

Speciation of Elements in Lake Sediments Investigated Using X-Ray Fluorescence and Inductively Coupled Plasma Atomic Emission Spectrometry

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Radioisotope-excited energy-dispersive x-ray fluorescence (EDXRF) analysis and inductively coupled plasma atomic emission spectrometry (ICP-AES) were used to investigate the speciation of elements in sediment samples collected from a peat bog in Hungary. Lake and bog sediments are a mixture of allogenic material (clastic mineral particles resulting from erosion of the catchment soils or from dust) and authigenic components (deposited directly from aquatic solution through biological uptake or chemical sorption, biochemically precipitated carbonate minerals, Fe and Mn oxides, oxyhydroxides, sulphides, sulphates, phosphates, etc.). After removing the authigenic fraction by wet digestion, element concentrations in the acid insoluble residue were determined by XRF and those in the authigenic part by ICP-AES. On the basis of chemical composition, the sediment sequence was divided into three zones reflecting different environmental regimes during sediment accumulation. Allogenic and authigenic species of elements provided relevant information on environmental processes which changed the soil and vegetation in NE Hungary during the early postglacial. © 1988 John Wiley & Sons, Ltd.

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INTRODUCTION

X-ray fluorescence (XRF) analysis is widely used for the determination of the element content in environmental samples.¹ As this technique is not capable of discriminating between different chemical forms of the elements, usually the total amounts of the elements present in the sample are investigated.² The information derived from bulk analysis is generally very important and useful in characterizing environmental processes. For example, the heavy metal content of environmental samples is considered to be a good indicator of anthropogenic pollution of the environment.³ On the other hand, measuring only the total content of the elements may mask some valuable information. In many cases, important additional information can be derived from the analysis of the different chemical phases of the samples, revealing the causes of environmental processes which would remain undetected on determining only the total content of the elements in question.

In the present work, radioisotope-excited energy-dispersive (ED) XRF analysis and inductively coupled plasma atomic emission spectrometry (ICP-AES) were used to investigate the speciation of elements in sediment samples collected from a peat bog in Hungary.

Lake and bog sediments are a mixture of materials which can be classified according to their origin. Components derived from outside the lake proper are termed allogenic, whereas those deposited directly from aquatic solution through biological uptake or chemical sorption and precipitation are designated authigenic⁴. Authigenic components include biochemically precipitated carbonate minerals, Fe and Mn oxides, oxyhydroxides, sulphides, sulphates, phosphates, etc. In contrast, the allogenic fraction consists entirely of clastic mineral particles resulting from erosion of the catchment soils or from dust. In most paleo-environmental studies the authigenic part is removed by acid digestion.^{3,4} The insoluble residue is fused with lithium metaborate or sodium hydroxide,^{4,5} then solutions are analysed using atomic absorption spectrometry (AAS) or ICP-AES. However, the allogenic part can be measured directly by XRF after removing the authigenic fraction by wet digestion, while the authigenic part is analysed by ICP-AES. To demonstrate the potential of the method in investigating environmental processes, we analysed sediment samples from Kis-Mohos, a small peat bog situated in a narrow valley in NE Hungary.

EXPERIMENTAL

Two continuous sedimentary sequences of length 879 cm were obtained from Kis-Mohos peat bog using a modified 5 cm diameter Livingstone piston corer.⁶ This

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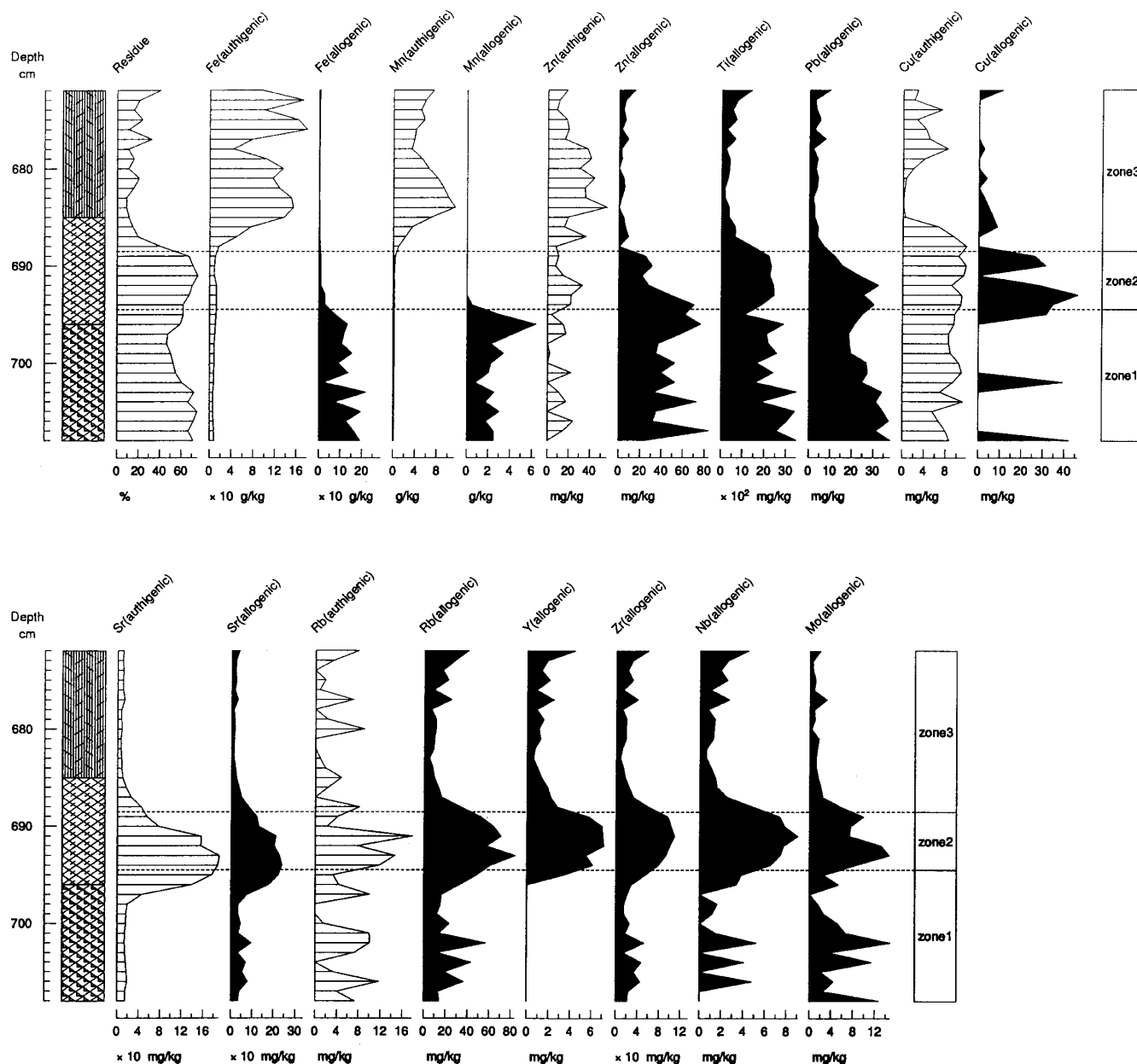


Figure 1. Physical characteristics and elemental compositions from the Kis-Mohos sediment plotted against depth. The allogenic fraction (filled) was determined using XRF and the authigenic fraction (open) using ICP-AES. Sediment type: ~ 685 cm, Th3Dg1 = *Turfa herbacea* with *detritus granulosus*, fibrous peat with visible plant remains; 685–696 cm, Ld2Dg2 = *Limus detrituosus* with *Detritus granulosus*, Lake mud with detritus; 696–710 cm, Ld2As2 = *Limus detrituosus* with *Argilla steatodes*, Lake mud with silt.

small peat bog (ca. 60 m diameter) has no inflowing or outflowing streams. The surrounding slopes are covered with an acidic non-podzol brown forest soil upon which is situated a mixed deciduous woodland. The climatic, geological and historical characteristics of the site are given in detail elsewhere.⁷

Pollen analysis was carried out on the first and chemical analysis on the second sedimentary sequence. Both sequences were radiocarbon dated by bulk and accelerator mass spectrometric (AMS) analysis. The relative standard deviations of radiocarbon dates were $<5\%$. The time-scale for the sediment section was published previously;⁷ radiocarbon ages in this paper are expressed as calibrated years before present (yr BP). Results from the 13 radiocarbon dates indicated a linear relationship of sediment deposition with time. The sediment section between 708 and 672 cm was subsampled

at 1 cm intervals, making 37 samples overall. Radiocarbon ages of the different subsamples were calculated from the linear relationship mentioned earlier. The sediment type was identified and described according to Troels-Smith.⁸

The element content representing the authigenic part was investigated by ICP-AES after acid digestion as described elsewhere.⁷ The acid-insoluble residue, representing the allogenic part, was analysed by XRF analysis after homogenization in an agate mortar. Pressed pellets of 10 cm diameter and $50\text{--}150\text{ mg cm}^{-2}$ weight were prepared for the x-ray measurements.

ICP-AES measurements were carried out with a Spectroflame instrument (Spectro Analytical Instruments, Cleve, Germany) in the simultaneous multi-element and sequential operation mode. Excitation was performed with a 27.12 MHz r.f. generator at 1.05 kW

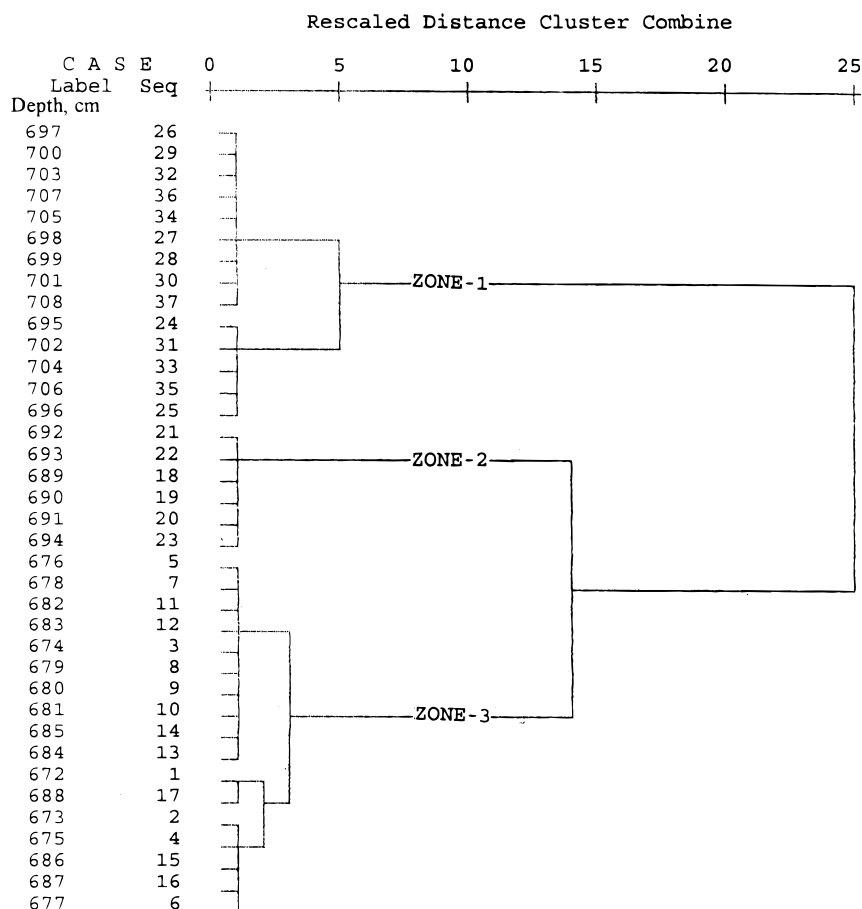


Figure 2. Dendrogram using the Ward method. Individual samples were classified by cluster analysis based on principal component scores.

energy, and nebulization with a cross-flow nebulizer using Ar at 0.6 l min^{-1} as nebulizing gas, at 1.5 l min^{-1} as cooling gas and at 4.0 l min^{-1} as plasma gas. Both the line and the background intensities were integrated for 25 s. Two-sided background correction was applied.

An Si(Li) detector (made at the Nuclear Research Centre of the Hungarian Academy of Sciences, Debrecen, Hungary) with 200 eV FWHM at the Mn $K\alpha$ line

and an IBM AT compatible computer with an S100 MCA card (Canberra) were used for the XRF measurements. Characteristic x-rays were excited by an annular ^{125}I radioisotope source. Live time was $>95\%$. Net peak intensities were determined with AXIL software. The elemental sensitivity (AXIL) and the emission transmission methods were used for the calculation of concentrations.

Table 1. Average composition of zones 1–3

Component	Zone 1	Zone 2	Zone 3
Residue (%)	61 ± 5	69 ± 4	19 ± 5
$\text{Fe}_{\text{Authigenic}}$ (g kg^{-1})	8.3 ± 0.9	11 ± 1.5	112 ± 23
$\text{Fe}_{\text{Allogenic}}$ (g kg^{-1})	129 ± 28	16 ± 9	2.0 ± 0.6
$\text{Mn}_{\text{Authigenic}}$ (g kg^{-1})	0.18 ± 0.01	0.24 ± 0.05	6 ± 1
$\text{Mn}_{\text{Allogenic}}$ (g kg^{-1})	2.8 ± 0.7	0.08 ± 0.07	<0.001
$\text{Zn}_{\text{Authigenic}}$ (mg kg^{-1})	9 ± 5	18 ± 7.5	26 ± 7
$\text{Zn}_{\text{Allogenic}}$ (mg kg^{-1})	50 ± 10	37 ± 15	5 ± 2
$\text{Ti}_{\text{Allogenic}}$ (g kg^{-1})	2.4 ± 0.4	2.2 ± 0.2	0.5 ± 0.2
$\text{Pb}_{\text{Allogenic}}$ (mg kg^{-1})	35 ± 13	23 ± 6	4 ± 1
$\text{Cu}_{\text{Authigenic}}$ (mg kg^{-1})	8.8 ± 0.8	10.6 ± 0.7	4 ± 1.7
$\text{Cu}_{\text{Allogenic}}$ (mg kg^{-1})	8 ± 8	28 ± 12	2 ± 1
$\text{Sr}_{\text{Authigenic}}$ (mg kg^{-1})	39 ± 27	137 ± 46	13 ± 4.5
$\text{Sr}_{\text{Allogenic}}$ (mg kg^{-1})	74 ± 31	189 ± 40	27 ± 8.5
$\text{Rb}_{\text{Authigenic}}$ (mg kg^{-1})	5 ± 2	10 ± 5	3 ± 2
$\text{Rb}_{\text{Allogenic}}$ (mg kg^{-1})	26 ± 8	65 ± 9	16 ± 5
$\text{Y}_{\text{Allogenic}}$ (mg kg^{-1})	<0.5	6.4 ± 0.6	1.7 ± 0.5
$\text{Zr}_{\text{Allogenic}}$ (mg kg^{-1})	30 ± 8	97 ± 8	26 ± 7
$\text{Nb}_{\text{Allogenic}}$ (mg kg^{-1})	2 ± 1	7.6 ± 0.7	1.9 ± 0.6
$\text{Mo}_{\text{Allogenic}}$ (mg kg^{-1})	5 ± 2	10 ± 2	1.6 ± 0.6

Element concentrations were expressed on a sediment dry matter basis. Element concentrations were plotted against sediment depth using Psimpoll 2.25.⁹ Correlations among elements and element species were evaluated using principal components analysis (PCA).¹⁰ Individual samples were classified by cluster analysis based on principal component scores.¹⁰

RESULTS

The elemental content of the sediment samples is given in Fig. 1(a) and (b). Radiocarbon ages indicated on the figures were calculated assuming constant sediment deposition with time, as mentioned earlier. On the basis of chemical composition plotted against depth, the sediment sequence was divided into three zones (Fig. 2). The mean concentrations of the zones are given in Table 1.

In zone 1 (708–695 cm, 9920–9540 yr bp), 61% of the sediment was made up of the acid-insoluble residue (allogenic part), with concentration peaks of Fe, Mn, Zn and Pb. Fe, Mn and Zn in the authigenic fraction showed minimum concentrations [see Fig. 1(a) and (b)].

In zone 2 (695–688 cm, 9540–9330 yr bp), the acid-insoluble residue was high (69%) and some elements in the allogenic fraction had peak concentrations: Cu, Sr, Rb, Y, Zr, Nb and Mo. Authigenic Sr and Rb had concentration maxima. The concentration of authigenic Cu and Zn in this zone was higher than in zone 1.

In zone 3 (688–672 cm, 9330–8870 yr bp), the contribution of the residue was markedly lower (19%) and the authigenic part became dominant (Fe, Mn, Zn). Most elements in the allogenic fraction had concentration minima.

PCA revealed two principal axes representing 78% of the sample variation. The first principal axis comprised the acid insoluble residue, the allogenic Fe, Mn, Pb, Zn and Ti, which had a strong positive correlation. This indicates the presence of unweathered siliceous particles in the sediment. However, this principal axis also included authigenic elements such as Fe, Mn and Zn, being negatively correlated with the former variables, except authigenic Cu, which showed a positive relationship.

The second principal axis involved the allogenic Y, Zr, Nb, Rb, Sr, Mo and Cu and authigenic Sr and Rb. These elements had a single concentration peak in zone 2.

DISCUSSION AND CONCLUSION

XRF analysis combined with ICP-AES proved useful in modelling the environmental processes which changed the soil and vegetation in NE Hungary during the early postglacial. Most of our knowledge of soil development is based on observations of contemporary phenomena.¹¹ Many data are available on the diversity of soils developed in different vegetation zones, under varied climatic conditions and often on considerably different parent material. However, relatively few data

are available on the course of soil development over time. Particularly little is known of how closely soil change follows major climatic change. In the case of Kis-Mohos, chemical analysis of the lake sediment sequence allowed us to reconstruct the development of the soil of the surrounding slopes as the chemical composition of the sediment represents mainly elements from the surrounding soils carried into the basin by overland flow, throughflow and precipitation. Concentrations of elements entering the lake from the atmosphere are thought to be low.

It is clear from Fig. 1(a) that the origin of Fe, Mn and Zn is different in the sediment samples from different depths. The high concentrations of allogenic Fe, Mn, Zn, Ti and Pb in the samples originating from the 708–695 cm layer indicate that unweathered mineral particles had been transported to the basin. Under a cold climate around 9920–9540 yr bp the physical weathering of the soil parent material was probably the dominant environmental process. Since small amounts of authigenic elements deposited in the sediment, it can be inferred that the soil was shallow and poor in organic matter, probably a podzol type of late glacial age.⁷

The steep decline of allogenic Fe and Mn and the gradual decrease in allogenic Ti, Pb and Zn in samples from the 695–688 cm sediment section reflect that major changes occurred in the catchment around 9540–9330 yr bp. The peak of authigenic Sr indicates that Sr, having accumulated in the leaf litter of the coniferous forest,⁷ leached into the lake after litter decomposition. Allogenic Sr, Rb, Y, Zr, Nb and Mo show intense erosion on the surrounding slopes. This agrees with evidence of a major wildfire which destroyed the coniferous woodland.⁷ These elements also indicate that weathering of the parent material of the soil, rich in silicates, intensified. The XRF analysis of the allogenic fraction demonstrated that during soil development Fe, Mn, Zn and Pb leached from the silicate matrix. ICP-AES analysis of the authigenic fraction showed that these elements transported to the lake water as aqueous solution, precipitated and deposited in the sediment. This process became predominant when deciduous forest established and replaced the coniferous woodland around 8870–9330 yr bp.

Table 2. Detection limits (mg kg⁻¹) for the elements measured

Element	XRF	ICP-AES
Fe	200	0.4
Mn	150	0.08
Zn	4	0.8
Ti	200	1.5
Pb	3	5
Cu	5	0.5
Sr	2	0.05
Rb	4	5
Y	1	0.5
Zr	2	0.5
Nb	1	1
Mo	1	1.5

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