

Natural and anthropogenic influences on the geochemistry of Quaternary lake sediments from Holzmaar, Germany

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Abstract The accumulation of heavy metals and trace elements has been investigated in a well laminated sequence of Holocene and late Pleistocene lake sediments composed of diatomaceous gyttja, tuff and silt and clay sediments. Varve chronology of the annually deposited gyttja yielded a continuous high-resolution time sequence and allowed the absolute age dating of the sediment. Fluxes of elements remained largely uniform from the late Pleistocene into the Holocene (12 867–2364 VT years ago; VT: varve time, years before 1950). Higher trace element and heavy metal fluxes occur from 2322 to 862 VT years ago and reached their maxima in the uppermost sediments (<845 VT years ago). These increasing element fluxes correlate with increasing inputs of clastic material. The changing accumulation rates are the result of elevated soil erosion in the lake catchment caused by human settlement, deforestation and agricultural activities. Thus disturbances of the natural geochemical cycles of the Holzmaar region have occurred since the beginning of the Iron Age and especially since the beginning of the Middle Ages.

Key words Lake sediments · Heavy metals · Geochemistry · Element fluxes

Introduction

The chemistry of lake sediment is a function of the flux and chemical characteristics of detritus from the watershed to the depositional site and the proportions of inorganic and organic material incorporated into the sediment (Norton and others 1992). Allochthonous atmospheric materials can also be added to the sediments from industrial activities and combustion of fossil fuels. Methods to recognize the anthropogenic influence include the investigation of samples deposited in discrete sedimentary layers (for example, Nriagu and others 1979; Oldfield and others 1980; Farmer and others 1980). Down core variations in pollutant concentrations in dated sediments can yield information about the temporal changes in pollutant inputs to a particular sedimentary environment. However, the chemistry of sediments may be modified after deposition by bioturbation, diagenesis, and changes in the pH of the overlying water column; the interpretation of such chemical stratigraphies can be exceptionally difficult.

This contribution documents a detailed chemical stratigraphy obtained on Quaternary lake sediments from the Holzmaar, Eifel, Germany (Fig. 1). The sediment has been deposited as identifiable varves which allow a high-resolution time sequence for the Holocene and late Pleistocene (Negendank 1989; Zolitschka 1989; Negendank and others 1990). The chemical data provide information on the temporal changes in element fluxes to a sedimentary trap due to natural processes and anthropogenic activities in the last 13 000 years.

Geological setting

The Holzmaar is located 100 km south of Bonn, in the West Eifel Volcanic Field (Fig. 1). This area is characterized by abundant Quaternary ash, cinder cones, and craters. Some of the craters including the Holzmaar, are filled with water. Phreatomagmatic volcanism is thought to be responsible for the formation of the Holzmaar. The crater developed on the palaeosurface of the Rhenohercynian basement comprising Devonian low-grade metamorphic slates, greywackes and quartzites. Formation of the crater probably occurred between 40 000 and 70 000 years BP (Büchel 1984).

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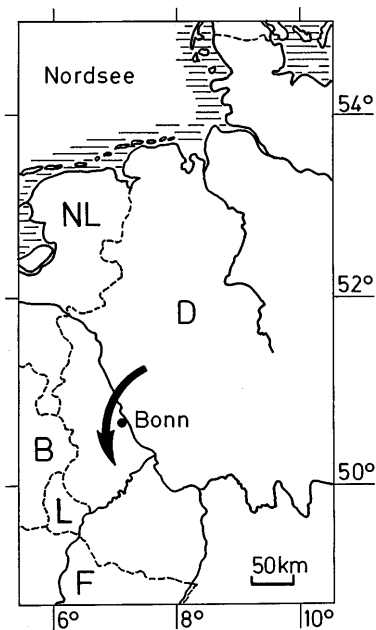


Fig. 1

Location map of the Holzmaar

Volcanism in the West Eifel was of a silica-undersaturated, alkali-rich nature with xenoliths of ultramafic and carbonatitic compositions, suggesting the parent magma(s) was derived from mantle sources (Frechen and Thiele 1979; Mertes 1983). The volcanics are phonolites, basanites and tephrites, and foidites (Mertes 1983). Such volcanics have also been found as country rocks within the immediate periphery of the Holzmaar. In addition, soils of the West Eifel Volcanic Field contain volcanic material from various volcanic eruptions including the Laacher See Tephra. The Laacher See Tephra is a late Quaternary marker bed, widespread in central and northern Europe, which resulted from the instantaneous explosive eruption from the Laacher See volcano (Bogaard and Schmincke 1985).

Ingress of water occurred after crater formation and the Holzmaar developed as a local sedimentary trap. Hydrological inputs occur via atmospheric deposition, groundwater, and surface run-off from the immediate periphery of the crater lake. A small creek is an insignificant source of water, solids, and dissolved material (Sammetbach; Fig. 2). The Devonian country rocks are largely impermeable. However, subsurface fissures are likely present within the basement which could provide channels for limited groundwater movement.

The lake has a catchment of 2.06 km² (Scharf 1987; Fig. 2). Current dimensions of the crater and the enclosed lake are as follows: crater depth 26–51 m, diameter 450 m by 300 m (Noll 1967); crater lake surface area 58000 m², maximum water depth 20 m, mean water depth 11 m (Scharf 1987). Current oxygen concentrations in the water column generally decrease with depth (0 mg/L at 15 m depth; Haaren 1988). The lack of bioturbation in sedi-

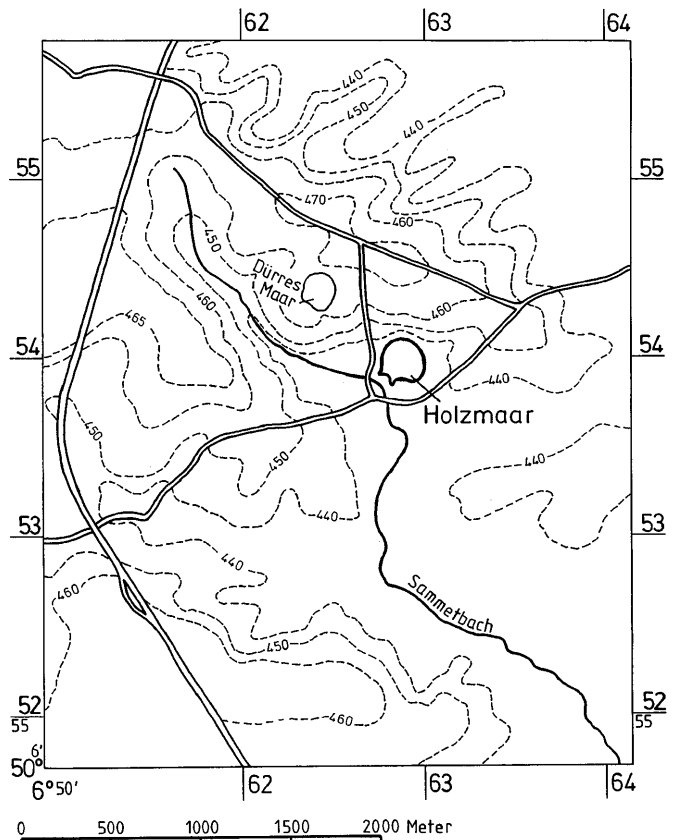


Fig. 2

Topographic map of the Holzmaar region with contour lines and major roads

ments from the deepest area and the preservation of diatomaceous varves indicate anoxic bottom waters since the late Pleistocene (Negendank and others 1990).

Holzmaar sediments

Sediments within the lake are well laminated with the lower part consisting of graded clastic sediments (rhythmites) and an upper part of diatomaceous gyttja and tuff layers (Fig. 3; Negendank 1989; Zolitschka 1989; Negendank and others 1990). Sedimentation was apparently continuous. Turbidites within the sediment column are rare and only present in the lower part of the sequence. Thin sections revealed that the gyttja is laminated on a mm-scale. Individual laminae generally consist of several varves: chrysophyta cysts (early spring), diatoms (spring), calcite (summer), vivianite and organic matter (autumn), and silt-clay-sized particles (winter; Zolitschka 1989). Using these varves and diatomological and palynological investigations, we have dated every layer within the entire gyttja sequence (Zolitschka 1989, Fig. 3). The sediments have a minimum thickness of 29 m with annual sedimentation rates ranging from 0.4 to

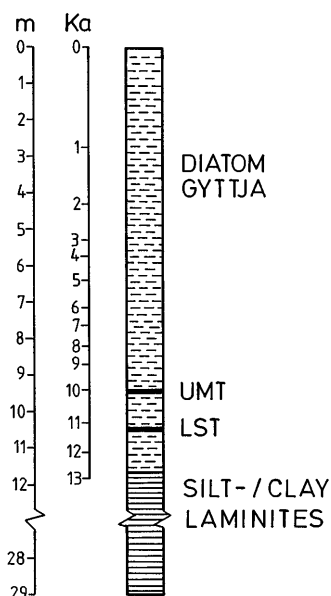


Fig. 3

Simplified stratigraphic column of the Holzmaar sediments showing depth and varve chronology. UMT: Ulmener Maar Tephra; LST: Laacher See Tephra

12.0 mm (Zolitschka 1989). Tephra layers, the Ulmener Maar Tephra (UMT) and the well-documented isochronous Laacher See Tephra (LST), occur within the sedimentary sequence and range from a few mm (UMT) to several cm in thickness (LST; Fig. 3). Both tephra horizons are from volcanic eruption centres which are located in the immediate vicinity; NE of the Holzmaar. Dating by varve chronology gave an age for the Ulmener Maar Tephra of 10 170 VT years (VT: varve time, years before 1950). The Laacher See Tephra has been dated radiometrically by various authors at different locations at 11 000–11 400 years BP; varve chronology yielded an age of $11,200 \pm 120$ VT years (Zolitschka 1989). Sediment cores were taken from the deepest part of the Holzmaar and consist of inorganic (amorphous and crystalline Fe- and Mn-oxhydroxides, volcanic glass, opal, quartz, kaolinite, montmorillonite, biotite, illite, chlorite, olivine, augite, feldspars, and authochthonous calcite, vivianite and siderite) and organic sediment fractions as determined by X-ray diffractometry (XRD) and optical microscopy studies. Inorganic sediment particles are present as individual minerals or as fragments of country rocks (sand- and siltstones, greywackes, shales, quartzites).

Materials and methods of analysis

Sampling and sample preparation

Sediments were recovered by Negendank and Zolitschka in 1984 with a modified Livingstone piston corer (Negendank 1989) in three parallel and overlapping cores. Cores

were retrieved from the center of the lake and stored at 4 °C. In 1990, 216 samples of 2-cm thickness were chosen at 2–4-cm intervals. The extended storage and evaporation made investigations of pore waters impossible. In addition, analytical techniques required several grams of starting material, and thus most samples represent 5–20 years of sediment deposition. Samples were dried at 60 °C for 48 hours and then ground in an agate mill. These powdered samples were then used for total, partial, and sequential element analyses. Gytja sediments and tephra layers were also analyzed for their major mineralogical composition by XRD. Sixteen handspecimens of Devonian metasediments were collected in the immediate vicinity of the Holzmaar and subsequently prepared for X-ray fluorescence (XRF) analysis. Detailed mineralogical and chemical data may be obtained from the senior author.

Total element analyses

Sediments were analyzed by XRF for Fe, Mn (0–253 cm sample depth) and trace elements (Ba, Co, Cr, Cu, Ga, Nb, Ni, Pb, Rb, Sr, V, Y, Zn, Zr) (0 to 1,189 cm sample depth) at the University of Mainz. Total element concentrations were determined in order to compare the composition of the Holzmaar sediments with the chemistry of the Laacher See and Ulmener Maar tephra, the surrounding country rocks, and the sum of the eluents and residuals of the extraction analyses, and to calculate total element fluxes into the lake. Organic sulphur (S_{org}), total sulphur (S_{total}), organic carbon (C_{org}), and total carbon (C_{total}) concentrations were determined using a Leco C/S-225 analyser at the University of Mainz.

Partial and sequential extraction analyses

Partial and sequential extraction studies provide an insight into the speciation of elements in the sediments (Schütz 1993; Boenecke 1993). They can also provide indirect information about the early diagenetic exchange of elements between the various sediment particles, and about possible mobilization and transportation processes for elements during early diagenesis. This study documents analytical results of two extraction techniques. The first extraction analysis was performed on samples of the uppermost 253 cm of the sediment column. The analytical procedure largely follows that of Tessier and others (1979) and Salomons and Förstner (1980), using the following sequence of chemical reagents: $MgCl_2$, NaOAc, $NH_2OH-HCl$, $NH_4Ox-HOx$, $HNO_3-H_2O_2$ and $HF-HClO_4-HNO_3$. The extractants were analyzed for Cr, Cu, Ni and Zn by graphite furnace atomic absorption spectrophotometry (GAAS). The wet chemical extraction procedure allowed the differentiation between exchangeable, carbonate, easily reducible Mn^{2+} , strongly reducible Fe^{2+} , oxidizable organic phases and sulphides, and residual heavy metal fractions. The successive extractions are assumed to remove individual phases of the material selectively, while causing relatively insignificant dissolution of other phases. However, it is obvious that these differentiated wet chemistry analyses are associated with several problems (Rendell and others 1980; Tipping and oth-

ers 1985; Förstner 1986): (a) the reactions involved in the leaching procedures are not selective; (b) readsorption and precipitation processes may occur; and (c) sample preparation, including drying, commonly causes transformation of labile phases to more stable components. In addition, the effects of long-term storage (7 years) of the investigated sediments on the speciation of metals are unknown. In spite of these limitations, sequential extraction analysis gives information on the relative speciation of metals within solid products of the Holzmaar sediments (Belzile and others 1989).

The second extraction analysis used a H_2O_2 - HNO_3 mixture (Boenecke 1993). Sediment samples of 1 g were extracted with 6 ml of 0.02 M HNO_3 and 8 ml 30% H_2O_2 adjusted to a pH of 2 with HNO_3 . The mixture was heated to 85 °C for 4 h. After cooling the sample was diluted to 20 ml and centrifuged at 5000 rpm for 30 min. The supernatant was removed, diluted to 50 ml and analyzed for Cr, Cu, Ni, Pb and Zn by flame atomic absorption spectrophotometry (FAAS) (Cr_{org} , Cu_{org} , Ni_{org} , Pb_{org} , Zn_{org} ; heavy metal concentrations in the oxidizable sediment fraction). In addition, residues from the extractions have been dissolved in a HF - HNO_3 - HClO_4 mixture and analyzed for heavy metals by FAAS in order to evaluate the extraction technique. The H_2O_2 - HNO_3 treatment was intended to extract metals which are principally attached to the organic material. However, the high acidity may have caused some leaching of silicate minerals. Dissolution of sulphides likely occurred, but the sulphide concentrations of the sediments are exceptionally low (S_{total} of 98 samples; min = 0.01 wt%, max = 1.66 wt%, arithmetic mean = 0.47 wt%, standard deviation $\pm 1\sigma = 0.47$ wt%). In addition, the applied extraction procedure leaches metals from clays, Mn^{2+} and Fe^{2+} particles. Similar extractions have been performed by other authors in order to destroy organic material in sediments and to liberate metals attached to these particles for further analysis (Papp and others 1991). Repetitive processing of several different sediment samples gave the precision of the partial extraction and FAAS techniques. Standard deviations ($\pm 1\sigma$) from the arithmetic mean value are for less than 10% Pb_{org} and generally less than 3% for Cr_{org} , Cu_{org} , Ni_{org} and Zn_{org} .

Geochemistry

Total element concentrations

Iron oxide (Fe_2O_3) and MnO concentrations of the gyttja sediments ranged from 6.2 to 10 wt% and 0.09 to 0.31 wt%, respectively (Fig. 4). Iron and Mn concentrations do not correlate with any of the analyzed heavy metals. Sediments from the lower part of the sediment column tend to have slightly higher Fe_2O_3 and MnO concentrations than those at the top of the sequence. Concentrations of S_{org} , S_{total} , C_{org} and C_{total} ranged as follows: S_{org} : 0.001–0.42 wt%; S_{total} = 0.01–1.66 wt%; C_{org} = 1.74–8.2 wt%; C_{total} = 2.03–10.1 wt% (Fig. 4). Silt

and clay laminae from the bottom of the sequence had distinctly lower S_{total} and C_{total} concentrations than the overlying gyttja sediments. Concentrations of S_{total} and C_{total} have similar profiles over the entire sequence and there are positive correlations between S_{org} and C_{org} ($r^2 = 0.5$) and between S_{total} and C_{total} ($r^2 = 0.5$). Concentration profiles of C_{org} and C_{total} largely correspond to the C_{org} profile detected in the lake sediments of the Meerfelder Maar (20 km SW of the Holzmaar; Negendank and others 1990). The analytical technique did not allow differentiation between allochthonous and autochthonous C_{org} ; however, the delicate layering of the varves with seasonal variations in microfossils suggests that most of the C_{org} is autochthonous in origin.

The trace elements (Ba, Co, Cr, Cu, Ga, Nb, Ni, Pb, Rb, Sr, V, Y, Zn, Zr) show variations throughout the profile, and horizons with volcanoclastic material have pronounced concentration changes for individual elements (Fig. 4). At a depth of 1087–1075 cm, layers of the Laacher See Tephra have lower Cr, Cu, Ni and V; and higher Y, Ga, Ba, Sr and Nb values compared to those of the underlying gyttja. Similarly, at a depth of 965–958 cm layers of the Ulmener Maar Tephra have lower V, and higher Ga, Ni, Zn and Y concentrations than the underlying organic varves. These compositional differences are a result of different magmatic sources and reflect the phonolithic composition of the Upper Laacher See Tephra and the more basic, nephelinitic nature of the Ulmener Maar Tephra (Zolitschka and others 1995).

Gyttja deposits above the tephra horizons have variable trace element concentrations (Fig. 4). Most trace elements and heavy metals show a strong increase in concentration from a depth of 253 cm to the top of the stratigraphic profile. In addition, some elements (for example, Ni, Pb, V, Zn, Zr) reach their maxima in the uppermost layers of the sequence. Sediments deposited above 253 cm have higher mean Co, Cr, Ga, Nb, Ni, Pb, Rb, V, Y, Zn, and Zr, and lower mean Ba, Cu and Sr concentrations than those deposited below this level (Table 1).

Sequential extraction

The heavy metal data are presented as the mass of the extracted species divided by the mass of the particular fraction (for example, Pb in residual fraction/mass of residual fraction). Such a presentation illustrates the percentages of metal distributions in one sample. The calculations indicate that Cu, Cr, Ni and Zn are preferentially associated with the Fe^{2+} fractions and the organic material and sulphide particles. Large amounts of Ni are also bound to the adsorptive phases of each sample (Fig. 5). The carbonate, Mn^{2+} , and residual fractions generally contain smaller amounts of heavy metals compared to the other extractable forms.

The heavy metal data are also presented as the mass of the extracted species divided by the mass of the entire starting material before sequential extraction (1g for all samples; for example, Pb in residual fraction/1g). Such a presentation illustrates the behaviour of one heavy metal in the same fraction of all samples. Relative proportions

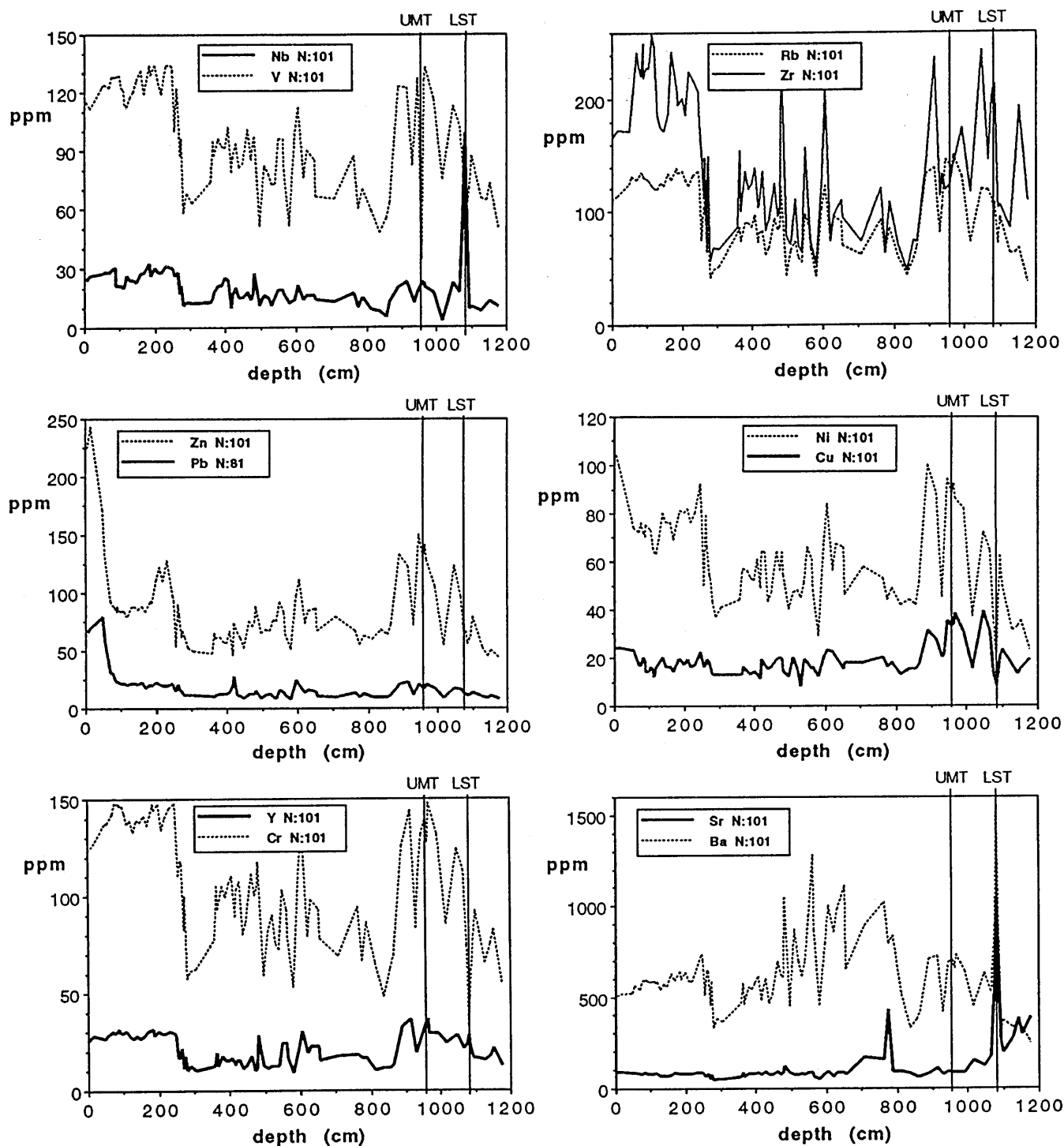


Fig. 4

Depth profiles of total element concentrations within the Holzmaar sediments. The positions of the Ulmener Maar Tephra (UMT) and Laacher See Tephra (LST) are indicated. Total Fe and Mn contents are given as Fe_2O_3 and MnO

of separated metals in the residual phases remain largely constant (Fig. 6). Above 69cm the carbonate and Mn^{2+} particulate forms of Zn and the adsorptive particulate form of Ni increase (Fig. 6). In contrast, Cu and Cr do not change in their particulate fractions. Thus, higher percentages of labile Zn and Ni occur in recent sediments than in deeper sediments.

Below approximately 200cm a discontinuity occurs in the Fe^{2+} , and organic and sulphide fractions. Whereas approximately 5–15% of Zn, Cr and Ni are found in the

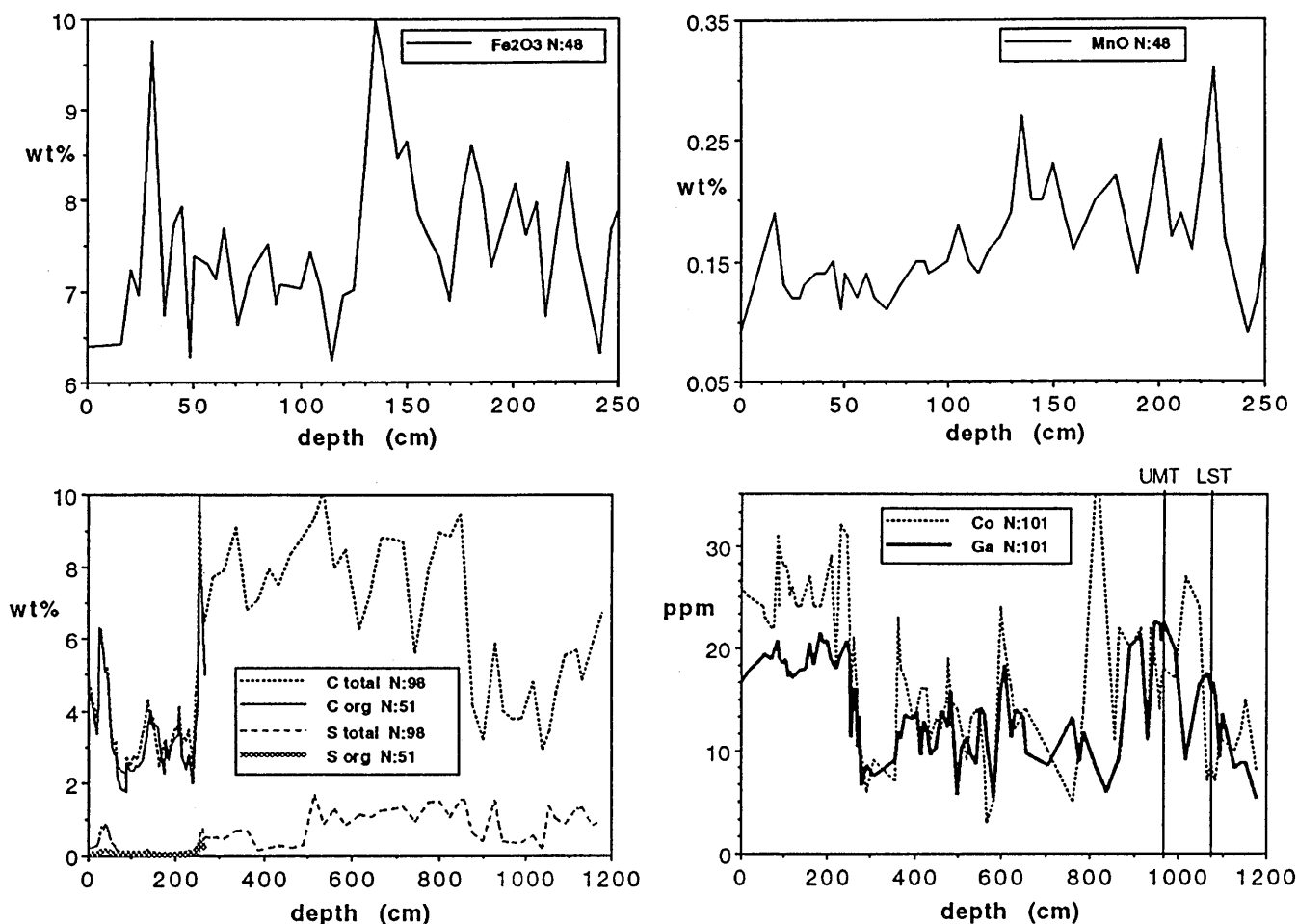


Fig. 4
(Continued)

Table 1
Trace element concentrations in Holzmaar sediments

Number of samples analyzed	27		74	
	Depth (cm)		Depth (cm)	
	Less than	253	Greater than	256
	x	s	x	s
(ppm)				
Ba	589	51	627	248
Co	26	3	14	6
Cr	140	6	94	26
Cu	18	3	19	7
Ga	19	1	13	4
Nb	26	4	19	14
Ni	77	9	55	17
Pb	28	17	13	4
Rb	127	7	87	28
Sr	78	6	141	167
V	124	7	86	22
Y	29	2	19	8
Zn	107	42	74	24
Zr	209	29	134	72

x: arithmetic mean; s: standard deviation ($\pm 1\sigma$)

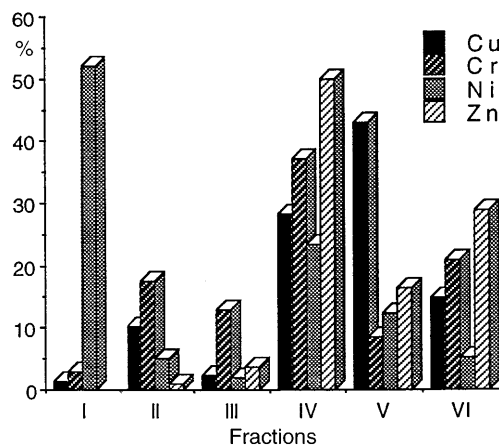


Fig. 5
Calculated proportions of Cr, Cu, Ni and Zn in each of the sequential extraction fractions for sample 50 (251–253cm depth). Metal calculations have been based on the mass of each extracted fraction (for example Pb in fraction IV/mass of fraction IV). I: adsorptive fraction; II: carbonate fraction; III: Mn-oxide fraction; IV: Fe-oxide fraction; V: organic matter/sulphide fraction; VI: residual fraction

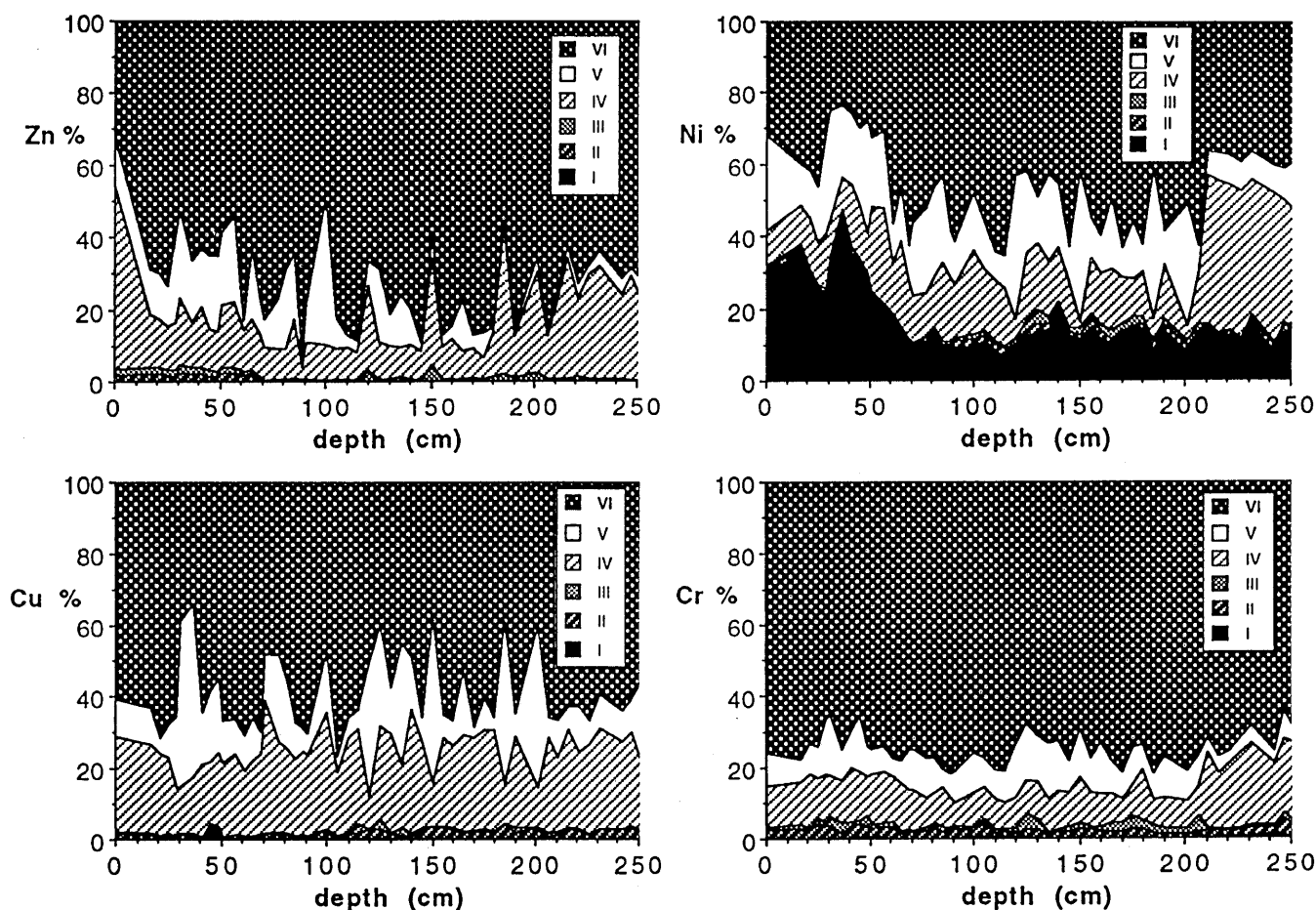


Fig. 6

Depth profile of calculated proportions of Cr, Cu, Ni and Zn in the sequential extraction fractions of the uppermost 50 sediment samples. Metal calculations have been based on the mass of the starting material (1g) before sequential extraction (for example Pb in fraction IV/1g). I: adsorptive fraction; II: carbonate fraction; III: Mn-oxide fraction; IV: Fe-oxide fraction; V: organic matter/sulphide fraction; VI: residual fraction

Fe^{2+} fraction in the upper parts, higher percentages of Fe^{2+} extractable forms (15–40%) occur below this level (Fig. 6). Distribution of the particulate organic and sulphide forms of Zn, Cr and Ni, on the other hand is the inverse. Organic and sulphide fractions for Zn, Cr and Ni increase from 5–10 percent to 10–25% above 200cm. Also the Mn^{2+} fraction of Ni is lower below 200cm (<1%) than in the upper parts of the sedimentary profile (1–3%). The inverse relationship between the Fe^{2+} and the organic and sulphide fractions suggests the redistribution of metals between these two sediment proportions. However, such postdepositional changes do not necessarily imply mobilisation of metals over great distances, as metals liberated from organic materials may have been immediately incorporated into the Fe^{2+} particulate form. A possible explanation may also be that more labile C_{org} with a higher trace element concentration is present in the upper part of the core, while that in

the lower part is degraded. Similarly, the depth distribution of labile and more refractory Fe-oxides may have changed through diagenesis.

Partial extraction

The reagent mixture used an extractant which leached approximately 1–20% of Cr, 2–80% of Cu, 5–50% of Ni, 2–60% of Pb, and 3–60% of Zn. Extraction percentages increase at higher levels in the stratigraphy. All metals possess highly variable concentration distributions. However, they exhibit distinctly similar trends over the entire sedimentary column: (a) exceptionally low Cr_{org} , Cu_{org} , Ni_{org} , Pb_{org} and Zn_{org} concentrations are present in samples taken from the lower part of the sedimentary column representing graded clastic sediments with low concentrations of organic matter (lower than 1,154cm); and (b) Cr_{org} , Cu_{org} , Ni_{org} , Pb_{org} and Zn_{org} concentrations generally increase towards the top, and Ni_{org} , Pb_{org} and Zn_{org} reach their maxima in the uppermost sediment (Fig. 7). Heavy metal values correlate positively with the C_{org} concentrations. Samples ($n=18$) between 0 and 80cm have the following element correlations: $C_{\text{org}}-\text{Cr}_{\text{org}}$ ($r^2=0.7$), $C_{\text{org}}-\text{Cu}_{\text{org}}$ ($r^2=0.8$), $C_{\text{org}}-\text{Ni}_{\text{org}}$ ($r^2=0.4$), $C_{\text{org}}-\text{Pb}_{\text{org}}$ ($r^2=0.6$), and $C_{\text{org}}-\text{Zn}_{\text{org}}$ ($r^2=0.5$). These positive correlations indicate that the observed increases in Cr_{org} , Cu_{org} , Ni_{org} , Pb_{org} and Zn_{org} at the top of the core

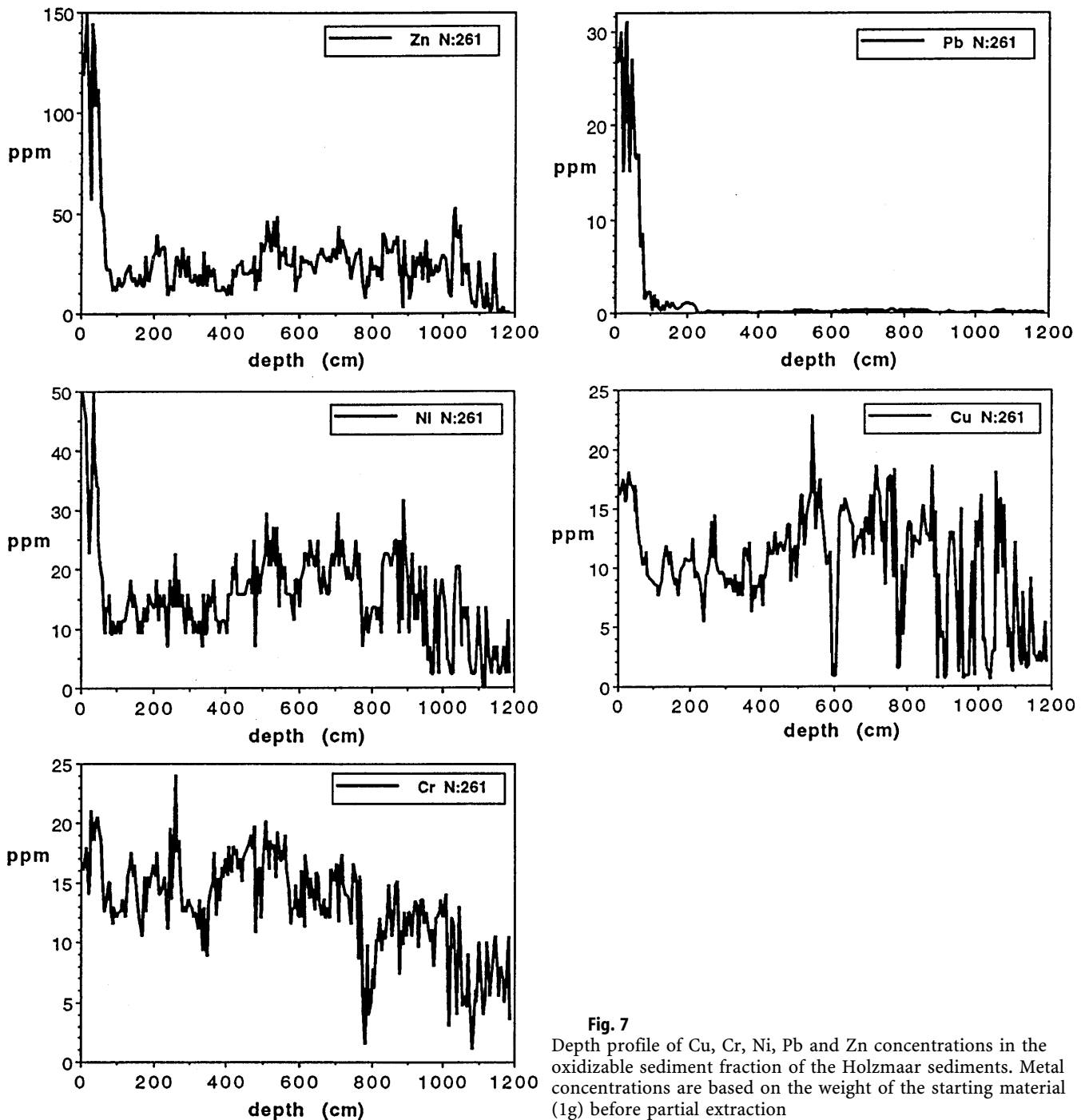


Fig. 7

Depth profile of Cu, Cr, Ni, Pb and Zn concentrations in the oxidizable sediment fraction of the Holzmaar sediments. Metal concentrations are based on the weight of the starting material (1g) before partial extraction

are simply a result of variable percentages of organic material present. This also implies that the sediments incorporated variable amounts of organic material with relatively constant heavy metal concentrations.

Element fluxes

Fluxes are constant for much of the sequence until 2,322VT years ago (Fig. 8; Table 2). Exceptionally high

trace element fluxes for some layers reflect the input of pure clastic material into the basin (for example, 2321–2285VT years; 1782 to 1717VT years; and 823–822VT years). Fluxes increase sharply around the time of the Laacher See Tephra (ca. 11600VT years; Fig. 8) and to a lesser degree around the time of the Ulmener Maar Tephra (ca. 10200VT years, Fig. 8). Fluxes of heavy metals and trace elements increase in pulses in sediments deposited from 2322 to 862VT years and since 845VT years (Fig. 8; Table 2), coincident with higher accumulation rates of clastic material (Zolitschka 1989).

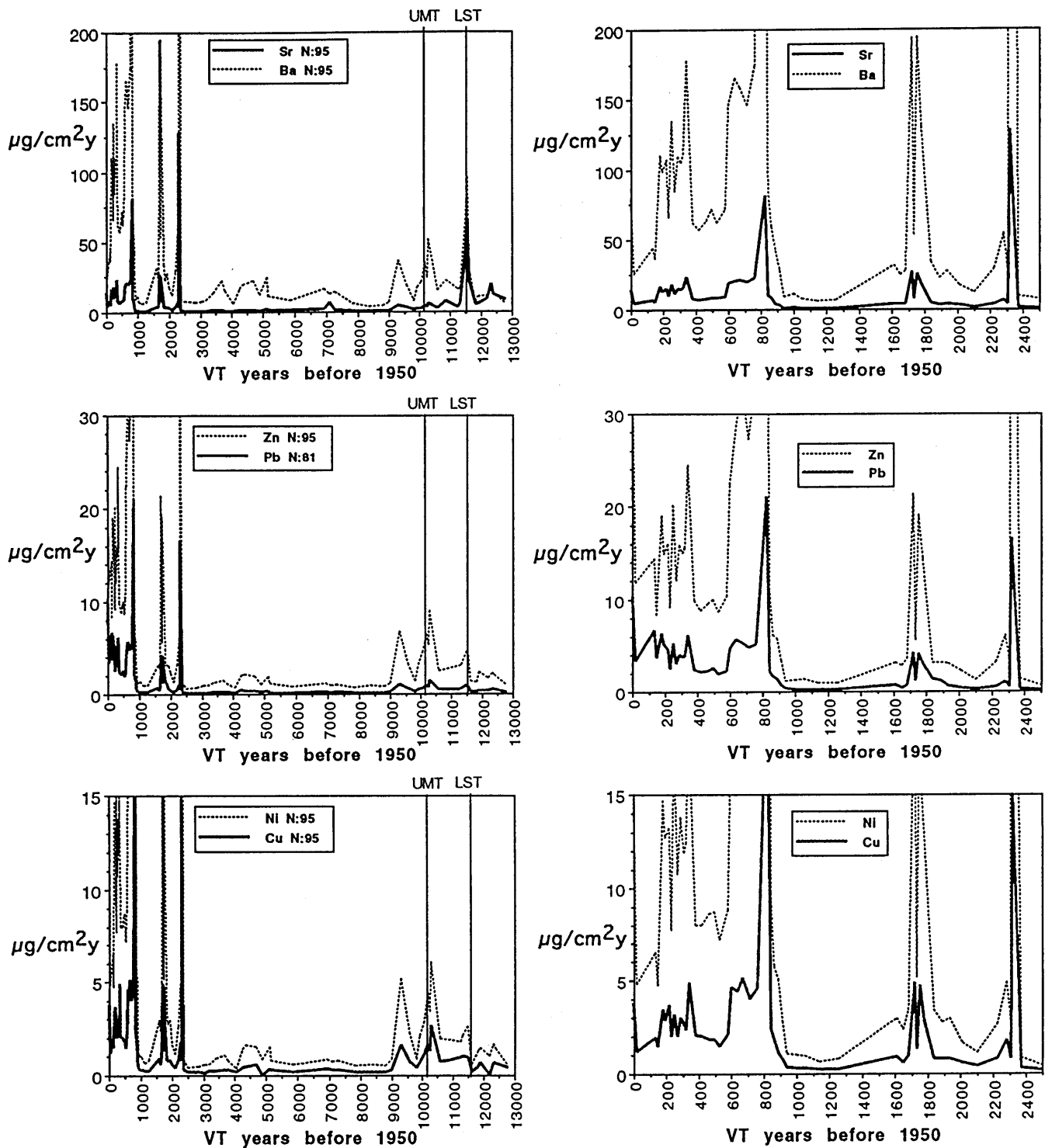


Fig. 8

Selected total element fluxes of the Holzmaar sediments. Each sample has been dated using varve chronology. The positions of the Ulmener Maar Tephra (UMT) and Laacher See Tephra (LST) are indicated

Origin of element loads

The increases in element fluxes in sediments could be due to (a) postdepositional mobilization and redistribution of elements and subsequent concentration of mobilized elements at higher or lower levels of the sedimentary column during diagenesis; or (b) increased input to the lake from bedrock and soils within the crater rim.

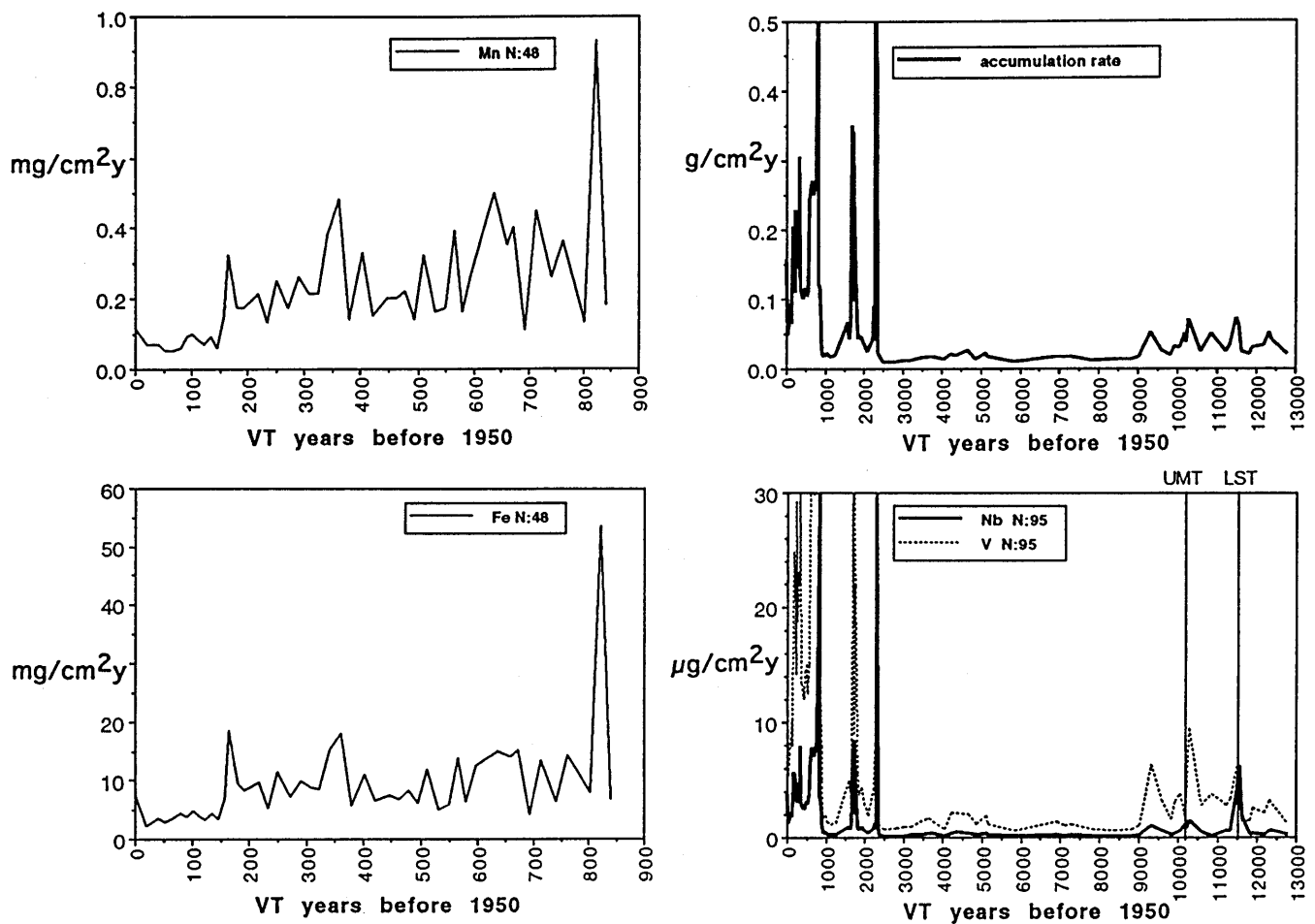


Fig. 8

Table 2

Trace element fluxes into Holzmaar sediments

Number of samples analyzed	26		24		45	
	Less than 253		256-485		498-1184	
Depth (cm)	Less than 253		862-2322		2364-12 867	
Age (VT years)	Less than 845					
	x	s	x	s	x	s
($\mu\text{g}/\text{cm}^2\text{y}$)						
Ba	123	132	91	231	18	17
Co	5	6	2	3	0.4	0.3
Cr	28	26	13	26	2	2
Cu	4	4	2	3	0.5	0.5
Ga	4	4	2	4	0.4	0.4
Nb	5	5	3	6	0.6	1
Ni	16	16	7	12	1	1
Pb	5	4	2	3	0.3	0.3
Rb	26	24	12	27	3	2
Sr	16	14	11	26	6	11
V	25	24	12	22	2	2
Y	6	5	2	6	0.6	0.5
Zn	20	18	9	19	2	2
Zr	43	37	21	55	3	3

x: arithmetic mean; s: standard deviation ($\pm 1\sigma$)

Post-sedimentary mobilization

The increases in element fluxes in the upper part of the sediment column cannot be due to postdepositional translocation because:

- (a) a diagenetic origin for all the high fluxes at the top of the profile would require the mobilization of elements which are commonly regarded as immobile (Co, Cr, Nb, Y, Zr);
- (b) the lack of Fe- or Mn-enriched layers at the top of the sedimentary column (Fig. 4) indicates that a distinct redox boundary did not exist between lake waters and sediments; and
- (c) the Holzmaar has conditions conducive for the incorporation and fixing of elements in sediments: Neutral pH, a non-turbulent environment, steady deposition, and the presence of suitable fine-grained particles for element adsorption.

Natural flux of detritus and anthropogenic influence

Weathering of low-grade metamorphic greywackes, slates, quartzites, and silica-undersaturated volcanics with slightly variable, yet similar trace element concentrations (Table 3), cannot explain the higher concentrations of elements.

Many maar lakes including the Holzmaar have been the focus for human settlements for the last 5000 years (Zolitschka 1989). Their activities are documented in the sedimentary sequence by charcoal remains and higher sedimentation rates caused by deforestation adjacent to the crater lakes and associated erosion (Zolitschka 1989). Distinct increases in heavy metal and trace element fluxes occurred in the Holzmaar sediments deposited since the beginning of the Iron Age (2322VT years), approximately 2150 years before the industrial revolution of central Europe, and especially since the beginning of the Middle Ages (845VT years). This coincides with greater inputs of clastic material (Fig. 8).

Increases in metal concentrations occur in central European lake and river sediments deposited since the latter half of the last century. These increases have been interpreted as being caused by mining activities, and industrialization and associated pollution of the hydrosphere and atmosphere as early as the nineteenth century (for example, Müller and others 1977; Oldfield and others 1980; Vernet and Favarger 1982). In contrast, this investigation did not find higher metal fluxes starting at that time (Fig. 8).

Conclusions

A well-laminated, undisturbed sequence of Holocene and late Pleistocene diatomaceous gyttja, glacial silt and clay laminates, and tuff layers provides a paleolimnological record of long-term variations in sedimentation rates, instantaneous historical events such as forest fires and vol-

Table 3

Trace element concentrations in metasediments exposed at the crater rim

Number of samples analyzed	16	
	x	s
(ppm)		
Ba	309	101
Co	15	5
Cr	145	62
Cu	12	10
Ga	12	5
Nb	17	3
Ni	51	17
Rb	72	36
Sr	58	9
V	71	22
Y	25	6
Zn	41	14
Zr	333	251

x: arithmetic mean; s: standard deviation ($\pm 1\sigma$)

canic eruptions, and volcanically and anthropogenic caused disturbances of natural geochemical cycles. Sequential extraction and analyses of recent sediments show that Ni is preferentially associated with the adsorptive particulate form, whereas Cu, Cr and Zn are associated with in the Fe²⁺-oxyhydroxide and organic fractions. Metal concentrations in the organic fraction vary in proportion to the organic matter.

Fluxes of trace elements increase in pulses in sediments deposited since the Middle Ages and since the Iron Age. They are the result of deforestation, agricultural activities and soil erosion in the immediate vicinity of the Holzmaar and associated increasing element inputs in the form of clastic material.

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Note added in proof

The chronology presented in this study is upon data obtained until 1993. Since then calibration with AMS-14C data (Hajdas and others 1995) and investigation of additional sediment cores (Zolitschka 1996) changed the ages older than 3500 VT years slightly.

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