Changes in pore water chemistry of desiccating freshwater sediments with different sulphur contents


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Abstract

Especially in dry summers, such as 2003 in Europe, wetlands may become subject to desiccation and oxidation processes may affect sediment top layers. In this paper, we present the results of a study in which the development of the pore water chemistry (major ions, nitrate, ammonium, phosphate and some metals) was monitored during experimental desiccation of previously anaerobic freshwater sediments. Three sediments with different concentrations of oxidizable sulphur were compared. Sediments appeared to respond very differently to prolonged oxidation due to desiccation. It can be concluded that oxidizable sulphur pools play an important role in freshwater wetlands. Water level fluctuations may have beneficial effects in sediments of which the buffer capacity is large enough to prevent acidification as a result of oxidation of reduced sulphur compounds. Oxidation of such sediments will result in net nitrogen losses and a decrease of the phosphate availability. Desiccation of sediments with high oxidizable sulphur contents, however, might lead to reactions that resemble those observed in acid sulphate soils. Extreme acidification might occur resulting in the mobilisation of high concentrations of potentially toxic metals such as aluminium and zinc. Dissolution of oxidized iron at very low pH will also result in the release of previously adsorbed phosphate. In freshwater systems, high concentrations of reduced sulphur will especially accumulate in reductive and iron-rich sediments which are fed by sulphate-enriched groundwater and which almost never fall dry.

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1. Introduction

In anaerobic/reductive sediments, sulphate reduction results in the formation of sulphide which may be reoxidized, escape from the sediment as gaseous H₂S or be bound in the sediment as insoluble metal sulphides. Usually iron is quantitatively the most important metal by which sulphide is bound (Drever, 1997). Therefore, the concentration of sulphur accumulating in reductive sediments depends on the concentration of sulphur supplied and the concentration of iron available to bind sulphide. High sulphur accumulation rates are found in sediments which are influenced by...
water rich in both sulphate and iron (Postma, 1982; Dellwig et al., 2001; Lucassen et al., 2002). In coastal regions, for instance, sediments commonly contain high concentrations of FeS as seawater provides large concentrations of sulphate while terrestrial sources supply iron (Dellwig et al., 2001).

In general, sulphate levels tend to be much lower in freshwater environments. However, atmospheric deposition, contaminated surface water and groundwater (seepage) may form important sources of sulphur (Postma, 1982; Schuurkes, 1987; Ritsema et al., 1992; Roelofs, 1991; Smolders and Roelofs, 1993; Dellwig et al., 2001; Lucassen et al., 2004a). Atmospheric sulphate deposition rates have been very high in the second half of the last century (Roelofs, 1983, 1986; Schuurkes, 1987). In large parts of The Netherlands, ground water sulphate concentrations have shown a strong increase over the last decades. This increase can be explained by the oxidation of geological pyrite-rich formations in the subsoil owing to decreased groundwater levels and increased nitrate losses from agricultural lands and forests (Stuyfzand, 1993; Lamers et al., 1998, 2002; Lucassen et al., 2004a,b). In pyrite containing subsoil, denitrifying bacteria use nitrate to oxidize sulphides to sulphate (Stuyfzand, 1993; Aravena and Robertson, 1998). In many European countries, nitrate concentrations in groundwater have increased strongly due to losses from agricultural lands (Ruano Criado, 1996; Iversen et al., 1998). Lucassen et al. (2002) showed that high concentrations of pyrite may accumulate in sediments of wetlands that are fed by sulphate and iron enriched groundwater.

In dry summers, such as 2003 in Europe, wetlands may become subject to desiccation and oxidation processes may affect sediment top layers. In general, temporary oxidation of reductive sediments might have beneficial effects. Oxidation of reduced iron, for instance, may increase the phosphate-binding capacity of sediments (Smolders et al., 1995a,b; Golez and Kyuma, 1997; Lamers et al., 1998; Lucassen et al., 2005). Next, oxidation of the top layer may stimulate nitrogen losses from the sediment by so-called coupled nitrification/denitrification reactions (D’Angelo and Reddy, 1993; Risgaard-Petersen and Jensen, 1997). On the other hand, if reduced sulphur concentrations are high, oxidation reactions may lead to a strong acidification of sediments and to a concomitant strong increase of (heavy) metal concentrations (Van Breemen, 1973; Harmsen and Van Breemen, 1975; Banks et al., 1997; Ludwig and Balkenhol, 2001; Lucassen et al., 2002). After re-wetting of such sediments, the water layer may become acidic and remain so for a considerable time (Lucassen et al., 2002). In such cases, metal toxicity may provoke lethal effects in fish and other fauna elements (Leuven, 1988).

In this paper, we present the results of a study in which the development of the pore water chemistry (major ions, nitrate, ammonium, phosphate and some metals) was monitored during experimental desiccation of previously anaerobic freshwater sediments. Three sediments with different concentrations of sulphur were compared.

2. Material and methods

2.1. Sediment types

Sediments were collected at three locations in The Netherlands. These locations were selected primarily for their total sulphur content of the sediment.

One sediment with total sulphur content of 0.002% consisted of sand and was collected from a location called “De Berendonck” (5°46’40” E, 51°48’44”). The Berendonck is a large open water which has been created after sand extraction and is not influenced by sulphate-rich seepage. Another sediment consisted of clay from an ox-bow lake in the former flood plain of the river Waal located in the Ooypolder (“Oude Waal” 5°53’35” E, 51°51’16” N). This sediment had a total sulphur content of 0.033%. Finally a silty/loam, sulphur-rich sediment with a total sulphur content of 0.272%, was collected from a ditch in “De Bruuk” (5°57’45” E, 51°47’10” N). “De Bruuk” is a small nature reserve near the village of Groesbeek, which receives sulphur and iron-rich seepage (Smolders et al., 1995a,b).

2.2. Total oxidizable sulphur

Total oxidizable sulphur was determined by mixing 50 ml of fresh sediment with 450 ml of demineralised water and flushing the sediment in a 1-L cylinder with compressed air or with compressed nitrogen gas for 30 days. The dissolved sulphur concentrations were determined in filtered (0.45 μm) water at the end of
the experiment. The concentration of sulphur reached in the aerated cylinder minus the concentration reached in the nitrogen flushed cylinder (which were very low compared to the concentrations reached in the cylinders flushed with compressed air) was used to calculate the maximum concentration of oxidizable sulphur in \( \mu \text{mol L}^{-1} \) sediment.

2.3. Experimental set-up

Glass aquariums (40 cm \( \times \) 40 cm \( \times \) 40 cm), six for each sediment type, were filled with 20 cm of fresh sediment. In each aquarium, two inert porous ceramic cups (Eijkelkamp Agrisearch Equipment) were installed in the upper 10 cm of the sediment layer to allow collection of pore water samples. Next, 20 cm of demineralised water was carefully poured on top of the sediment without disturbing the sediment. For each sediment type, the water layer was siphoned off in half of the aquariums after 25 days. Next, these three aquariums were allowed to desiccate. Extreme desiccation was prevented by spraying small amounts of water on top of the sediments (water content of the sediment was kept at \( \pm 50\% \) of the original values). In the remaining three aquariums, the water level was maintained constant by adding demineralised water. The aquariums were kept in the dark at a temperature of 18 \( ^\circ \text{C} \) and a humidity of \( \pm 70\% \). Pore water samples were collected at regular time intervals by connecting the samplers (by airtight tubing) to nitrogen pre-flushed vacuumed infusion flasks. Both samplers from the same aquarium were connected to the same flask (pooled during sampling). After determination of pH and alkalinity, the samples were kept at \(-20\ ^\circ \text{C}\) until analysis.

2.4. Bulk density

Bulk density was determined by weighing 1 L of fresh sediment and re-weighing it after drying for 48 h at 105 \( ^\circ \text{C} \). Bulk density values were used to predict maximum concentrations of dissolved sulphate in sediment pore water during desiccation.

2.5. Chemical analysis

Total sulphur (S) and iron (Fe) concentrations were determined in digestates of dried and ground sediment. Digestates were prepared by combusting sediment samples in nitric acid and hydrogen peroxide for 16 min with the aid of a Milestone microwave (type mls 1200 Mega). After dilution with demineralised water, the digestates were kept at \(-20\ ^\circ \text{C}\) until analysis.

Alkalinity and pH of the samples were determined immediately after collection. Alkalinity was determined by titrating a known volume of sample with 0.01 M HCl down to pH 4.2 (Roelofs, 1983). Sulphate was measured according to Technicon Auto Analyser Methodology (1981), ortho-phosphate according to Henriksen (1965), ammonium according to Grasshoff and Johannsen (1977) and nitrate according to Kamphake et al. (1967). Fe, Mn, Ca, Mg, S (wavelength, 182 nm), Al and Zn were analysed using an inductively-coupled-plasma emission spectrophotometer (ICP) (Spectroflame, Spectro Inc., Littleton, USA). Saturation indices of calcite and gypsum were calculated using Visual MINTEQ version 2.30. Quality assurance measures included blanks and replicate analysis. Repeated analyses did not reveal differences greater than 6%.

3. Results

The three sediments show clear differences in total S and oxidizable S content (Table 1). In the Bruuk sediment, oxidizable S content amounts to 32,349 \( \mu \text{mol L}^{-1}\) which is 64.8% of the total S content (49,780 \( \mu \text{mol L}^{-1}\)). In the sandy Berendonck sediment and the Oude Waal sediment, mean oxidizable S contents amount to 981 and 4289 \( \mu \text{mol L}^{-1}\), respectively which respectively accounts for 53% and 53.8% of the total S contents of the sediments (1830 and 7980 \( \mu \text{mol L}^{-1}\), respectively). The non-oxidizable S content could consist of organic-S or pyrite forms that are very resistant to oxidation (Morse, 1991). This is probably the case for the Oude Waal and the Bruuk sediments as these sediments have a relatively high organic matter content (Table 1). For the sandy, and thus less-reductive, Berendonck sediment, the relatively low percentage of oxidizable S can most likely be explained by the presence of insoluble sulphate minerals, such as iron sulphates (Drever, 1997).

Fig. 1 shows the amount of pore water that remained in the top layer of the sediment as calculated from the increases of the chloride concentrations during the desiccation process. The calculations were compared with values obtained by drying sediment
sub-samples from the aquarium during the experiment. The measured and calculated values appeared to show a strong correlation and never differed more than 10%. Immediately after onset of the experiment, water contents of the sediment dropped strongly down to 70% of the original water content at 25 days after removing the water layer. Next water content declined more slowly during the rest of the experiment and reached values between 50 and 60% of the original water content at the end of the experiment (Fig. 2). Initially, the water content showed the strongest decline at the sandy Berendonck sediment. However, at the end of the experiment, the lowest water content was measured in the silty/loamy Bruuk sediment.

Based on the lowest residual water content measured during the experiment, we have calculated the maximum concentration of sulphate in the remaining pore water that theoretically could be observed given that all the oxidizable sulphur would be oxidized and consequently remained dissolved upon desiccation. These values are given in Table 1.

### 3.1. Desiccation of Berendonck sediment

Within 30 days after removal of the water layer, sulphate concentrations reached a maximum value of $\pm 7000 \mu\text{mol L}^{-1}$ and remained more or less stable during the remaining period of the experiment (Fig. 2). The same pattern was observed for calcium and magnesium, which reached concentrations of $\pm 6200$ and $1000 \mu\text{mol L}^{-1}$, respectively. Alkalinity and iron, manganese and ammonium concentrations strongly declined to very low levels within the first 25 days after the start of desiccation. Nitrate concentrations strongly increased to values as high as $2500 \mu\text{mol L}^{-1}$ at day 80, and from then on remained more or less stable. pH showed a sharp decline from pH $\pm 6.8$ to pH 6.0 around day 75. After day 55, phosphate concentrations dropped from 13 $\mu\text{mol L}^{-1}$ to $\pm 5 \mu\text{mol L}^{-1}$. Zinc (Zn) and aluminium (Al) concentrations showed more or less the same pattern of change as Ca and Mg (Fig. 2).

### 3.2. Desiccation of Oude Waal sediment

In the Oude Waal sediment, ammonium, iron, manganese and phosphate levels declined from day 30 and reached very low levels at the end of the experiment (Fig. 3). Around day 60, sulphate levels increased from very low levels to concentrations of $\pm 1000 \mu\text{mol L}^{-1}$. Around day 130, sulphate levels showed a further increase to values of $\pm 4000 \mu\text{mol L}^{-1}$. Alkalinity showed a gradual decrease from day 50 until the end of the experiment with a more or less stable period in which no change occurred from day 75 until day 150. Calcium and magnesium concentra-

<table>
<thead>
<tr>
<th>Sediment Type</th>
<th>Berendonck</th>
<th>Oude Waal</th>
<th>De Bruuk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total S content (%)</td>
<td>0.004</td>
<td>0.062</td>
<td>0.419</td>
</tr>
<tr>
<td>Oxidizable S content (%)</td>
<td>0.002</td>
<td>0.033</td>
<td>0.272</td>
</tr>
<tr>
<td>Total Fe content (%)</td>
<td>0.024</td>
<td>0.103</td>
<td>0.462</td>
</tr>
<tr>
<td>Total S content ($\mu\text{mol L}^{-1}$ sediment)</td>
<td>1830</td>
<td>7980</td>
<td>49,780</td>
</tr>
<tr>
<td>Oxidizable S content ($\mu\text{mol L}^{-1}$ sediment)</td>
<td>981</td>
<td>4289</td>
<td>32,349</td>
</tr>
<tr>
<td>Total Fe content ($\mu\text{mol L}^{-1}$ sediment)</td>
<td>5890</td>
<td>7576</td>
<td>31,344</td>
</tr>
<tr>
<td>Predicted pore water S concentration ($\mu\text{mol L}^{-1}$)</td>
<td>8637</td>
<td>6227</td>
<td>79,164</td>
</tr>
<tr>
<td>Soil characteristics</td>
<td>Sandy</td>
<td>Clay</td>
<td>Silty loam</td>
</tr>
<tr>
<td>Organic matter content (%)</td>
<td>1</td>
<td>15</td>
<td>9</td>
</tr>
</tbody>
</table>

Total (oxidizable) sulphur and iron content are given in percent as well as in $\mu\text{mol L}^{-1}$ sediment. Sediment characteristics are according to Scheffer and Schachtschabel (1992).

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Fig. 1. Amount of soil water remaining during desiccation based on chloride measurements. The dashed line indicates the start of the desiccation treatment (day 25). At day 0, the experiment started and the sediments were submerged.
tions showed a gradual decline in the control treatment as well as the desiccation treatment until day 100. In the desiccation treatment, Ca and Mg concentrations showed an increase at day 125. Aluminium and zinc concentrations did not differ much between the treatments during the experiment (Fig. 3) and showed more or less the same pattern of change as Ca and Mg (Fig. 3).

Fig. 2. Changes in pore water chemistry in the control treatment (open symbols) and the desiccation treatment (closed symbols) for the Berendonck sediment. Water was removed from the desiccation treatment at day 25. Mean values (n=3) and SD (vertical bars) are presented. All pore water concentrations are given in µmol L⁻¹.
3.3. Desiccation of Bruuk sediment

In the Bruuk sediment, sulphate, calcium and magnesium showed an increase to values of respectively 8000, 6000 and 1000 µmol L⁻¹ between day 30 and day 55. Next, from day 80 until day 150, sulphur, calcium and magnesium concentrations gradually increased to values as high as respectively 30,000, 13,000 and 4000 µmol L⁻¹. After day 90, pH dropped strongly from pH 6.0 to pH 3.0. After day 150, pH...
dropped to values as low as $\pm 2.5$. Between day 100 and day 150, iron as well as aluminium concentrations increased to 2300 and 7500 $\mu$mol L$^{-1}$, respectively. After day 150, sulphur concentration showed a strong increase to $\pm 70,000$ $\mu$mol L$^{-1}$. Iron, aluminium and magnesium showed a concomitant increase to values as high as 10,700, 19,000 and 11,300 $\mu$mol L$^{-1}$, respectively, at the end of the experiment. Manganese and zinc concentrations more or less showed the same pattern as iron and aluminium. Nitrate levels remained low during the experiment and did not show any differences between the control and the desiccation treatment. Ammonium levels gradually increased between days 60 and 140 from 200 to 600 $\mu$mol L$^{-1}$. After day 150, ammonium concentrations increased strongly to $\pm 1600$ $\mu$mol L$^{-1}$.

4. Discussion

4.1. Effects of desiccation on water chemistry

As soon as anaerobic reductive sediments fall dry and oxygen enters the sediment, oxidation reactions start to affect pore water chemistry. Reduced sulphur, largely present in the form of metal sulphides such as FeS and pyrite FeS$_2$, will become oxidized (reaction 1).

$$4\text{FeS}_2 + 15\text{O}_2 + 10\text{H}_2\text{O} \rightarrow 4\text{FeOOH} + 16\text{H}^+ + 8\text{SO}_4^{2-}$$ (Reaction 1)

As a result, pore water sulphate concentrations will increase which was observed in all three sediments. Oxidation of iron sulphides generates protons and hence will lead to an acidification of the sediment if the buffering capacity is not adequate to compensate for the acid produced (Ritsema et al., 1992; Lucassen et al., 2002). Buffering can be provided by the consumption of alkalinity (Reaction 2), dissolution of carbonates such as calcite and dolomite (Reactions 3 and 4, respectively), cation exchange reactions (Reaction 5), and finally by the weathering of aluminium and iron(hydr)oxides and silicates (for instance Reaction 6) (Van Breemen, 1973; Ritsema et al., 1992; Scheffer and Schachtschabel, 1992; Ritsema and Groenenberg, 1993; Lucassen et al., 2002).

$$\text{HCO}_3^{- (aq)} + \text{H}^+_\text{(aq)} \rightarrow \text{H}_2\text{O} + \text{CO}_2^{(g)}$$ (Reaction 2)

$$\text{CaCO}_3^{(s)} + 2\text{H}^+_\text{(aq)} \rightarrow \text{Ca}^{2+ (aq)} + \text{CO}_2^{(aq)} + \text{H}_2\text{O}$$ (Reaction 3)

$$\text{CaMg(CO}_3^{(s)} + 4\text{H}^+_\text{(aq)} \rightarrow \text{Ca}^{2+ (aq)} + \text{Mg}^{2+ (aq)} + 2\text{CO}_2^{(aq)} + 2\text{H}_2\text{O}$$ (Reaction 4)

$$-\text{Ca}^{2+ (aq)} + 2\text{H}^+_\text{(aq)} \rightarrow -2\text{H}^+ + \text{Ca}^{2+ (aq)}$$ (Reaction 5)

$$[\text{Al}_6(\text{OH})_15^{3+ (s)} + 15\text{H}^+_\text{(aq)} \rightarrow 6\text{Al}^{3+ (aq)} + 15\text{H}_2\text{O}$$ (Reaction 6)

The rate by which sediments become oxidized will strongly depend on sediment characteristics such as particle size and organic matter content. Water potentials of coarser sediments are relatively low (Scheffer and Schachtschabel, 1992). Therefore, the sandy Berendonck sediment dried out more rapidly than the other sediments and oxidation of reduced sulphur started immediately after the sediment fell dry. In this sediment, most changes in pore water chemistry took place during the first 25 days after the sediment fell dry. Maximum sulphate concentrations of $\pm 7800$ $\mu$mol L$^{-1}$ were reached, which are more or less in accordance with the predicted concentrations assuming that all oxidizable sulphur would be oxidized and remain in solution (Table 1). This means that precipitation of gypsum (calcium sulphate) was not an important process in this sediment, which was confirmed by calculated saturation indices for gypsum which remained negative during the entire experiment (Fig. 5). Consumption of dissolved alkalinity, carbonate dissolution and possibly cation exchange seemed to be the main buffering reactions involved. pH did not drop below pH 6.0 and alkalinity appeared to be just sufficient to prevent a further decrease of the pH (Fig. 4).

The strong increase of nitrate concentrations upon desiccation in the Oude Waal sediment indicates that nitrification of ammonium to nitrate also played an important role in acid formation in this sediment (Reaction 7).

$$\text{NH}_4^+ + 1.5\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+$$ (Reaction 7)

Approximately 25% of the acid produced during the oxidation of the sediment can be ascribed to nitri-
Nitrate concentrations appeared to increase more strongly than can be explained by the observed decline of the ammonium concentrations, probably because ammonium becomes de-sorbed from the adsorption complex and oxidized consequently.

In the more finely grained sediments of the Oude Waal and the Bruuk, changes in pore water chemistry only started to occur approximately 25 days after the water layer was removed. This can be explained by the relatively slow penetration of oxygen in these fine sediments.
grained sediments compared to the sandy Berendonck sediment.

The Oude Waal sediment appeared to be supersaturated in calcium/magnesium (bi)carbonate (Figs. 3 and 5). Therefore, the gradual decrease of the calcium, magnesium and carbonate concentrations in this sediment probably resulted from calcium (magnesium) carbonate precipitation. Sulphate levels increased in two distinct periods which might be explained by the intensity of pyrite oxidation reactions. Buffering was provided mainly by consumption of dissolved alkalinity in this strongly buffered pore water. After day 125, sulphate concentrations showed a further increase to 4000 μmol L⁻¹ to remain stable again until the end of the experiment. We assume that an increased oxygenation of the sediment resulted in a further increase of the sediment oxidation. Calcium and magnesium now do show an increase in the desiccation treatment, indicating a contribution of carbonate dissolution in the buffering reactions. Fig. 5 confirms that at this stage, calcite saturation indices have declined sufficiently (owing to carbonate consumption) to enable net calcite dissolution. Concentrations of sulphate and calcium reach a maximum value of ±4000 μmol L⁻¹. However, not all oxidizable sulphur was dissolved at these concentrations, while gypsum saturation (Ritsema and Groenenberg, 1993) was not reached either (Fig. 5). This might indicate that sulphur concentrations did not increase further because not all oxidizable sulphur (Table 1) was yet oxidized under the prevailing conditions.

In the Oude Waal sediment, the increase of nitrate was much less pronounced than in the Berendonck sediment. The total ammonium content might have been lower in this sediment. However, it also seems probable that oxygenation of the sediment did not become sufficiently high before the later stages of the experiment. Between days 50 and 125, for instance, ammonium showed a very gradual decline from 300 to 100 μmol L⁻¹ while nitrate levels only slightly increased. This could be explained by the presence of anaerobic niches in the sediment where nitrate could be denitrified following nitrification. In the sandy and thus permeable Berendonck sediment, these anaerobic sides were probably not present and most nitrate produced remained present in sediment pore water. After day 125, the ammonium concentration suddenly dropped to very low levels while nitrate concentration increased progressively. In this stage, the observed increase of nitrate can be explained again by the rapid oxidation of ammonium that becomes desorbed from cation exchange sites.

“De Bruuk” is a small nature reserve which receives sulphur and iron-rich seepage (Smolders et al., 1995a,b). Therefore, high concentrations of FeS₀ have accumulated in this sediment. The oxidation of large amount of FeS₀ explains the strong acidification of this sediment and hence the totally different reaction of this sediment following desiccation. Initially, however, only a small amount of the oxidizable sulphur pool was oxidized, which was largely buffered by consumption of dissolved alkalinity, carbonate dissolution and cation exchange. In contrast to the other sediments, ongoing oxidation of the Bruuk sediment resulted in such a high acid production that buffering reactions were not able to prevent a strong decrease in pH of the sediment. Pore water pH dropped strongly and sulphate concentrations gradually increased to values as high 30,000 μmol L⁻¹. Under acid conditions, the solubility of gypsum is

Fig. 5. Time versus saturation indices for calcite and gypsum for the desiccation treatments for the three sediments. Saturation indices were calculated with Visual MINTEQ version 2.30.
much higher and hence gypsum saturation indices remained negative. Weathering of aluminium and iron(hydr)oxides and silicates became involved in acid buffering as was clearly indicated by the strongly increased concentrations of aluminium and iron during ongoing soil acidification.

The strong increase of sulphur concentrations around day 150 can be explained by a sudden and rapid oxidation of reduced sulphur, probably due to a further desiccation of the sediment (Fig. 1). This was accompanied by a further and strong drop of the pH (to pH 2.5) and a concomitant increase of aluminium and iron concentrations. Calcium concentrations did not show any further increase, indicating that carbonate buffering and calcium exchange did no longer play a role in acid buffering reactions at these very low pH values. The strong increase in magnesium at this stage can be explained by the increased weathering of magnesium silicates (Drever, 1997). The sulphate concentrations of $+80,000 \text{ mmol L}^{-1}$ that were reached in the pore water at the end of the experiment were close to the predicted pore water concentrations assuming that all oxidizable sulphur would be oxidized (Table 1).

In the desiccated Bruuk sediment extremely high Al and Zn concentrations were reached at the end of the experiment. This in contrast to the Berendonck and the Oude Waal sediments. Such concentrations are highly toxic to benthic invertebrates. The strong increase of Zinc can most probably be explained by a decreased sorption of Zn$^{2+}$ to iron(hydr)oxides owing to a decreased pH (Drever, 1997).

In the Bruuk sediment, no net ammonium oxidation was observed, not even at the initial stage of the experiment when pH was still high enough to enable nitrification. Due to the relatively high oxidizable sulphur pool in this sediment, most oxygen entering the sediment was probably consumed by the thermodynamically more favourable sulphide oxidation reactions so preventing nitrification of ammonium. In a later stage, pH became too low for nitrification reactions to occur (Roelofs, 1983, 1986).

4.2. Effects of desiccation on nutrient availability

Desiccation results in an increase of insoluble iron(III) (hydr)oxides due to the oxidation of dissolved Fe$^{2+}$ and of FeS$_x$. Therefore, initially a clear decrease of dissolved iron concentrations could be observed in all sediments following desiccation. Manganese more or less shows the same behaviour. Only at very low pH (pH $<3.5$) iron(hydr)oxides dissolve (Drever, 1997), which was only the case in the Bruuk sediment at the final stage of the experiment.

In general, oxidized iron (III) compounds adsorb phosphate much better than reduced iron (Patrick and Khalid, 1974; Khalid et al., 1977; Ponnampерuma, 1984; Golterman, 1988; Lamers et al., 1998; Lucassen et al., 2004a,b). Therefore, phosphate becomes adsorbed onto iron(hydr)oxides under oxidized conditions and hence is immobilised following desiccation. Only in the sandy Berendonck sediment, phosphate concentrations remained higher than 1 mmol L$^{-1}$ after desiccation. In the Bruuk sediment phosphate concentrations increased strongly during the sharp decline of the pH at the end of the experiment. This can be explained by the dissolution of aluminium and iron(hydr)oxides at very low pH (2.5) values which, as a consequence, also resulted in the release of adsorbed phosphate. Phosphate concentrations increased much stronger than would be expected by the initial concentrations in the sediment pore water. This can be explained by the fact that calcium- and aluminium-bound phosphate dissolves and becomes bound to iron(hydr)oxides during the strong acidification occurring in the Bruuk sediment.

It can be concluded that the oxidation of iron, as a result of desiccation of sediments, will increase the phosphate-binding capacity of the sediment. Reduced sulphur will strongly reduce the phosphate-binding capacity in reductive sediments as it will form insoluble iron (II) sulphide precipitates. Desiccation of such sediments will result in the oxidation of iron sulphides into sulphate and iron(hydr)oxides. Sulphate is highly mobile and will be (at least partly) lost from the sediment to the surface water after re-flooding. Oxidized iron, on the other hand, is rather insoluble at pH $>3.5$, and will hence remain in the sediment. As a net result, the iron to sulphur ratio may be affected favourably resulting in a lasting increase of the phosphate-binding capacity after re-flooding (Lucassen et al., 2002, 2005).

In the Oude Waal and Berendonck sediments, desiccation leads to the nitrification of accumulated ammonium. Under field conditions denitrification of nitrate (in deeper still anaerobic sediment layers or
after re-wetting) will result in net nitrogen losses from the system. Nitrate can also oxidize reduced sulphur and iron compounds (Straub et al., 1996; Nielsen and Nielsen, 1998), which might even result in a further oxidation of these compounds once the sediment is reflooded.

5. Conclusions

It can be concluded that sediments may respond very differently to prolonged oxidation due to desiccation. If the oxidizable sulphur concentration is relatively low, oxidation of anaerobic sediments will normally result in net nitrogen losses and a decrease of the phosphate availability. Therefore, regular desiccation of wetlands might be essential to prevent eutrophication of such systems (Smolders et al., 1995a,b; Lamers et al., 2002; Lucassen et al., 2005).

However, desiccation of sediments with high oxidizable sulphur contents, particularly in combination with low acid buffering capacity, might lead to reactions that resemble those observed in acid sulphate soils (Van Breemen, 1973; Ritsma et al., 1992; Lucassen et al., 2002). Extreme acidification might occur resulting in the mobilisation of high concentrations of toxic metals such as aluminium and zinc. Dissolution of oxidized iron at very low pH will also result in the release of previously adsorbed phosphate. High concentrations of reduced sulphur will accumulate especially in iron-rich sediments which are fed by sulphate-enriched groundwater and which almost never fall dry (Lucassen et al., 2002, 2004a,b). When, in extremely dry years, such sediments become subject to desiccation severe negative effects may occur. In restoration activities, high oxidizable sulphur contents may also present a potential threat. Artificial drainage and consequent dredging of accumulated sediment in ‘de Venkoelen,’ a shallow lake fed with sulphate-rich groundwater located near the city of Venlo, The Netherlands, resulted in a strong acidification of the water layer (Lucassen et al., 2002). This was the result of oxidation of reduced sulphur following exposure of the sediment to the atmosphere.

It can be concluded that oxidizable sulphur pools play an important role in freshwater wetlands. The presented method to estimate the potentially mobilizable sulphur pool appeared to be very useful for the prediction of acidification related biogeochemical changes during desiccation. Water level fluctuations may have beneficial effects in sediments where the buffer capacity is large enough to prevent acidification as a result of oxidation of reduced sulphur compounds. The Bruuk sediment reacted as a classical acid sulphate soil. So, ‘acid sulphate soils’ are not restricted to coastal areas but are also formed in freshwater wetlands that are fed by seepage rich in both iron and sulphate.

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References
