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Effects of winter versus summer flooding and subsequent desiccation on soil chemistry in a riverine hay meadow

Roos Loeb *, Leon P.M. Lamers, Jan G.M. Roelofs

Department of Aquatic Ecology and Environmental Biology, Institute for Water and Wetland Research, Radboud University Nijmegen, The Netherlands

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Flooding of riparian meadows along rivers leads to a switch to anaerobic soil respiration, causing iron reduction and a corresponding release of phosphate. In addition, pollution of river water with sulphate may lead to higher phosphate release as a result of sulphide–iron interactions. As global climate change is expected to increase both temperature and the risk of summer flooding, floods may occur at higher temperatures, leading to faster anaerobic processes in soils. In a mesocosm experiment we tested the effects of flooding with or without 1 mmol L^{-1} SO_4^{2-} at two temperatures on sods from a riverine hay meadow. In the control treatment, the water level was kept 10 cm below the soil surface. After four weeks at 5 °C, the temperature was changed to 20 °C, mimicking the effects of summer flooding. After seven more weeks, all sods were allowed to dry out. In the inundated sods, redox potential dropped during flooding, leading to higher concentrations of Mn^{2+}, Fe^{2+}, PO_4^{3-}, NH_4^+ and Ca^{2+} and a higher alkalinity of the soil pore water. Upon desiccation, redox potential increased immediately, leading to the oxidation of Mn^{2+}, NH_4^+ and Fe^{2+} and causing immobilisation of PO_4^{3-} and a temporary drop in pH. Inundation at 20 °C resulted in a much faster release of Mn^{2+}, Fe^{2+}, PO_4^{3-} and Ca^{2+} and a higher acid consumption compared to flooding at 5 °C. Reduction of the added sulphate did not lead to additional mobilisation of phosphate through competition with the produced sulphide for binding to iron, because of the high iron concentration in the soil, which is characteristic of many floodplains. It is concluded that seasonality of flooding determines accumulation rates of potential phytotoxins and the release rate of phosphate, which has important implications for floodplain management.

1. Introduction

Upon flooding or waterlogging of a soil, oxygen depletion leads to a switch from aerobic to anaerobic respiration. As a result, potentially toxic substances such as Fe^{2+}, NH_4^+ and S^{2-} may accumulate. Additionally, the reduction of Fe^{3+} can cause a release of PO_4^{3-} that was originally adsorbed to Fe (hydr)oxide particles (Patrick and Khalid, 1974; Ponnamperuma, 1984), as the affinity of P to Fe(III) is higher than to Fe(II). It has been shown that in fen and lake systems, extra phosphate can be released by the binding of S^{2-} to Fe (Caraco et al., 1989; Smolders and Roelofs, 1993; Roden and Edmonds, 1997; Lamers et al., 1998a). Sulphide could also chemically reduce iron, also leading to the release of phosphate (Sperber, 1958). Notwithstanding the high iron (hydr)oxide concentrations in floodplain soils compared to fen systems, sulphate reduction can still play a role in the release of phosphate during floods (Zak et al., 2006; Loeb et al., 2007). This might be of great importance, as many rivers are polluted with sulphate (e.g. Van der Weijden and Middelburg, 1989).

During the last decade, summer floods have tended to occur more frequently in Central and Eastern Europe than before. Severe summer and late-spring floods have occurred in the major rivers Odra, Vistula, Labe (Kundzewicz et al., 2005) and Danube in the past ten years. Christensen and Christensen (2003) showed that global climate change may cause periods of heavy precipitation in Europe in summer, which may lead to more frequent summer floods, even though summers may become drier on average. Summer floods are known to have a greater impact on floodplain vegetation than winter floods. Koutecký and Prach (2005) showed that only 20% of the plant species present in a floodplain of the river Morova were able to regenerate from belowground parts after a flood in July 1997, and that recovery of the vegetation took several years. Van Eck et al. (2004, 2006) also found that floodplain species are less tolerant to summer floods than to winter floods and that tolerance to summer floods explains the distribution of plant species along elevation gradients in floodplains of the river Rhine. Less attention has been paid to the influence of seasonality of flooding on biogeochemical processes in the soil, although it is generally known that bacterial processes accelerate with increasing temperatures. We therefore expected that the above biogeochemical processes would take place at a higher rate during summer floods than during winter floods.

We selected a species-rich floodplain meadow to test the effects of temperature and water quality at the time of flooding. In a mesocosm experiment with intact soil–vegetation units (sods), we simulated

* Corresponding author. Department of Aquatic Ecology and Environmental Biology, Institute for Water and Wetland Research, Radboud University Nijmegen, Toernooiveld 1, 6525 ED, The Netherlands. Tel.: +31 243652337; fax: +31 243652409.
E-mail address: r.loeb@science.ru.nl (R. Loeb).

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winter flooding, succeeded by summer flooding and subsequent desiccation as in a summer drought.

2. Materials and methods

2.1. Area description

In February 2003, 15 vegetated soil cores 18 cm in diameter and 20 cm in height were taken from a floodplain along the River Overijsselse Vecht in the Netherlands (N 52°33.3′, E 6°7.3′). This specific meadow is being managed as a nature reserve by the State Forestry Service and is mown several times a year. The vegetation on this species-rich hay meadow can be characterised as a form of the *Fritillario-Alopecuretum pratensis* (Horsthuis et al., 1994). This vegetation is characterised by the presence of the endangered bulb species *Fritillaria meleagris*. The soil, characterised as a fluvisol, consisted of a mixture of clay and sand on a deeper peat layer. The vegetated topsoil which we used in our experiment consisted mainly of silt (>50%), but also contained clay (approximately 15%) and sand (approximately 10%), which formed the C-horizon. On top of this horizon, a distinct A-horizon (12% organic matter) of approximately 5 cm was present. The high Fe concentration (Table 1) in the soil originated from historical discharge of groundwater towards this meadow. This discharge is no longer present, due to drainage of surrounding fens and peatlands, which historically had a higher hydrological elevation. The soil was poor in inorganic N and K and had a low concentration of Fe- and Al-bound P, compared to other Dutch floodplain soils. The concentration of total P was, however, comparable to that in other, mostly eutrophic, floodplains. Eighty-six percent of the cation adsorption complex was occupied by Ca and Mg, preventing the soil from severe acidification.

2.2. Experimental set-up

The vegetated soil cores (sods) (19 plant species per 4 m^2), placed in pots perforated at the bottom, were hung in containers with a volume of approximately 10 L with outflows at 5 cm above and 10 cm below the soil surface (Fig. 1; Lamers et al., 1998b). Each soil core received water of controlled quality from its own 10 L reservoir, from which it was pumped at a rate of 10 L $week^{-1}$ to the top of the soil cores, where it infiltrated. The surplus water was discharged either from the outflow at 5 cm above or that at 10 cm below the soil surface. Three rhizon samplers (Rhizon SMS — 5 cm, pore size 0.1 µm, Rhizosphere Research Products) were used to collect soil pore water.

The soil cores were kept in a climate room at 5 °C with a day/night regime of 8 h light (approximately 100 µmol m^{-2} s^{-1}) and 16 h dark. After one week of acclimatisation, soil cores received one of the following treatments (n=5): (1) inundation up to 5 cm above the soil surface with sulphate-rich artificial river water, (2) inundation up to 5 cm above the soil surface with sulphate-poor river water, or (3) perfusion with the same sulphate-poor river water, but with the water table fixed at 10 cm below the soil surface. The composition of the

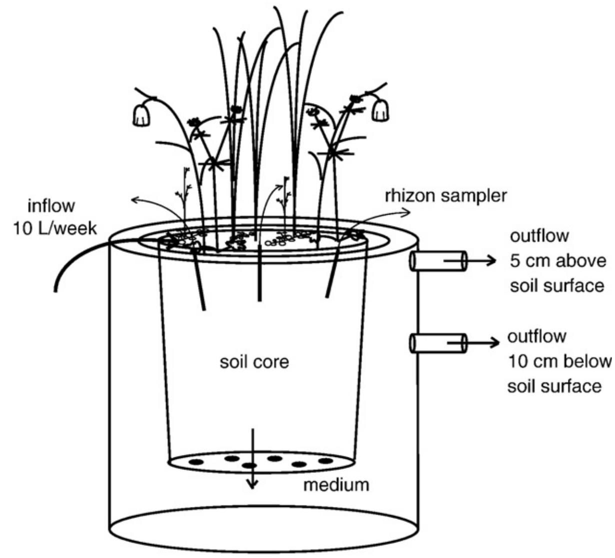

Fig. 1. Experimental set-up.

artificial river water resembled the local river water quality. The characteristics of the artificial river water are listed in Table 2. After 4 weeks, temperature was increased to 20 °C during the daytime and 15 °C at night to imitate summer flooding. The day/night regime was changed to 12 h/12 h. After 7 more weeks, treatments were stopped and outer containers were emptied to let the soils dry out. For three weeks, the soil cores then only received artificial rain water (1650 mL in total over this period, containing 0.005 g/L seasalt (Wiegandt GmbH), 3.1 µmol L^{-1} KCl, 1.6 µmol L^{-1}, $CaCl_2{\cdot}2H_2O$, 0.15 µmol L^{-1} KH_2PO_4, 67 µmol L^{-1} NH_4NO_3 and 87 µmol L^{-1} NH_4Cl.

2.3. Analysis of plant material

In order to determine the total concentrations of elements in plant material, 200 mg of homogenised and dried sample was digested for 17 min with 4 mL concentrated HNO_3 and 1 mL 30% H_2O_2 (Milestone microwave MLS 1200 Mega). Concentrations were analysed by ICP-OES (ICP, Spectroflame VML2).

2.4. Analysis of soil pore water

Each week, pore water samples were taken from the soil cores with the help of vacuumed glass bottles and analysed for pH, alkalinity, S^{2-}, NO_3^-, NH_4^+, PO_4^{3-}, Na^+, K^+, Cl^-, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, total dissolved S and total dissolved P. Samples from the three rhizon samplers of one soil core were pooled to reduce the effects of heterogeneity. At the end of the experiment, aboveground biomass was clipped and dry weight was determined after 24 h drying at 70 °C. Internal concentrations of P, Fe, Mn, Ca, Mg, Na, K and S were determined after digestion (see above).

Table 1
Soil characteristics in µmol g^{-1} dry weight

Organic matter	12
Amorphous Fe (oxalate)	459
Total Fe (digestion)	693
Fe- and Al-bound P (Ca-EDTA)	3.3
Total P (digestion)	24
NO_3 (MilliQ)	0.43
NH_4 (NaCl)	0.12
K (NaCl)	0.06
CEC	24
Base saturation Ca	82
Base saturation Mg	3.8

Organic matter content and base saturation in %, CEC in cmol+ kg^{-1}.

Table 2
Composition of the artificial river water

	SO_4-poor medium	SO_4-rich medium
Ca	1300	1300
Mg	250	250
K	250	250
Na	2000	4000
Cl	3300	3300
HCO_3	2000	2000
SO_4	0	1000
HPO_4	0.3	0.3
NO_3	35	35

Concentrations in µmol L^{-1}.

The pH was measured with a Radiometer Copenhagen type PHM 82 standard pH meter. Alkalinity was determined by titrating 10 mL of sample with 0.1 mol L^{-1} HCl down to pH 4.2. The concentration of dissolved sulphide species was determined in a 10 mL subsample, fixed with S^{2-} antioxidant buffer containing NaOH, NaEDTA and ascorbic acid. S^{2-} was detected using an S^{2-} ion-specific Ag electrode and a double junction calomel reference electrode (Thermo Orion) (Van Gemerden, 1984). For the ICP analyses (ICP-OES, Spectroflame VML2), 1.17% of concentrated nitric acid was added to the samples to avoid precipitation of elements. Samples were stored in polypropylene tubes at 4 °C. For the other analyses, 0.12 g citric acid L^{-1} was added to the samples, which were stored in iodated polyethylene bottles at −24 °C until further analysis. Total concentrations of Ca, Mg, P, Fe, Mn and S were analysed by ICP-OES (ICP, Spectroflame VML2). Total Fe and Mn measured in the pore water was regarded as Fe^{2+} and Mn^{2+}, since these are the dominant soluble species at the pH we measured. Total S was regarded as SO_4^{2-}, as, at the concentrations occurring in our samples, only a very small part will be in organic form and no dissolved sulphide species were found to be present. *o*-PO_4 and Cl^- (Technicon AutoAnalyser II), NH_4^+ and NO_3^- (+NO_2^-) (Bran+Luebbe, TRAACS 800+ AutoAnalyser) were analysed colorimetrically using ammonium molybdate, ferriammonium sulphate, salicylate and hydrazine sulphate, respectively. We will consider this molybdate reactive phosphorus as phosphate. Na and K were measured by photospectrometer (FLM3 Flame Photometer, Radiometer Copenhagen) using lithium nitrate.

2.5. Soil analysis

Organic matter content of the sediments was determined by loss-on-ignition (4 h, 550 °C). In order to determine the total concentrations of elements in the soil material, 200 mg of homogenised and dried sample was digested for 17 min with 4 mL concentrated HNO_3 and 1 mL 30% H_2O_2 (Milestone microwave MLS 1200 Mega). Redox potential of the soil was measured weekly with an mV-meter with a platinum electrode and an Ag/AgCl reference electrode. Measured potentials

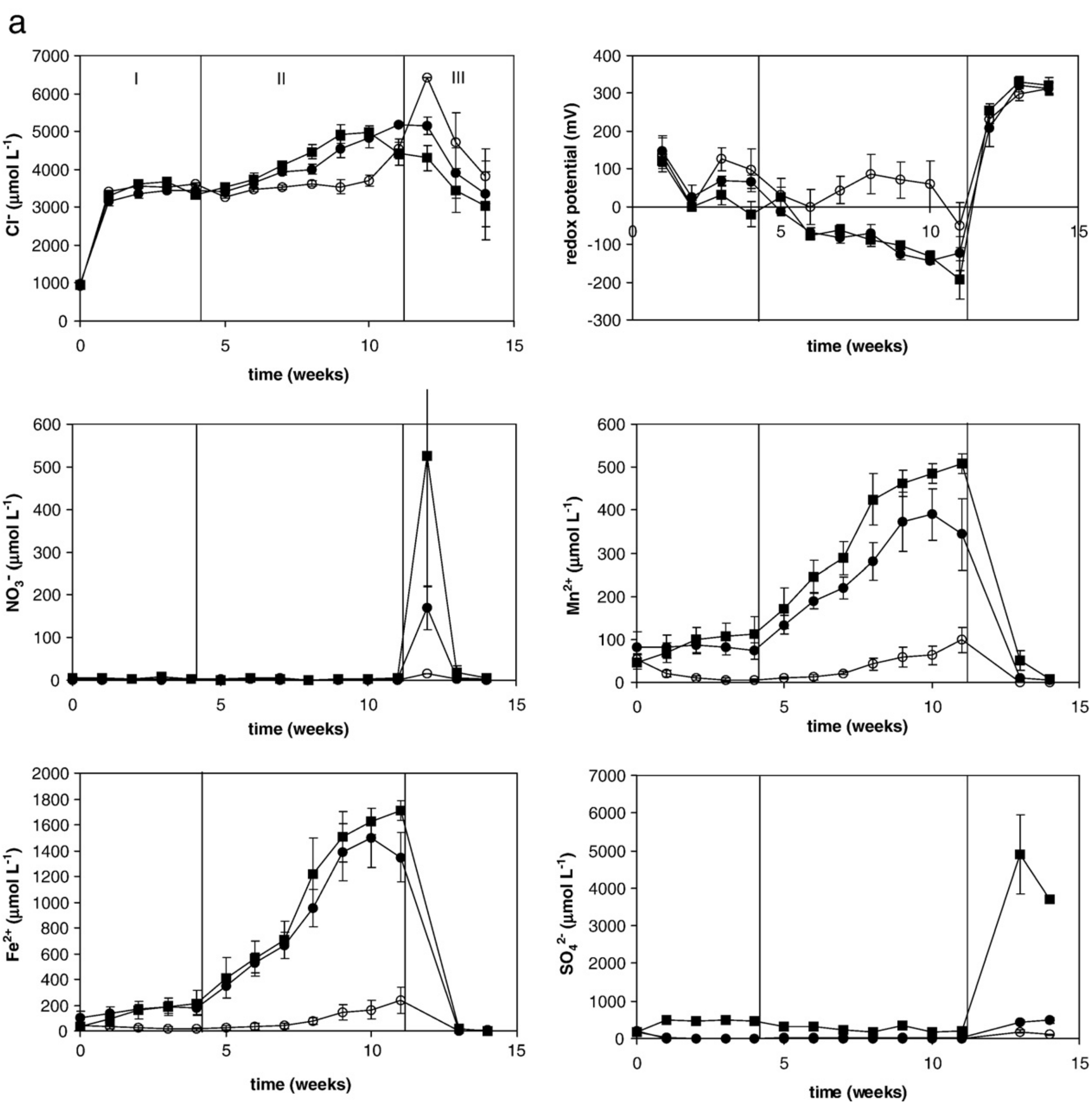

Fig. 2. Soil pore water characteristics during the cold flooding period (I), the subsequent warmer flooding period (II) and the warm period of drought (III). Squares symbolise sods receiving sulphate-rich water; circles symbolise sods receiving sulphate-poor water. Open symbols represent control sods with the water table at 10 cm below the soil surface during the flooding period; closed symbols represent inundated sods with the water table at 5 cm above the soil surface during the flooding period. Error bars represent standard error of the mean.

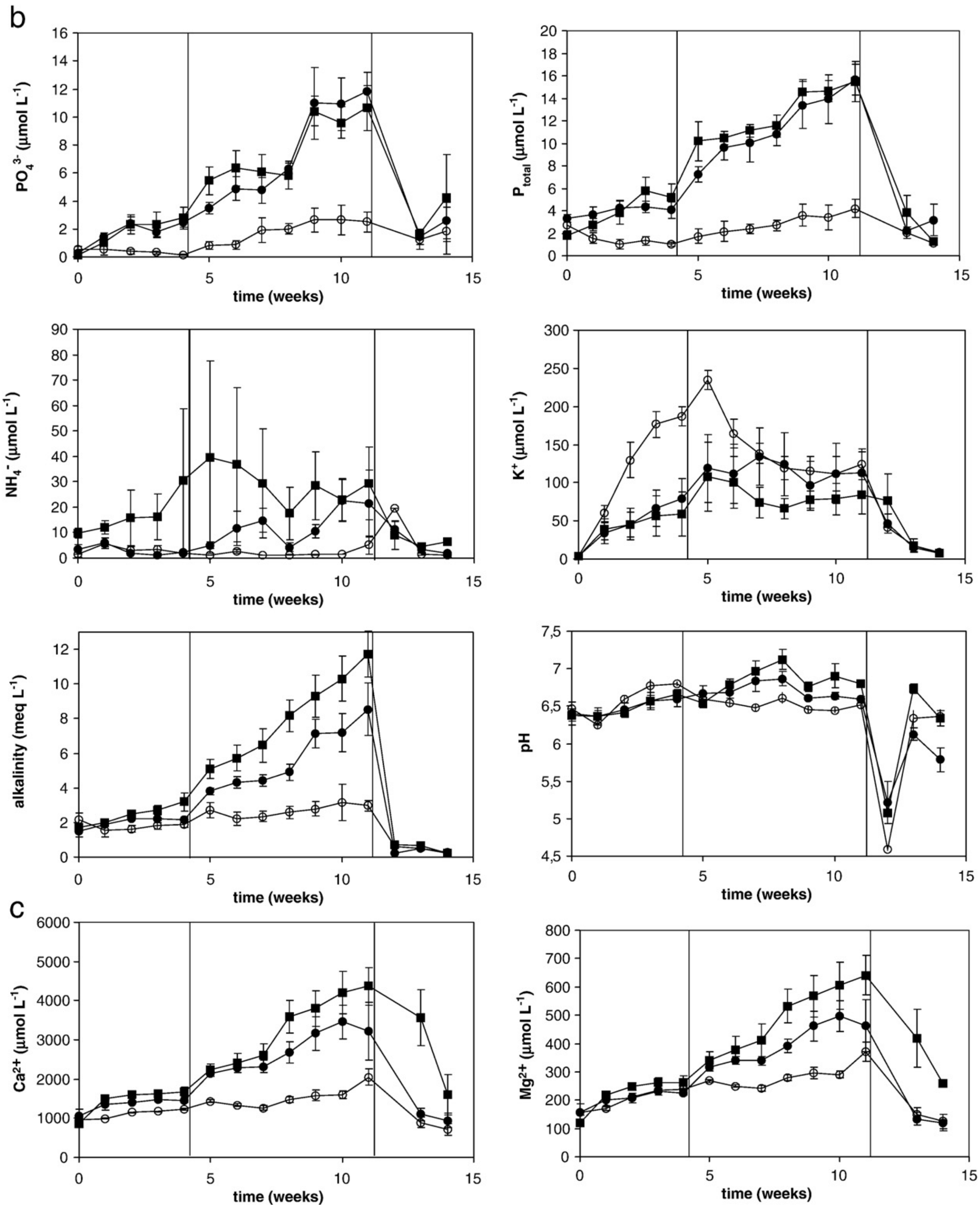

Fig. 2. (*continued*).

were converted to redox potentials relative to standard hydrogen potential (E_H). Soil extractions were performed on fresh sediments and were corrected for moisture content afterwards, after drying (24 h, 105 °C). CEC and base saturation were determined by a triple sequential extraction of 5 g of fresh soil with a 0.1 M $BaCl_2$ solution, followed by extraction with a 0.020 M $MgSO_4$ solution. The CEC was calculated from the surplus of Mg in this extract. Relative base saturations of Ca and Mg were calculated from the concentrations of Ca and Mg, respectively, in the $BaCl_2$ extract, relative to the CEC. The concentration of amorphous Fe was determined by oxalate extraction (2.5 g of sediment shaken for 2 h with 30 mL of a solution containing 16.2 g of $(COONH_4)_2{\cdot}H_2O$ and 10.9 g of $(COOH_2){\cdot}2H_2O$ per L (Schwertmann, 1964). To determine the Al- and Fe-bound P pools, a series of sequential P fractionations after Golterman (1996) was performed in duplicate: 2 g of field-moist soil was shaken twice (100 rpm) for 2 h with 25 mL 1 M NH_4Cl to extract loosely bound and water-soluble phosphorus. The pellet was then shaken twice for 2 h with 30 mL 0.05 M Ca-EDTA to extract Fe- and Al-bound P. NH_4 and K concentrations were determined by NaCl extraction, using 50 mL 0.1 M NaCl per 17.5 g of soil. In the MilliQ (ultrapure water, 18.2 MΩ cm) extraction, 17.5 g of soil was shaken with 50 mL MilliQ to determine NO_3 concentrations in soil. Digestions and extractions were measured as described above.

2.6. Statistical analysis

Net release rates were calculated by determining the regression coefficient per pot for a particular element in time during the cold or hot period. Rate differences in inundated sods were calculated by paired *t*-tests. Overall changes during the experiment, and the influence of the treatments, were assessed by repeated measures analyses (GLM) using log(x+1) transformed data. Significance was accepted at the 0.05 level. Effects of treatments on aboveground biomass and internal element concentrations were calculated by ANOVA using log (x+1) transformed data.

3. Results

Fig. 2 shows the ion concentrations measured during the experiment. Table 3 lists the results of changes in the parameters over time and the effects of the treatments. Concentrations of Cl^-, which is useful as an inert tracer, show that the artificial river water had already fully penetrated the soil during the first week of flooding. During the flooding period at 20 °C, Cl^- concentrations rose above those in the artificial river water, due to evaporation. At the end of the inundation period, Cl^- concentrations had increased to up to 1.5 times that in the artificial river water.

After inundation, the redox potential dropped steadily in the inundated sods, from +140 mV at the start of the inundation to approximately −150 mV in the last week of flooding. During this decrease, the concentrations of Fe^{2+}, Mn^{2+}, PO_4^{3-}, Ca^{2+} and NH_4^+ and the alkalinity increased. NO_3^- concentrations remained low, below the detection limit (3 µmol L^{-1}) in most of the measurements. Fe^{2+}, Mn^{2+} and PO_4^{3-} in the soil pore water showed particularly large increases. Fe^{2+} concentrations rose from about 70 µmol L^{-1} at the start of the experiment to 1500 µmol L^{-1} at the end of the inundation period (a 21-fold increase), while Mn^{2+} rose from 65 to 430 (7-fold) and phosphate from 0.2 to 11 µmol L^{-1} (55-fold). Concentrations of Fe^{2+}, PO_4^{3-} and NH_4^+ also increased in the sods with the water level at 10 cm below soil surface compared to the increase in Cl^-, but the increase was much smaller than in the inundated sods.

Table 3
p-values of the effects of time and time * treatment interactions (within-subject effects) and treatment effects (between-subject effects) (GLM for repeated measures)

	Time	Time * treatment	Treatment	Non-inundated	Inundated −SO_4	Inundated +SO_4
PO_4	0.000	0.021	0.000	a	b	b
P_{total}	0.000	0.000	0.000	a	b	b
NO_3	0.000	n.s.	n.s.	a	a	a
NH_4	0.007	n.s.	0.007	a	ab	b
K	0.000	n.s.	n.s.	a	a	a
Fe	0.000	0.000	0.000	a	b	b
Mn	0.000	0.000	0.000	a	b	b
Ca	0.000	0.000	0.000	a	b	c
Mg	0.000	0.000	0.003	a	a	b
SO_4	0.000	0.000	0.000	a	b	c
Cl	0.000	n.s.	n.s	a	a	a
pH	0.000	0.000	0.024	a	a	b
Alkalinity	0.000	0.000	0.000	a	b	c
Redox potential	0.000	0.000	0.000	b	a	a

Different letters indicate differences between treatments for a particular element (Tukey post-hoc test). Due to insufficient values in week 12, results from this week were not included in the analysis, except for the redox potential measurements. For the same reason, the results of week 14 were omitted from the analysis for Fe, Mn, P_{total}, Ca and Mg.

During the warmer period, rates of biogeochemical processes increased significantly. In the inundated sods, the net release of Fe^{2+} to the soil pore water was 7 times higher (32 µmol L^{-1} pore water per day; p=0.000) than during the colder period. Net PO_4^{3-} release rates were 3 times higher (0.18 µmol L^{-1} d^{-1}; p=0.007), Ca^{2+} rates 2 times (45 µmol L^{-1} d^{-1}; p=0.002) and Mn^{2+} rates 6 times (6.9 µmol L^{-1} d^{-1}; p=0.001). Alkalinity production (acid consumption) was 9 times higher on average (1.1 meq L^{-1} d^{-1}; p=0.000). Concentrations of SO_4^{2-} in the pore water of the sods inundated with the SO_4-rich river water were 1.9 times higher during the colder inundation period than during the warmer period (p=0.005), although they were both significantly lower than the concentration of 1000 µmol L^{-1} we had added. When the cold period is compared with an equal time span of the warmer period (i.e. the first four weeks), the net release rates of phosphate did not differ significantly anymore, due to the temporal drop that we measured in the release rate during the fourth week of the warmer period. Release rates of total P did however still show the same trend as observed for phosphate when considering the complete warmer period (0.2 µmol L^{-1} d^{-1}; p=0.056; 3 times higher than in the colder period).

The sods receiving sulphate-rich river water showed higher concentrations of Na^+ and SO_4^{2-}, Ca^{2+} and Mg^{2+} in the soil pore water than the sods receiving sulphate-poor water. Concentrations of S^{2-} remained below the detection limit (1 µmol L^{-1}), just as in the other treatments. Alkalinity was higher in the treatment with sulphate than in the treatments without sulphate during the inundation period, and pH was slightly higher.

During desiccation, the redox potential increased from −150 to +300 mV. This led to a severe drop in pH, from an average of 6.6 to 5.0 in the first week after desiccation. During the following weeks, however, pH recovered to an average of 6.3. After desiccation, Fe^{2+}, Mn^{2+} and PO_4^{3-} concentrations and alkalinity in the soil pore water decreased and remained low. In the first week of desiccation, NO_3^- concentrations showed a steep increase in the formerly inundated soils, up to values of 1000 µmol L^{-1}. In the subsequent weeks, concentrations of NO_3^- decreased again. SO_4^{2-} also showed an increase after desiccation, up to an average of 5000 µmol L^{-1} for the soils inundated with sulphate.

No effects of the treatments were found in the dry weight of the aboveground biomass at the end of the experiment. Some elements, however, did show significantly different concentrations in the aboveground biomass in the three treatments. Concentrations of Mn were 1.7 times higher in biomass from the inundated treatments than in the non-inundated control (p=0.005). The addition of SO_4 caused 1.7 times higher concentrations of S in the biomass of the sods treated with SO_4 (p=0.002), and concentrations of the Na added with the SO_4 were 1.5 times higher in the biomass of the sulphate-treated sods than in the biomass of the sods inundated with the sulphate-poor water (p=0.039). Fe concentrations in vegetation from the inundated sods were 1.6 times higher on average than in the controls, but the difference was not significant (p=0.375). We found no effects of SO_4 addition on the Fe concentration in plant material.

4. Discussion

4.1. Redox processes

Despite the fact that the inundated sods were flooded with the same water quality as the control sods with the water table fixed at 10 cm below surface, they contained much higher concentrations (2–40 times) of PO_4^{3-}, NH_4^+, Fe^{2+}, Mn^{2+}, Ca^{2+} in their pore water, and had a higher alkalinity. The higher availability of Fe and Mn was also reflected in increased concentrations of these metals in the plant tissue. The PO_4^{3-} concentrations reached after flooding were in the same order of magnitude as recorded in other studies (Loeb et al., 2007; Zak and Gelbrecht, 2007), although values 10 times higher have also been described for more heavily loaded floodplain soils (Kleeberg and Schlungbaum, 1993). The higher water level in the inundated sods clearly decreased the redox potential compared to the non-inundated sods. In these treatments, organic matter was decomposed anaerobically by the reduction of Mn^{4+} (resulting in increased concentrations of soluble Mn^{2+}) and of Fe^{3+} (resulting in increased concentrations of soluble Fe^{2+}), and by the reduction of SO_4^{2-} to S^{2-}. The use of NO_3^- as an electron acceptor may have contributed less to the decomposition of organic matter, due to the low concentrations of NO_3^-. Concentrations of Fe^{2+} in the pore water rose to 1700 μmol L^{-1}, which is in the same range as recorded in other wetland soils after 10 weeks of flooding (Zak and Gelbrecht, 2007) Note that the reduction of Mn, Fe and SO_4 occurred simultaneously, indicating heterogeneity of the soil.

Van der Welle et al. (2007) found in a laboratory experiment that *Caltha palustris*, a species present in the field site from which we took our sods, already had reduced growth on peat soils at an Fe^{2+} concentration of 350 μmol L^{-1}. In a field survey, Lucassen et al. (2000) found clear symptoms of iron toxicity in *Glyceria fluitans* at pore water Fe^{2+} concentrations of 2600 μmol L^{-1}. It can therefore be said to be quite possible that iron toxicity occurs in the field that we examined and that toxic levels are reached much sooner at higher temperatures than at colder temperatures.

Our results show that water level, by determining redox potential, also formed a key factor for the availability of NH_4^+ and PO_4^{3-}. The anoxic circumstances in the soils led to inhibition of nitrification, and decomposition of organic material therefore led to accumulation of the NH_4^+ produced. As regards the extremely low nitrate concentrations we measured, it is unlikely that the accumulated NH_4^+ originated from dissimilatory reduction of nitrate to ammonium. After desiccation, NH_4^+ was immediately oxidised to NO_3^-, resulting in high NO_3^- concentrations in the first week after desiccation. The high release of PO_4^{3-} during inundation can be attributed to the reduction of Fe^{3+} including iron from oxides and iron hydroxides, which effectively adsorb PO_4^{3-} (Patrick and Khalid, 1974; Reddy et al., 1999). Since the affinity of PO_4^{3-} for Fe(II) compounds is much smaller, reduction of Fe^{3+} leads to a release of PO_4^{3-} increasing the availability of the nutrient in pore water and, by diffusion, in the surface water (Ponnamperuma, 1984). The actual mobilisation of P to the pore water is determined by the concentration of amorphous Fe and its saturation by P (Young and Ross, 2001). The release of P from the soil pore water to the surface water is decisive for the eutrophication of surface waters and the discharge of P by river water. Since the sediment–water interface often also forms the interface between the anaerobic and aerobic environments, and the top layer of the sediment may also be oxic, the release of P to the water layer cannot be directly predicted by the release of P to the pore water. Reoxidised Fe adsorbs phosphates diffusing towards the surface water and in this way prevents release to the water layer (e.g. Boström et al., 1988; Moore and Reddy, 1994). Release of P to the surface water has been reported to be determined by a number of factors, including the Fe:P ratio in the pore water (Smolders et al., 2001), the Fe:P ratio in the aerobic top layer of the sediment (Jensen et al., 1992), wind and bioturbation, precipitation with $CaCO_3$ (Boström et al., 1988) and by the phosphate concentration in the soil pore water itself (Young and Ross, 2001).

The drought period showed large differences with the preceding period, as all substances whose reduction was described above were oxidised again. Even the non-inundated treatment manifested a different pore water composition during the dry period than before. Although the differences for Mn^{2+} and Fe^{2+} concentrations and alkalinity between this dry period and the period preceding were not as large as in the inundated sods, they still showed that when the water level is set at −10 cm, the anaerobic processes deeper in the soil still play an important role for the mobility of nutrients and metals.

High increases of concentrations of Fe^{2+} and Mn^{2+} indicated increased anaerobic respiration by Fe^{3+} and Mn^{4+} reduction at higher temperatures. In addition, the lower concentrations of soluble total S – this was mainly SO_4^{2-}, because no S^{2-} was present – in the pore water during the warmer period, suggested a higher sulphate reduction rate. The higher temperature also led to higher increases of concentrations of PO_4^{3-}. Increased PO_4^{3-} availability at the temperatures we applied was of the same order of magnitude as found by Zak et al. (2006) for a floodplain soil and by Koerselman et al. (1993) for peat soils. It is also in line with Van 't Hoff's rule, according to which the turnover rates in our experiment should increase by a factor of 3. Jensen and Andersen (1992) also found that in shallow, eutrophic lakes, phosphate release from the sediment to the water phase is much higher at higher temperatures, due to the reduced P binding capacity of the thinner oxidised layer at the sediment–water interface.

4.2. Acid–base processes, desorption and cation exchange

Since the reduction of Mn^{4+}, Fe^{3+} and SO_4^{2-} are acid-consuming processes, alkalinity increased during inundation. The higher alkalinity in the pore water of the inundated sods treated with sulphate can be attributed to the reduction of SO_4^{2-}, which generates a significantly higher alkalinity than that in the inundated sods without sulphate. Upon desiccation, the oxidation of NH_4^+, Mn^{2+}, Fe^{2+} and S^{2-}, as indicated by the results, resulted in a high acid production, leading to a drop in pH during the first week. The re-establishment of the circumneutral pH in the subsequent weeks can be explained by the buffering effect of bicarbonate and subsequently by cation exchange of protons from the solution with other cations from the cation adsorption complex (not shown by the results). After desiccation, NO_3^- concentrations rose to values of 5000 μmol L^{-1}, whereas the concentrations of NH_4^+ in the soil pore water just before desiccation did not exceed 100 μmol L^{-1} in any of the sods. Therefore, it seems likely that the nitrified NH_4^+ originates mostly from the adsorption complex (Lucassen et al., 2006), either by desorption induced by the low ammonium concentrations in solution, or by cation exchange.

The Ca^{2+} concentrations in the soil pore water of the inundated sods greatly exceeded the concentrations of Ca^{2+} supplied with the artificial river water. The sods with added SO_4 showed an even higher Ca and Mg release than those without added SO_4^{2-}. There are two possible explanations for the release of Ca and Mg. In the inundated soils CO_2, originating from decomposition of organic matter, could be trapped in the soil and could cause dissolution of $CaCO_3$ and $MgCO_3$, which could be present in the soil in small amounts, notwithstanding the low initial pH of the soil. In the sods receiving sulphate, decomposition of organic matter was increased by the higher availability of electron acceptors. Additionally, part of the raised concentrations of Ca and Mg compared to the non-inundated soils may be explained by cation exchange of the newly formed soluble cations generated in the soil itself during the inundation period, such as Fe^{2+}, Mn^{2+}, and NH_4^+. As shown in Table 1, initially 82% of the adsorption sites of the soil were occupied by Ca. Only a small part of the additional release of Ca and Mg in the inundated soils receiving sulphate could be explained by the exchange of Na, added as Na_2SO_4, against Ca or Mg, because a larger release by the monovalent Na against the divalent Ca and Mg would only be possible at higher concentrations of Na.

4.3. Effects of sulphate pollution

No free sulphide was detected in the soil pore water of the sods, as S^{2-} binds to Fe and the examined soil contained high concentrations of Fe. However, it was shown by the additional increase in alkalinity during flooding and by the release of sulphate after desiccation in the treatment with sulphate-rich water that sulphate reduction did take place. During dessication FeS_x was oxidised, leading to high sulphate concentrations in the pore water. Several other authors (Caraco et al., 1989; Smolders and Roelofs, 1993; Roden and Edmonds, 1997; Lamers et al., 1998a) have shown that the competition of S^{2-} – generated by the reduction of sulphate – with PO_4 for binding to Fe largely controls the release of PO_4 in fens and peatlands. Zak et al. (2006) and Loeb et al. (2007) showed that, depending on the soil type, inundation with sulphate-rich water may also increase the phosphate mobilisation in floodplain soils, which generally have higher soil Fe concentrations and lower organic matter content than fens and peatlands. The addition of sulphate to the river water did not have any effect on phosphate release in this particular soil. In this soil, the ratio of amorphous iron, which can be reduced by bacteria, to the amount of phosphate bound to it, was very high (Table 1). Hence, this soil is expected to be less sensitive to sulphate pollution (Zak et al., 2006).

5. Conclusions

We showed that seasonality of flooding largely determines the accumulation of potential phytotoxins and the release of phosphate. This is not only important for floodplain soils, but also at other locations where water is stored or retained as a measure in flood prevention strategies. Whether the release of phosphate to the soil pore water will actually lead to changes in the vegetation composition depends on the type of nutrient limitation. Although the vegetation type studied in the present experiment appeared to be limited by N in a greenhouse fertilisation experiment (Loeb, unpublished results), greatly increased phosphate mobilisation to the surface water may lead to algal blooms and to eutrophication in downstream areas. The expected increase in the risk of summer floods will therefore have significant effects on floodplain biogeochemistry in terms of the potential for eutrophication and accumulation of potential phytotoxins, especially on fertilised meadows.

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