Annual sulfate budgets for Dutch lowland peat polders: The soil is a major sulfate source through peat and pyrite oxidation

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SUMMARY

Annual sulfate mass balances have been constructed for four low-lying peat polders in the Netherlands, to resolve the origin of high sulfate concentrations in surface water, which is considered a water quality problem, as indicated amongst others by the absence of sensitive water plant species. Potential limitation of these plants to areas with low sulfate was analyzed with a spatial match-up of two large databases. The peat polders are generally used for dairy farming or nature conservation, and have considerable areas of shallow surface water (mean 16%, range 6–43%). As a consequence of continuous drainage, the peat in these polders mineralizes causing subsidence rates generally ranging between 2 and 10 mm y^{-1}. Together with pyrite oxidation, this peat mineralization the most important internal source of sulfate, providing an estimated 96 kg SO$_4$ ha^{-1} mm^{-1} subsidence y^{-1}. External sources are precipitation and water supplied during summer to compensate for water shortage, but these were found to be minor compared to internal release. The most important output flux is discharge of excess surface water during autumn and winter. If only external fluxes in and out of a polder are evaluated, inputs average 37 ± 9 and exports 169 ± 17 kg S ha^{-1} y^{-1}. During summer, when evapotranspiration exceeds rainfall, sulfate accumulates in the unsaturated zone, to be flushed away and drained off during the wet autumn and winter. In some polders, upward seepage from early Holocene, brackish sediments can be a source of sulfate. Peat polders export sulfate to the regional water system and the sea during winter drainage. The available sulfate probably only plays a minor role in the oxidation of peat: we estimate that this is less than 10% whereas aerobic mineralization is the most important. Most surface waters in these polders have high sulfate concentrations, which generally decline during the growing season when aquatic sediments are a sink. In the sediment, this sulfur is reduced and binds iron more strongly than phosphorus, which can be released to the overlying water and potentially fuels eutrophication. About 76% of the sampled vegetation-sites exceeded a threshold of 50 mg l^{-1} SO$_4$, above which sensitive species, such as *Stratiotes aloides*, and several species of *Potamogeton* were significantly less abundant. Thus high sulfate concentrations, mainly due to land drainage and consequent mineralization, appear to affect aquatic plant community composition.

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1. Introduction

In line with the pattern in most European countries (EEA, 2005), eutrophication abatement policies have substantially reduced N- and P-loading to surface waters in the Netherlands (Hosper

et al., 2011). However, notably in the low-lying, drained peatlands of the West and North, used for dairy farming, this has not lead to the hoped-for reduction in turbidity and algal blooms (Penning et al., 2013). Internal loading from the sediment (Geurts et al., 2010) and an increased release of phosphorus due to sulfate induced phosphorus mobilization have been proposed as mechanisms (Lamers et al., 1998, 2002; Smolders et al., 2006; Van der Welle et al., 2007). High sulfate concentrations have been attributed to external loading due to the extensive supply of river Rhine water to the polder districts in summer (Fiselier et al., 1992). Additional adverse effects of high sulfate inputs are sulfide toxicity to aquatic organisms (Lamers et al., 1989; Smolders et al., 2003; Lucassen et al., 2004) and enhanced anaerobic mineralization of organic sediments, which is suspected to contribute to oxidation of peat banks (Lamers et al., 2002).

Several other sources of sulfate exist besides inlet water from the river Rhine, but their importance has not yet been quantified simultaneously in annual budgets for these drained peatland polders with extensive networks of ditches. Atmospheric deposition of sulfate has declined to ∼10% of its value in the 1980s as a consequence of the successful abatement of acid rain (Van Dam, 2009; Buijsman et al., 2010). Around 2000, deposition amounted to 30–45 kg SO_4 ha^{-1} y^{-1}. Farmers add sulfate to their land in artificial fertilizer and manure but remove it via milk and meat (Oenema and Postma, 2003). Drainage causes the continuous mineralization of peat leading to a soil subsidence of 2–10 mm y^{-1} (Schothorst, 1977) and a release of macro-nutrients such as N and P (Vermaat and Hellmann, 2010), and also S. In many cases the peat has been under the influence of episodic contact with brackish and river water and contains sulfides such as pyrite (Lowe and Bustin, 1985; Pons, 1992). Oxidation of the organic matter bound as well as mineral S in the peat can form sulfate in the unsaturated zone. Elsewhere, peatland drainage and seasonal drying has led to marked sulfate pulses in drainage water after rewetting (Devito et al., 1999; Eimers et al., 2003; Kerr et al., 2012; Toivonen et al., 2013), leaving the system with the drainage water. The magnitude of such pulsed sulfate export rates has been found to be buffered by lakes and wetlands in the drainage network (Devito et al., 1999; Björkvald et al., 2009) as well as by a poor hydrological connectivity in the network (Kerr et al., 2012). Finally, specifically in some of these Dutch polders, upward groundwater seepage may deliver S from deeper sediment strata deposited in coastal lagoons during the earlier Holocene, which may contain pyrite (Pons, 1992).

Using monitoring data collected by water boards and research institutes (Alterra, B-WARE) and the polder unit approach of Vermaat and Hellmann (2010), we constructed annual budgets of sulfate as in Evans et al. (1997). These allowed us to derive a source apportionment and a reconstruction of the seasonal variability of the S fluxes. Subsequently, we address two potentially adverse environmental effects of high sulfate concentrations. Based on the annual fluxes, we estimate the oxidative capacity of sulfate to quantify its possible contribution to peat mineralization. Finally, we use empirical data on aquatic macrophyte distribution and sulfate concentrations from monitoring data of three water boards in a spatial match-up to verify predicted indirect effects of sulfate on macrophyte distribution: Smolders et al. (2003) and Lamers et al. (2013) suggest a critical upper limit of 50 mg l^{-1} SO_4 above which submerged plant communities are affected and several sensitive species decline. We verify whether this is reflected in plant community composition, which is an important indicator of water quality in lowland water bodies (Birk et al., 2013).

In short, we address the following research questions:

(1) Based on annual sulfate budgets of a peat polder, what are the most important components of these budgets, and what is the contribution of external loading?

(2) What is the oxidative capacity and the contribution to peat oxidation of sulfate?, and

(3) Is the predicted adverse effect level of 50 mg l^{-1} sulfate (or 0.52 mmol l^{-1}) confirmed by correspondence of higher sulfate concentrations with reduced species richness in the field?

2. Materials and methods

Annual sulfate budgets were compiled for individual polders as in Vermaat and Hellmann (2010). Each polder is a separately managed well-delimited water management unit, where inputs and outputs of water and concentrations of numerous water quality parameters including nutrients and sulfate are either monitored directly or can be derived from other data available. These peat polders differ greatly in size, are generally used for dairy farming or nature conservation, and can have large areas of shallow ditches and ponds (mean 16%, range 6–43%). Polder units are connected to surface water outside via pumping stations. In our budget approach, each polder unit contains the ditches full of water, the land surface and the first meter of active topsoil, which is the layer where rain water infiltrates, ground water level moves up and down and oxygenation may vary (Fig. 1; Van Beek et al., 2004; Vermaat and Hellmann, 2010). We include this upper meter because it strongly interacts with the ditch water and because here land use and water management have direct and strong effects on water, nutrient and sulfur dynamics (Vermaat and Hellmann, 2010). This surface layer interfaces with deeper groundwater through upward and downward seepage, and with the atmosphere through precipitation, evapotranspiration and volatilization (Fig. 1). Ditch sediment and the deeper subsoil are treated as separate, external storage components, where reducing conditions have major consequences for nutrient and sulfur dynamics (Smolders et al., 2006) and fluxes of water and matter are often much slower (e.g. Dekker et al., 2005).

The following inward fluxes of S into the active surface layer were distinguished discerned: precipitation, upward seepage, inlet water supplied from outside the polder to maintain the water level, mineralization of peat and pyrite (FeS_2), deposition of dredged sediment from the ditches during maintenance, and farming fertilizer. It must be noted that we do not separate peat mineralization from pyrite oxidation as sources of sulfate here. Lowe and Bustin (1985) found a predominance of organic S in the peatlands of the Fraser river delta (mineral S maximally 5% of total S), where peat accumulation started 4500 years ago. For Dutch lowland peats, Van Kempen and Griffioen (2011) suggested 2–4% of the dry subsoil mass from 1 to 2 m depth to be pyrite, but they pooled all forms of S into pyrite after ashing the full soil sample, hence may have included variable quantities of organic S.

Outward fluxes are: volatilization (as H_2S, neglected), downward seepage, surface water discharge outside the polder, sediment retention, which is a compounded estimate taking together assimilation, sedimentation and (co-) precipitation into the ditch sediment, and export of farming produce (silage, milk, meat). Complex geochemical processes in ditch sediment and deeper subsoil, such as sulfate reduction, pyrite formation and oxidation, competition with phosphate for iron and sorption to organic matter (Smolders et al., 2006) were not modeled separately, but are pooled in the net annual fluxes to and from subsoil and sediment included in our budget.

We report here on the budgets for four polders studied earlier by Vermaat and Hellmann (2010): the Nieuwe Keverdijkse Polder, polder Zegveld, the Krimpenerwaard and the Vlietpolder. Annual budgets of water, N and P were made up for the year 2000 and can be found in Vermaat and Hellmann (2010). We have not normalized our budgets to a standard hydrological year and have