

Evidence for aluminium precipitation and phosphorus inactivation in acidified watershed-reservoir ecosystems

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Abstract

Downstream from the confluence of acidic, aluminium-rich brooks and circumneutral brooks the precipitation of Al was observed in the forested catchment of the Neunzehnhain reservoir (Ore Mountains, Germany). A similar phenomenon known from the slate mining area of Thuringia was studied for comparison. Laboratory simulation experiments showed that this Al precipitation was due to a slight pH increase and the presence of sulphate or phosphate ions which were in part included in the precipitates. In competition with Fe, Al bound orthophosphate more effectively under these chemical conditions. The same mechanism was evident in the sediments of three reservoirs with acidified watersheds. Sequential extraction revealed that P was mainly associated with Al. In spite of low redox conditions linked with strong iron release, no P release was observed in the interstitial water. These results were in contrast to the findings for the sediment of the Saldenbach reservoir with non-acidified catchment. The acid-induced Al mobilization from the bedrock is partly moderated by alkalinity-generating processes which enhance the Al retention in sediments. Simultaneously, the elevated Al content in sediments leads to inactivation and burial of phosphorus even under low redox conditions.

Key words: acidification, aluminium precipitation, phosphorus cycle, sediment composition

This contribution is dedicated to Prof. Dietrich Uhlmann (Germany) on the occasion of his 70th birthday

Introduction

The phosphorus (P) cycle of lake ecosystems is regulated by both biotic and abiotic factors (BOSTRÖM & al. 1982, 1988, FORSBERG 1989, GÄCHTER & MEYER 1993, DE MONTIGNY & PRAIRIE 1993). Concerning the abiotic factors, the sorption of orthophosphate onto inorganic compounds (colloids, clays, minerals) of iron (Fe), aluminium (Al), and calcium (Ca) as well as humic substances and the subsequent sedimentation are relevant processes of P removal from the water column. The ultimate phosphorus removal in the P cycle is determined by the capacity of anoxic sediments to retain the buried P (LIJKLEMA 1994, HUPFER & al. 1997). Ferric iron is widely accepted as the primary active P-retaining inorganic compound in fresh waters (LIJKLEMA 1977, BUFFLE & al. 1989, JENSEN & al. 1992). However, the adsorption capacity of sediments is drastically reduced under anoxic conditions, and P is liberated when Fe(III) is reduced to Fe²⁺ and dissolved (EINSELE 1936, MORTIMER 1941, 1942). The chemistry of phosphate in sediments is also connected to Al, especially in soft waters (PORTIELJE & LIJKLEMA

1993), and to Ca in hard waters (MURPHY & al. 1983, GOLTERMAN 1998). Concerning soft-water reservoirs and lakes, it has recently been shown that Al might play a key role in phosphorus inactivation and burial in the sediment under low redox conditions (HUPFER 1993, ULRICH 1997, UHLMANN & al. 1997, KOPACEK & al. 2000). These processes seem to be influenced by strong or episodic acidification in the watershed and subsequent neutralization in the water column or near-bottom water. Regarding non-acidified reservoirs with acidified watersheds, HORN & al. (2000) and HOEHN (1998) calculated a significant Al retention in the sediments of Neunzehnhain Reservoir in the Ore Mountains and Kleine Kinzig Reservoir in the Black Forest, respectively. ULRICH (1997, 1998, 2000) confirmed the enrichment of Al in the sediments of these reservoirs and demonstrated the P binding onto Al compounds by means of sequential extraction.

The aims of this study are (1) to give some insight into the processes of precipitation of Al mobilized from the bedrock by acidification, and (2) to illustrate that the Al precipitation process might strongly be connected with binding and immobilization of phosphate in the sediment even under low redox conditions.

Study sites

The main study sites of this investigation are located in the Ore Mountains, Germany. Four reservoirs of which the first three mentioned below are used for drinking-water supply were compared: (1) the oligotrophic and circumneutral reservoir Neunzehnhain II, (2) the mesotrophic (formerly eutrophic) Saidenbach reservoir, and the oligo-mesotrophic acidified reservoirs Sosa (3) and Falkenstein (4). The main characteristics of the reservoirs and their catchments are listed in Table 1. Contrary to the catchment of Saidenbach reservoir which is

Table 1. – Selected characteristics of the investigated reservoirs and their catchments. Data from STIEBER (1992) and HORN & HORN (1995).

Reservoir	Neunzehnhain	Saidenbach	Sosa	Falkenstein
Drainage area (km ²)	13.7	60.7	24.4	13.3
- agricultural area (%)	18	73	4	0
- forested area (%)	80	19	94	88
Population density (inhab./km ²)	0	86	15	31
Altitude (m a.s.l.)	525–680	439–701	638–1037	562–785
Annual mean rainfall (mm)	980	830	1200	834
Bedrock geology	mica slate, gneiss	gneiss	tourmaline granite	phyllite slates
Lake area (ha)	29	146	39	13.2
Lake volume (hm ³)	2.93	22.4	5.94	1.2
Maximum depth (m)	33	48	49	20
Mean depth (m)	10.1	15.3	15.2	9.1
Mean retention time (a)	0.74	0.58	0.45	0.21
Range of pH	6.0–7.5	6.3–9.7	4.5–5.9	4.1–5.3
Mean NO ₃ ⁻ concentration (mg/L)	16	25	5	5
Mean SO ₄ ²⁻ concentration (mg/L)	42	57	22	33
Mean alkalinity, K _{S+3} (mmol/L)	0.11	0.4–0.6	0–0.04	0–0.05
Reservoir starting	1914	1933	1952	1977

dominated by farmland, the catchments of the other three reservoirs are mainly covered by forest. Due to the siliceous bedrock with a high Al content, the catchments are highly sensitive to acid rain and Al leaching. The inlets of the Sosa and Falkenstein reservoirs are permanently, the inlets of the Neunzehnhain reservoir episodically acidified. In the Saidenbach catchment, acid rain is buffered due to the higher carbonate content of the bedrock (grey gneiss) and the application of lime to the agricultural areas (UHLMANN & al. 1997).

Apart from the reservoirs, in the Neunzehnhain watershed small unnamed brooks were studied which sometimes showed whitish precipitates on their streambed sediment. Since this phenomenon is well known from streams in the slate mining area around Lehesten and Ludwigstadt (southeastern Thuringia), the confluence of the Loquitz and the Aubach was investigated for comparison. The Loquitz was characterized by strong acidification and high Al and sulphate concentrations due to acid mine drainage from slate stone dumps, whereas the Aubach was affected by municipal sewage. A detailed site description is given by PEIFFER & al. (1997).

Material and Methods

Sampling and preparation – Stream water was sampled with a polyethylene beaker and water temperature, pH, and conductivity were measured immediately. In addition to the unfiltered water samples, subsamples were filtered through 0.45 μm cellulose acetate filters and stabilized by addition of nitric acid to pH 2. The precipitates were either scraped from stones of the riverbed using a plastic spoon or washed down from leaf litter with distilled water. After centrifugation the precipitates were dried at 30°C and carefully homogenized.

The reservoir sediments were sampled with a gravity corer (Uwitech, Austria). In the laboratory, the preparation of the cores was performed in a glovebox under argon atmosphere. Before slicing the sediment, the overlying water was separated with a syringe and filtrated. To obtain the pore water, sediment samples of the horizons 0-0.5, 0.5-1, 1-2, 2-3, 3-4, and 4-5 cm were centrifuged (11,000 rpm) and 0.45 μm -filtrated in the glovebox. Then, redox potential, pH, and conductivity were measured by means of electrodes. Stabilization of the pore water was performed with HNO_3 as described above. Subsamples of the sediment were oven-dried at 105°C and combusted at 550°C to give the loss on ignition (LOI).

Phosphorus fractionation – According to PSENNER & al. (1984, 1988) and HUPFER (1995), four fractions were extracted from the sediment layers 0-1, 1-2, and 4-5 cm by the following sequence: (1) deoxygenated distilled water (' H_2O ') at 6°C (10 min) to remove P dissolved in the pore water and adsorbed onto surfaces, (2) 0.11 M $\text{Na}_2\text{S}_2\text{O}_4$ and 0.11 M NaHCO_3 (circumneutral buffered dithionite, 'BD') at 40°C (30 min) to extract P from Fe-oxyhydroxides under anoxic conditions, (3) 1 M NaOH at 20°C (16 h) to obtain soluble reactive P (SRP) from amorphous Al- and Fe-oxyhydroxides and non-reactive P from organisms, detritus and humic substances after oxidative digestion, and (4) 0.5 M HCl at 20°C (24 h) followed by oxidative digestion (0.074 M $\text{K}_2\text{S}_2\text{O}_8$) to release P associated with carbonates, apatite, and refractory organic matter. P fractionation was generally performed in duplicate. In the fractions not only SRP and total dissolved P (P_{diss}), but also co-extracted metals (Al, Fe, Mn, Ca, Mg) were analysed. Dissolved elements X with different possible species are written in the form X_{diss} .

Laboratory experiments – Precipitation experiments under controlled conditions were performed to test and confirm the chemical key parameters which trigger Al precipitation in the field. This way, precipitates were gained for comparative speciation analyses. The batch experiments were started with acid (pH 3) Al(III)- and/or Fe(III)-chloride solutions and various concentrations of sulphate and/or phosphate. By stirring the solution, 0.01 M NaOH was

carefully titrated until a precipitation started. The influence of Ca^{2+} and Mg^{2+} on the precipitation reaction was tested as well.

Nearly undisturbed sediment cores (diameter 85 mm) of the acidified Sosa reservoir were used to exemplify the release of Al, Fe, and P under in-situ temperature (6°C) and various pH and oxygen conditions in the overlying water. Three pH ranges were simulated: pH~4.7 (in-situ pH of the water column), pH~6.5 (in-situ pH of the sediment) and pH~3.5 (simulated strong acidification of the inlet). Additionally, either oxic conditions by bubbling of air or anoxic conditions by bubbling of argon into the overlying water were simulated. Unfortunately, the combination of pH 3.5 and anoxia failed due to a technical problem. During six days, the pH, redox potential, water temperature, and the concentrations of Al_{diss} , Fe_{diss} , and P_{diss} were determined in the overlying water.

Analyses – Orthophosphate was analysed photometrically according to the standard molybdate method (DIN 38405-D11–1/4). Aliquotes of samples were digested 2 h under pressure with persulphate to turn P_{diss} of filtrates or the total P (P_{tot}) of unfiltered samples into orthophosphate. The digestion of dried sediment and precipitate samples was performed as described in ULRICH (1997). Al, Fe, Mn, Mg, Ca, Zn, and Si concentrations were measured by inductively coupled plasma atomic emission spectrometry (ZEISS Plasmaquant 110) using ultrasound nebulization.

Results

Aluminium precipitation in the watershed

In the Neunzehnhain watershed as well as in the slate mining region of Thuringia, direct precipitation of Al was obvious in some brooks and streams especially downstream from confluences. Digestive analyses and combustion of the whitish precipitates which covered rocks and leaf litter on the streambeds showed a clear dominance of Al up to 25% of dry weight and a relatively high loss on ignition (Table 2). Scanning electron microscopy combined with energy-dispersive X-ray (SEM-EDX) analyses confirmed the dominance of Al besides oxygen, sulphur, and traces of silicium in the Neunzehnhain precipitate which was shown to be amorphous with respect to the X-rays. Infrared spectra of both the Neunzehnhain and the Loquitz precipitate were different from spectra of freshly precipitated or crystalline Al-hydroxide, but gave evidence for basic Al compounds including hydroxyl (OH^-) and sulphate (SO_4^{2-}) or phosphate (PO_4^{3-}) groups (ULRICH & PÖTHIG 1999). However, typical Al-SO_4 -salts such as alunite, basaluminite, zaheerite, jurbanite, and others were not detectable.

Analyses of pH and Al_{diss} concentrations upstream and downstream the confluences revealed that Al precipitation occurred when acidic ($\text{pH}<5$) brook water with an elevated Al_{diss} concentration (0.8–4 mg/L) mixed with circumneutral brook water with nearly undetectable Al_{diss} concentration (0.05 mg/L). Due to this precipitation process, the Al_{diss} concentrations downstream the confluences were significantly lower than expected from the mixing of both brooks (Table 3). In addition, in the mixed stream water the pH was higher than expected

Table 2. – Element concentration (mg/g) and loss on ignition (LOI, % of dry weight) in the dried precipitates from the Neunzehnhain brook (08/10/96) and the Loquitz downstream the Aubach confluence (22/05/98). n.a.: not available.

Location	Al	Fe	Mn	Zn	Ca	Mg	Si	P	LOI
Neunzehnhain brook	190	6.2	0.31	0.19	0.66	1.3	22.1	0.28	42
Loquitz stream	254	1.7	0.04	0.27	0.67	0.2	n.a.	7.44	34

Table 3. – pH, concentrations of dissolved metals (mg/L) and phosphorus ($\mu\text{g/L}$) in the Neunzehnhain brooks (08/10/96, 05/05/97, 25/03/99) and in the Loquitz stream system (22/05/98). $F = 100 \cdot (\text{concentration in the confluence brook}) / (\text{expected mixing concentration})$, n.a.: not available.

Date	Sampling location	pH	Al	Ca	Mg	Mn	Zn	P
08.10.96	neutral brook	6.85	0.05	23.5	10.5	0.01	0.03	n.a.
	acidic brook	4.98	2.31	20.0	8.5	0.43	0.43	n.a.
	confluence brook	5.47	0.94	21.1	9.2	0.28	0.30	n.a.
	F (%)	49.4	61.6	99.3	99.9	99.9	103	n.a.
05.05.97	neutral brook	6.66	0.05	20.6	10.1	0.01	0.02	3.7
	acidic brook	4.83	0.84	18.5	8.7	0.28	0.33	2.5
	confluence brook	5.40	0.56	18.7	8.8	0.23	0.28	2.5
	F (%)	28.3	69.8	98.4	99.3	85.4	90.0	97.7
25.03.99	neutral brook	6.5	0.06	19.3	9.4	0.01	0.03	1.1
	acidic brook	5.02	1.61	16.5	7.8	0.32	0.36	1.9
	confluence brook	5.54	0.49	17.2	8.3	0.20	0.24	0.2
	F (%)	49.2	49.7	97.5	98.5	105	103	11.5
22.05.98	Loquitz stream	5.2	3.8	50.3	12.1	2.02	0.67	2
	Aubach stream	7.8	0.04	48.8	5.1	0.06	0	560
	confluence stream	7.0	0.14	49.9	9.6	1.32	0.42	6
	F (%)	2.4	5.6	100.2	100.1	99.3	95.6	3.2

from the dilution, indicating that neutralization processes were involved. The concentrations of dissolved Ca, Mg, Mn, and Zn followed the expected dilution, a change towards particulate fractions was not significant. Concerning P_{diss} , the concentrations in the Neunzehnhain brooks were near to the detection limit. Consequently, P precipitation was not significant in the Neunzehnhain brooks studied here. However, concerning the confluence of the Aubach and Loquitz stream, a phosphate precipitation was observed under similar chemical conditions, and this was linked with a pronounced Al precipitation (Table 3). Only 3.2 and 5.6 % of the expected P and Al concentration were found after the mixing of both streams, and a neutral pH resulted. In the precipitate, both the Al and P concentration were elevated (Table 2).

Laboratory precipitation experiments

The chemical conditions (pH, Al, Ca, Mg concentrations) of the Al precipitation in the brooks were simulated in batch experiments in the laboratory. Starting with pH 3, OH^- was added to solutions with different Al concentrations. With 2.5–5.0 mg/L Al, no precipitation was observed until sulphate or phosphate were added to the solutions. Then, the Al precipitation started around pH 5.2. After the precipitation was finished, the pH was one order of magnitude higher (Table 4). The infrared spectra of the precipitates gained from these laboratory experiments and from the streams showed similar absorption bands (ULRICH & PÖTHIG 1999). Ca^{2+} and Mg^{2+} did not affect the Al precipitation.

Precipitation experiments with Al and phosphate under these chemical conditions revealed a pronounced P removal from the solution (Table 4, exp. 1–3). When replacing Al by Fe, phosphate was removed to a much lower extent (Table 4, exp. 4–5). However, when both Fe and Al were present in the solution, the phosphate removal was as high as with Al alone (Table 4, exp. 6–7). SEM-EDX analysis of the precipitate of experiment No. 6 showed similar

Table 4. – Phosphorus precipitation experiments with Al and Fe. Initial concentrations of the components in solution (mg/L), pH at the start of the precipitation, and final pH and P concentrations in the solution after the precipitation are given. x: component of the solution.

Experiment	No.	Initial concentration						pH, start of prec.	Final values	
		Al	Fe	Ca	Mg	P	SO ₄		pH	P
Precipitation with Al	1	5	-	-	-	2	-	5.2	6.3	0.008
	2	5	-	-	10	2	x	5.2	6.2	0.006
	3	10	-	-	-	4	x	5.0	6.2	0.007
Precipitation with Fe	4	-	5	20	-	2	-	5.0	6.5	0.276
	5	-	5	-	20	2	x	5.2	6.7	0.269
Precipitation with Al and Fe	6	2.5	2.5	10	10	2	x	5.2	6.2	0.030
	7	3.0	0.1	20	10	1	x	5.3	6.3	0.008

mappings of Al, P, and S, but a different mapping of Fe (Fig. 1). Therefore, it can be concluded that under the simulated chemical conditions phosphate was mainly bound by Al.

Phosphorus binding and mobility in the sediment

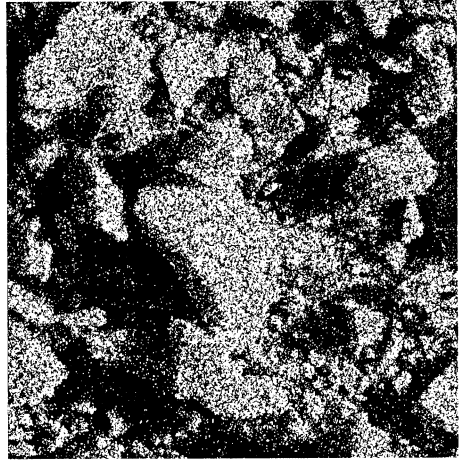
Comparing anoxic pore waters of reservoirs with different acidity and trophic state, sediment investigations revealed phosphate concentrations increasing with sediment depth up to more than 1.5 mg P/L in meso- and eutrophic waters (e.g. Saidenbach reservoir, Forchheim pre-reservoir, Dittmannsdorfer Teich; ULRICH 1998) and very low P_{diss} concentrations (<30 µg/L) in the circumneutral Neunzehnhain reservoir with acidified watershed (Fig. 2). In the pore waters of the acidified reservoirs Sosa and Falkenstein, the phosphate concentration was also relatively low. Figure 2 shows that the shapes of the P concentration profiles differed from the Fe²⁺ profiles, but resembled more the Al profiles which showed elevated concentrations up to 3–4 mg/L in the pore waters of the Sosa and Falkenstein reservoir. Especially in Neunzehnhain reservoir, in spite of a significant Fe²⁺ release into the pore water no P release was found under anoxic conditions. This result was consistent with the phosphorus fractionation in the sediment: In spite of high Fe concentrations in the BD-fraction P was not extracted by the strong reducing agent as it was the case in Saidenbach sediment (Fig. 3). However, most of the P_{tot} was extracted by NaOH solution together with Al. This effect was observed not only in the Neunzehnhain sediment, but also in the sediments of the acidified Sosa and Falkenstein reservoir.

Sediment core incubation

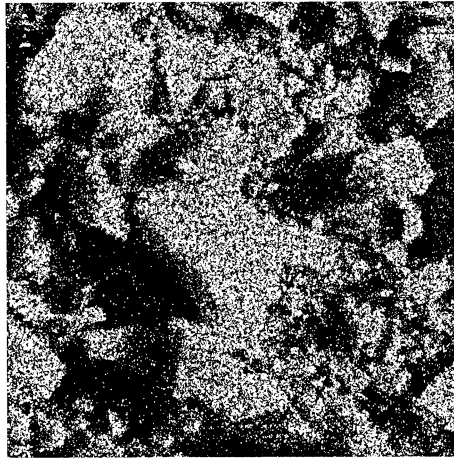
The sediment core incubation showed that Fe²⁺ was released from the sediment and reached high concentrations in the overlying water in the case of acid oxic (pH<4) and anoxic conditions (pH 4.7). No phosphate was released under anoxic conditions. However, when the pH dropped below 3.5, the P_{diss} concentration increased (Fig. 4). Under the same conditions, the Al concentration increased considerably up to 8 mg/L in the overlying water. However, compared with the high Al and Fe release due to the strong acidification, and compared to experiments with sediments from eutrophic lakes (ULRICH 1998), the P release was only moderate.



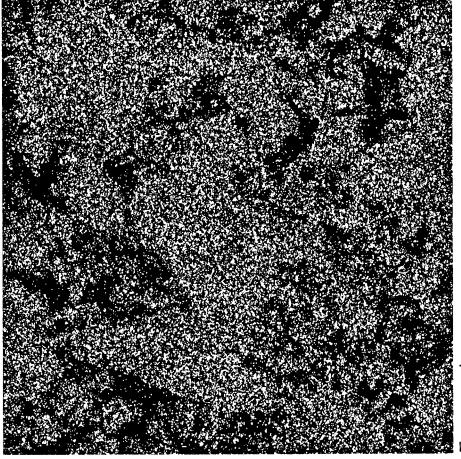
SEM view of the precipitate No. 6, 200x



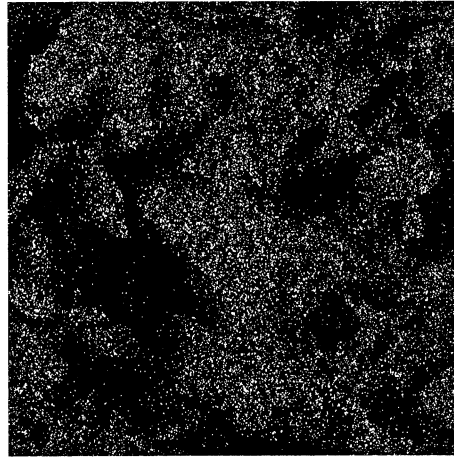
Al mapping



P mapping



Fe mapping



S mapping

Precipitation experiment No. 6

Initial concentrations in the solution:

- $c(\text{Al}) = 2.5 \text{ mg/L}$
- $c(\text{Fe}) = 2.5 \text{ mg/L}$
- $c(\text{P}) = 2.0 \text{ mg/L}$
- $c(\text{Ca}) = 10 \text{ mg/L}$
- $c(\text{Mg}) = 10 \text{ mg/L}$

Fig. 1. – Scanning electron-microscopic (SEM) view (200 x) of the precipitate resulting from the precipitation experiment No. 6 (Table 4) and corresponding energy-dispersive X-ray mapping for the elements P, Al, Fe, and S.

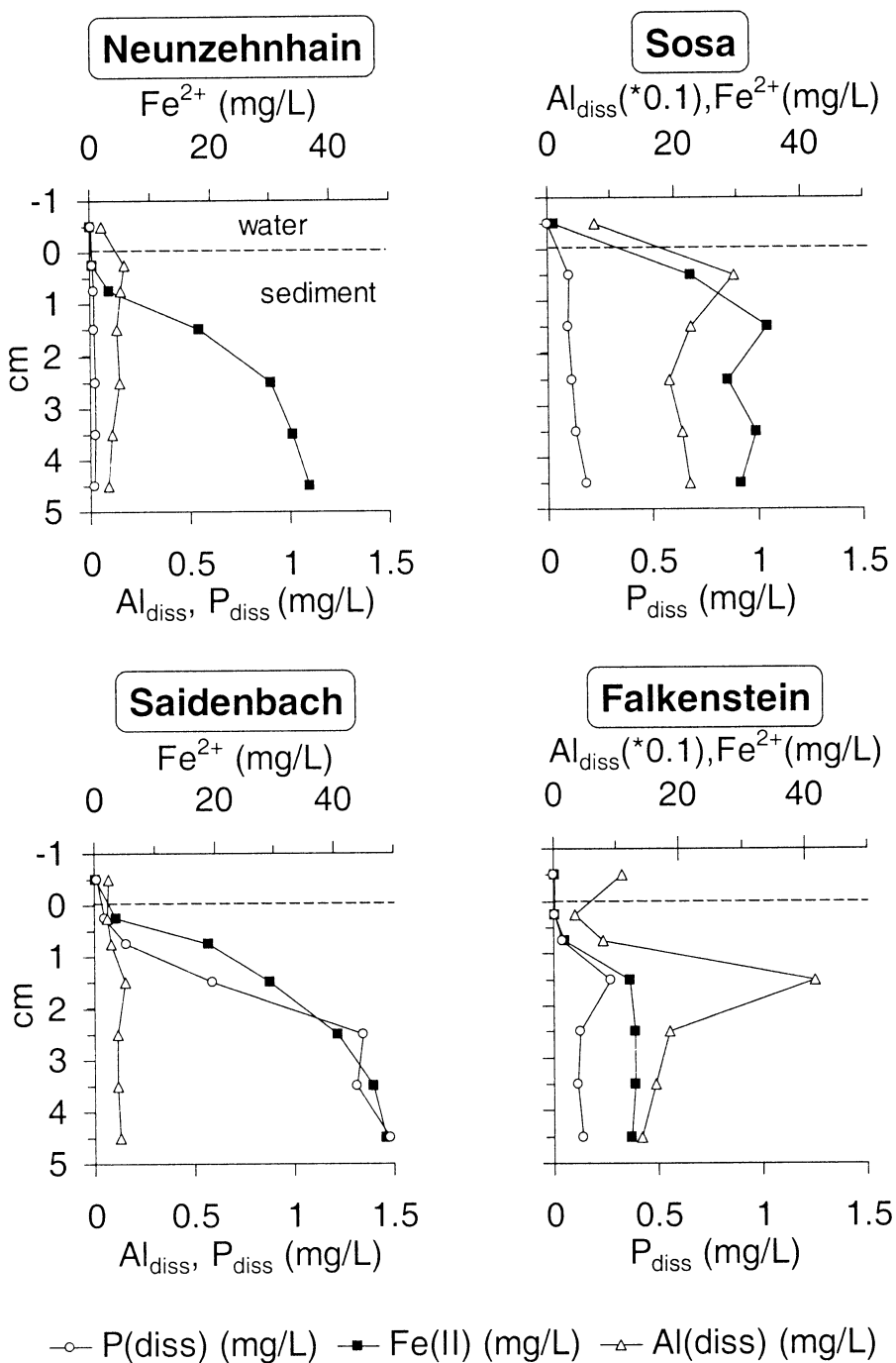


Fig. 2. – Concentration of dissolved Fe^{2+} , Al, and P in the overlying water and in the pore water of sediment cores from the reservoirs Neunzehnhain II (station 11, 07/05/96), Sosa (04/06/96), Falkenstein (17/03/97), and Saldenbach (station 12, 22/04/97). Please note the different scaling of the parameters.

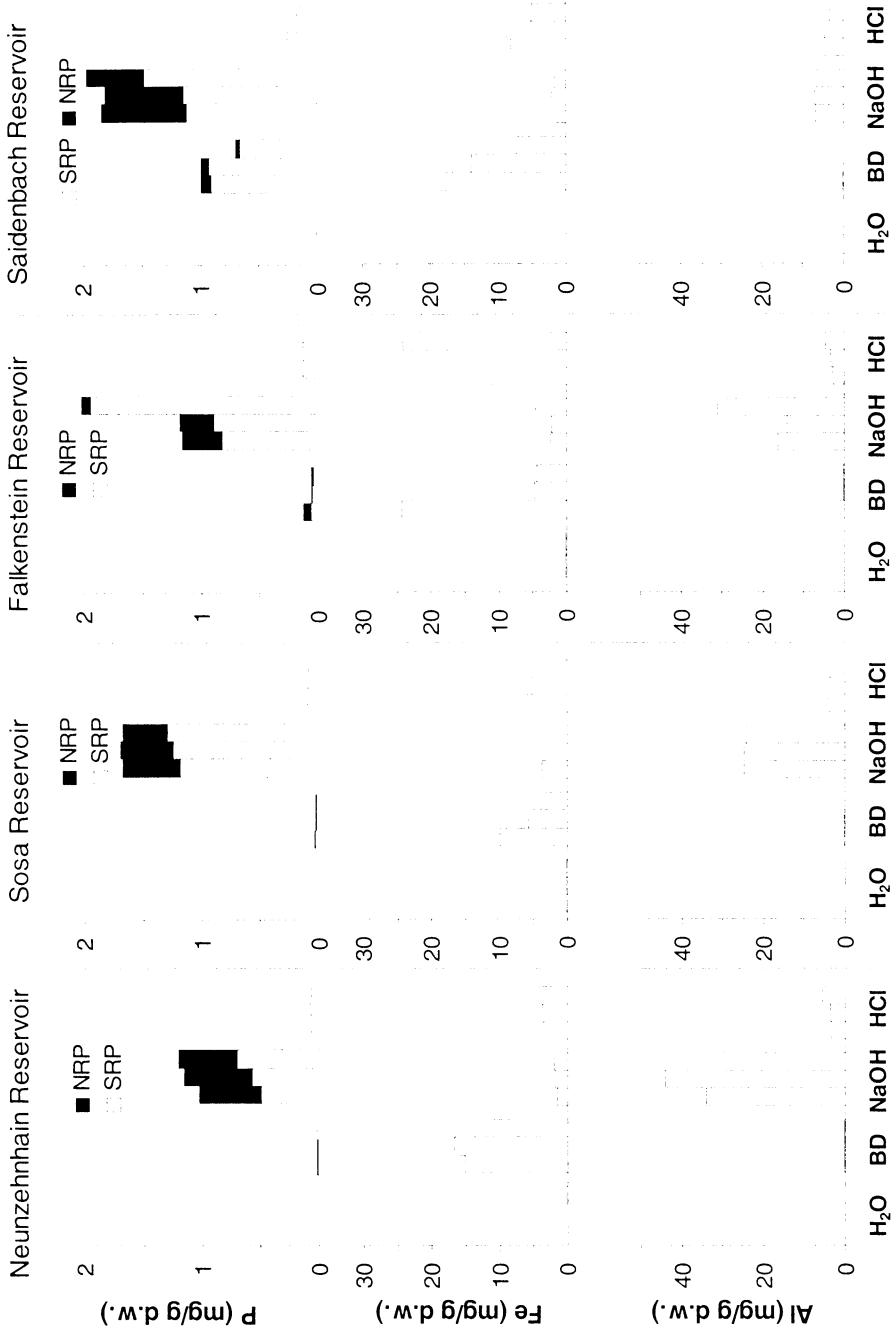


Fig. 3. – Concentrations of P, Fe, and Al related to dry weight (d.w.) in the four fractions (H₂O, BD, NaOH, HCl) of the sequential P extraction of sediment samples from the four reservoirs. The three columns represent from left to right the sediment horizons 0–1, 1–2, and 4–5 cm. Both BD and NaOH fraction are further divided into soluble reactive (SRP) and non-reactive (NRP) P fractions. For details see methods.

Discussion

The results clearly demonstrate that the process of Al mobilization from the bedrock by strong acidification may be moderated in the liquid phase under certain chemical conditions, especially when the pH is increasing towards neutrality. Then Al precipitates naturally and rapidly as apparent from the streambeds of certain confluences and ground-water seepages in the Neunzehnhain watershed. Similar observations were reported from the Rocky Mountains (McKNIGHT & BENCALA 1990), and in Germany from the Senne/Teutoburger Wald (LÜKEWILLE & VAN BREEMEN 1992) and the Fichtelgebirge (PEIFFER, pers. comm.). Our results give evidence that the Al precipitation is not only depending on the Al concentration and the pH conditions, but also on the presence (and concentration) of polyvalent anions like sulphate and phosphate. These anions, if present, seem to be regular components of the Al precipitate. The existence of sulphate in Al precipitates is known e.g. from the slate mining region of Thuringia (PEIFFER & al. 1997) and from the Senne region (LÜKEWILLE & VAN BREEMEN 1992). The laboratory experiments showed that especially in case of low Al concentrations the precipitation of Al is favoured by the presence of these polyvalent anions. This is consistent with literature on the Al chemistry (e.g. MARION & THOMAS 1946, HSU 1979, NORDSTROM 1982). PORTIELJE & LIJKLEMA (1993) have found that the precipitation of Al-hydroxide was hampered without addition of phosphate. DICKSON (1978) has demonstrated by addition of orthophosphate to acid lake water with 0.5 mg/L Al and subsequent pH adjustment that the Al-P precipitation was most pronounced between pH 5–6. Both citations confirm our results.

A second important observation was the increase of pH connected with the Al precipitation process in both the investigated streams and the laboratory experiments. Whereas in the field this effect may in part be due to the neutralization of H^+ by HCO_3^- (at least in the Aubach confluence), in the experiments the exchange of SO_4^{2-} or PO_4^{3-} against OH^- on the Al-hydroxide surface or in the lattice as reported by VAN MIEGROET (1994) is the most suitable explanation. A release of OH^- is also due to the sorption of phosphate onto FeOOH (MILTENBURG & GOLTERMAN 1998) and might explain the pH increase in the precipitation experiment No. 4 & 5 (Table 4). However, in the presence of both Al and Fe, the binding of phosphate onto Al is favoured as shown by the experiment No. 6 & 7 (Table 4). This effect was also illustrated by mixing sediment samples of Neunzehnhain and Saidenbach reservoir prior to sequential P fractionation (ULRICH 1997). It was found that 74 % of the Fe-bound P (BD-P) from the Saidenbach sediment changed towards Al-bound P (NaOH-SRP) after mixing with Neunzehnhain sediment. The redox-sensitive phosphate was in part inactivated due to the higher P sorption capacity of the Al-rich Neunzehnhain sediment (ULRICH, unpublished data). Very similar results, but with Al-sulphate dosing instead of using natural sediment, were published by RYDIN & WELCH (1998). At pH 7, Al has a considerably higher affinity towards orthophosphate than Fe according to LIJKLEMA (1980). In contrast to Fe, Al maintains its adsorption capacity also under low redox conditions by which sediments are usually characterized (DANEN-LOUWERSE & al. 1993).

However, it is necessary that the 'reactive' Al species settle from the water column or form on the sediment. The pH seems to be the decisive factor: in the circumneutral Neunzehnhain reservoir, Al precipitates are formed in the water column, and perhaps already in the mouth region, where sometimes milky turbidity was observed. In the acidified Sosa and Falkenstein reservoir, it is more likely that Al precipitates are formed in the sediment-water interface or below, because of the pH increase due to alkalinity generation by both assimilatory and dissimilatory nitrate and sulphate reduction (ULRICH 1998). The precipitated Al is then available to bind phosphate either liberated from organisms and detritus or from FeOOH after Fe(III) reduction. The sorbed P is stable under both oxic and reducing conditions because the Al

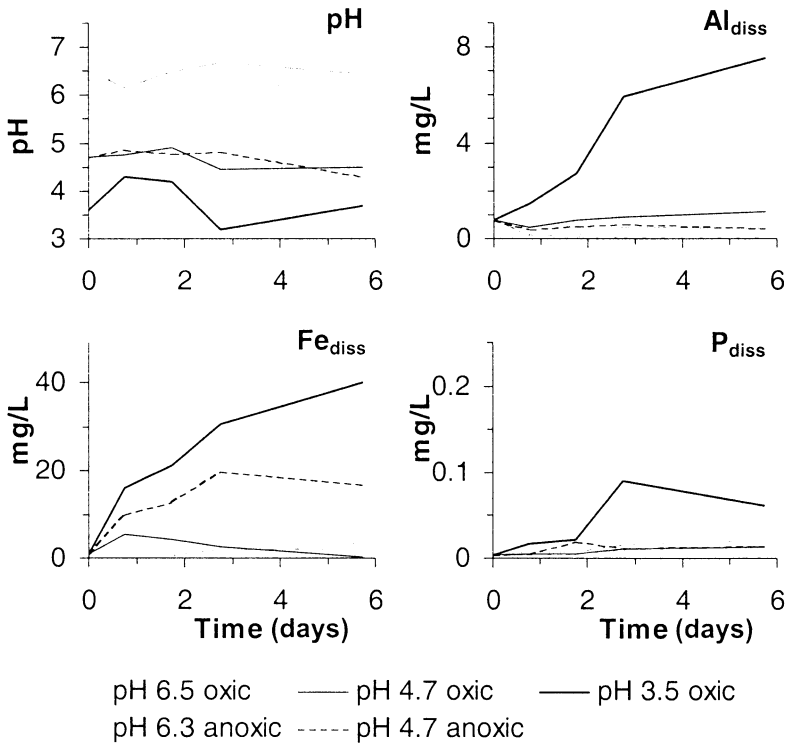


Fig. 4. – pH and concentrations of dissolved Al, Fe, and P in the overlying water of sediment cores from the acidified Sosa reservoir (04/06/96). In the water different pH and oxygen conditions were simulated (oxic: oxygen saturation, anoxic: oxygen depletion).

compounds are not sensitive to redox changes. This fact was confirmed by the pore water profiles and by the sediment core experiment which both agreed in showing no significant phosphate release in spite of severe Fe^{2+} release under anoxic conditions. The missing Fe^{2+} release in the anoxic sediment core with pH 6.3 (Fig. 4) can be explained by the redox potential which decreased from about 510 down to 350 mV only. The natural inactivation of phosphate by Al was also observed by KOPACEK & al. (2000), emphasizing the significance of these processes.

Discussing these processes, the reversibility should be pointed out as well. Our experiments showed the dissolution of the Al-P compounds by (1) high alkalinity (extraction with NaOH), which can be explained by the exchange of PO_4^{3-} against OH^- and the formation of highly soluble $\text{Al}(\text{OH})_4^-$, and (2) by strong acidity ($\text{pH} < 4$). Both conditions are extreme and not relevant in the sediments investigated, because these sediments were characterized by a sufficient buffering capacity and circumneutral pH values (ULRICH 1998). Based on these facts, the danger of severe Al^{3+} and phosphate release from the sediments is considered to be only hypothetical. However, this argument is contradictory to the Al_{diss} concentrations sometimes analysed in the interstitial water of acidified reservoirs. Several investigations revealed elevated Al_{diss} concentrations up to more than 4 mg/L (related to higher P_{diss} and DOC concentrations) in distinct sediment layers as shown by Fig. 2 for the Sosa and Falkenstein reservoir. In these cases, a large portion of Al_{diss} might be represented by organically complexed Al. Further investigations including Al speciation are needed.

Conclusion

In acidified regions a reduction of Al^{3+} mobilized from the bedrock is possible under special conditions of pH increase. This was directly observed by Al precipitation in the confluence of brooks with different acidity and Al concentration in the forested and episodically acidified Neunzehnhain watershed. Laboratory simulation experiments showed that at low Al concentrations, the precipitation was triggered by sulphate or phosphate ions. With both ions present in the solution, the elimination of phosphate was more effective. This was also evidenced by the data from the confluence of the wastewater-polluted Aubach and the acidified, Al-rich Loquitz river in the slate mining area of Thuringia. Furthermore, when Fe competed with Al for phosphate in the simulated acid neutralization process, Al dominated in binding P more effectively. A similar mechanism is supposed to be primarily responsible for the efficient P inactivation in the sediment of reservoirs with acidified watersheds. A pH increase caused either by photosynthetic activity in the water column or by alkalinity-generating decomposition processes in the overlying water and sediments favours Al precipitation together with adsorption and/or binding of phosphate liberated from organisms, detritus, or dissolving Fe-oxyhydroxides. This way, P is buried in sediments even under low redox conditions. These natural processes enhance the Al retention in sediments of acidified watershed-lake ecosystems and simultaneously enable an effective and lasting inactivation and burial of phosphorus.

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