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Differential responses of freshwater wetland soils to sulphate pollution

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Abstract. Sulphate (SO_4^{2-}) reduction rates are generally low in freshwater wetlands and are regulated by the scarce availability of the ion. Increased concentrations of this electron acceptor due to sulphur (S) pollution of groundwater and surface water may, however, lead to high SO_4^{2-} reduction rates now regulated by the availability of appropriate electron donors. Due to variations in this availability, the response to S pollution (e.g. from surface water or groundwater) is expected to differ between soils. This hypothesis was tested in laboratory mesocosm experiments by comparing two wetland soil types with distinctly different humus profiles: a Hydromoder and a Rhizomull type. In the first type, expected to have a higher availability of degradable soil organic matter (SOM), SO_4^{2-} availability appeared to be rate limiting for SO_4^{2-} reduction. In the Rhizomull soils, in contrast, the electron acceptor did not limit SO_4^{2-} reduction rates at higher concentrations. These differences in response could not, however, be attributed to differences in the various SOM fractions or in SOM densities. Eutrophication and free sulphide accumulation, two major biogeochemical problems caused by SO_4^{2-} pollution, occurred in both types. The absolute extent of phosphorus mobilisation was determined by the concentration of this element in the soil (C/P ratio), while the level of sulphide accumulation was governed by the concentration of dissolved iron in the pore water. It was therefore concluded that neither the humus profile nor the concentrations of different SOM fractions in the soils are reliable indicators for the sensitivity of wetland types to S pollution.

Introduction

Sulphate (SO_4^{2-}) concentrations in freshwater wetlands are generally low, in contrast to marine and brackish wetlands. The increased availability of this ion due to anthropogenic sulphur (S) pollution of the atmosphere, and more importantly of surface water and groundwater, has been shown to cause severe problems in freshwater wetlands. Pollution of groundwater and surface water is caused by anthropogenic S input into rivers (agricultural, industrial and mining activities) and the use of S-enriched river water to compensate for water shortage in wetlands (Roelofs 1991; Smolders & Roelofs 1993; Lamers et al. 1998a). In addition, large amounts of SO_4^{2-} are mobilised by the oxidation of sulphide deposits (mainly pyrite) by oxygen during desiccation of wetlands (Schuurkes et al. 1988; Van Dam 1988; Lamers et al. 1998b) and by nitrate in aquifers (fertiliser efflux from arable land) through chemolithotrophic denitrification (Paul & Clark 1989; Appelo & Postma 1993). SO_4^{2-} pollution often leads to eutrophication and to accumulation of sulphide in the pore water reaching phytotoxic concentrations (Ohle 1954; Boström et al. 1982; Caraco et al. 1989; Roelofs 1991; Smolders & Roelofs 1993, 1996; Lamers et al. 1998a; Beltman et al. 2000). As a result of this process, fast growing, sulphide resistant plant species may outcompete characteristic plant species, leading to loss of biodiversity in wetlands (Lamers et al. 1998a).

The response of different freshwater wetlands to S pollution is, however, expected to vary because of the variation in factors controlling SO_4^{2-} reduction rates. In acidic environments SO_4^{2-} reduction rates are much lower than in more alkaline environments (Roelofs 1991). The availability of electron donors such as acetate and lactate is another important factor regulating SO_4^{2-} reduction rates. As these organic acids of low molecular weight are the product of overall decomposition, one may predict that the easier decomposable a soil is, the stronger its response to SO_4^{2-} pollution will be. Soils with a humus profile indicative of a higher concentration of easily decomposable soil organic matter (SOM) are therefore expected to be much more sensitive to S pollution (Kemmers 1996).

To test the hypothesis that the humus profile can be used as an indicator of the response of different wetland types to S pollution, we repeated an earlier laboratory mesocosm experiment using intact soil cores from the field (see Lamers et al. 1998a). This time, however, we collected cores from a location that was expected to contain much lower amounts of readily decomposable SOM as indicated by a stronger decomposed humus profile. It was expected that SO_4^{2-} reduction rates during S pollution, and thereby phosphate (PO_4^{3-}) mobilisation rates and sulphide accumulation, were lower or even negligible in soils in which SOM had been largely decomposed. In order to compare and discuss the results, graphs show the combined results from both experiments.

Material and methods

Sampling sites

Soil cores were collected from two different freshwater fen meadows. The first location was in the nature reserve 'De Bruuk' (51°45′N; 5°58′E) near Nijmegen, the Netherlands, where the vegetation comprised of a Caricion nigrae (Ellenberg 1988) vegetation. The soil used for the experiment was classified as Rhizic Hydromoder, abbreviated in the text as Moder. Moder is a noncompact humus form in which organic matter accumulates on the soil surface, with dominant zoogenous decomposers. Hydromoders are moders that have developed under the influence of excessive moisture (Green et al. 1993; Van Delft 1995). The second location was in the 'Urkhovensche Zeggen' (51°26′N; 5°32′E) near Eindhoven, the Netherlands, and characterised by a Molinion (Ellenberg 1988) vegetation. Here, the soil was classified as Rhizomull, abbreviated as Mull (Figure 1). Mull is a humus form in which organic matter is intimately incorporated into the upper mineral soil, unlike Moder in which organic matter is accumulating on top of the soil. Decomposition rates are much faster than in Moder (Green et al. 1993). The terms rhizic and rhizo- refer to the abundance of roots in the humus (Van Delft 1995).

The cores (diameter 18 cm, depth 10–12 cm) including their vegetation were collected and transferred into plastic containers, suspended in larger (12 L) plastic containers (Lamers et al. 1998a).

Experimental set-up

The containers were placed in a climate control chamber at a light level (Photosynthetically active radiation) of 110 μmol m^{-2} s^{-1}, a daily photoperiod of 12 hrs, an ambient air temperature of 20 °C and an air humidity of 50–60% saturation. Each experimental flow-through unit received water from its own stock container through black silicon tubes, at a flow rate of 10 L wk^{-1} maintained by peristaltic pumps. The water level in the outer container could be manipulated by changing the overflow level. Three different SO_4^{2-} concentrations, added as Na_2SO_4 (0, 2, and 4 mmol L^{-1}), were used in addition to the basic medium composition (Table 1). Each experimental group consisted of either 6 (De Bruuk) or 5 (Urkhovensche Zeggen) replicates, randomly assigned to the units. Three soil moisture samplers (Rhizon SMS-10 cm; Eijkelkamp Agrisearch Equipment, Giesbeek, the Netherlands) were placed in each container, and the collected samples were pooled in order to collect a representative pore water sample. The removal of the sods did not result in experimental artefacts, and variation among the sub-samples proved to be moderate (standard deviation, at most, 10–15% of the means

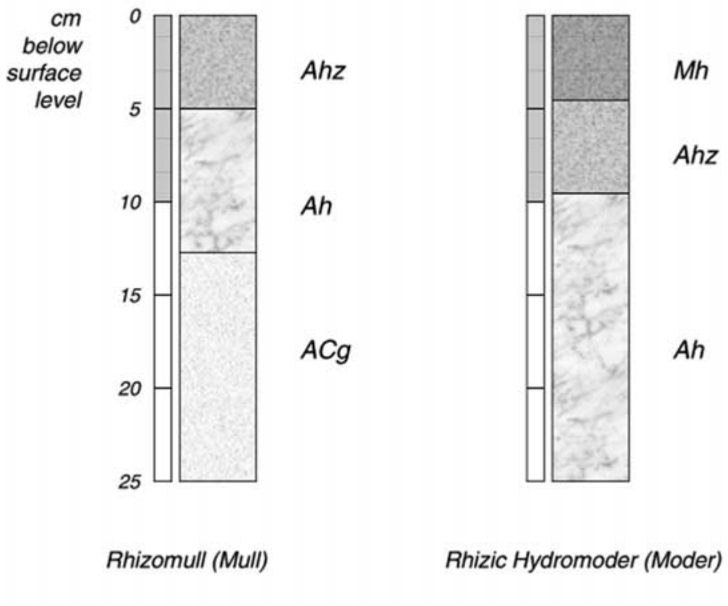

Figure 1. Humus profiles at the locations from which monoliths were collected; the upper 10 cm was used in the experiments. Classification according to Green et al. (1993) and Van Delft (1995); Ah – mineral horizon enriched with humified organic matter ($< 17\%$), Ahz – idem but rich in (dead) roots, ACg – transitional horizon between A and C (weathered) horizons, showing gley symptoms, Mh – horizon mainly composed of (dead) Hypnaceae mosses and (dead) roots.

Table 1. Composition of the basic medium used (in μmol L^{-1}). For the sulphate treatments, either 2000 or 4000 μmol L^{-1} Na_2SO_4 was added.

Ca	2000	Mg	400
Na	2000	K	5
Cl	4885	Mn	0.9
HCO_3	2000	Zn	0.7

for all parameters measured). Further details are provided by Lamers et al. (1998a).

Chemical analysis

The pH was determined with a standard Ag/AgCl electrode and alkalinity was estimated by titrating part of the sample down to pH 4.2 using 0.01 mol L^{-1} HCl. Measurements of free sulphide were performed as described by

Lamers et al. (1998a). The concentrations of ortho-phosphate (SRP, soluble reactive phosphorous), nitrate (and nitrite) and ammonium in the pore water samples were estimated colorimetrically (Lamers et al. 1998a). The data were corrected for colour caused by humic acids. Potassium was determined by flame photometry (Technicon Flame Photometer IV). Total concentrations of dissolved S, P and Fe in the moisture samples were determined by inductively coupled plasma emission spectrometry (ICP; Jarrell Ash IL Plasma-200). At the relatively high SO_4^{2-} concentrations used, total S gives a good estimate of SO_4^{2-} because only a small percentage of S is present in organic forms. This was verified by parallel analysis using capillary ion analysis (Waters Technologies), in which SO_4^{2-} concentrations were shown to match the total S concentrations within the uncertainty of both analytical methods.

Soil samples from the field (between 0 and 10 cm depth) were dried at 70 °C until constant weight, and ground and mixed in liquid nitrogen. From each well-mixed sample 1 g was sequentially fractionated into cell soluble, hemicellulose, lignine, cellulose (+ cutine) and insoluble ash fractions using the Neutral Detergent Fibre (NDF), Acid Detergent Fibre (ADF) and Permanganate Lignine methods as described by Goering and Van Soest (1972). Sulphite and ethoxy ethanol were excluded from the NDF-solution.

Bulk density was estimated after drying a constant volume of fresh material at 70 °C until constant dry weight, SOM density from weight loss after subsequent ignition for 4 h at 450 °C. For the analysis of total (non-carbonate) carbon, nitrogen, phosphorus and other elements, 10 mL of 1 mol L^{-1} HCl was added to 5 g dry ground material, after which the samples were stored at 105 °C overnight to remove carbonate. After carefully mixing each sample, carbon and nitrogen concentrations were determined in 20 mg dry matter using a CNS analyzer (Carlo Erba Instruments NA1500). Total P, Fe, Al, Ca, and S were estimated by ICP after microwave destruction (Milestone MLS 1200 Mega) of 500 mg dry sample in 4 mL HNO_3 (65%) and 1 mL H_2O_2 (30%). All concentrations were corrected for weight loss due to carbonate removal.

Statistical analysis

A repeated measures analysis was used to examine the response for both soil types to treatments (Potvin et al. 1990), using the SAS procedure GLM, model two-way ANOVA, for repeated measures (SAS 1989). Data were log-transformed to make the variances less dependent on the sample means and to fit a normal distribution. Differences between SOM fractions and iron concentrations in pore water were tested using a two-tailed ANOVA at the 0.05 confidence limit. For clarity of presentation, the means and standard errors presented in the figures represent the non-transformed data.

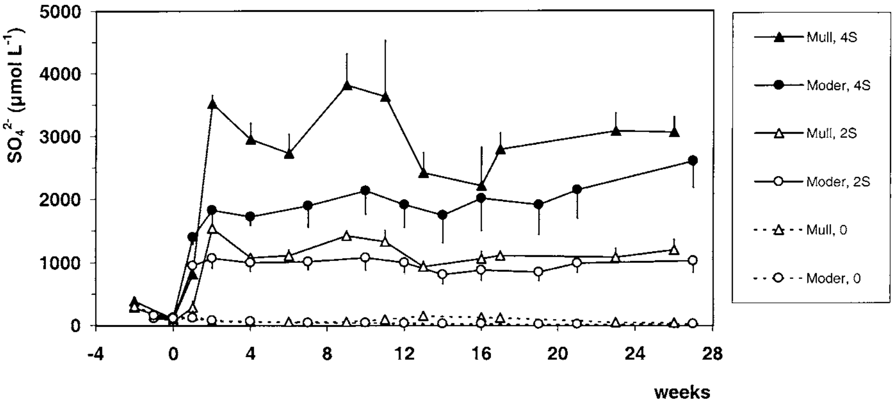

Figure 2. Sulphate (SO_4^{2-}) concentrations in the pore water of Rhizomull (Mull) and Hydromoder (Moder) soils (see Figure 1) during waterlogging treatment with 0, 2 or 4 mmol L^{-1} SO_4^{2-} (indicated 0, 2S, 4S). Means are given, with their standard error (n = 5 and 6 for Mull and Moder, respectively).

Table 2. Repeated measures analysis of variance (general linear models) of the effects of sulphate addition and soil type on 4 pore water chatacteristics.

	independent variable				
	between subjects effects		within subject effects		
dependent variable	SO_4 treatment	soil type	time	time * treatment	time * soil
SO_4^{2-}	282.77^c	10.52^a	58.07^c	35.69^c	16.07^c
PO_4^{3-}	8.90^b	79.56^c	44.55^c	3.64^c	17.89^c
NH_4^+	14.15^c	1.37^{NS}	5.03^b	3.81^b	13.23^c
HS^-	53.35^c	0.39^{NS}	80.90^c	25.02^c	23.46^c

F values are given, with their level of significance: $^aP \leqslant 0.01$; $^bP \leqslant 0.001$; $^cP \leqslant 0.0001$; ^{NS}not significant; d.f. = 2, 1 and 11 for SO_4 treatment, soil type, and time, respectively (for sulphide, time d.f. = 9).

Results and Discussion

Sulphate reduction

Treatment with 2 mmol SO_4^{2-} L^{-1} led to the consumption of 1 mmol L^{-1} for both the Rhizomull (Mull) and the Hydromoder (Moder) soils (Figure 2, Table 2). At the 4 mmol SO_4^{2-} L^{-1} treatment this concentration was reduced to 2 mmol L^{-1} in the Moder soils. By contrast, only about 1 mmol L^{-1} was consumed in the Mull soils, similar to the lower SO_4^{2-} treatment. This clearly shows that SO_4^{2-} reduction rates were limited by the availability of the electron acceptor SO_4^{2-} for the Moder soils at lower concentrations. The Mull soils, however, showed equal SO_4^{2-} reduction rates at both concentrations. Therefore, it is most likely that electron donor availability must have become the rate-limiting factor. The overall decomposition rates in this soil type were apparently too low for the sufficient provision of organic electron donors, such as acetate and lactate. This seemed to confirm the theory that the humus profile can be used as an indicator for the expected response of SO_4^{2-} reduction rates during SO_4^{2-} pollution.

However, chemical analysis of the soils did not support this. C/N ratios showed no differences and were both below 20–25, a range above which decomposition is believed to be N-limited (Swift et al. 1979). This can be explained by of the high atmospheric nitrogen deposition in the Netherlands caused by the vast anthropogenic emission of this nutrient (Roelofs 1986, Bobbink et al. 1998). SOM density was even lower for the high-response (Moder) soil (Table 3). Moreover, the soil composition showed that this soil type had lower weight fractions of soluble constituents, cellulose and hemicellulose (Figure 3(a)). These fractions are considered relatively easily decomposable (Swift et al. 1979; Paul & Clark 1989), in contrast to the refractory lignin fraction. The differences could be completely attributed to the larger insoluble ash fraction in the Moder soil. Figure 3(b) shows that SOM fractions were, unexpectedly, completely equal between both soil types. Therefore, the different responses can neither be attributed to differences in humus concentrations nor to C and N chemistry. Contrastingly, the total P concentration was significantly higher, and consequently the C/P ratio much lower, in the Moder soil (Table 3). C/P ratios averaged 157 for the Moder and 366 for the Mull soil. It is supposed that C/P values above 200 indicate P-limitation for decomposition (Brinson 1977). Apparently, the higher C/P ratio for the Mull soil suggests that both the overall decomposition and the potential SO_4^{2-} reduction rate were limited by P (Redfield 1958; Walker 1965). Furthermore it has been suggested that the relatively high earthworm activity in Mull soils promotes SOM aggregate formation, thereby reducing C availability and decomposition rates (Van Delft et al. 1999). An additional explanation could lay in ecological and physiological differences between microbial communities in both soils, a hypothesis calling for further testing.

Sulphide accumulation

The problems caused by SO_4^{2-} pollution are, however, of an indirect nature. The first is the increased production and accumulation of the potentially phytotoxic compound, sulphide. As shown in Figure 4 and Table 2, sulphide production, and thereby its concentration, was exceptionally high in both Mull and Moder soils. Although SO_4^{2-} reduction rates were lower in the Mull

Table 3. Total element concentrations of both soil types (in %, ratios in g g^{-1}), and bulk and SOM densities (in g cm^{-3}).

	C	N	P	K	C/N	C/P	C/K	Fe	Al	Ca	S	Bulk density	SOM density
Rhizomull	17.6	1.1	0.050	0.086	15.5	366	210	0.38	0.30	0.43	0.19	0.49	0.24
(Urkhoven)	*(0.7)*	*(0.0)*	*(0.005)*	*(0.006)*	*(0.4)*	*(36)*	*(18)*	*(0.01)*	*(0.02)*	*(0.02)*	*(0.01)*	*(0.02)*	*(0.01)*
Hydromoder	18.2	1.1	0.117	0.080	16.4	157	233	1.17	1.21	0.66	0.34	0.18	0.07
(Bruuk)	*(1.7)*	*(0.3)*	*(0.008)*	*(0.007)*	*(0.8)*	*(14)*	*(58)*	*(0.11)*	*(0.09)*	*(0.05)*	*(0.03)*	*(0.01)*	*(0.00)*
Significance	NS	NS	***	NS	NS	**	NS	***	***	*	**	***	***

Means *(SEM)*; $^{*}P \leqslant 0.01$; $^{**}P \leqslant 0.001$; $^{***}P \leqslant 0.0001$; ^{NS}not significant (n = 5).

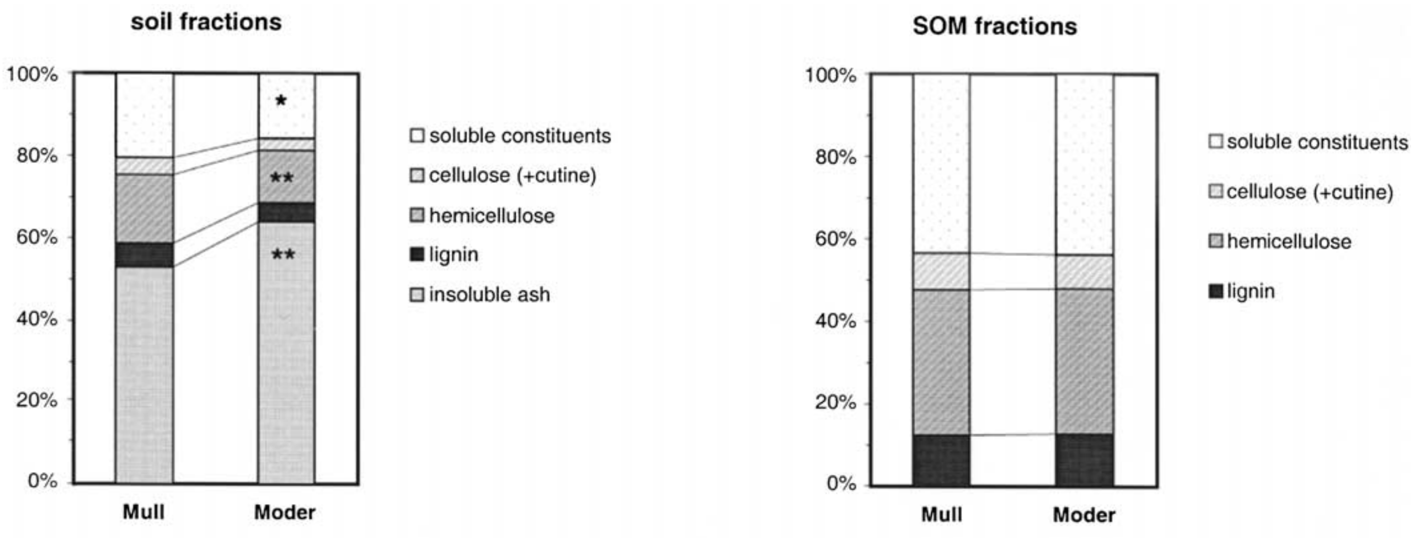

Figure 3. Soil (a) and soil organic matter (SOM); b) fractions for (Rhizo)mull and (Hydro)moder soils; $^{*}P \leqslant 0.05$, $^{**}P \leqslant 0.01$ (n = 5).

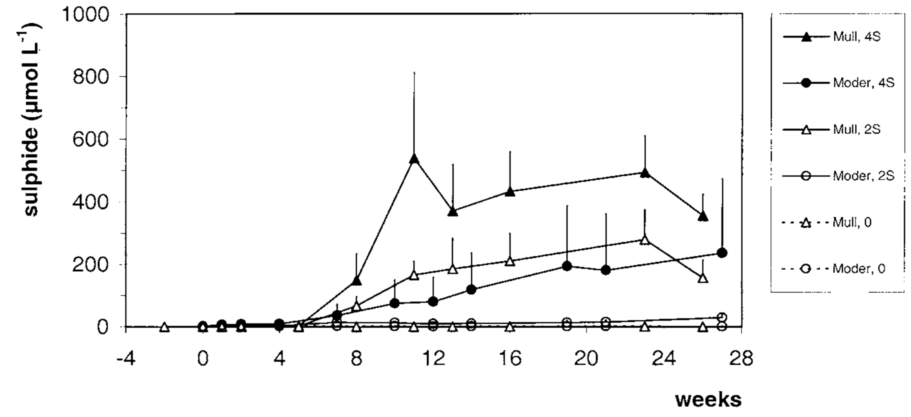

Figure 4. Sulphide concentrations in the pore water of Rhizomull (Mull) and Hydromoder (Moder) soils during waterlogging treatment with either 0, 2 or 4 mmol L^{-1} SO_4^{2-} (indicated 0, 2S, 4S). See caption Figure 2 for further information.

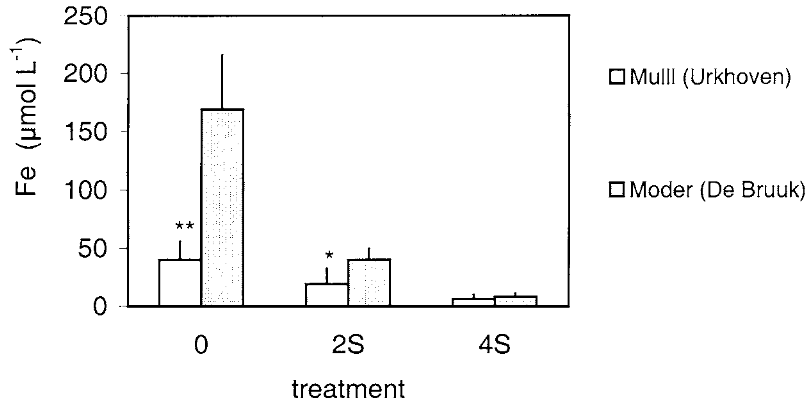

Figure 5. Concentrations of dissolved iron (Fe) in soil pore water of (Rhizo)mull and (Hydro)moder soils after 27 weeks of treatment with 0, 2 or 4 mmol L^{-1} SO_4^{2-} (indicated 0, 2S, 4S); $*P \leqslant 0.05$, $**P \leqslant 0.01$. See caption Figure 2 for further information.

soils, free sulphide concentrations in the pore water were significantly higher for the final two sampling efforts ($p \leqslant 0.05$ Tukey post test) as compared to the Moder soils. This is most likely caused by the low availability of free iron in the pore water, governed by both the net mobilisation rate and the concentrations of this metal. The formation of iron sulphides (FeS_2 and FeS) strongly influences free sulphide concentrations (Smolders et al. 1995; Smolders & Roelofs 1996). A comparison of the Fe concentrations in the pore water supports this explanation (Figure 5). In addition, aluminium and calcium might be involved in sequestering sulphide (Table 3).

Higher SO_4^{2-} concentrations led to increased sulphide concentrations at levels expected to cause toxicity problems. For both soil types, biomass regrowth after 21 (Mull) or 16 (Moder) weeks was negatively influenced by SO_4^{2-} addition (Lamers et al. 1998a; results not shown). This response could be almost completely attributed to the decreased growth of *Carex* spp. Sulphide toxicity to freshwater plant species has been reported at levels as low as 20 μmol L^{-1} (Smolders & Roelofs 1996). Recent experiments strongly support the idea that *Carex* spp. are highly susceptible to raised concentrations of free sulphide in contrast to *Juncus* spp. (Lamers 2001).

Eutrophication

The second indirect problem caused by SO_4^{2-} pollution is eutrophication. Especially the mobilisation of PO_4^{3-}, and thereby the higher availability of this nutrient to plants, has been shown to be regulated by SO_4^{2-} reduction (Sperber 1958; Patrick & Khalid 1974; Boström et al. 1982, 1988; Roelofs 1991; Smolders & Roelofs 1993; Lamers et al. 1998a). As early as 1936, SO_4^{2-} addition was proposed as an indirect fertiliser to raise lake productivity (Einsele 1936). This SO_4^{2-} induced PO_4^{3-} mobilisation occurred in both soil types. In the Moder pore water, however, the PO_4^{3-} concentrations were significantly higher than in the Mull soils (Figure 6, Table 2). This was most probably caused by the high total P concentration of this soil type, providing a larger pool of mineralisable P (Table 3). Total iron concentrations were three times as high in the Moder soil, strongly indicating that a significant amount of PO_4^{3-} was bound in Fe$\sim$P complexes, and therefore susceptible to PO_4^{3-} mobilisation by sulphide (Sperber 1958; Patrick & Khalid 1974; Boström et al. 1982; Smolders & Roelofs 1993). Moreover, higher SO_4^{2-} addition caused stronger eutrophication for the Moder soils. In the Mull type, both SO_4^{2-} concentrations caused equal PO_4^{3-} eutrophication levels, and the effect was transient. While the effect lasted about 20 weeks in this soil type, PO_4^{3-} concentrations stayed high or even further increased in the Moder type. Apparently, the pool of PO_4^{3-} that could be mobilised by increased SO_4^{2-} reduction became exhausted in the Mull soils.

At circumneutral pH, anion binding capacity is very low (Scheffer & Schachtschabel 1992) and it is therefore unlikely that PO_4^{3-} mobilisation was caused by ion exchange, all the more because PO_4^{3-} binding is much stronger than SO_4^{2-} binding. Moreover, chloride treatment of Mull soils to check for ion exchange effects did not show any PO_4^{3-} mobilisation at an ion strength equivalent to the 4 mmol^{-1} SO_4^{2-} treatment (results not shown). This is in contrast to findings of Beltman et al. (2000), who found increased PO_4^{3-} availability in fen peat monoliths after adding 3 mmol L^{-1} Cl^{-}.

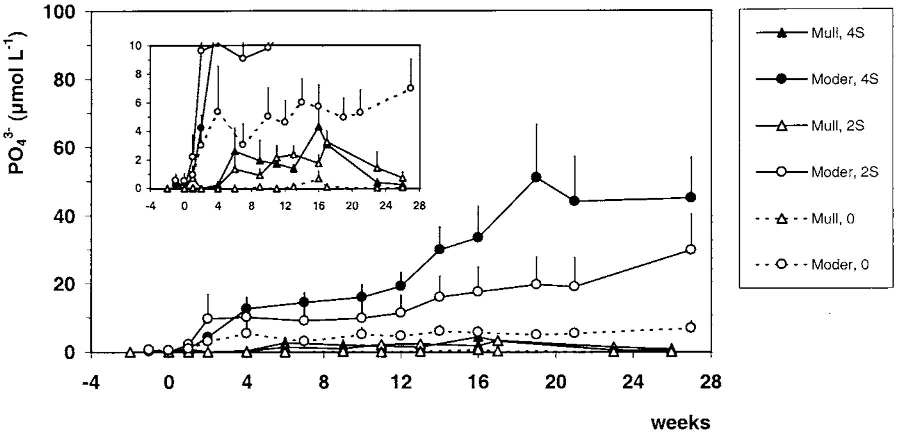

Figure 6. Phosphate (PO_4^{3-}) concentrations in the pore water of (Rhizo)mull and (Hydro)moder soils during waterlogging treatment with either 0, 2 or 4 mmol L^{-1} SO_4^{2-} (indicated 0, 2S, 4S). See caption Figure 2 for further information.

The most probable cause for the observed PO_4^{3-} mobilisation in the present experiment is the interaction of the sulphide produced with the formation of Fe~P compounds like iron phosphate (strengite), iron (hydr)oxides-phosphates and humic-iron-phosphates. The reduction of Fe(III) to Fe(II) and the formation of Fe sulphides leads to the release of PO_4^{3-} and reduces the pool of Fe available for PO_4^{3-} binding (Einsele 1936; Sperber 1958; Patrick & Khalid 1974; Boström et al. 1982; Smolders & Roelofs 1993; Lamers et al. 1998a). A second cause for increased PO_4^{3-} concentration could be increased mineralisation rates due to SO_4^{2-} reduction (Jørgensen 1982) and concomitant alkalinisation (McKinley & Vestal 1982; Brock et al. 1985; Kok & Van de Laar 1991), root die-off caused by sulphide toxicity (Lamers et al. 1998a), or a combination. Figure 7 and Table 2 show that ammonium concentrations in the Moder soils were raised by the addition of SO_4^{2-}. This did not occur in the Mull soils. Potassium concentrations (not shown) displayed an identical response. Apparently, eutrophication was caused by both Fe-P-S interactions and increased mineralisation in this soil, and only by Fe-P-S interactions in the Mull soil, although part of the cation mobilisation in this soil type may also be caused by the simultaneous addition of Na^+. This means that one can expect that SO_4^{2-} induced eutrophication causes vegetation shifts on Moder type soils regardless of the type of nutrient limitation (P, N, K), whereas on Mull type soils shifts are only expected for P (co)limited systems. However, for the ecosystem on the Mull site, a litter fen (Molinion vegetation), it is known that P is (co)limiting vegetation growth (Pegtel 1983; Vermeer 1986) and the increased availability of this nutrient leads to uncontrolled growth

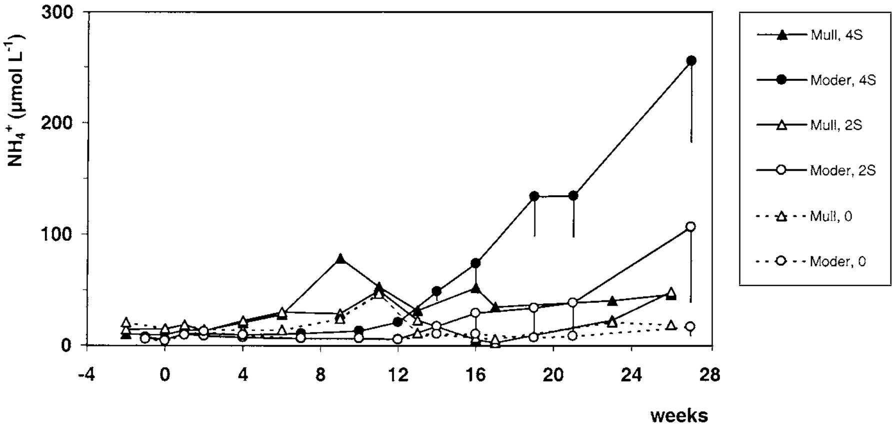

Figure 7. Ammonium (NH_4^+) concentrations in the pore water of (Rhizo)mull and (Hydro)moder soils during waterlogging treatment with either 0, 2 or 4 mmol L^{-1} SO_4^{2-} (indicated 0, 2S, 4S). See caption Figure 2 for further information.

of graminoid species such as *Agrostis canina* (Pegtel 1983). Although the absolute increase of the PO_4^{3-} concentration due to SO_4^{2-} pollution was much lower in the Mull soils as compared to the Moder soils, the relative increase in PO_4^{3-} availability was between 3 and 6 times that of the control values for both soil types after 27 weeks treatment. Litter fens, typically occurring on Mull soil types, are characterised by a much lower nutrient level than small sedge fen meadows occurring on Moder soils. Therefore, it is plausible that a fivefold increase of PO_4^{3-} concentrations in the Mull soil pore water will have a much stronger impact on the vegetation composition and ecosystem functioning than in more eutrophic systems. A similar experiment with soils from more calcareous coastal fen meadows, low in humus, showed a similar increase in PO_4^{3-} availability after SO_4^{2-} pollution. Waterlogging treatment with the addition 2 mmol L^{-1} SO_4^{2-} resulted in an increase from 4–5 μmol L^{-1} PO_4^{3-} to 15–20 μmol L^{-1} in pore water within 1 month (Lamers, unpublished results).

Conclusions

The absolute accumulation level of free sulphide in pore water, and thereby possible phytotoxic effects, could not be correlated to the soil profile. It was shown that the availability of free iron in the soil, and not the humus profile, determines the extent to which free sulphide accumulation (and thereby toxicity) occurs.

With respect to P eutrophication, we conclude that different types of freshwater fen soils show the same pattern of response to SO_4^{2-} pollution. The absolute extent of this phenomenon, however, and whether the mobilisation of other nutrients is also accelerated, depends on the soil type. Although it seems plausible that this is related to the availability of electron donors, no indication for this could be derived from the extraction of different SOM fractions. Differences in SOM aggregate formation might provide a partial explanation for this. The soil type with the highest P concentrations (both total P and PO_4^{3-} in pore water) showed the strongest eutrophication response after SO_4^{2-} addition. Care must be taken, however, because plant communities on low P soils are adapted to low trophic levels, and a small absolute acceleration of PO_4^{3-} mobilisation rates will easily lead to adverse effects in these systems.

We conclude that neither the description of the humus profile nor SOM fraction analysis are reliable indicators for wetland sensitivity to S pollution, as phytotoxicity and vegetation responses to eutrophication are not (directly) coupled to these variables. Instead, Fe and P were defined as key factors in the response of wetland soils to SO_4^{2-} pollution.

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References

Appelo CAJ & Postma D (1993) Geochemistry, Groundwater and Pollution. AA Balkema, Rotterdam

Beltman B, Rouwenhorst TG, Van Kerkhoven MB, Van der Krift T & Verhoeven JTA (2000) Internal eutrophication in peat soils through competition between chloride and sulphate with phosphate for binding sites. Biogeochemistry 50: 183–194

Bobbink R, Hornung M & Roelofs JGM (1998) The effects of airborne nitrogen pollutants on species diversity in natural and semi-natural European vegetation. J. Ecol. 86: 717–738

Boström B, Jansson M & Forsberg C (1982) Phosphorus release from lake sediments. Arch. Hydrobiol. 18: 5–59

Boström B, Andersen JM, Fleischer S & Jansson M (1988) Exchange of phosphorus across the sediment-water interface. Hydrobiologia 170: 229–244

Brinson MM (1977) Decomposition and nutrient exchange of litter in an alluvial swamp forest. Ecology 58: 601–609

Brock ThCM, Boon JJ & Paffen BGP (1985) The effects of the season and water chemistry in the decomposition of *Nymphaea alba* L.: Weight loss and pyrolysis mass spectrometry of the particulate matter. Aquat. Bot. 22: 197–229

Caraco NF, Cole JJ & Likens GE (1989) Evidence for sulphate-controlled phosphorus release from sediments of aquatic systems. Nature 341: 316–318

Einsele W (1936) Über die Beziehungen des Eisenkreislaufs zum Phosphatkreislauf im eutrophen See. Arch. Hydrobiol. 29: 664–686

Ellenberg H (1988) Vegetation ecology of Central Europe. 4th ed., Cambridge University Press, Cambridge

Goering HK & Van Soest PJ (1972) Forage Fiber Analyses; Agriculture Handbook 379. US Agricultural Research Service, Washington

Green RN, Trowbridge RL & Klinka K (1993) Towards a taxonomic classification of humus forms. Forest Science Monograph 29, Bethesda

Kemmers RH (1996) Using humus forms to monitor processes. Landschap 13: 1157–167 (in Dutch, with Engl. abstract)

Kok CJ & Van de Laar BJ (1991) Influence of pH and buffering capacity on the decomposition of *Nymphaea alba* L. detritus in laboratory experiments: a possible explanation for the inhibition of decomposition at low alkalinity. Verh. Internat. Verein Limnol. 24: 2689–2692

Jørgensen BB (1982) Mineralization of organic matter in the sea bed – the role of sulphate reduction. Nature 296: 643–645

Lamers LPM, Tomassen HBM & Roelofs JGM (1998a) Sulfate-induced eutrophication and phytotoxicity in freshwater wetlands. Environ. Sci. Technol. 32: 199–205

Lamers LPM, Van Roozendaal SME & Roelofs JGM (1998b) Acidification of freshwater wetlands: combined effects of non-airborne sulfur pollution and desiccation. Water, Air, Soil Pollut. 105: 95–106

Lamers, LPM (2001) Tackling Some Biogeochemical Questions in Peatlands. PhD thesis University of Nijmegen, Nijmegen

McKinley VL & Vestal JR (1982) Effects of acid on plant litter decomposition in an arctic lake. Appl. Environ. Microbiol. 43: 1188–1195

Ohle W (1954) Sulfat als 'Katalysator' des limnischen Stoffkreislaufes. Vom Wasser 21: 13–32

Patrick WH & Khalid RA (1974) Phosphate release and sorption by soils and sediments: effect of aerobic and anaerobic conditions. Science 186: 53–55

Paul EA & Clark FE (1989) Soil microbiology and biochemistry. Academic Press Inc., San Diego

Pegtel D (1983) Ecological aspects of a nutrient-deficient wet grassland (Cirsio-Molinietum). Verh. Ges. Ökol. X: 217–228

Potvin C, Lechowicz MJ & Tardif S (1990) The statistical analysis of ecophysiological response curves obtained from experiments involving repeated measures. Ecology 71: 1389–1400

Redfield AC (1958). Biological control of chemical factors in the environment. Am. Sci. 46: 205–221

Roelofs JGM (1986) The effect of airborne sulphur and nitrogen deposition on aquatic and terrestrial heathland vegetation. Experientia 42: 372–377

Roelofs JGM (1991) Inlet of alkaline river water into peaty lowlands: effects on water quality and on *Stratiotes aloides* stands. Aquat. Bot. 39: 267–293

SAS (1989) SAS/STAT Users Guide, Version 6. SAS Institute Inc., Cary

Scheffer F & Schachtschabel P (1992) Lehrbuch der Bodenkunde. Enke, Stuttgart

Schuurkes JAAR, Kempers AJ & Kok CJ (1988) Aspects of biochemical sulphur conversions in sediments of a shallow soft water lake. J. Freshwater Ecol. 4: 369–381

Smolders AJP & Roelofs JGM (1993) Sulphate mediated iron limitation and eutrophication in aquatic ecosystems. Aquat. Bot. 46: 247–253

Smolders AJP & Roelofs JGM (1996) The roles of internal iron hydroxide precipitation, sulphide toxicity and oxidizing ability in the survival of *Statiotes aloides* roots at different iron concentrations in sediment pore water. New Phytol. 133: 253–260

Smolders AJP, Nijboer RC & Roelofs JGM (1995) Prevention of sulphide accumulation and phosphate mobilization by the addition of iron(II)chloride to a reduced sediment: an enclosure experiment. Freshwater Biol. 34: 559–568

Sperber JI (1958) Release of phosphate from soil minerals by hydrogen sulphide. Nature 181: 934

Swift MJ, Heal OW & Anderson JM (1979) Decomposition in Terrestrial Ecosystems. University of California Press, Berkeley & Los Angeles

Van Dam H (1988) Acidification of three moorland pools in The Netherlands by acid precipitation and extreme drought periods over seven decades. Freshwater Biol. 20: 157–176

Van Delft SPJ (1995) Humus- and Soil Profiles in Wet Grasslands. SC-DLO, Wageningen (In Dutch)

Van Delft SPJ, Marinissen JCY & Didden WAM (1999) Humus profile degradation as influenced by decreasing earthworm activity. Pedobiologia 43: 561–567

Vermeer JG (1986) The effect of nutrient addition and lowering of the water table on shoot biomass and species composition of a wet grassland community (*Cirsio-Molinietum* Siss. et de Vries, 1942). Act. Oecol. 7: 145–155

Walker TW (1965) The significance of phosphorus in pedogenesis. In: Hallsworth EA & Crawford DV (Eds) Experimental Pedeology (pp 295–315). Butterworth, London