

## DISTRIBUTION OF PHOSPHORUS AND HEAVY METALS IN THE SEDIMENTS OF LAKE ARENDSEE (ALTMARK, GERMANY)

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### Abstract

Lake Arendsee is a dimictic lake with a surface area of about 5 km<sup>2</sup> and a maximum depth of about 50 m. Due to the input of untreated sewage rich in P the lake turned to eutrophic state in the 1950s. Sediment cores were taken by different methods: short cores (0–50 cm) with a gravity corer, long cores (0–160 cm) with a piston corer. The sediments were sliced into subsamples under argon atmosphere in a glove box. The samples were analysed by ICP-OES and ICP-MS on main and trace elements after digestion in either *aqua regia* or HF-HNO<sub>3</sub>-HClO<sub>4</sub>. Analogous cores were dated by varve counting and radiometric methods. The enforced build-up of industry and agriculture since the 1950s is displayed in the sediment composition. The P concentrations increase from a background of about 600 ppm (oligotrophic state of the lake) to more than 4,000 ppm in a depth of 14 cm, which corresponds to the 1970s. In 1976, a hypolimnetic withdrawal and a sewage plant were built. Above the corresponding depth the concentrations of P and heavy elements decrease in the sediments but are still by far higher than the background values. The bonding form analyses document mineral equilibration by diagenetic processes. Stable sulfidic bonding forms become predominant with increasing depth.

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**Key words:** phosphorus, lake sediments, heavy metals, sequential extraction, Lake Arendsee

### INTRODUCTION

Lake Arendsee is situated in Northern Germany near the River Elbe (Fig. 1). It developed in a sinkhole due to the subsidence of an underlying salt dome. In 822 A.D. and in 1682, two main collapses formed the lake's basin. The geographic characteristics of Lake Arendsee are as follows: surface area – 5.2 km<sup>2</sup>; mean depth – 28.6 m; maximum depth – 49 m.

A bench of lake marl as a relict of an older lake crops out in the north of Lake Arendsee (Scharf 1998). This older lake, Wendischer See, has an age of more than 4,000 years. Lake Arendsee is dimictic, with overturns in spring and fall. Since the 1950s, the trophic state of the former oligotrophic Lake Arendsee turned to eutrophic due to the input of untreated sewage water from the city Arendsee. The long retention time of 114 years limits the self-purification potential of the lake. To combat the eutrophication symptoms and improve the water quality, different countermeasures have been undertaken. In 1976, a hypolimnetic withdrawal was constructed to increase the water exchange. Later a sewage treatment plant was built. In 1995, lake marl was flushed across the lake in order to precipitate dissolved phosphate and to cover the phosphate-rich sediment. The cover was in-

tended to inhibit the reflux of phosphate from the sediment into the water column. These measures have not been successful so far (Hupfer *et al.* 2000).

The study traces the development of element concentrations in the lake sediments caused by anthropogenic activities during the last decades. Bonding form analyses yield an assessment of the diagenetic influences on the stability of heavy elements.

### METHODS

#### Sampling and sample preparation

The sediment cores were taken according to Table 1 and Fig. 1. The sediment cores were kept in a dark and cool (4 °C) place until subsampling, which was done in an argon-flushed glove box. The upper parts of the cores were sliced into 2 cm thick subsamples; the lower parts had a thickness of 5 cm. The subsamples were put into polyethylene containers, which were then kept in larger glass containers filled with argon, sealed airtight, and stored in the dark at 4 °C until further analyses.

## Chemical analysis

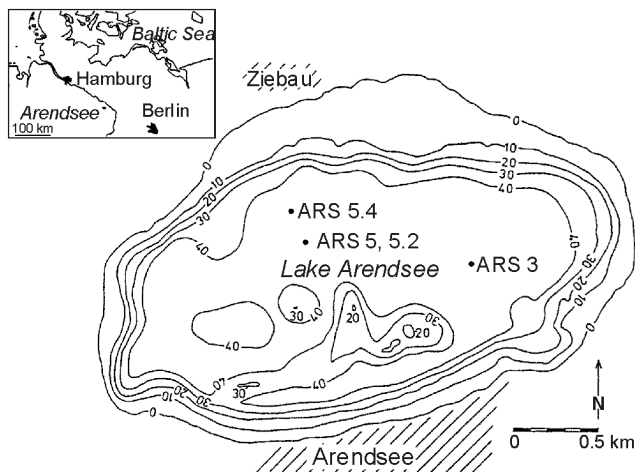
Concentrations of C and S were determined by infrared spectroscopy after combustion of the dry unfractionated sample material in an induction furnace flushed with oxygen (Leco CS 144). The procedure is described in detail in DIN ISO 10694. Total carbon (TC) and S were measured directly without specific treatment on the finely ground sample powders. Total organic carbon (TOC) was determined after treatment with HCl. Total inorganic carbon (TIC) results from the difference between TC and TOC.

In core ARS 5.4, total element concentrations were analyzed after digestion in HF-HNO<sub>3</sub>-HClO<sub>4</sub>. Samples from the other cores were digested by *aqua regia*. Both methods are known to yield nearly the same analytical results for heavy metals, Ca, and S. Differences occur mainly for P, Al, Ti, and K. However, also for these elements a parallelization of concentration tendencies and distribution patterns in core profiles is possible (on different concentration levels).

The analyses of the main elements were performed by ICP-OES (ARL 3250; Fisons Maxim); trace elements by ICP-MS (Micromass Platform).

The lake eutrophication enhanced biotic activity, which caused the precipitation of CaCO<sub>3</sub>. In addition, marls were flushed across the lake. Due to carbonate precipitation and the supply of marls the portion of calcium carbonate reaches values of about 75% in the uppermost sediment layers (< 20 cm). Bonding form studies show a negligible concentration of most elements in the carbonate phase (exceptions: Sr, Mn). Therefore, the element concentrations are corrected for the content of calcium carbonate.

The bonding form of the heavy metals was determined according to a sequential extraction scheme that stems from a method published by Tessier *et al.* (1979). As natural substances may be composed partially from poorly defined substances (amorphous, transitional, metastable), the results of the sequential elution procedures should be considered as an approximation of the "true" mineralogical composition of the samples (Wippermann *et al.* 1997). In this study, we applied a six-step-scheme based on Zachmann & Block (1994). It was modified to anoxic processing from step 1 up to 4



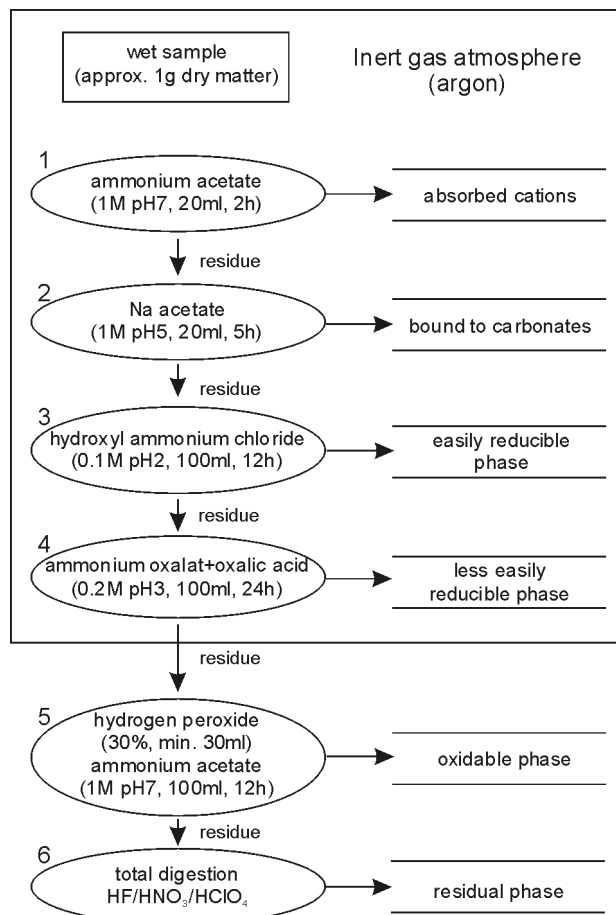
**Fig. 1.** Bathymetric map of Lake Arendsee and sampling sites ARS 3, ARS 5, ARS 5.2, and ARS 5.4 (modified after Scharf 1998).

**Table 1**  
Methods and parameters of sampling used in the present work

Sediment	Date	Corer type	Diameter	Length [cm]
ARS 3	April 1999	piston corer (Niederreiter)	6	160
ARS 5	April 1999	gravity corer (Mondsee)	9	50
ARS 5.2	April 1999	piston corer	9	105
ARS 5.4	September 1999	gravity corer	9	46

(Fig. 2). This was achieved by working in an argon-flushed glove box and by purging the extractants with argon. To avoid any unwanted oxidation, the wet untreated sediment was used. Other modifications concern steps 5 and 6. In step 5, hydrogen peroxide was added up to 5 times until a bleaching effect could be detected. In step 6, a total digestion with a mixture of HF-HNO<sub>3</sub>-HClO<sub>4</sub> replaced the digestion of the residue with *aqua regia*.

The easily reducible phase (Fig. 2) comprises elements, which are bound to amorphous hydroxides and oxides (mainly Mn). In the less easily reducible phase, the elements are associated with more crystalline oxides and hydroxides



**Fig. 2.** Sequential extraction modified after Zachmann and Block (1994).

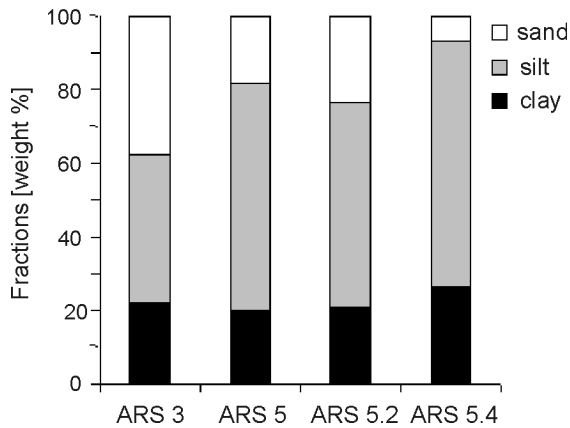


Fig. 3. Mean grain size composition in Arendsee cores.

(mainly Fe). Phase 5 (Fig. 2) comprises sulfides and elements bound to organic substances. Silicates and some stable oxides (e.g. hematite) are defined by the residual phase.

RESULTS

Element concentrations

The layers of the sediment cores ARS 5, ARS 5.2, and ARS 5.4 show similar mean grain size compositions with about 10–20% of sand (Fig. 3). Core ARS 3 contains nearly 40% sand. Therefore, the results for core ARS 3 and cores ARS 5 are only approximately comparable.

The uppermost sediment sequence could be sampled completely by the short cores (0–50 cm). Due to the corer type (Table 1), the upper parts of the deep cores have been more or less mixed up whereas the lower parts are well preserved. Therefore, only the short cores were used as a record of the recent environmental changes. The lower parts of the deep cores record the local background conditions. In the following studies, only the short cores and the lower parts of the deep cores are considered (> 50 cm).

The cores ARS 5, ARS 5.2, and ARS 5.4 show rather identical patterns of element concentrations with depth, and of element correlations. Similar patterns are indicated for the core ARS 3.

The lower parts of the lake sediments show a rather constant concentration of 700 (± 97) ppm P and 1.1 (± 0.5)% Ca. Starting in a depth of 35 cm, the concentrations of P and Ca increase simultaneously (ARS 5; Fig. 4) up to a depth of 12–15 cm. At this depth, the P values reach a maximum of about 2,500 ppm. The P concentrations decrease to the uppermost sediment parts whereas the Ca concentrations increase continuously towards the uppermost sediment layers. The Ca carbonate reaches concentrations of nearly 70%. The decrease of concentrations of P, Ca, and C-org. corresponds to an increase of Al and K with depth (Fig. 5).

The P-Ca-scattergram (Fig. 6) displays three sections in the core with different correlations. The section below 30 cm shows no correlation (samples m–r). Between 30 and 15 cm, P and Ca increase simultaneously (samples g–n). The uppermost series is characterized by a negative correlation (samples A–E).

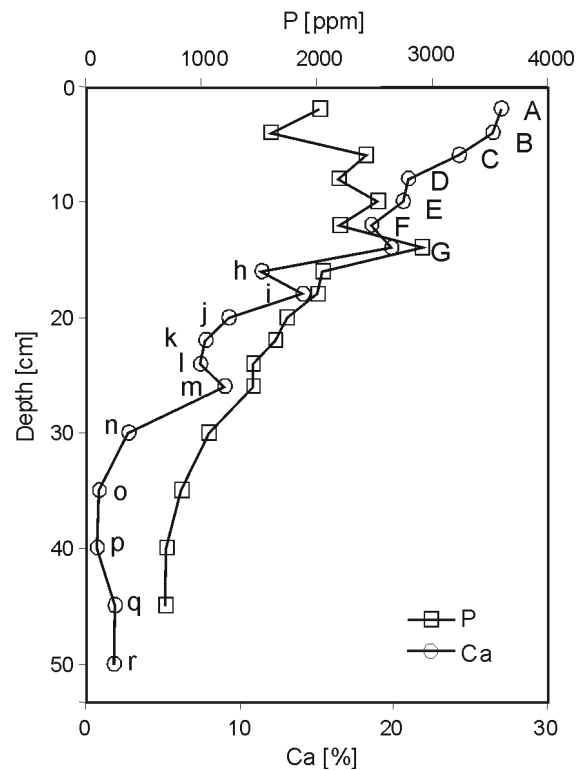


Fig. 4. Concentrations of P and Ca as a function of depth in core ARS 5 (Ca represents the carbonate portion in the sediments; shapes A–r: c.f. appendix “analytical data”).

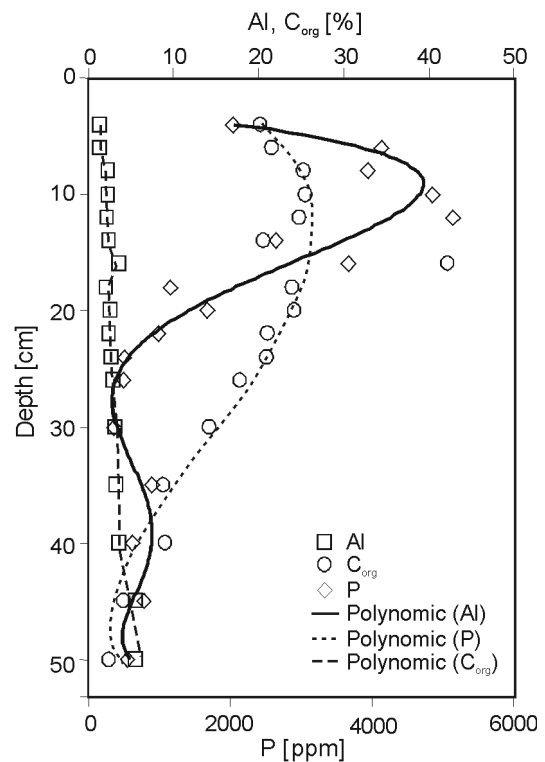


Fig. 5. Concentrations and trendlines of Al, C-org., K, and P as a function of depth in core ARS 5.4.

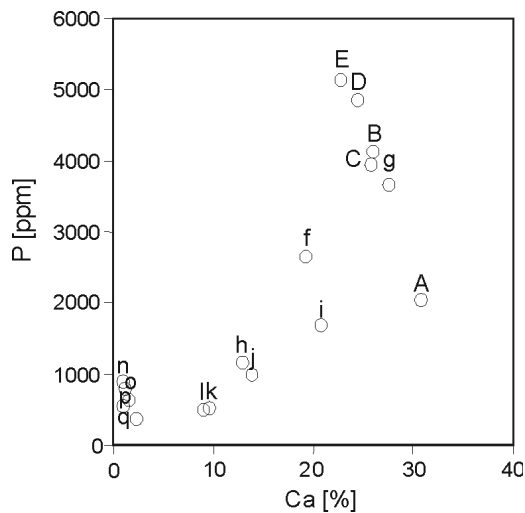


Fig. 6. Concentrations of Ca and P in core ARS 5.4.

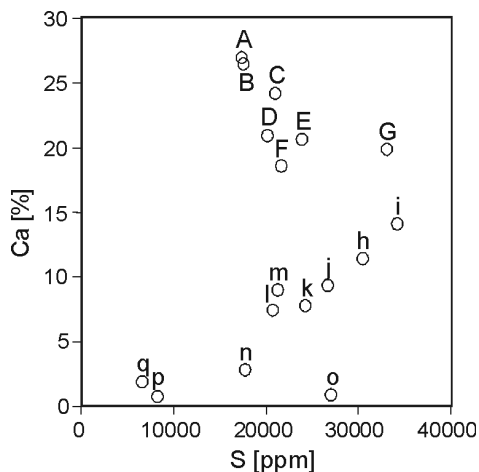


Fig. 7. Scattergram Ca–S in core ARS 5 (shapes A–q: c.f. appendix “analytical data”).

The scattergram Ca–S of core ARS 5 (Fig. 7) is similar to scattergram Ca–P (ARS 5.4); furthermore, similar Ca–S patterns are found in all other cores. The correlation between Ca and S seems to indicate the occurrence of gypsum in the sediments. However, the Ca and S concentrations do not fit the stoichiometry of gypsum. In addition, the strong correlation between C-org. and S (*r*-values: ARS 5.4 = 0.85; ARS 5.2 = 0.77; ARS 5 = 0.75) and the occurrence of Mn carbonate (c.f. bonding form analysis) indicate reducing conditions and the formation of sulfides.

The concentrations of the heavy metals Fe, Cu, Pb, and Zn correlate positively with S, P, and C-org. A similar element cluster can be found in all sediment cores. The elements Fe, Cu, Pb, and Zn are known to form mineralizations with sulfur as well as with phosphate. Due to the very high amounts of S in comparison to P (about factor 10), the formation of sulfides is supposed as predominant in the control of heavy metal concentrations. (Fig. 8). X-ray diffraction analyses document the presence of pyrite. A geochemical control of Co, Ni, and Cd by S, P, and C-org. could not be observed. Cr correlates with Al.

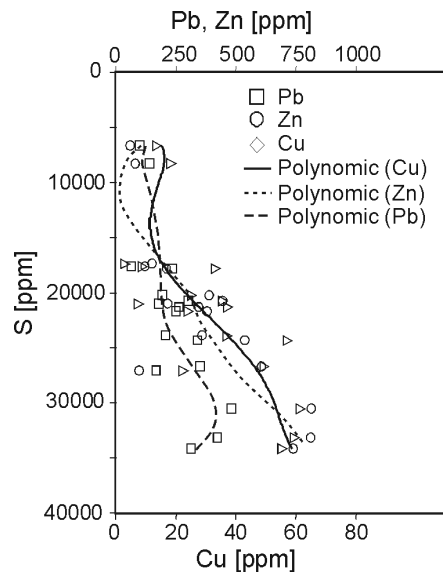


Fig. 8. Control of Pb, Zn, and Cu by S.

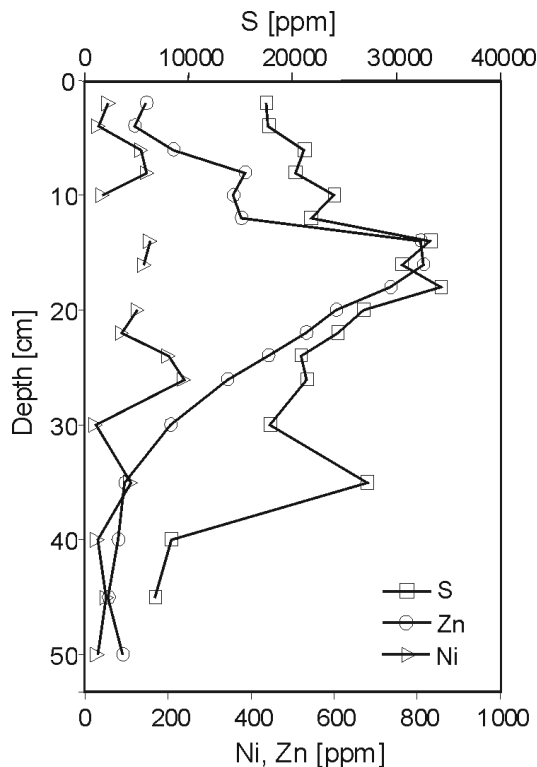
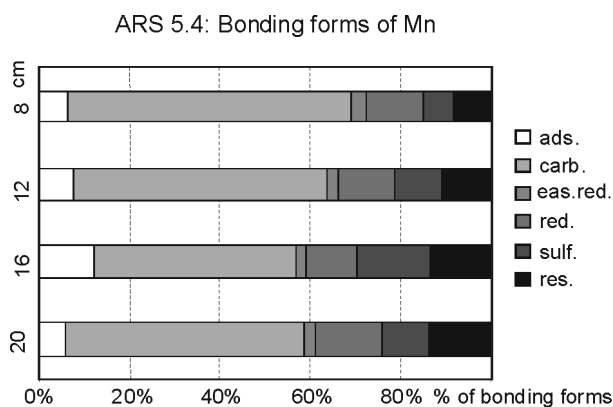
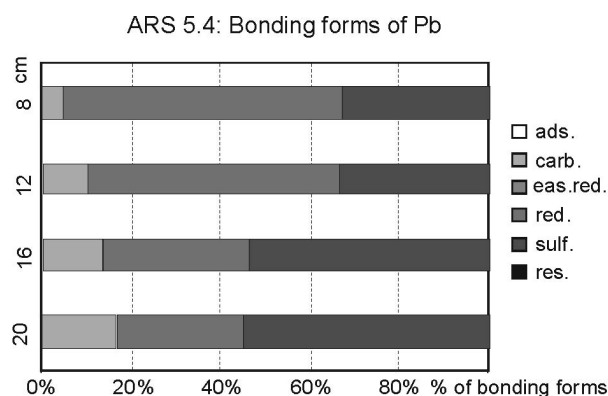


Fig. 9. ARS 5 – distribution of S, Zn and Ni with depth; the distribution patterns of Cu, Pb, P, and C-org. show a maximum concentration at a depth of about 18 cm; the elements Ni, Co, Cr, and Cd, are without trend.

The concentrations of the elements S, P, Fe, Cu, Pb, Zn, and C-org. show a very similar distribution pattern in the cores. Zn and S represent this element group in Fig. 9. In the depth, the values are nearly identical to the local background concentrations, which are documented, in the lower parts of the deep core ARS 5.2 (535 ppm P, 0.54% S, 6.9% C-org., 1.2% Fe, 7.4 ppm Cu, 19 ppm Pb, 48 ppm Zn). Starting from the background, the concentrations increase continuously to



**Fig. 10.** Bonding forms of Mn. Ads. – adsorption; carb. – carbonates; eas. red. – easily reducible (generally amorphous hydroxides of Mn and Fe); red. – reducible (more crystalline oxides / hydroxides); sulf. – sulphides (and organic C); res. – residual: silicates, some oxides.



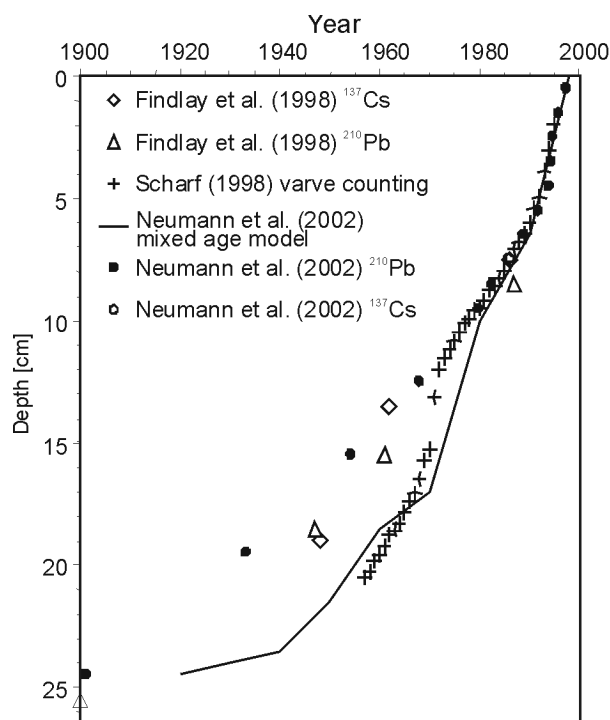
**Fig. 11.** Bonding forms of Pb. Ads. – adsorption; carb. – carbonates; eas. red. – easily reducible (generally amorphous hydroxides of Mn and Fe); red. – reducible (more crystalline oxides / hydroxides); sulf. – sulphides (and organic C); res. – residual: silicates, some oxides.

a maximum in approximately 18 cm. An abrupt decrease of concentrations follows to the sediment surface. In contrast, the concentrations of Ni, Co, Cr, and Cd remain on a rather low and constant level.

### Bonding forms

In general, the main findings of the bonding form analyses from the different cores are consistent. Therefore, only the results of core ARS 5.4 are represented (Fig. 10, 11).

The mineralizations of Mn are predominated by the carbonatic bonding form, *i.e.*  $Mn^{2+}$  prevails over the more oxidized valencies of Mn (Fig. 10). Some core sections show minor amounts of siderite ( $FeCO_3$ ). The distribution pattern of heavy metal bonding forms in the cores is represented by Pb (Fig. 11). The distribution is dominated by the reducible and sulfidic (including organic) bonding forms. The proportions of bonding forms change with depth from more oxidic (reducible) to sulfidic. The portion of the carbonate bonding form increases likewise with depth.



**Fig. 12.** Comparison of sediment dating of Lake Arendsee.

### Sediment dating

Sediments from Lake Arendsee have been dated by radiometric methods ( $^{137}Cs$ ,  $^{210}Pb$ ; Findlay *et al.* 1998, Neumann *et al.* 2002), and varve counting (Scharf 1998). The sediment cores were taken from localities in the eastern part of Lake Arendsee from 1993 to 1998. The results shown in Fig. 12 are corrected for additional sedimentation in the younger cores that are the basis of our study.

Varves are formed by autochthonous calcite precipitation each year in the month June and July (Scharf 1998). They occur and are well recognizable in the upper 20 cm. A detailed comparing discussion of age determination by the different methods and of age-depth-correlations for the Lake Arendsee sediments is given by van der Veen (2003). While the results of the varve counting correspond to the radioisotope dating in the upper 12 cm, the calculated age values from both radiometric methods differ below that level. Radioisotopes yield older ages than the varves in these sediments.

The good correlation of the dating and of the occurrence of varves between the different localities in the eastern and the central part allows the interpolation of the sediment ages.

### DISCUSSION

A table of enrichment factors was calculated using the values of core ARS 5.4 (Table 2). The enrichment factors compare the concentrations of the lower with the upper core portions (ARS5.4: 0–30 cm; 30–50 cm). Similar enrichment factors can be found for all ARS5 cores.

The concentration increase of P, Ca, S, Cu, Pb, Zn, and C-org. indicates most probably an increasing anthropogenic influence on the sediment quality. The amount of P reaches mean values of about 2,500 ppm in the upper sediment layers

**Table 2**  
Background values and enrichment factors of ARS 5.4

Element	Background values [in ppm, Ca and P in %]	Mean enrichment tfactor
Ca	0.9	15.9
P	498	5.1
C <sub>org</sub>	7.0	3.3
S	4628	2.6
Zn	43.5	5.7
Mn	172	4.9
Pb	17.8	2.0
Cu	5.3	1.9
Mg	805	1.8
Ni	21.5	1.3
Fe	11297	1.0
Cr	6.3	0.8
Al	3872	0.5
K	595	0.5
Co	3.2	0.4

with maximum concentrations of 5,000 ppm. In the same period (since *ca.* 1950) a similar development of P-concentrations can be found in the sediments of Lake Constance (dimictic lake). The concentrations reach values of 1,700 ppm (Müller 1997). The background values of both lakes are similar (Lake Constance: 600 ppm). The very high enrichment of P and other elements in Lake Arendsee is due to the slow water turnover with a retention time of 114 years.

The function of P for the eutrophication of lakes is well known; P is the controlling factor for algal (and bacterial) growth and the associated primary production of organic substance (Müller *op. cit.*; Fig. 5). Due to the discharge of untreated sewage and waters from agricultural fertilizing, Lake Arendsee turned eutrophic in the 1950s.

Positive correlations between P, S, Ca, and C-org. occur above a depth of 25 cm. They indicate an at least intermediate causally connection of element enrichment in the sediment.

Between 50 and 30 cm the concentrations increase slowly (Figs. 4, 8). High increments occur above a depth of about 25 cm. A maximum concentration is reached in a depth of about 14 cm. With the exception of Ca (Ca carbonate) the concentrations decrease to the uppermost sediment layers.

The findings fit the sediment dating by varve counting (Scharf 1998; Fig. 12). The depth of about 25 cm corresponds to the years 1948–1950. This time is characterized by the beginning impact of industrialization and intensification of agricultural productivity in the area. The depth of maximum concentrations (*ca.* 14 cm) corresponds roughly to the year 1975. In 1976, a hypolimnetic withdrawal was constructed to increase the water exchange. Later a sewage treatment plant was built. Since that time the input of P, Ca, S, Cu, Pb, Zn, and C-org. to the sediments decreased continuously. In 1995, the sea floor was flushed with about 56,000 m<sup>3</sup> carbonate rich marls. This year corresponds to a depth of 4 cm. Indications on this remedial attempt are not recorded in the sediment cores.

According to the physical chronometry the depth of 14 cm would yield the year 1960. This year belongs to the period of massive building up of agriculture and industry. Measurements of environmental management are not reported from this time. In contrast to the varve counting method, the physical chronometry does not fit the concentration record of the sediment cores and historical events at Lake Arendsee.

The history of the lake environment is corroborated by the P–Ca correlation (Fig. 6). The older series show no correlation between P and Ca (samples r–m). The time of intensified agricultural productivity since about 1950 can be traced by the positive correlation P–Ca (samples g–l). After 1976, the concentrations of P decrease whereas those of Ca continue to increase (negative correlation, samples A–F). Evidently, the P concentrations in the lake water are high enough for an intensified seasonal photosynthesis which triggers the precipitation of carbonate (Garbe-Schönberg *et al.* 1997, Gruber *et al.* 2000, Neumann *et al.* 2002).

The accumulation of organic material is a prerequisite for sulfate reducing bacteria (Klapper 1992). Production of organic material is controlled by phosphorus. Therefore, the input of P triggers not only the precipitation of Ca carbonate, but also the production of sulfide in the sediment (cf. Tables in Appendix 1–4). The causal connection is documented by similar correlation patterns for Ca–P and Ca–S (Fig. 8). The portion of S controls the concentration of heavy metals in the sediment (Fig. 8). The simultaneous decrease of P, S, and heavy metals in the sediments can be attributed to a lower waste water discharge into the lake after the year 1976 (construction of a sewage plant). Most of the year the lake shows a thermic stratification with short periods of oxygenation of the hypolimnion occur during overturns in spring and fall. The extent of reducing conditions in the sediments is verified by the occurrence of siderite. The occurrence of siderite indicates the very low  $E_h$ -values necessary for methanogenesis (Berner 1981). The occurrence of a reducing environment is corroborated by the massive occurrence of Mn carbonate (Fig. 10).

During diagenesis, the mineralogical composition of the sediments equilibrates with the reducing environment. Mn occurs predominantly in the reduced, *i.e.* divalent, form (Fig. 10).

Due to sedimentation processes, many heavy elements are bound to Fe–Mn-oxides-hydroxides. This bonding form predominates in the uppermost sediment layers. The portions of sulfide increase with increasing depth. This development is found for lead (Fig. 11) and other heavy metals (not displayed). Under reducing conditions, heavy metal sulfides are very stable.

## CONCLUSIONS

The sediments of Lake Arendsee record the industrial and agricultural development in the lake environment. The fast development since 1950 led to the accumulation of a lasting pool of a eutrophic nutrient, particularly phosphorus, potential in the sediments. The slow water turnover with a retention time of 114 years supports the high enrichment of P and the other elements. The construction of a sewage treatment plant proved a reversal in the pollution trend. However,

the state of the lake is far from the former oligotrophic state. The P concentrations in the recent sediments are in the range of 1,500 ppm. An oligotrophic state can be expected when the P concentrations in the upper sediment layers approximate the background values in the range of 600–700 ppm P.

During diagenesis the (stable) sulfidic bonding form of heavy metals becomes predominant in the reducing environment of Lake Arendsee sediments

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