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Primary Research Paper

Sediment and pore water composition as a basis for the trophic evaluation of standing waters

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Abstract

Sediments and pore water samples from four reservoirs in eastern Germany with different trophic characteristics have been examined (Neunzehnhain I – oligotrophic; Muldenberg – oligotrophic, dystrophic; Saidenbach – mesotrophic; Quitzdorf – highly eutrophic). Several parameters were analyzed regarding the dependence on the trophic state and the possibility to use them for the trophic evaluation of standing waters. The strongest influence of the trophic state could be found in the case of the parameters SRP, alkalinity and ammonium in the pore water. For the dry sediment, it could be concluded that the most important factor affecting the trophic state is the ratios of Fe:P and Al:P, which were summarized to a metal:phosphorus sum ratio (MPS) and showed a clear threshold value for the potential to immobilize phosphorus in the sediment. Also, with the P fractions of the sediment samples, differences between the trophic levels became evident. Higher percentages of the reductively soluble, iron-bound fraction and of the biogenic fraction occurred in the reservoirs with higher trophic state, while comparitively higher percentages of the stable aluminum-bound fraction could be measured in the reservoirs with lower trophic state.

Abbreviations: BD – bicarbonate-dithionite-extractant; DW – dry weight; MPS – metal:phosphorus sum ratio; Mul – Muldenberg; Neu – Neunzehnhain; NRP – non-reactive phosphorus; POC – particulate organic carbon; Qui – Quitzdorf; R. – reservoir; Sai – Saidenbach; SRP – soluble reactive phosphorus; TP – total phosphorus

Introduction

In most countries, the determination of the trophic conditions of standing waters is based on the load concept of Vollenweider (OECD, 1982). Here, the total phosphorus concentration in the water body is used for the description of the nutrient conditions, while the parameters chlorophyll *a* and Secchi depth are used for the estimation of the trophic conditions (e.g. Klapper et al., 1989; LAWA, 1989). The restriction on total phosphorus is substantiated by the fact that eutrophication in most standing waters can only be controlled by reduction of the P load. Based on the three parameters of total phosphorus, Secchi depth and chlorophyll *a*, each of the determined parameters is arranged in a trophic system, which contains the trophic states ultra-oligotrophic, oligotrophic, mesotrophic, eutrophic and hypertrophic. The state hypertrophic marks the highest trophic state and occurs only rarely under natural conditions.

However, with an examination of the above parameters in the water body, it is not possible to determine the causes of eutrophication and to predict future water quality in the context of restoration measures. The parameters total phosphorus, Secchi depth and chlorophyll *a*, often show strong fluctuations, which make an estimation of the trophic state comparatively difficult. In many lakes and reservoirs, a substantial P release from the sediment can be detected, which may, even to a greater extent than the external load, cause a high trophic state or its increase in subsequent years.

The intensity of microbial and chemical processes has a strong influence on the release of nutrients and other dissolved substances from the sediment (Boström et al., 1982; Boers et al., 1998). It is shown in this study that sediments may be utilized as an additional source of information for the evaluation of the trophic state and of future trophic development.

Sediment in standing water bodies may react relatively delayed on changes in the catchment area such as P reduction (van der Molen & Boers, 1994). Thus, many chemical parameters in the sediment may show smaller fluctuations than the corresponding parameters in the water body. Several parameters in the sediment (e.g. metals, phosphorus) can provide important information about the phosphate immobilization potential, although almost no seasonal fluctuations can be measured. Thus, a potential exists for a general assessment of the sediment characteristics, and also of the trophic character of the water on the basis of few sediment samples. By the calculation of release rates and internal loads, it may be possible to estimate future developments of the trophic state of lakes and reservoirs.

On the other hand, there are severe constraints. The composition of sediment samples very often exhibits a strong spatial heterogeneity. Therefore, it is necessary to take several sediment cores in parallel. It can be assumed in most cases, that the sediment at the greatest water depth is most suitable for examination, since this spot is subject to an integrating effect (enrichment of materials by sediment focusing) (Hilton, 1985; Nürnberg, 1991).

The aim of this study was to investigate the relationship of chemical and microbial parameters in the sediment of reservoirs with different trophic states. In particular, we examined to what extent the chemical and microbial structure of the upper 5 cm sediment layer can be used as a basis for a comparative evaluation of water bodies, and which parameters show the strongest relation to the trophic state.

Sampling sites

Sediment cores from four different reservoirs in Saxony (Germany, humid temperate climate zone) were examined, which represent a broad range of trophic conditions: Neunzehnhain I (oligotrophic),

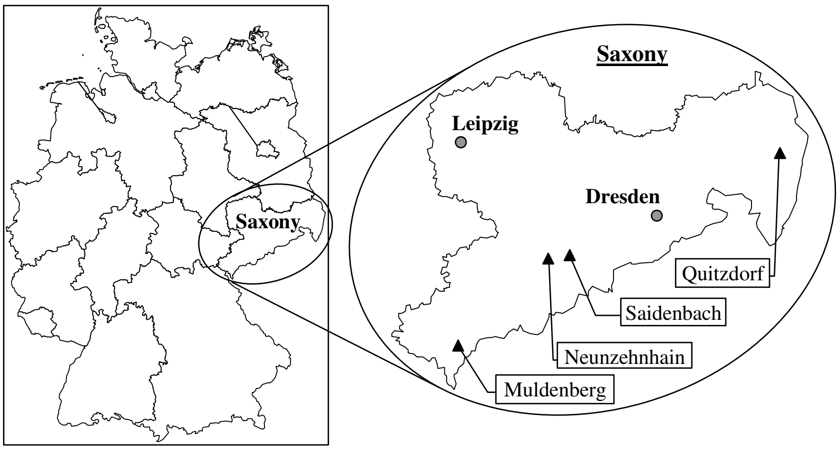

Figure 1. Germany with the reservoirs under investigation in Saxony.

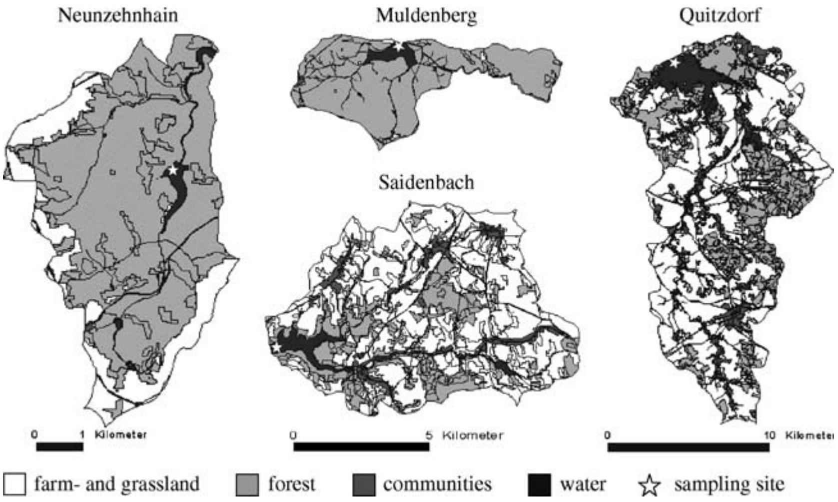

Figure 2. Catchment areas of the reservoirs and sampling sites.

Muldenberg (oligotrophic, dystrophic), Saidenbach (mesotrophic), Quitzdorf (highly eutrophic) (Figs. 1 and 2). With the exception of Quitzdorf, all of the reservoirs are used for drinking water supply (Table 1).

The Muldenberg drainage basin mainly consists of forested bogs, which cause an increased input of humic substances and a reduced Secchi depth. Since the 1970s, acid rain deposition has been significant, but there have been recent

Table 1. Characteristics of the reservoirs (according to Sieber, 1992; Reservoir Administration of Saxony, personal communication)

Reservoir	Neunzehnhain	Muldenberg	Saidenbach	Quitzdorf
Trophic state	Oligotrophic	Oligotrophic, dystrophic	Mesotrophic	Highly eutrophic
Catchment area (km^2)	10.7	20.3	60.8	174.5
Catchment	80% forest 18% agriculture	98% forest	19% forest 73% agriculture	29% forest 64% agriculture
Geological substrate	Mica schist	Slate	Gneiss	Glacial clay
annual precipitation (mm)	821–1026	628–648	821–1026	550–600
Surface area (ha)	8.5	92	146	750
Max. depth (m)	16.5	23	48	9.3
Mixis	Dimictic	Dimictic	Dimictic	Polymictic
Residence time (yr)	0.33	0.63	0.39	0.67
pH pore water	6.5–7.2	5.7–7.0	7.3–8.0	7.5–8.4
pH water body	6.6–7.4	4.7–5.8	7.4–9.0	7.3–10.4
Thermocline depth (m)	9–10	8–9	12–13	–
Stratification (period)	May–Aug.	May–Sep.	May–Sep.	No stabile strat.
Anoxia (period)	–	July–Sep.	–	May–Sep.
Dissolved oxygen epilimnion	8.5–12.4	8.4–13.0	8.8–13.1	No stratification
Dissolved oxygen hypolimnion	6.9–11.9	0.2–11.9	4.3–12.7	No stratification
Secchi depth (m)	4.7–10	2.1–3.9	2.4–7.0	0.4–2.9
Total phosphorus (mg/l)	0.005–0.014	0.004–0.016	0.007–0.06	0.04–0.3
Chlorophyll *a* (μg/l)	0.7–4.9	0.3–10.3	1.5–11.5	5.9–141

reductions in the deposition (Sieber, 1992). Accordingly, the average pH of the water increased from pH 3.5 in 1990 to pH 5 in the year 2000, and the pH in the pore water tends to lean towards the neutral range. Quitzdorf has a very shallow mean depth of 2.8 m and is characterized by mass growths of *Microcystis* during the summer months. In this period, the entire water body warms with no stable stratification apparent.

Methods

The reservoirs were examined at intervals of approximately two months. Ten sediment cores were taken at the greatest water depth (Kajak Sampler with a diameter of 6 cm, Uwitec). In the laboratory, the cores were sliced into layers of 1 cm thickness and for P fractionation the upper centimeter was additionally sliced into layers of 0.5 cm thickness. In order to obtain a representative sample, all 10 sediment cores were pooled in each case. To obtain the pore water, the sediment samples were centrifuged for 10 min at 20500 × *g* and filtered (HT-Tuffryn membrane 0.2 μm, Pall Corporation). During the summer months it was impossible to obtain pore water from the samples of Quitzdorf by centrifugation without a very high content of *Microcystis* colonies, and hence the separation was performed with dialysis samplers according to Hesslein (1976), which were exposed for about 3 weeks. Preliminary analyses with a dialysis sampler revealed similar pore water concentrations as with centrifugation/filtration. The diaphragm membrane was the same as was used for water filtration (see above), and the chamber volume was 10 ml. The pore water was sampled directly at the reservoir and transported to the laboratory in a cooling box.

The chemical examination of pore water was performed according to German standards for water analysis (DIN, 1982-94; "Ausgewählte Methoden der Wasseruntersuchung" 1976). Ammonium was analyzed photometrically at 655 nm and phosphate (soluble reactive phosphate – SRP) at 665 nm with a U-2000 photometer (Hitachi Ltd.), dissolved organic carbon (DOC) was measured using a DC 190 TOC-analyzer (Tekmar-Dohrmann). Inorganic anions (nitrate, sulfate) were analyzed by ion chromatography (Dionex Corp.) and metals (Fe, Al, Mn, Ca) with ICP-AES. Alkalinity was determined by titration with 0.01 M HCl. The determination of ammonium, SRP and alkalinity was performed directly after filtration of the samples (for pore water from the dialysis sampler after arrival at the laboratory), samples for the analysis of DOC, nitrate and sulfate were stored at −20 °C, while H_2SO_4 was added to the samples for the determination of metals.

Pooled samples of fresh sediment were used for P fractionation (Psenner et al., 1984; Hupfer & Gächter, 1995) and the photometric determination of sulfide (665 nm, fixation with zinc acetate). The sediment samples were subjected to drying, homogenization and determination of the dry weight (DW). Metals (Fe, Al, Mn, Ca) were extracted with aqua regia and measured with ICP-AES, phosphorus was extracted with K_2SO_8 and analyzed photometrically. With intact sediment cores, the penetration depth of O_2 and the redox potential were measured using microelectrodes (Kurt-Schwabe-Institut Meinsberg, Saxony).

The diffusion-controlled phosphorus release rates were calculated according to Fick's law (e.g. Berner, 1980; Sinke et al., 1990). For comparison of the pore water profiles, a Mann–Whitney *U* test was performed using the software Statistica 5.0 (StatSoft, Inc.).

Results

The SRP concentrations in the pore water increased with the trophic state (see Fig. 3) and displayed significant differences between the reservoirs ($p < 0.05$) with different trophic states. The maximum SRP concentration of the pore water in the oligotrophic Neunzehnhain R. was 0.1 mg/l, while in the highly eutrophic Quitzdorf R., values up to 5.2 mg/l were detected. These extremely high values were measured in October 2001. In the reservoirs with an increased trophic state, strong seasonal fluctuations were detectable (see Fig. 4).

In terms of sediment TP, only small differences between the trophic states could be found (see Fig. 5). Here, the Muldenberg R. showed the smallest values with a mean TP content of 2.3 mg/gDW, and the Quitzdorf R. showed the highest with a mean TP content of 3.5 mg/gDW.

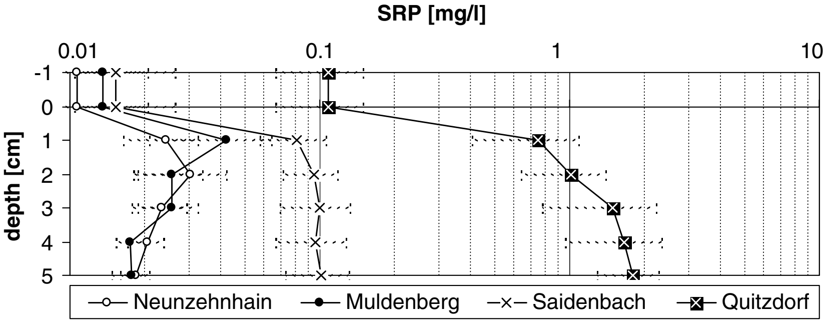

Figure 3. SRP concentrations in the pore water of the reservoirs (means and standard deviations for the sampling period 2000–2001).

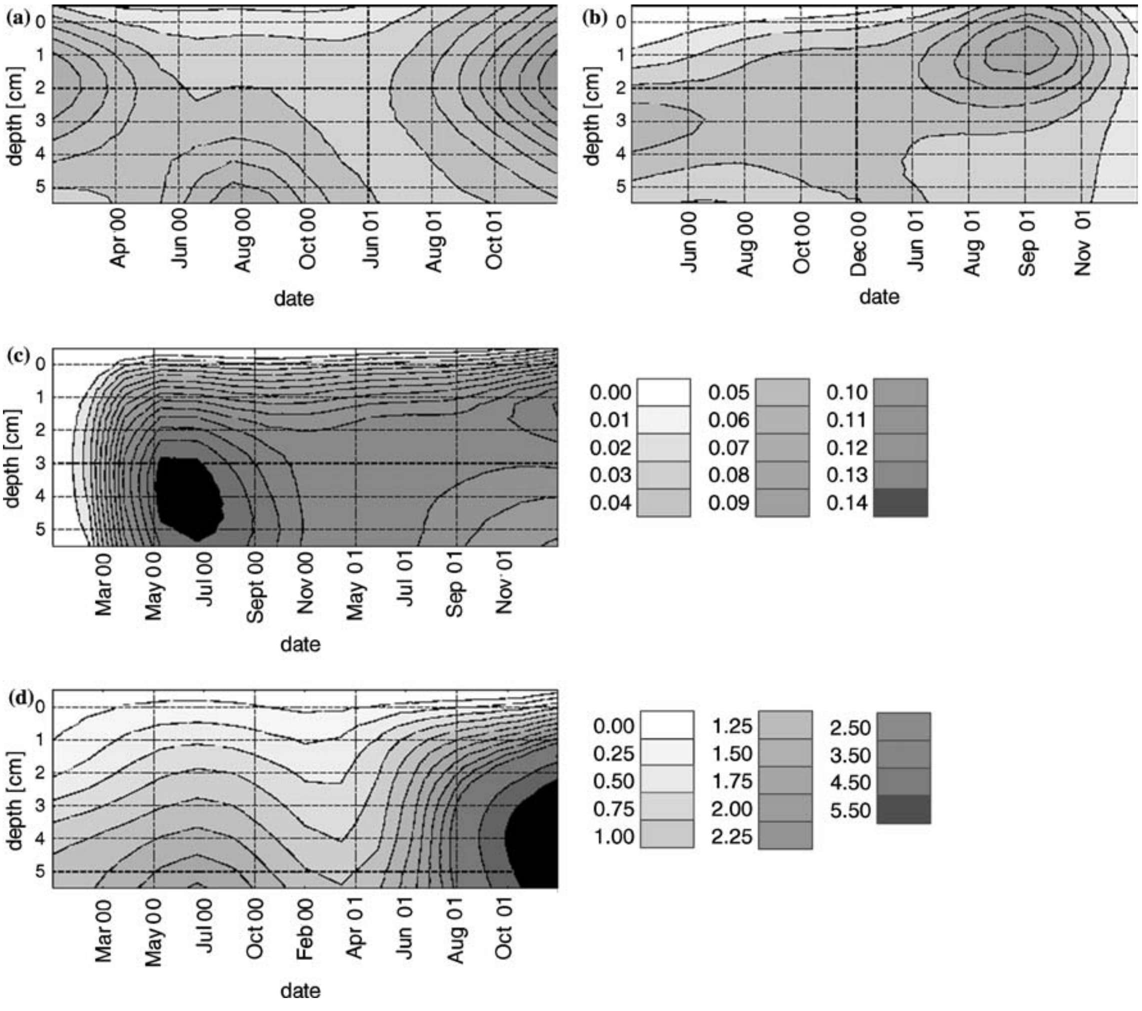

Figure 4. Seasonal variability of the SRP concentrations (mg/l) in the pore water of the reservoirs. (a) Neunzehnhain R.; (b) Muldenberg R.; (c) Saidenbach R.; (d) Quitzdorf R.

In order to examine the potential for sediment phosphorus release, the TP in the sediment was divided by a sequential extraction into different fractions (Psenner et al., 1984). With the comparison of the P fractions, clear differences between the reservoirs are evident, in particular, in the

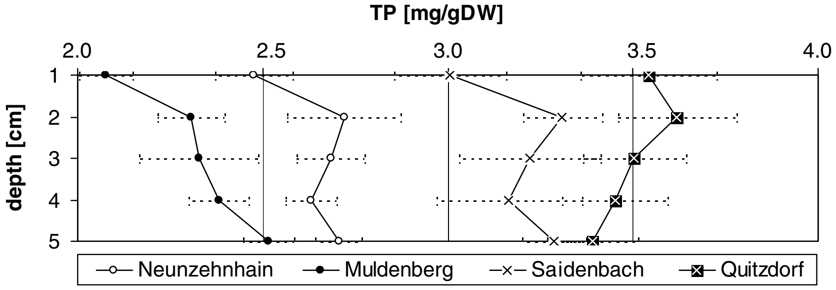

Figure 5. TP contents of the sediment of the reservoirs (means and standard deviations for the sampling period 2000–2001).

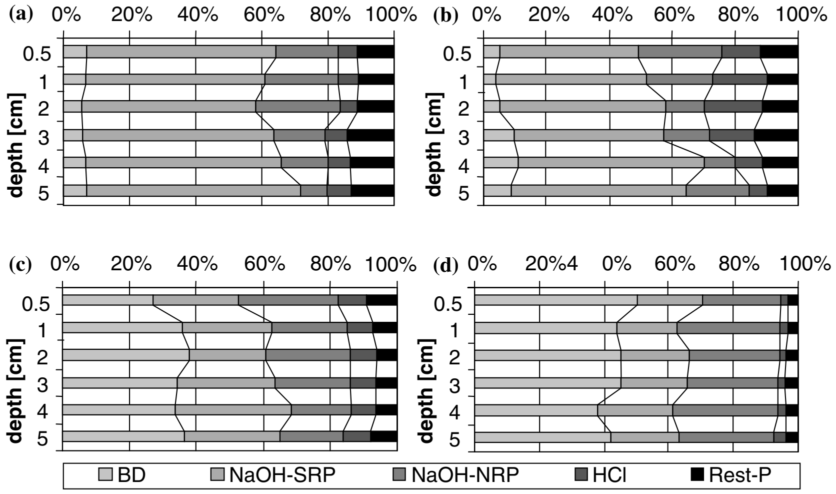

Figure 6. P fractions in the sediment of the reservoirs. (a) Neunzehnhain R.; (b) Muldenberg R.; (c) Saidenbach R.; (d) Quitzdorf R.

reductively soluble iron-bound BD fraction and the reductively insoluble aluminum-bound NaOH–SRP fraction (see Fig. 6). Thus, the contents of the bicarbonate-dithionite-fraction (BD) increased with the trophic state. For example, in the oligotrophic Neunzehnhain R., the mean percentage of the BD fraction was 7%, whereas in the highly eutrophic Quitzdorf R., up to 50% was present. On the other hand, a clear decrease of the stable NaOH–SRP fraction was recognizable with an increasing trophic state, with about 55% in Neunzehnhain and only 21% in Quitzdorf. In the NaOH–NRP fraction, which is assumed to be mainly of autochthonous origin (Penn et al., 1995), differences between the reservoirs could likewise be found. The percentages of this P fraction were slightly increased in the reservoirs with a higher trophic state. In Quitzdorf, a proportion of about 32% could be found, whereas in Neunzehnhain, there was only an average of 18%.

Oxygen profiles in the pore water showed that the penetration depth of oxygen was in agreement with the trophic level. Thus, dissolved oxygen could be detected in Neunzehnhain up to a mean sediment depth of 1.2 cm, in Muldenberg of 0.7 cm, in Saidenbach of 0.4 cm, and in Quitzdorf of 0.1 cm.

In all reservoirs, with exception of the oligotrophic Neunzehnhain R., nitrate was already depleted in a sediment depth of 1 cm. Even in the oligotrophic reservoir Muldenberg, nitrate was generally not found below 1 cm in depth, which was most likely caused by the intensified microbial respiration processes due to the increased allochthonic input of organic ('humic') materials.

The vertical gradients of the sulfate decrease underneath the sediment surface also reflected the trophic condition of the reservoirs (Fig. 7). However, the mesotrophic Saidenbach R. and the P-oligotrophic Muldenberg R. showed almost

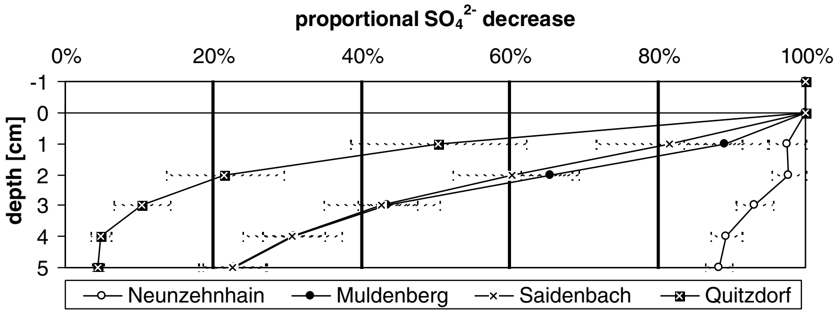

Figure 7. Proportional sulfate decrease in the pore water underneath the sediment surface (means and standard deviations for the sampling period 2000–2001).

similar sulfate gradients. Sulfate losses by microbial sulfate reduction resulted in an accumulation of sulfide in the sediment (Fig. 8). With the sulfide concentration, a dependence on the trophic state was proven. Here however, the values of the P-oligotrophic, but greatly allotrophic (i.e. impacted by humic material) Muldenberg R., exceeded those of the mesotrophic Saidenbach R. The increased sulfide concentrations and sulfate gradients in the sediment of Muldenberg are most likely caused by the intensified input of organic matter, and hence the high organic content of the sediments. The sulfide concentrations were particularly high in the sediment of the highly eutrophic and shallow Quitzdorf R. during the summer months, which may reflect the strong temperature dependence of the sulfate reduction (Urban et al., 1994).

The highest concentration of ammonium in the pore water was attained in the Quitzdorf R. (up to 18 mg/l NH_4^+–N). A clear rise of the ammonium concentration with increasing sediment depth is evident. In addition, a clear increase of the NH_4^+ concentration with rising trophic state can also be

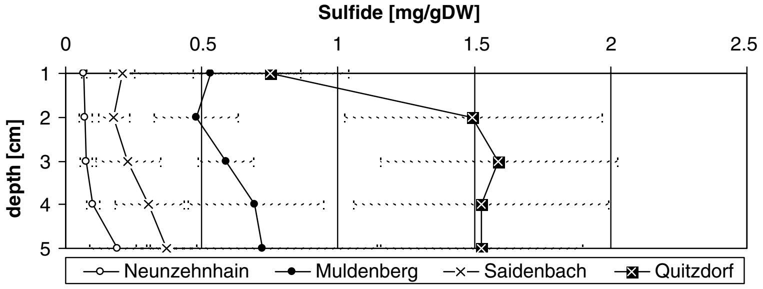

Figure 8. Sulfide concentration in the sediment of the reservoirs (means and standard deviations for the sampling period 2000–2001).

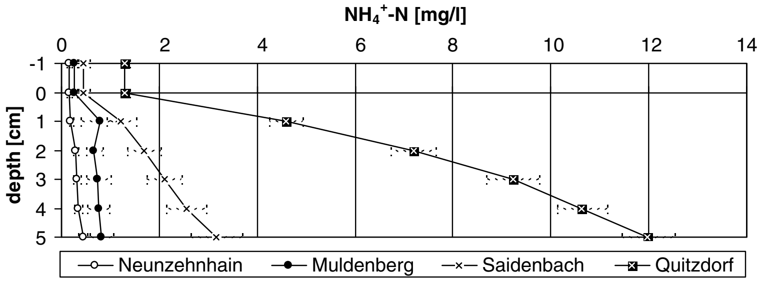

Figure 9. Ammonium concentration in the pore water of the reservoirs (means and standard deviations for the sampling period 2000–2001).

recognized (Fig. 9). During the summer months, the values were highest in the reservoirs Saidenbach and Quitzdorf.

Alkalinity in the pore water showed a clear correlation to the trophic state, with the highest concentrations (up to 7 mmol/l) in the pore water of Quitzdorf (Fig. 10). Furthermore, in Quitzdorf, the sharpest rise in alkalinity with increasing sediment depth was also found. In the more eutrophic reservoirs (Saidenbach and Quitzdorf), the alkalinity was highest during the summer period.

It became obvious, that DOC concentrations increased with rising trophic state (e.g. Quitzdorf up to 90 mg/l DOC, see Fig. 11). However, the Muldenberg R. should be regarded separately, due to its dystrophic character, since high DOC concentrations could be found here, too. Furthermore, with statistical methods, no significant differences could be stated between the reservoirs with a higher trophic level (Saidenbach versus Quitzdorf) and between the highly eutrophic Quitzdorf R. and the dystrophic Muldenberg R. ($p > 0.05$). Therefore, it has to be concluded, that the DOC concentrations of the Muldenberg R. are similar to those of the reservoirs with higher trophic states (Saidenbach, Quitzdorf) and cannot be used as a trophic indicator. As for the other parameters which represent end products of microbial decomposition, higher concentrations of DOC could be found during the summer months.

The concentrations of metals in the pore water and in the sediment showed significant differences between the reservoirs and specific patterns for each of the examined waters (see Fig. 12). The oligotrophic Muldenberg R. displayed the highest iron concentrations in the pore water and in the dry sediment. In the pore water, the seasonal differences were relatively high, which is shown by the relatively high standard deviation. The concentration of manganese was highest in the Saidenbach R., both in the sediment and in the pore water, while the concentration in the pore water showed high seasonal differences. Here, the highest concentrations were measurable in the summer months, which was related to the strong decrease of the redox potential in this period (down to −270 mV). Since the reoxidation of dissolved, reduced manganese occurs only very slowly (Waite et al., 1988), a strong accumulation in the sediment occurred. The Quitzdorf R. is characterized by a high concentration of calcium in the sediment and in the pore water. This may be related to the

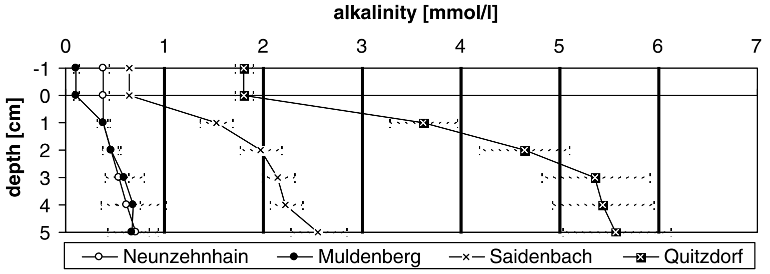

Figure 10. Alkalinity in the pore water of the reservoirs (means and standard deviations for the sampling period 2000–2001).

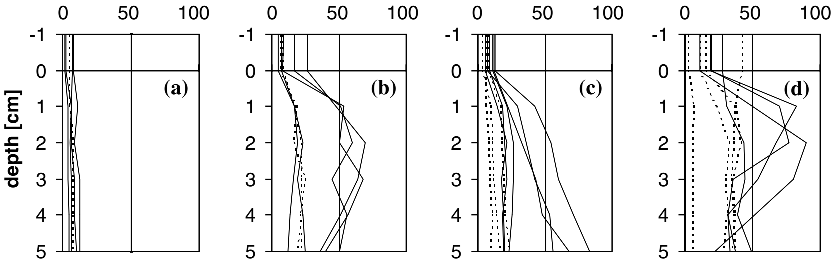

Figure 11. DOC concentrations (mg/l) in the pore water of the reservoirs (dotted lines: fall/spring turnover, full lines: summer months). (a) Neunzehnhain R.; (b) Muldenberg R.; (c) Saidenbach R.; (d) Quitzdorf R.

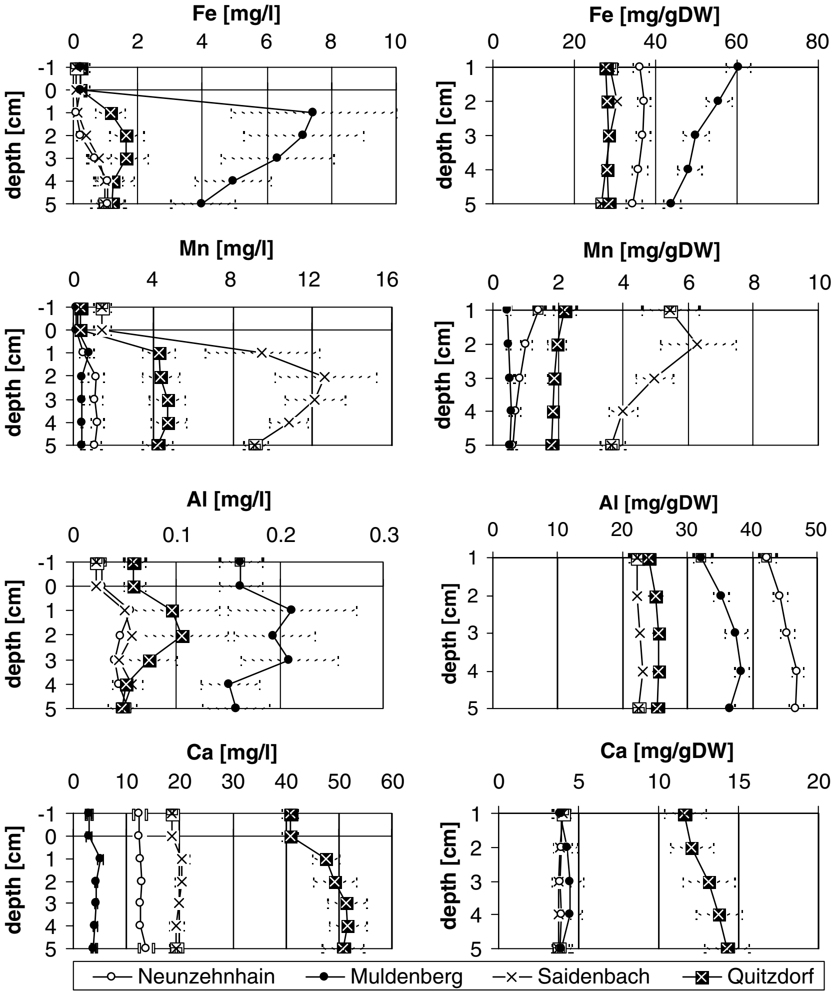

Figure 12. Metal concentrations (Fe, Mn, Al, Ca) in the pore water (mg/l) and in the dry sediment (mg/gDW) of the reservoirs (means and standard deviations for the sampling period 2000–2001).

higher calcium content of the inflowing water and to biogenous decalcification due to the strong CO_2 depletion by the phytoplankton. In late summer, the pH of the water body may attain a level up to 10.5 near the surface (S. Jähnichen, personal communication).

Discussion

In the Saidenbach and Quitzdorf reservoirs, the SRP concentration of the pore water increased during the summer months, due to the strong input of phytoplankton biomass and high water temperatures, which in turn increased the microbial decomposition and the intensity of diffusion processes in the sediment.

The differences in the concentrations underneath the sediment surface and the resulting different concentration gradients affect the phosphorus release at the sediment-water interface. In terms of P inputs into the reservoirs (Fig. 13), it is recognizable that these correspond to the respective trophic state. The Quitzdorf R. showed the highest total P input, which amounted up to 11705 kgP/yr, whereas the input into the oligotrophic Neunzehnhain R. was only 24 kgP/yr. The increased P inputs into the reservoirs with higher trophic state are caused on the one hand by the P load from the catchment areas, since a higher percentage

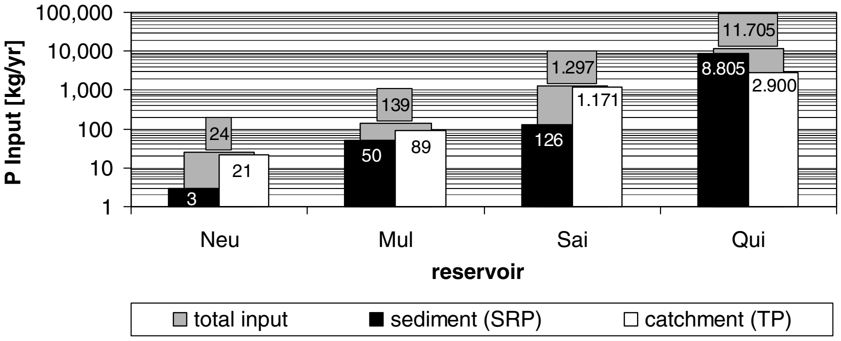

Figure 13. P inputs into the reservoirs from their catchment areas (raw data: Reservoir Administration of Saxony) and from the sediment.

of agriculturally used areas is present here than around the reservoirs with lower trophic state. On the other hand, in the highly eutrophic Quitzdorf R., a substantial percentage of the total P input is caused by the sediment as is evident from Fig. 13. In Quitzdorf, this internal P input with 8800 kg/yr is about three times higher than the external input with 2900 kg/yr. Thus, the sediment in Quitzdorf has a decisive influence on the trophic state of the reservoir, and should therefore be included into the P budget of the reservoir when restoration measures come into consideration.

The strong influence of the sediment in the Quitzdorf R. is a typical phenomenon, which occurs in nutrient-rich shallow waters. Here, the water body is usually strongly mixed and warmed to the bottom in the summer months, so that microbial processes and diffusion from the sediment are strengthened by the increased temperatures. Furthermore, because of the absence of a stable stratification, the nutrients are transported rapidly into the euphotic zone.

Comparing the TP contents in the sediment with the SRP concentrations in the pore water and the resulting P release rates, no significant correlation could be determined. Thus, the assumption of Uhlmann et al. (1997) could be confirmed that the P release is not, or only slightly, affected by the TP content of the sediment, which therefore cannot be used for trophic evaluation.

In terms of the SRP release relative to the TP concentrations in the epilimnion, a clear correlation could be found during the summer months or summer stratification, respectively (see Fig. 14). This can be explained by the microbial decomposition of P containing detritus in the sediment. This detritus forms in the water body by intensified phytoplankton growth, and thus leads to the formation and release of bioavailable SRP from the sediment. Also, the TP content in the water body is affected by the SRP release from the sediment.

Regarding the P fractions in the sediments, it becomes obvious that the reductively soluble BD

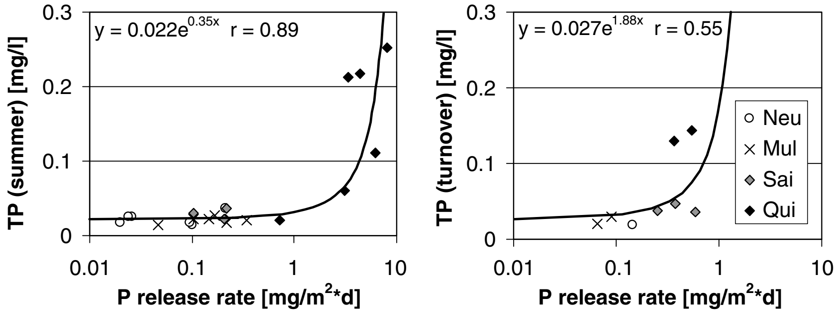

Figure 14. Correlation between the SRP release from the sediment and the TP concentration in the epilimnion during the summer months and during turnover.

fraction, in which the phosphate is bound to iron and manganese oxides is highest in the reservoirs with higher trophic state. On the other hand, the aluminum-bound P fraction (NaOH–SRP) is relatively small. This confirms the results of other authors that the Fe/Mn-bound P fraction has a strong influence on the P release potential of the sediments (e.g. Boström et al., 1982; Søndergaard, 1989; Petticrew et al., 2001). The correlation between phosphate and the corresponding metals becomes particularly clear in the comparatively stable Al–P fraction. Thus, in the oligotrophic Neunzehnhain R., in which the aluminum content of the sediment is highest, the Fe/Mn–P fraction is very small and a high percentage of the phosphorus is stably bound to aluminum. In the reservoirs Saidenbach and Quitzdorf, which exhibit smaller aluminum concentrations in the sediment, the percentage of the aluminum-bound P fraction accordingly is smaller, as might be reasonably expected.

The NaOH–NRP fraction mainly represents the biologically bound phosphorus (e.g. Psenner et al., 1984; Hupfer & Gächter, 1995). This contains, besides organic phosphorus (Uhlmann et al., 1990) and phosphorus bound to humic substances (Pettersson, 1986), also inorganic polyphosphates (Uhlmann et al., 1990; Hupfer et al., 2004). The increased portion of the biogenic phosphorus in the Quitzdorf R. is most likely caused by the high content of *Microcystis* cells in the sediment, many of which contain poly-P granules. Also, many algae and other bacteria are able to store poly-P (Hupfer & Uhlmann, 1991; Hupfer et al., 2004). When the environment becomes anoxic, SRP is released due to degradation of poly-P with consequent P release from the sediment (e.g. Gächter & Meyer, 1993; Goedkopp & Pettersson, 2000). Thus, also the NaOH–NRP fraction can be regarded as a parameter for trophic evaluation.

The vertical concentration gradients of the electron acceptors such as nitrate and sulfate became steeper with rising trophic level, and thus correspond to the classical conception of Mortimer (1941, 1942). The intensified microbial consumption of nitrate and of sulfate in the Quitzdorf and Saidenbach sediments during the summer months was in agreement with the findings from other standing waters of high trophic state (e.g. Sinke et al., 1992; Sherman et al., 1994).

As has been stated already by Ohle (1954), microbial sulfate reduction induces, by the formation of sulfide, the displacement of phosphate from iron-phosphorus complexes of lake sediments. If not enough iron is available for the formation of largely insoluble iron sulfides, phosphate is released into the water (Nürnberg 1996; Kleeberg 1997; Kleeberg & Dudel 1997). Thus, the highest concentration of sediment sulfide and the highest SRP release were observed in the Quitzdorf R. (Figs. 8 and 13, see also Murray, 1995; Giordani et al., 1996). Other parameters closely related to the trophic conditions and to the microbial activity in the sediments were ammonium, alkalinity and DOC in the pore water. Significant differences between the four reservoirs ($p < 0.05$) could be found (with the exception of DOC). In the reservoirs with a higher trophic state (Saidenbach, Quitzdorf) the upward flux of ammonium was higher and NH_4^+ concentration showed a strong seasonal variability with higher values in the summer months due to an increased sedimentation flux of phytoplankton and higher

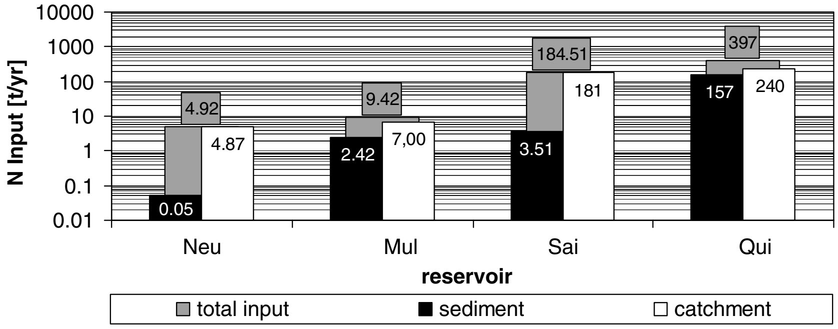

Figure 15. N inputs into the examined reservoirs from their catchment area (raw data: Reservoir Administration of Saxony) and from the sediment.

temperatures. In Fig. 15, the nitrogen inputs into the examined reservoirs are shown.

Figure 15 indicates that both the internal and the external N inputs increased with the trophic state. However, the internal N load in the Quitzdorf R. increased not as drastically as the P input (Fig. 13). In addition, the external N load exceeded the internal one in Quitzdorf, in contrast to the P loads in this reservoir. The high external nitrogen inputs into the Saidenbach R. and the Quitzdorf R. are a consequence of the agricultural use and the associated surface discharge of N fertilizers (Uhlmann & Paul, 1994).

In the pore water, significant correlations, could be found between alkalinity and SRP ($r = 0.82$) and alkalinity and ammonium ($r = 0.93$), respectively. The close correspondence between alkalinity and SRP can be explained with the increase of both parameters under anaerobic conditions, since the solubility of phosphate is strongly dependent on the presence of electron acceptors, such as oxygen, nitrate or sulfate. Both alkalinity and SRP mainly result from microbial decomposition processes. This explanation is affirmed by the strong correlation between alkalinity and ammonium, since both parameters are clear indicators of microbial mineralization processes. Significant correlations between ammonium concentration and the rate of carbon mineralization have been described for different sediment habitats (e.g. Thamdrup & Canfield, 1996). The significant correlation between alkalinity and SRP confirms the statement of Ohle (1952), that alkalinity is an important trophic indicator.

DOC in the pore water can be regarded as a relatively stable end product of microbial decomposition. In the non-dystrophic reservoirs, a higher trophic state (i.e. phytoplankton production) leads to an increased microbial activity and thus to higher DOC in the pore water. The high DOC concentrations in the dystrophic reservoir Muldenberg are predominantly of allochthonous origin (Maassen, 2003). In particular, the POC from the catchment is microbially metabolized into DOC.

Iron concentrations in the pore water and in the dry sediment were highest in the dystrophic Muldenberg R.. Reductive dissolution of particulate iron cannot be the reason in the case of the pore water, since the redox potential was relatively high. As in one of the two main tributaries iron and DOC are strongly correlated (W. Schmidt, personal communication), this complexation might also be relevant in the pore water. The relatively low concentration of dissolved iron in the pore water of the highly eutrophic Quitzdorf R. points to the fact that it has been converted into iron sulfides. This assumption is confirmed by the high concentrations of sulfide in the sediment (up to 3.5 mg/gDW). Consequently, no iron is available to immobilize the phosphate (Roden & Edmonds, 1997; Clavero et al., 1997).

Unlike the binding of phosphate to oxidized iron, the stability of the Al–P complexes is redox-independent and accordingly high. From the literature, it is well-known that the sediment P can only be robustly immobilized if the ratio between metal and phosphorus exceeds a certain value. For iron, the molecular ratio should be higher than 15 (Jensen et al., 1992), and for aluminum, higher than 11 (Kopáček et al., 2000; Rydin et al., 2000).

From Fig. 16 it is evident that in the reservoirs with lower trophic state (Neunzehnhain, Muldenberg), the Al:P ratios are higher than the values

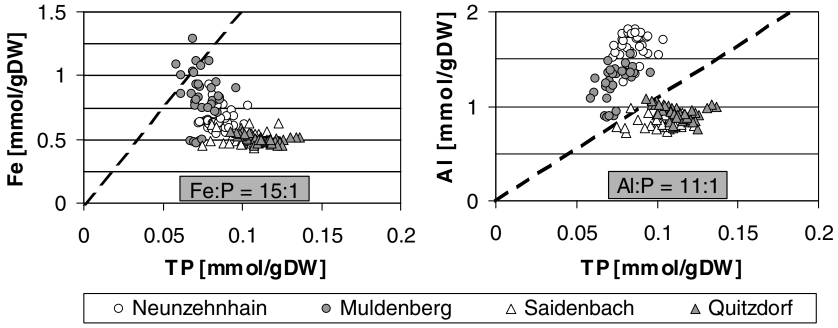

Figure 16. Molecular Fe:P and Al:P ratios in the sediments of the reservoirs. The broken line corresponds to the critical ratios mentioned in the text.

mentioned. In the reservoirs with higher trophic level (Saidenbach, Quitzdorf), the ratios are lower than 11. The Fe:P ratios for all examined reservoirs, with the exception of some values of Muldenberg, are lower than the values described in the literature. It can be concluded that above all, the aluminum content in the sediments of the examined reservoirs has a crucial influence on the P binding capacity, and thus on the trophic state.

The relation between the SRP concentrations in the pore water and the molecular Fe:P and Al:P ratios of the sediments is shown in Fig. 17. Underneath a certain threshold with both metal: phosphorus ratios, an increased SRP release becomes evident. For the Al:P ratio, the critical value was between 11 and 12 and so it was similar to the values described in the literature. For the Fe:P ratio, however, the critical value was 6, and thus smaller than the data given in the literature.

In all of the examined reservoirs, a strong correlation between the Fe:SRP and Al:SRP ratios could be found (see Fig. 18). This confirms that both metals have a high affinity for the phosphate in the pore water, and thus strongly affect the SRP release.

Both iron and aluminum are important in the formation of metal–P complexes and the immobilization of phosphorus. Thus, using a metal: phosphorus sum ratio (MPS), which is calculated from the sum of the Al + Fe content and the TP of the sediment, an estimate of the phosphorus binding capacity of sediments can be derived. The molecular MPS can be computed according to the following formula:

$$\mathrm{MPS} = \frac{\left(\frac{C_{\mathrm{Fe}}}{M_{\mathrm{Fe}}} + \frac{C_{\mathrm{Al}}}{M_{\mathrm{Al}}}\right)}{\frac{C_{\mathrm{P}}}{M_{\mathrm{P}}}}$$

with MPS: molecular metal:phosphorus sum ratio (dimensionless)

C_i: concentration of the respective element (Fe, Al, P) (g/kgDW)

M_i: molecular weight of the respective element (Fe, Al, P) (g/mol)

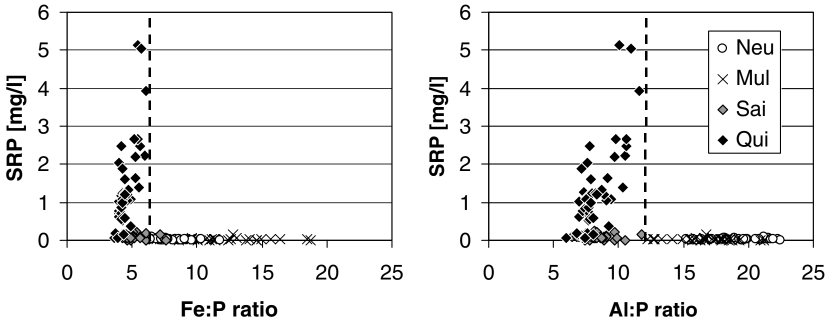

Figure 17. Relation between the SRP concentration in the pore water and the molecular metal:phosphorus ratios in the sediment of the reservoirs.

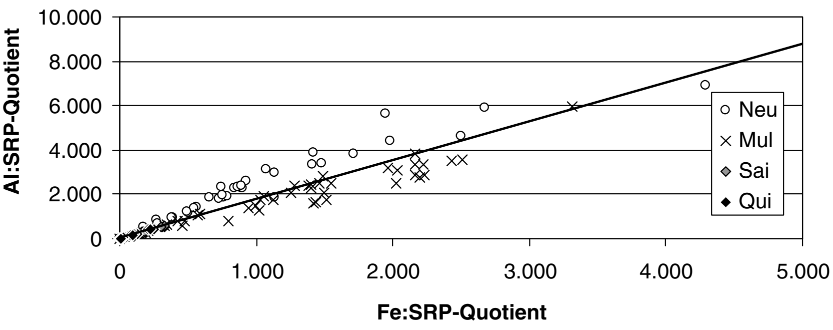

Figure 18. Correlation between the ratios of aluminum (dry sediment):SRP (pore water) and iron (dry sediment):SRP (pore water) ($r = 0.95$).

($M_{\mathrm{Fe}} = 55.85$ g/mol; $M_{\mathrm{Al}} = 26.98$ g/mol; $M_{\mathrm{P}} = 30.97$ g/mol)

For the reservoirs examined in this study, a significant increase of the SRP concentration in the pore water resulted if the MPS in the sediment was smaller than 18 (see Fig. 19). From this fact it can be concluded that the sediments at a MPS < 18 have a P binding potential, which is too small to prevent the release of dissolved phosphate. Therefore, the MPS can be used as a parameter for the trophic evaluation of waters.

The investigation of the sediments of the four reservoirs revealed that some parameters of the pore water and of the sediment show significant correlations to the trophic state. Particularly, the pore water concentration of dissolved phosphate (SRP), ammonium and alkalinity, as well as the Fe:P and Al:P ratio (or the MPS, respectively), and the P fractions in the sediment exhibited clear relations to the trophic state. Since the determination of the P fractions is a relatively time-consuming procedure, it would not be applicable for a routine investigation of sediments. The other parameters, however, appear suitable components for the evaluation of the trophic state of standing waters and of future trends in water quality.

The pore water parameters SRP, ammonium, alkalinity and MPS correspond to the criteria for the trophic evaluation of standing waters (LAWA, 1989): practicability, applicability to waters with different characteristics and scientific justification. All parameters can be determined relatively easily. Unlike these parameters, which preferably should be examined at the beginning and the end of the summer, the values of the metal:phosphorus ratios (Al:P, Fe:P, MPS) are relatively constant and thus can be determined at any time of the year.

In Table 2, a preliminary trophic system is specified, which is based on the commonly used trophic classification system (Klapper et al., 1989).

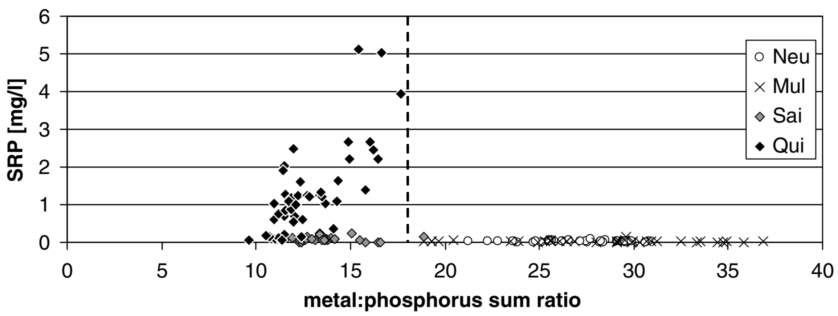

Figure 19. Relation between the SRP concentration in the pore water and the molecular MPS in the sediment.

Table 2. Preliminary evaluation system for the trophy-relevant parameters of the pore water and the dry sediment (on the basis of the examined reservoirs)

	Oligotrophic	Mesotrophic	Eutrophic	Eutrophic–hypertrophic	Hypertrophic
1. mean values during the vegetation period (maximum of the upper 5 cm of the pore water, sampling distance between sediment layers 1 cm):					
SRP (mg/l)	< 0.10	0.10–0.25	0.25–1.00	1.00–2.50	> 2.50
NH_4^+-N (mg/l)	< 3.00	3.00–5.00	5.00–10.0	10.0–18.0	> 18.0
alkalinity (mmol/l)	< 1.00	1.00–3.00	3.00–5.00	5.00–7.00	> 7.00
2. seasonally independent parameters (minimum of the upper 5 cm of the dry sediment, sampling distance between sediment layers 1 cm):					
mol. Al:P-ratio	> 12	> 12	< 12	< 12	< 12
mol. Fe:P-ratio	> 6	> 6	< 6	< 6	< 6
sum ratio (MPS)	> 18	> 18	< 18	< 18	< 18

All parameters relevant for the trophic level and threshold values between the individual trophic states in the table are based on the results of the investigations of the four reservoirs with a sampling distance between the sediment layers of 1 cm. The trophic state hypertrophic is regarded as the highest and open upper limit. Despite a different thickness of the sediment layer depending upon depth and morphology of the water body, it mostly can be assumed that the layer of the uppermost 5 cm of the sediment is involved in the vertical exchange processes, and thus well suitable as a basis for monitoring. The values from the greatest depth should in each case be regarded as 'worst case', i.e. as maximum pore water concentration and minimum metal:phosphorus ratio. To assure the relevance of the sediment and pore water parameters for the evaluation of the trophic state, more standing waters with different trophic states need to be studied, in particular those with a very high calcium carbonate content in the sediment and in the pore water.

The results of this study may form an important basis for the trophic evaluation of standing waters. Sediment and pore water both reflect the trophic characteristic of the water body, and are, in turn, also strongly affected by it. Therefore, it seems reasonable to attach a greater importance to the parameters in the sediment and the pore water, and to include these parameters into common trophic evaluation systems.

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