. The headwaters of the Ilm river are geochemically characterized by accumulations of elements Aq-Pb-Cu-Ni-Ba-Mn corresponding the attributed mineralization paragenesis, which can be to hydrothermal mineralizations in the geologic range of Rotliegendes series of the Thüringer Wald-highlands. Extremely enhanced Ba-concentrations belonging to still exploited vein deposits of the Schmalkalden hydrothermal district (mineralization paragenesis fluorite-baryte-calcite-sideritequartz-sulphides) at Trusetal (mine Mommel) and Steinbach were detected at the medium course of the Werra river.

Towards the lower course of the river these characteristic patterns of element distribution increasingly diminish and receive a superposition by unspecific accumulations of different elements, mainly of a high geochemical mobility, originating from most different sources. The tendency of an element to accumulate towards the lower course of a river is growing with an increasing anthropogenic percentage of its total intake in a soil.

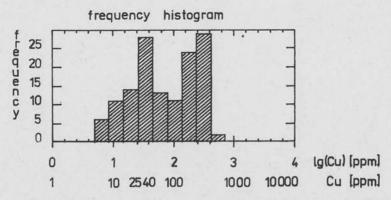


Fig. 2: absolute frequency distribution of the concentration of lg (Cu) in flood plain soils.

These results are supported by the factor analysis carried out on the complete soil profiles, which are partially very different from the point of view of geology and pedology (pH-value, redox potential - influence of groundwater, organic soil matter and sesquioxide contents). Elements with similar geochemical properties, which also frequently show similar frequency distribution patterns of their concentrations, are summarized in the same factors (Fig. 1).

Thus the elements Pb-Ag-Cu-Be-(Sn) highly loaded in factor 1 show at least a bimodality of the frequency distribution of their concentrations (Fig. 2). This factor amounting to 35,2 % has the greatest percentage of the total variance.

The mode value of lower concentration mostly lying near the Clarke value for soils represents samples (parts of horizons, horizons, profiles) with element concentrations in the range of the geological background, whereas the mode value of higher concentration shows most frequently occuring contents in case of additional secondary intakes into soil from anthropogenic sources or pedologically conditioned accumulations in certain profile zones. These patterns of distribution refer to the existence of at least two independent sources of intake for the elements concerned in flood plain soils.

The elements Zr, Nb and Ti with high loadings in factor 4 (9,2 percentage of the total variance) are characterized by a completely contrary picture of the frequency distribution of their concentrations (Fig. 3). These elements providing a Normal distribution of their concentrations are almost exclusively

primarily and geogenicallly transported into soil in the course and as a result of weathering and soil formation and they are accumulated in the heavy mineral fraction of the sediments. So these elements do not show any regional specific variations in concentration in case of the flood plain soils investigated.

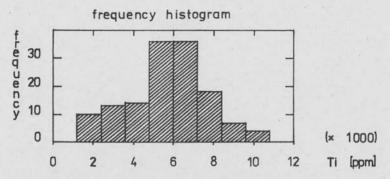


Fig. 3: absolute frequency distribution of the concentrations of Ti /ppm/ in flood plain soils

On the contrary to elements with high loadings in factor 1 the elements Ga-B-Mn-Sn-Co-V highly loaded in factor 2 (14,2 % total variance) show a percentage of definite positive correlation with the pH-value). Their geochemical behaviour is determined by pedological parameters like pH-value substantially larger extent than that of the elements Ni-Cr-Mo-(Co) highly loaded in factor 3 (10,5 % percentage of total variance). Beside geochemical similarities the intake into soil from the same sources is mainly responsible for the common occurrence of those elements finally mentioned. All elements highly loaded in factor 2 and 3 are characterized by a lognormal frequency distribution of their concentrations which is marked to a different degree.

The strongest positive dependence on the pH-value however shows the element Ba (factor 5: Ba-pH; 6,4 % percentage of total variance).

The geochemical behaviour of elements in soil profiles concerning their vertical distribution is mainly determined by pedological parameters (pH-value, organic soil matter and sesquioxides contents, influence of groundwater etc.).

Hierarchical cluster analysis provides a summary of single samples in the following order: soil horizons/soil profiles ---> river ---> river system ---> region. The subregional geochemical

character of the single rivers and river systems selected for investigation is distinctly evident. The flood plain soil profiles of the Spree river (profile D 25; SE-part of the G.D.R.) and the Warnow river (profile B 27; N-part of the G.D.R.) were separated from all other flood plain soils investigated with the greatest Jistance.

In flood plain soils of the southern part of the G.D.R. no indications for an insufficient trace element supply could be found. On the contrary for the low-moor soils widely distributed in the northern part of the country and characterized by a general, partly serious trace element depletion a potential danger of occurrences of diseases in consequence of trace element deficiency for the elements Cu, Cr and Mn is existing. Diseases as a result of trace element deficiency of such a kind were already reported from similar soils of other regions by several authors (MENGEL, 1961).

The estimation of load levels and possibly existing potential risks of intoxications realized by comparison with the limiting values of the concentrations admissible in arable soils after KLOKE et. al. (1984) is problematically on the basis of total concentrations determined and because of the frequently occurring complex enrichment of different elements with partly antagonistic effects.

Finally the Kloke values for the trace elements Cr, Ga, Ni, Ti, V and Zr must be called in question because of their unreal position within the range of or below the Clarke value for soils, respectively, and require a revision.

### summary

The investigation of 20 selected vertical profiles of soil on flood plain and lowland areas allows a characterization of the specific geochemistry of these soils.

Both universal and special regional regularities of element distribution could be derived.

Elements of a high geochemical mobility and with a prevailing anthropogenic part of total intake into soil show a wide range of element concentrations with tendency for accumulation towards the lower course of a river.

On the contrary elements with typically or exclusively geogenic properties are characterized by a narrow range of concentration without any tendencies for accumulation in certain regions in case of the flood plain soils investigated.

## Literature

- Schwermetalldaten der Elbe. Bericht über die Ergebnisse der Schwermetalluntersuchungen im Elbabschnitt von Schnackenburg bis zur Nordsee 1979/80 Arbeitsgemeinschaft für die Reinhaltung der Elbe der Länder Hamburg-Niedersachsen-Schleswig-Holstein-ARGE-ELBE. Hamburg: Wassergütestelle Elbe, 1980
- Baumann, L.; Nikolskij, I.; Wolf, M.: Einführung in die Geologie und Erkundung von Lagerstätten.- 2., durchgesehene Auflage.- Leipzig: VEB Deutscher Verlag für Grundstoffindustrie, 1982.- 503 S.
- Claussen, T.: Schwermetallverunreinigungen in überschwemmungsgebieten von Niederrhein und Ruhr.- In: Umwelt.- Düsseldorf 13 (1983).- S. 426-427
- 4. Kloke, A.; Sauerbeck, D.R.; Vetter, H.: The contamination of plants and soils with heavy metals and the transport of metals in terrestrial food chains.— In: Changing Metal Cycles and Human Health/hrsg. von J. O. Nriagu.— Berlin/West/; Heidelberg; New York; Tokyo: Springer Verlag, 1984.— S. 113-141
- 5. Kovalskij, V.V.M.: Geochemische Ökologie-Biogeochemie (deutschsprachige Ausgabe)/hrsg. von A. Hennig.- Berlin: VEB Deutscher Landwirtschaftsverlag, 1977.- 351 S.
- Mengel, K.: Ernährung und Stoffwechsel der Pflanze. Jena: VEB Gustav Fischer Verlag, 1961. - 322 S.
- Mohr, F.; Luft, B.; Bombach, H.: Bestimmung von Spurenkonzentrationen in hochreinem Phosphor mittels Hydridtechnik am AASiN. Jenaer Rundschau. - Jena (1983) 3.- S. 120-122
- Müller, G.: Sedimente als Kriterium der Wassergüte. Die Schwermetallbelastung des Neckars und seiner Nebenflüsse.- In: Umschau.- Frankfurt/Main 81 (1981) 15.- S. 455-459
- Salomons, Wim; Förstner, Ullrich: Metals in the Hydrocycle.-Berlin/West/; Heidelberg; New York; Tokyo: Springer Verlag, 1984.- 333 S.
- 10. Thornton, İain: Applied Environmental Geochemistry. London; New York; Paris; San Diego; San Francisco; Sao Paulo; Sydney; Tokyo; Toronto: Academic Press, 1983. 501 S.
- 11. Voland, B.; Metzner, I.; Bombach, G.: Zur Selenverteilung in Böden der DDR.- In: Mengen- und Spurenelemente (Teil 1)/hrsg. von Manfred Anke; Christoph Brückner; Herbert Gürtler; Manfred Grün.- Leipzig: Karl-Marx-Universität. 1987.- S. 1-10