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ENVIRONMENTAL GEOCHEMISTRY OF SALT-AFFECTED SEDIMENTS AT THE FEHÉR-LAKE, SZEGED, HUNGARY

Theses of PhD dissertation

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I. PRELIMINARIES, RELEVANCE AND AIMS

The primary aim of the present PhD research was to shed light on the distribution of chemical elements important from an environmental perspective in saline lake sediments, characterised by similar geology but different hydrology and anthropogenic influence. The research also aimed at determining those geochemical and mineralogical factors which may affect prevailing concentration patterns. In relation to the above a further scope of the study was to investigate the heavy-metal adsorption potential of saline lake sediments.

The relevance of the research is supported by the following facts: 1) As a matter of global climatic change larger and larger territories – mainly agricultural – are exposed to the process of salinization, which fundamentally alters geochemical conditions in these areas. 2) Due to an explosive economic growth and progress in the 20th century a significant amount of toxic elements or other physiologically harmful components have been released to the environment, and changed the trace element household of soils almost everywhere on Earth. During the process of salinization the significant reduction of element adsorption capacity as a consequence of geochemical changes in sediments previously having a preferable buffer capacity is a potential hazard. Due to their hydrology and closed sedimentary system saline lakes are sensitive indicators of both salinization processes and anthropogenic pollution, thus they provide an adequate setting for studying the relationship and effects of salinization and trace element accumulation processes.

Although numerous researchers have already addressed the topic of salinization or the distribution of chemical elements important from an environmental aspect, comprehensive studies on the environmental geochemistry of saline sediments are hardly available. Besides, we also have limited information on what geochemical processes determine the distribution, ad- and desorption of chemical elements in saline environments.

The present research aims to provide fundamental results on element adsorption processes in saline, high salt content geochemical environments, and the distribution characteristics of organic and inorganic phases responsible for the immobilisation of trace elements. Besides, the research also introduces several practical results aiding the interpretation of secondary, anthropogenic salinization processes affecting soils under cultivation, and the further investigation of element mobilisation induced by salinization. Beyond their agrochemical importance our results have major implications in terms of thermal water drainage related to geothermal applications and in terms of planning waste dumps and waste disposal.

II. APPLIED METHODS

During laboratory analyses the following parameters were determined for the evaluation of sediment profiles: pH, total electric conductivity, grain size distribution, carbonate content, qualitative and quantitative parameters of the accumulated organic matter, mineralogical composition, clay mineral content, major and trace element composition. The precise evaluation of the large database received during the research also necessitated the application and testing of the most recent geostatistical methods. The assessment of the trace element adsorption features of sediments with different organic matter, clay mineral and carbonate content was also a key task during the laboratory work.

The pH and electric conductivity of sediments was determined by a CONSORT C561 type pH and conductometer, according to the relevant Hungarian standards.

The grain size distribution of 80 representatively selected sediment samples was determined at the Department of Geology and Palaeontology, University of Szeged by a SediGraph 5000ET type grain size analyser.

The carbonate content of 80 representatively selected samples was determined by the Dean-method.

The total organic matter content of sediments and the composition of organic matter was analysed by an Oil Show type Rock-Eval pyrolysator. Following a 3 minute preheat at 180°C the samples were pyrolised until 600 °C by applying a programmed 25 °C/min heating rate. The stabile isotope analysis of carbon and nitrogen was made with an NA 1500 NCS type fission instrument and a Finnigan DeltaPlusXp type mass spectrometer, connected to a Thermo Finnigan ConFlo III type sample digestion unit.

The mineralogical analysis was made with a DRON UM-1 type X-ray diffractometer in the 3-52 (1-16 in case of clay minerals) 2 θ angle interval. The instrument was equipped with a Cu-tube radiation source, a LiF monochromator, a scintillation detector and operated at a 35 kV excitation voltage and 20 ma anode current by applying a 1°/min step rate.

The major and trace element content was determined by a Horiba Jobin Yvon XGT-5000 X-ray fluorescent spectrometer, equipped with a Rh X-ray source. For the measurements a 30 kV excitation voltage and 1 mA anode current and a 100 μm diameter beam was applied. The net measurement time was 60 min/sample.

For trace element adsorption analyses five samples of different composition were selected. From each sample 200 mg of material was suspended separately in 20 ml zinc-, cadmium-, nickel-, lead- and copper-nitrate solutions of different concentrations. The initial metal concentration of the solutions was set to10, 20, 50, 100, 200, 500, 1000, 2000 mg/l.

III. NEW SCIENTIFIC RESULTS

1. **It has been established that beside hydrological effects and vegetation cover, anthropogenic factors can also greatly determine the differences observed in pH and salt content. On areas with dense vegetation cover and moderate ground water fluctuation salt content is significant and pH is highly alkaline. Whereas at sites with intensive anthropogenic water exchange salt content is considerably reduced, thus a kind of artificial leaching can be observed in the sediments**.

The greatest, and in terms of average values an extreme, salt accumulation can be observed in profiles “K” and “X/2” being under a permanent vegetation cover. It is apparent that in these profiles, differences in pH and salt accumulation are determined by water fluctuation and vegetation. While in profile “K”, representing a meadow with moderate water table variation and permanent vegetation cover, a very intensive and narrow salt accumulation zone can be identified, in profile “X/2” being similar in terms of vegetation cover but featured by a more significant water fluctuation the accumulation expands to a 50-60 cm thick zone.

The average pH and salt content of profiles “SZ-2” and “S1” lags far behind the values measured in profiles “K” and “X2”. The underlying reason is fish breeding, which necessitates the seasonal drainage and fresh water recharge of the territory, thus salts moving to the surface due to capillary lifting during the dry period can dissolve. As a consequence, these two profiles are practically leached artificially year by year when dissolved salts are removed from the system by the regular drainage of the lakes.

It has been established therefore that on territories with basically similar geological and mineralogical background the differences in salt content and pH and consequently in geochemical conditions are determined predominantly by anthropogenic influence.

2. **It has been shown that intensive chemical weathering and clay mineral formation can be observed in all of the studied profiles. Feldspars, as a consequence of alkalinity, are present in the form of colloidal, poorly crystallised lattice fragments with decreased adsorption capacity, and they migrate together with the ground water table and easily soluble salts.**

Intensive weathering close to the surface is also expressed by the fact that feldspars occur in horizons below a depth of 100 cm, i.e. they have been transformed or entirely decomposed in the upper sections of the profiles. In each case rubidium exhibits a distribution identical to that of clay minerals and Al, Si, K, Fe and Cu, supporting the fact that feldspars are highly weathered and their products are clay minerals. In such cases the strong adsorption of Rb to clay minerals is obvious in all of the studied profiles. The decomposition of the majority of feldspars in the upper horizons as a matter of intensive weathering processes is driven by the downward migration of salts during inundation periods, since feldspar weathering and clay mineral formation are going to be the preferred processes in the lack of Na^+ and K^+.

Clay mineral formation sediment weathering are simultaneous processes. An important evidence is the distribution of clay minerals which is completely identical to the distribution of Al, Si. K, Fe, Cu in all of the profiles. A further argument for the autigene formation of clay minerals is provided by X-ray diffractogramms resembling mixed and poorly crystallised clay mineral groups in all cases. This also leads to the conclusion that among alkaline conditions primarily lattice fragments develop during the formation of clay minerals. In all cases the vertical distribution of clay mineral groups (kaolinite-chlorite, illite, smectite) was very similar. Based on the investigations, it turned obvious that none of the groups are preferred during clay mineral formation, since the amount of either Mg, K or Na in the upper layers of the sediment is well enough for the formation of any of the groups, and there are also numerous clay minerals with a mixed structure. In profiles “K” and “X/2” each clay mineral group intensively accumulates at a depth of 50 cm. Since this horizon coincides with the accumulation zone of easily soluble salts it is claimed that clay minerals are present in the form of a colloidal, fine fraction material and their distribution is in close relation with variations in the water table.

3. **Based on X-ray diffractional, major and trace element geochemical analyses it has been proven that in case of each profile there is autigene dolomite formation. Dolomite enriches usually below strata of permanent inundation. Most probably it forms during inorganic co-precipitation along with calcite, but at certain areas bacterial formation cannot be excluded either.**

In profiles „K”, „SZ-2” and „X/2” the amount of dolomite starts to increase usually in depths below 100 cm, and it hardly occurs closer to the surface. As a matter of fact dolomite always forms below the ground water table. In case of profile “S1”, under permanent water cover, dolomite already appears on the surface. Based on this, it is claimed that inundation is a very important requirement during dolomite formation. The precipitation of dolomite occurs at the horizon of maximum magnesium concentration, thus increased Mg content is another key prerequisite of dolomite formation.

Since the amount of dolomite increases at the same horizon where the amount of calcite decreases in each case, and in the meantime no extreme changes can be observed in vertical calcite distribution, and increased magnesium concentration coincides with the presence of dolomite, autigene formation can be unambiguously supported, and detrital origin can be ruled out. It can also be established that dolomite formation preferentially occurs below salt accumulation zones, thus it is not affected by high ion strength. In the studied profiles dolomite is formed by inorganic precipitation, i.e. when the water table descends the soil solution gets oversaturated of calcium which in turn precipitates during which Mg enters its crystal lattice.

4. **It has been pointed out that the organic content of Fehér Lake saline sediments is not significant, highest concentrations of TOC do not exceed 2 %, which is far less than usual 10-15 % values characterising other lakes with similar geochemical background. In most of the cases only the top 100 cm of profiles contains a mentionable amount of organic matter. Investigations on the qualitative parameters of organic matter proved that the conditions of sediment accumulation were changing continuously on the Eastern part of the lake system, i.e. exsciccation and inundation periods were alternating throughout the history of the lake. In the uppermost horizons of profiles the effects of fish breeding are unambiguous.**

Very low organic matter content can mainly be explained by poor and scarce vegetation, i.e. the lack of organic rich material being ready to be preserved. Nevertheless, in profiles “K” and “X/2”, being densely vegetated, the amount of organic matter is still quite low and varies between 1-2 %. This observation is related to the characteristics of saline sediments, namely high salt content, alkaline pH and oxic conditions during dry periods. These intensify the degradation of organic matter, which is the most striking in case of profile “S1”. Organic matter accumulation in relation with inundation phases of the lake basin is minimal, and during the subsequent short but dry periods of draining the previously deposited organic material decomposes immediately. It has also been established that the investigated lake sediments primarily contain terrigenous organic matter, indicating that the lake system evolved under similar conditions like today, i.e. dry and wet periods were alternating seasonally, and inundations did not last too long (as in this case sediments should have preserved a larger amount of algaeic origin organic matter), but the lake exsiccated several times or at least water cover became minimal.

In the upper 15 cm of profiles “K” and “SZ-2” both the quality and quantity of organic matter significantly changes. The value of TOC along with the H-index increases considerably, which is the result of water regulation works carried out in the 1970s. The development of a saline meadow over profile “K” contributed to the fast accumulation of immature organic matter, while in case of “SZ-2” the continuous use as a fishery lead to the increase of TOC and HI. It has to be also highlighted that in the upper layers of the sediment the signs of anthropogenic use can be clearly identified.

The upper 100 cm of profiles “K” and “SZ-2” contained a reasonable amount of organic matter to determine the conditions prevailing at their accumulation. Investigations aiming at the qualitative description of organic matter have shown that the Eastern part of the lake system underwent several sedimentation cycles consisting of exsiccation and inundation phases. These alternating periods can be clearly identified with the help of the qualitative parameters of organic matter. Changes in organic matter quality can be observed at similar horizons in case of both profiles, indicating that organic matter quality recorded sensitively the changes in water cover and thus climate. In periods of inundation the degree of humification and algae production increased, while during exsiccation less organic matter could be preserved.

5. **It has been pointed out that the studied profiles are poor in trace elements, and mean concentrations are mostly close to, or below the Hungarian geochemical thresholds. The low trace element content is a result of the geological background, the relatively low level of anthropogenic contamination, and the low quantity of organic matter and clay minerals, having anyway high adsorption capacity.**

   It has been shown that the studied sediments are poor in trace elements for several reasons. Firstly, loess, being the base rock of the lake system, is poor anyway in trace elements, thus surface weathering processes are unable to produce large quantities of these elements. Secondly, the Szeged Fehér Lake is far from great industrial pollution sources, and apparently there are no other anthropogenic activities in the vicinity of the lake system that could endanger the anyway very large catchment in this respect. Thirdly, the operation of the fishery itself can lead to the reduction of trace element content, as by regular water exchange it maintains an artificial leaching process, and by the breeding and trawling of a huge quantity of fish a significant amount of trace elements can be removed from the sedimentary system.

   The most important environmental geochemical reason for the low trace element concentration is the lack of adequate geochemical conditions and those mineralogical and organic material components which could immobilise these elements. The amount of organic components, which can have a major role in the adsorption of elements, is very limited in the sediments. The presence of clay minerals of good adsorption capacity is also low, and moreover, as a consequence of weathering under alkaline conditions most of these minerals are represented by fragmented components with an inadequate crystalline structure, reducing adsorption capacity further. Decreased adsorption capacity is clearly indicated by the fact that no positive correlation can be identified between V, Cr, Cu, Zn, Ni, Pb having high adsorption affinity and the adsorption groups mentioned above. It is also unidentifiable that highly adsorptive Fe- and Mn-hydroxides would have a significant role in the immobilisation processes of Fehér Lake sediments.

6. **It was proven that the element distribution in the alkaline sediments of Lake Fehér is primarily determined by two background processes. The weathering of loess, forming the base rock of sediments, is the most significant factor in this respect. This process is the most relevant in the upper 100 cm zone of the sediment sequence where water table and pH fluctuation is the most intensive. The second background process (water level fluctuation and the migration of highly soluble weathering products) is in close relation with the previous one, and causes salt enrichment also in the upper zone.**

   The correlation between clay minerals and Al, Si, K, Fe, Zn and Rb concentrations has turned to be positive in all cases, however, these elements showed a negative correlation to the amount of Ca, Mg and Sr. This undeniably reinforces the results of mineralogical analyses, i.e. there is an intensive weathering of feldspar and subsequent autigene mineral formation, during which mobile Ca, Mg, Sr (entering the calcite lattice) are leached and separated from the original element composition.

   The results of the main component analysis revealed basically four processes determining element distributions and chemical parameters: weathering of loess, accumulation of salt, formation of dolomite and variation of the red-ox conditions. The most important process in all of the profiles is weathering, which is the most intensive in the upper 100 cm zone of profiles “K”, “SZ-2” and “X/2”. These findings verify previous conclusions on weathering processes.

   The second most important background process is the accumulation of easily soluble salts (primarily Na) in profiles “K”, “X/2” and “S1”. In each case total conductivity is related to the Na content and it is the strongest in the horizons close to the surface. In case of profile “SZ-2” the physical mixing of sediments can be well supported by the means of main component analysis, as processes were the least identifiable here, which is only possible if the fundamental parameters are disturbed by an external process, which is physical mixing in this case.

   The third significant background process is contemporary dolomite formation affecting primarily profiles “S1” and “SZ-2”.

7. **Heavy metal adsorption experiments have shown that both in single and multi element adsorption processes the value of maximum and specific adsorption is low and decreases following the Pb > Cu > Zn > Cd > Ni order due to the low organic**

matter and clay mineral content of the studied samples. In case of a high carbonate content lead, copper and zinc immobilised due to the precipitation of carbonate, while cadmium and nickel was mostly adsorbed by clay minerals. In case of a high organic content all heavy metals were primarily bound by the organic matter. When there was an increased salt content copper, nickel and in certain cases zinc remobilised from adsorption surfaces if their initial solution concentration was high.

Both the single element and competitive adsorption reactions of heavy metals can be adequatly described by the Langmuir-type isotherm. Adsorption curves refer to several different immobilisation processes at the different elements and samples. Precipitation, surfacial precipitation, adsorption, and in case of higher initial concentrations the desorption of previouly bound heavy metals are the key processes in general. Multi element adsorption reactions can aslo be well defined by the Langmuir-isotherm. It can be observed that in case of lead and copper the fitting is better than in case of nickel, zinc and cadmium. This can be traced back of the different adsorptive character of these elements. While lead and copper are highly susceptible to immobilisation, nickel, zinc and cadmium show decreased immobilisation potential in a competitive situation.

Changes of pH experienced both during single element and multi element reactions indicate that each of the studied heavy metals in each sample was bound very quickly, as usually from the 3rd hour of adsorptoin the pH of the equlibrium solutions got stabilised. This is partly caused by precipitation processes and the prevailing alkaline pH, since under these conditions the adsorption of the studied elements increases significantly.

It was proved that however the investigated sediment samples effectively immobilised the total heavy metal content up till a 200 mg/L initial concentration, in case of a more intensive contamination, adsorption would be highly limited by the relatively high Na content of the sediments. A further risk can be related to carbonate, which on the one hand immobilises effectively lead, copper, and in certain cases zinc, but carbonates can dissolve intensively which leads to the remobilisaton of previously adsorbed heavy metals. In case of lower initial concentrations copper and zinc is effectively immobilised in a highly saline, carbonate free environment, whereas at higher concentrations by the entrance of sodium ions into solution previously bound heavy metals are forced to remobilise.

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