



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 SO₄ 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 SO₄, 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 led 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 SO₄ 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 SO₄ 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 (FeS₂), 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 H₂S, 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

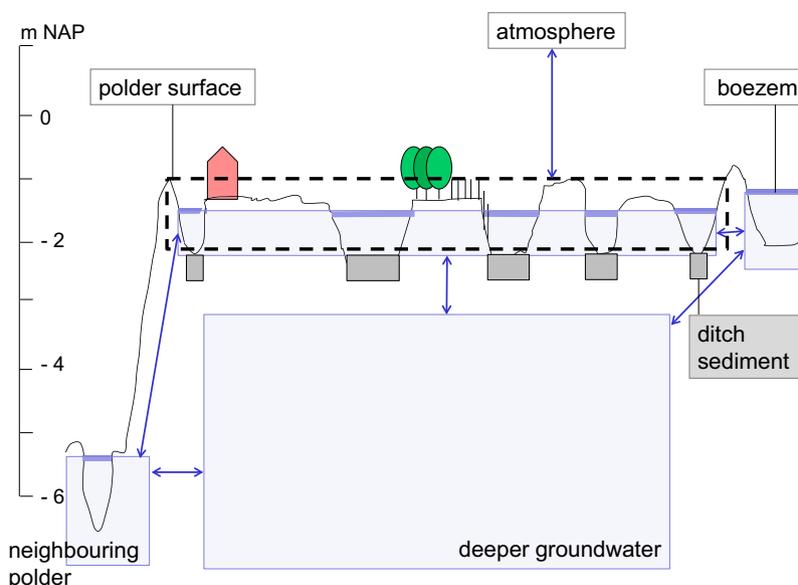


Fig. 1. Delineation of the upper, 'active' surface layer in a polder (bold box with broken lines) and the different entities to which inputs and outputs can occur. This hypothetical polder has a characteristic elevation around 1–2 m below sea level (NAP, Dutch ordnance level), whereas adjacent polders can be deeper when they are reclaimed lakes (left). The surface water storage system ('boezem') is used as a reservoir to redistribute water among polders, to cope with water shortage in summer, and for discharge of excess water to the sea. Different, more or less separate, volumes of water are indicated as light blue rectangles. Surface water has a darker blue bar. Blue arrows indicate flows of water. Areas of land and water are not drawn to scale. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

been consistently conservative in our estimates when we had a choice. Individual polder budgets can be obtained from the first author as excel sheets. The two most important external sources of fresh surface water are firstly river water from one of the Rhine distributaries, which differ in discharge, fraction of water from local Dutch drainage and sulfate concentration (these vary seasonally from 50 to 60 in the Lek to 40–200 mg $\text{SO}_4\text{-S l}^{-1}$ in the Hollandse IJssel), and secondly lake water from the nearby and large Lake IJmeer (concentration ~ 80 mg $\text{SO}_4\text{-S l}^{-1}$). Sulfate concentrations for these budget entries are taken from Specken and De Groot (2010) and Twisk (2010).

Sulfate production due to peat mineralization was estimated from subsidence rates, the density of the lower part of the peat column (0.15 kg dry matter l^{-1} soil volume and 80% organic dry matter, Schothorst, 1977; Smolders et al., 2011; Rob Hendriks pers. comm.), and the mineral S (2%) as well as organic S (0.2% of organic matter) content (Van den Akker et al., 2010). These values are within the range for deep peat soils available in an unpublished database of Smolders. Together they add up to 32.4 kg S mm^{-1} ha^{-1} y^{-1} , expressed as an annual rate per hectare for every mm subsidence. Vermeulen and Hendriks (1996) independently estimated 30 kg S mm^{-1} ha^{-1} y^{-1} . For each polder, locally observed specific subsidence rates have been used, ranging from a minimal subsidence value of 1 (Nieuwe Keverdijkse Polder) to 7 mm y^{-1} (Zegveld; Vermaat and Hellmann, 2010). Ditches are dredged every 6–10 years but vegetation which fills up the water column is removed every year. We estimated the S fluxes originating from this dredged material which is deposited on the adjacent fields from Smolders et al. (2011) and Harmsen et al. (2005). We assume that the adjacent bank area on which sludge is deposited equals the surface of the ditch. Annual cleaning produces a deposit of 1 mm of dredged sediment (density 0.56 kg l^{-1} , 80% organic matter) or 12 g $\text{SO}_4\text{-S m}^{-2}$ (ditch bank area) y^{-1} . Dredging is estimated to produce 3 cm of sludge every 10 years, leading to 36 g $\text{SO}_4\text{-S m}^{-2}$ y^{-1} on the banks. Together, this amounts to an output of 480 kg S ha^{-1} ditch bank y^{-1} , but part of this sulfate is rapidly flushed back into the ditch and we therefore use a

conservative 300 kg S ha^{-1} ditch bank y^{-1} . Using this estimate we then normalized from ditch bank area to total polder area. Net sulfate fluxes from farming were estimated from fertilizer practice advice (BLGG, 2010) and a farm gate balance by Oenema and Postma (2003).

For downward seepage we use a conservative low end sulfate concentration of 25 mg $\text{SO}_4\text{-S l}^{-1}$ observed in deeper peat soils by Hendriks and Van den Akker (2012) and multiplied this with the downward water flux. Upward seepage was taken from Vermaat and Hellmann (2010) or estimated from Post et al. (2002) for the Nieuwe Keverdijkse Polder, and verified from new seepage and groundwater quality maps prepared by Harry Massop (included in Vermaat et al., 2012) from the Dutch National Hydrological Instrument (De Lange et al., 2014). For the sulfate exported with surface water we used winter concentrations, since this is the time when water is pumped out of the polders. Sulfate loss to the ditch sediment was estimated from Meuleman et al. (2004) and Smolders et al. (2011) who found a distinct decrease in ditch water concentrations during the growing season. We use the conservative lower concentration difference of 13 mg $\text{SO}_4\text{-S l}^{-1}$ from Meuleman et al. (2004) and estimate a reduction scaled to ditch area of 76 kg ha^{-1} ditch area y^{-1} . We used an annual water balance and relevant sulfate concentrations for the area of 1100 km^2 managed by the waterboard Rijnland covering many individual polders, to verify the findings from our polder budgets at a larger spatial scale. Estimating uncertainty in compounded sums of data from variable sources is complicated. We did an order-of-magnitude estimate for the most important fluxes.

A geo-referenced database was compiled from water quality monitoring data provided by the water boards of Rijnland, 'Schie-land en de Krimpenerwaard', 'Amstel-en Gooiland' and 'Noordhollands Noorderkwartier', totaling 2780 sampling stations with a median growing season sulfate concentration of 89 and a standard error of 11 mg $\text{SO}_4\text{-S l}^{-1}$. When Smolders et al. (2003) proposed a critical upper sulfate limit of 50 mg $\text{SO}_4\text{-S l}^{-1}$ they also provided a list of sensitive and less sensitive species based on an extensive data base in Bloemendaal and Roelofs, 1988). We used distribution

data of these species in a spatial match-up in ARC-GIS of sulfate and water plant data and found 207 sites where both types of data have been collected. For each species or species group, the frequency distribution of presence against sulfate concentration classes was compared to that of the sites without the species using a χ^2 -test.

3. Results

3.1. Polder budgets and seasonality

Overall, the budgets are not in balance: our estimates suggest that the top layer is subject to a net enrichment with sulfate in three out of the four polders (Fig. 2). The major source of sulfate was oxidation of peat (and pyrite), with the exception of the Nieuwe Keverdijkse Polder, where upward seepage predominated inputs (Fig. 2; cf Post et al., 2002). The major output flux in all polders is surface water that is pumped out of the polder, which occurs mainly during winter. If we only evaluate external fluxes, inputs average 37 ± 9 and exports 169 ± 17 kg S $\text{ha}^{-1} \text{y}^{-1}$ for the three polders without deep brackish upward seepage (paired t -test: export is significantly higher at $p < 0.01$). This excludes internal peat mineralization, ditch sludge dynamics as well as manure. Thus, we can conclude that most polders generate sulfate through mineralization, and export it with excess drainage water during winter. This is confirmed by the seasonal pattern of sulfate in one of the main buffering water bodies of the Rijnland water board, the Oude Rijn, which receives discharged polder water during winter, and witnesses maximal sulfate concentrations during that same period (Fig. 3), with peaks reflecting particularly wet winters (2004) or winters with distinct spells of snow melt (2005, 2010). The budget for the buffer water body serving the whole water board management area ('boezem' in Fig. 1, see budget in Table 1) clearly confirms that pumped polder water is the main source of sulfate (70%), and that inlet of (largely) Rhine water (18%), and sewage works effluent (11%) are secondary sources. Thus, most of the sulfate that is discharged during winter ends up in the North Sea.

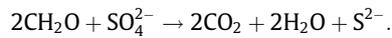
Uncertainty in our budgets is probably most substantial in two internal fluxes: peat mineralization and dredged ditch sediment deposition. Both are compound estimates that multiply conservative medians of uncertain and variable terms. For example, peat soil density is known to vary with depth and geography (coefficient of variation, CV = 78%, unpublished data set Smolders, $N = 1527$), and so is organic matter content (CV = 79%) as well as total sulfur content (CV = 117%). Our estimate of sulfur content of dredged ditch sediment is based on limited field data and assumptions on dredging frequency, dredging depth as well as deposition modes on the neighboring pastures. Thus, based on these CVs, our estimates could easily be wrong by a factor 2 when used for another, specific polder. All other budget entries, however, are either of minor importance, or based on well-supported water balances (Vermaat and Hellmann, 2010) and solid time series from routine monitoring programs (Fig. 3). Thus, the two major internal fluxes have higher uncertainty but still allow an assessment of the importance of the underlying processes, whereas we have higher confidence regarding the external fluxes.

3.2. Estimating the potential of sulfate as a peat oxidizer

The prime electron-acceptor for the mineralization of peat organic matter is oxygen, but sulfate may act as an alternative electron acceptor. We estimate this using the oxidative potential of two different sources of sulfate: (1) the mineralized sulfate from

the oxidized peat and, (2) the sulfate brought in with inlet water during summer.

The sulfate from the peat is an alternative electron-acceptor in the temporally anaerobic zone of the peat soil. To estimate its potential contribution to peat mineralization we assume that the anaerobic oxidation of peat proceeds as follows:



Mineralization of 1 mm of peat (0.15 kg l^{-1} , 80% organic matter, see above) corresponds to $1200 \text{ kg CH}_2\text{O ha}^{-1}$ or 40 kmol ha^{-1} . Oxidation requires 20 kmol ha^{-1} , which corresponds to $1920 \text{ kg SO}_4 \text{ mm}^{-1} \text{ ha}^{-1}$. Annual subsidence rates range between 1 and 10 mm, hence we use a median of 5 mm. The sulfate from the inlet water is brought into the polders during summer when a precipitation deficit is compensated by pumping in external surface water. This can have a sulfate concentration of $50\text{--}80 \text{ mg SO}_4 \text{ l}^{-1}$ (Rhine branch Lek or Lake IJmeer, in summer). We use the higher value, and assume that all this sulfate is available for oxidation, and at most 300 mm is pumped in during a very dry summer (for example 1976, with a probability of $1/100$, = $3000 \text{ m}^3 \text{ ha}^{-1}$). Then 80 mg l^{-1} this corresponds to 0.83 mol m^{-3} or 2.5 kmol ha^{-1} sulfate, which is 12.5% of the 20 kmol ha^{-1} sulfate required to fully oxidize one mm of peat, and hence 2.5% of what is needed to cause 5 mm subsidence. We conclude that this sulfate will not be a major oxidizer, when oxygen is freely available in the unsaturated zone, also along ditch banks where this inlet sulfate would encounter the underlying peat.

3.3. Water plant communities and sulfate concentrations

The spatial match up of water quality data and occurrence of aquatic angiosperm species allowed us to test the suggested no-effect level for sulfate of 50 mg l^{-1} (Fig. 4). All three distributions were significantly different: *Potamogeton pectinatus* occurred at significantly higher sulfate concentrations, but the four sensitive pondweeds and the water soldier occurred at significantly lower concentrations, than average. However, all three have a major proportion of their occurrences above the critical 50 mg l^{-1} . Thus, our crude presence data would rather suggest a critical level at 100 mg l^{-1} . If however we analyze the ratios of presence over absence calculated for each sulfate class, then *P. pectinatus* has a disproportionately higher presence above 100 mg l^{-1} , whereas for *Stratiotes aloides* and the sensitive pondweeds this is the case below 50 mg l^{-1} (Fig. 5). Only 24% of the sampled stations have such low sulfate concentrations, where the probability to observe one or more of these sensitive species is over 50% (sensitive pondweeds 60% and *S. aloides* 88%). The majority of the sampled waters, however, have higher sulfate concentrations, so the impoverishing effect on aquatic plant communities may well be widespread.

4. Discussion

Our annual sulfate budgets demonstrate that internal release from peat is the main source of sulfate, but we cannot distinguish between true peat mineralization and pyrite oxidation. In one case it is internal release from deeper mid Holocene sands and clays with upward seepage. Remarkably, external sources, such as the supply of surface water during dry summers, appear of minor quantitative importance. Our analysis of uncertainty, the larger-scale annual balance for the whole Rijnland water district (Table 1) and correspondence with water quality data from other polders and wetlands (De Mars and Garritsen, 1997; Van Dam, 2009; Vermaat and Hellmann, 2010; Smolders et al., 2011; Van Gerwen et al., 2011), lends us confidence that the observed pattern can be generalized. Indeed, elsewhere in the world drainage of coastal

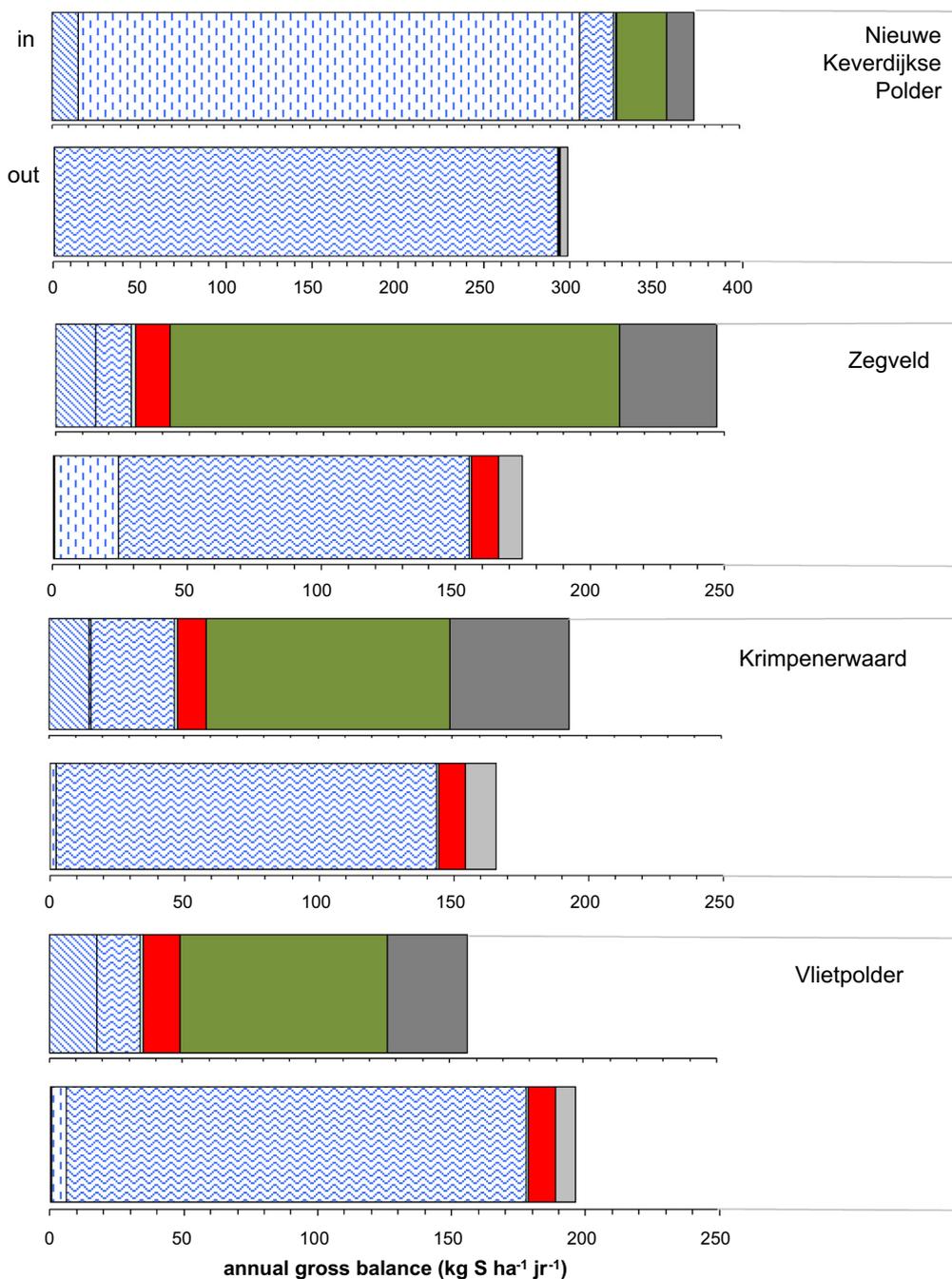


Fig. 2. Breakdown of annual inputs and outputs of sulfate ($\text{kg S ha}^{-1} \text{yr}^{-1}$) in 4 Dutch polders. Upper stacked bars are inputs, lower bars output. The budget is in kg S because some fluxes are mainly in reduced and other in oxidized form. Legend: blue diagonally hatched: precipitation, blue vertically hatched seepage, blue waves: surface water in or out, red: agriculture, green: mineralization, dark gray: dredged sludge on land, light gray: export to ditch sediment. Note that the scale for the Nieuwe Keverdijkse Polder deviates from the others. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

lowlands also leads to mineralization, subsidence, high sulfate releases and related water quality problems (Holden et al., 2004; Pedersen et al., 2007). Also in upland catchments, mineralization of organic matter has been shown to lead to a net release of sulfate (e.g. Devito et al., 1999; Likens et al., 2002; Eimers et al., 2003; Kerr et al., 2012; Toivonen et al., 2013).

Based on the pattern in our data, we postulate a general picture of sulfur dynamics for a Dutch peat polder, which may well be valid in numerous coastal lowlands worldwide. During the summer growing season, when the water table falls and evapotranspiration is an important loss of water, reduced sulfur (as pyrite) or organically bound sulfur in the peat is being oxidized to sulfate.

This sulfate remains in the unsaturated zone, as long as it remains dry. During winter, evapotranspiration is minimal and the water table rises. Rain infiltrates into the shallow top soil and drains superficially to the ditches, transporting the sulfate to the ditch water (indeed winter sulfate concentrations in drainage ditches are high, e.g. Smolders et al., 2011). Ditch water is pumped out of the polder into the water reservoirs, where the sulfate concentration rises (Fig. 3), and is subsequently pumped to the sea. During summer, a proportion of the sulfate dissolved in ditch water is assimilated in plants but mainly reduced in the anaerobic sediments. Our calculations suggest that the remaining dissolved sulfate will contribute little to peat mineralization. This is even

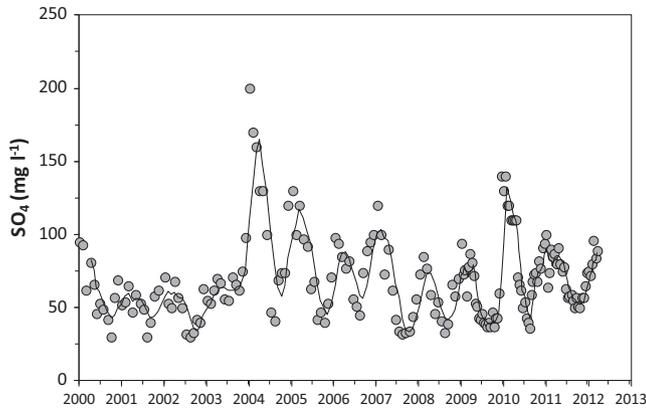


Fig. 3. Seasonal variation in sulfate concentration in the Ouden Rijn at Bodegraven, part of the storage reservoir ('boezem') of the Rijnland waterboard. The smoothed curve is a three-monthly running mean. Grand mean and standard deviation: $69 \pm 28 \text{ mg l}^{-1} \text{ SO}_4$ ($n = 187$).

Table 1

Annual balance of water and sulfate for the reservoir water ('boezem') of the whole management area of the Rijnland water board. Data courtesy Rijnland. For winter discharge out of the polder, the median winter concentration of the reservoir storage ('boezem') is used. Surplus precipitation is mainly discharged during winter, whereas outside water from the Rhine enters at Bodegraven. Note that water can be pumped in and out at several inlet stations (here Gouda).

	Water 10^6 m^3	Sulfate concentration ($\text{mg SO}_4 \text{ l}^{-1}$)	Sulfate load 10^3 kg SO_4	Percent
In				
Precipitation	41.8	4.8	201	0.4
Pumped out of polders to reservoir	431.4	90	38,826	70.4
Inlet at Gouda	29	120	3480	6.3
Inlet at Bodegraven	79.7	69	5499	10.0
Effluent sewage works	137.3	45	6179	11.2
Inlet other sluice gates	12.7	69	876	1.6
Storage = rest, closing term	0.9	69	62	0.1
Sum	732.8		55,123	100
Out				
Evapotranspiration	26	0	0	0
Pumped into polders	15.2	78	1186	2.2
Outlet at Spaarndam	105.1	78	8198	14.9
Outlet at Halfweg	310.4	78	24,211	43.9
Outlet at Gouda	40.7	78	3175	5.8
Outlet at Katwijk	209.9	78	16,372	29.7
Outlet at Leidschendam	0.2	78	16	0
Outlet at KvL sluice gate	8.8	78	686	1.2
Downward seepage from reservoir 'boezem')	16.4	78	1279	2.3
Sum	732.7		55,123	100

more so because ditch water is generally well oxygenated: daytime concentrations are often supersaturated when plant communities are dense (Kersting and Kouwenhoven, 1989). Ditch water exchanges with shallow, generally anaerobic ground water leading to redox and concentration gradients in the banks. In these ditch banks and lake shores, sulfate may accumulate due to spatial complexity in redox gradients and mineralization of dredge spoils. Burrowing by voles, muskrats and crayfish as well as trampling by cattle may also increase patchiness in peat aeration and erosion (e.g. Barends, 2002), but we lack the spatial resolution to estimate or compare these impacts at polder scale.

In organic aquatic sediments, sulfate reduction results in the production of sulfide which can cause sulfide toxicity but also

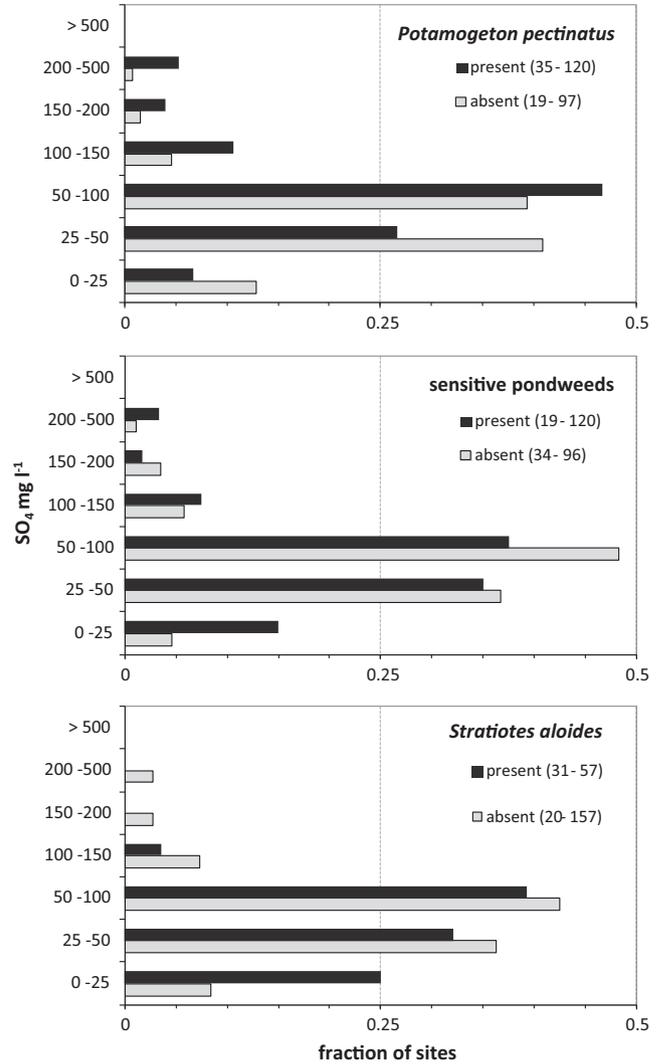


Fig. 4. Distribution of tolerant *Potamogeton pectinatus*, a pooled group of 6 sensitive pondweeds (*Potamogeton acutifolius*, *P. berchtoldii*, *P. compressus*, *P. lucens*, *P. mucronatus* and *P. trichoides*; categorized as sensitive by Bloemendaal and Roelofs, 1988), and *Stratiotes aloides* over different classes of sulfate concentration for 207 sites in the Vechtstreek area (data courtesy Waternet). Each graph shows the distribution of sites where the plant species is present and those where it is absent. In brackets following the legends are the truncated 10-maximum and 10-minimum values. These three paired distributions are all significantly different (χ^2 , $P < 0.001$).

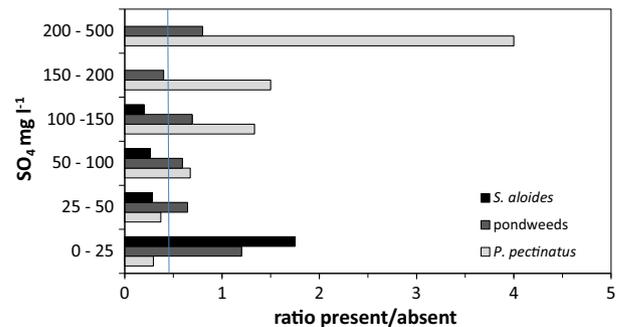


Fig. 5. Presence-absence ratios of tolerant *P. pectinatus*, a group of 6 sensitive pondweeds and *S. aloides* binned against classes of sulfate concentrations. Further as Fig. 4. Kolmogorov-Smirnov tests were significant for *S. aloides* and the pondweeds ($p = 0.012$), but not for *P. pectinatus* ($p = 0.318$).

binds to sediment iron complexes, hereby strongly decreasing the mobility of reduced iron and increasing the mobility of phosphorus. This may lead to shifts in plant community composition through the decline of 'sulfate-sensitive' species (Smolders et al., 2003) and ultimately to duckweed-covered ditches and cyanobacterial blooms in larger lakes and ponds (Lamers et al., 2013). Our spatially matched field data on plant communities and sulfate concentrations corresponded well with the pattern observed and the mechanism proposed by Smolders et al. (2003). Although correspondence does not equal causality, observed presence/absence ratios corresponded to the postulated no effect level of 50 mg SO₄ l⁻¹ (or 0.52 mmol l⁻¹) for five sensitive pondweeds and *S. aloides*.

Drainage, and the continual lowering of the water table needed to maintain agricultural practice, leads to continued mineralization of the peat and has been shown to turn these peat lands into sources of carbon dioxide and methane contributing to global warming (Winiwarer et al., 1999; Hendriks et al., 2007). We have shown that this also has turned these peat lands into sources of sulfate and asked ourselves how climate change would affect sulfate dynamics in these polders. Using the two most extreme climate change scenarios for the Netherlands (G and W+) developed by the Royal Dutch Meteorological Institute, Hellmann and Vermaat (2012) have modeled the plausible future seasonality in groundwater level in these peat polders for 2036–2065. Under W+, ground water levels will sink more deeply (10–40 cm depending on the year), and this will lead to increased subsidence and mineralization. To prevent accelerated subsidence, the demand for inlet surface water will increase. We estimated the increase in sulfate load due to either increased subsidence or increased external inlet water for the Krimpenerwaard. Increased subsidence would amount to 5 mm, whereas twice as much inlet water would be required to maintain the water level in the ditches. The former would correspond to an increase from 91 to 181 kg S ha⁻¹ y⁻¹, whereas the latter would lead to an increase from 31 to 61 kg S ha⁻¹ y⁻¹. Assuming that sulfate loading of Rhine water from the hinterland will remain unaltered, we conclude that extra inlet water will contribute far less to an increased sulfate loading than the alternative of increased subsidence resulting from a freely falling water table. In subsiding, drained peat lands, external inlet water is thus less adverse from a water quality perspective than further subsidence.

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References

Barends, F.K.N., 2002. The muskrat (*Ondatra zibethicus*): expansion and control in the Netherlands. *Lutra* 45, 97–104.

- Birk, S., Willby, N.J., Kelly, M.G., Bonne, W., Borja, A., Poikane, A., Van de Bund, W., 2013. Intercalibrating classifications of ecological status: Europe's quest for common management objectives for aquatic ecosystems. *Sci. Total Environ.* 454 (455), 490–499.
- Björkvald, L., Giesler, R., Laudon, H., Humborg, C., Mörth, C.M., 2009. Landscape variations in stream water SO₄²⁻ and δ³⁴S_{SO4} in a boreal stream network. *Geochim. Cosmochim. Acta* 73, 4648–4660.
- BLGG, 2010. Voorbeeldadvies bemesting. <www.blgg.nl> (in Dutch: Advice fertiliser application).
- Bloemendaal, F.H.J.L., Roelofs, J.G.M., 1988. Waterplanten en waterkwaliteit. KNNV Natuurhistorische Bibliotheek nr 54, 189 pp.
- Buijsman, E., Aben, J.M., Hetteling, J.P., Van Hinsberg, A., Koelemeijer, R.B.A., Maas, R.J.M., 2010. Zure regen, een analyse van dertig jaar verzuringsproblematiek in Nederland. PBL publicatie 500093007, Bilthoven [in Dutch: Acid rain, an analysis of 30 years of acidification in The Netherlands].
- Dekker, S.C., Barendregt, A., Bootsma, M.C., Schot, P.P., 2005. Modelling hydrological management for the restoration of acidified floating fens. *Hydrol. Proc.* 19, 3973–3984.
- De Lange, W.J., Prinsen, G.F., Hoogewoud, J.C., Veldhuizen, A.A., Verkaik, J., Oude Essink, G.H.P., van Walsum, P.E.V., Delsman, J.R., Hunink, J.C., Massop, H.T.L., Kroon, T., 2014. An operational, multi-scale, multi-model system for consensus-based, integrated water management and policy analysis: the Netherlands Hydrological Instrument. *Environ. Modell. Softw.* 59, 98–108.
- De Mars, H., Garritsen, A.C., 1997. Interrelationship between water quality and groundwater flow dynamics in a small wetland system along a sandy hill ridge. *Hydrol. Proc.* 11, 335–351.
- Devito, K.J., Hill, A.R., Dillon, P.J., 1999. Episodic sulphate export from wetlands in acidified headwater catchments: prediction at the landscape scale. *Biogeochemistry* 44, 187–203.
- Eimers, M.C., Dillon, P.J., Schiff, S.L., Jeffries, D.S., 2003. The effects of drying and rewetting and increased temperature on sulphate release from upland and wetland material. *Soil Biol. Biochem.* 35, 1663–1673.
- Evans, H.E., Dillon, P.J., Molot, L.A., 1997. The use of mass balance investigations in the study of the biogeochemical cycle of sulfur. *Hydrol. Proc.* 11, 765–782.
- European Environment Agency (EEA), 2005. Source Apportionment of Nitrogen and Phosphorus Inputs into the Aquatic Environment EEA Report 7/2005. Copenhagen 48pp.
- Fiselier, J., Klijn, F., Ducloux, H., Kwakernaak, C., 1992. The choice between desiccation of wetlands or the spread of Rhine water over the Netherlands. *Wetl. Ecol. Manage.* 2, 85–93.
- Geurts, J.J.M., Smolders, A.J.P., Banach, A.M., Van de Graaf, J.P.M., Roelofs, J.G.M., Lamers, L.P.M., 2010. The interaction between decomposition, N and P mineralization and their mobilization to the surface water in fens. *Water Res.* 44, 3487–3495.
- Harmsen, J., Van den Toorn, A., Zweers, A.J., 2005. Natuurlijke immobilisatie van zware metalen in de Roeventerpeel. Alterra-rapport 1125 (in Dutch: natural immobilisation of heavy metals in the Roeventerpeel).
- Hellmann, F., Vermaat, J.E., 2012. Impact of climate change on water management in Dutch peat meadows. *Ecol. Model.* 240, 74–83.
- Hendriks, D.M.D., Van Huissteden, J., Dolman, A.J., Van der Molen, M.K., 2007. The full greenhouse gas balance of an abandoned peat meadow. *Biogeosciences* 4, 411–424.
- Hendriks, R.F.A., Van den Akker, J.J.H., 2012. Effecten van onderwaterdrains op de waterkwaliteit in veenweiden. Alterra-rapport 2354 (in Dutch: effects of submerged drains on water quality in the peat meadow district).
- Holden, J., Chapman, P.J., Labadz, J.C., 2004. Artificial drainage of peat lands: hydrological and hydrochemical process and wetland restoration. *Prog. Phys. Geogr.* 28, 95–123.
- Hosper, H., Pot, R., Portielje, R., 2011. Meren en plassen in Nederland: toestand, trends en hoe verder? H₂O 44 (7), 25–28 (in Dutch: lakes and ponds in The Netherlands: state, trends, and the future?).
- Kerr, J.G., Eimers, M.C., Creed, I.F., Adams, M.B., Beall, F., Burns, D., Campbell, J.L., Christopher, S.F., Clair, T.A., Courchesne, F., Duchesne, L., Fernandez, I., Houle, D., Jeffries, D.S., Likens, G.E., Mitchell, M.J., Shanley, J., Yao, H., 2012. The effect of seasonal drying on sulphate dynamics in streams across southeastern Canada and the northeastern USA. *Biogeochemistry* 111, 393–409.
- Kersting, K., Kouwenhoven, P., 1989. Annual and diel oxygen regime in two polder ditches. *Hydrobiol. Bull.* 23, 111–123.
- Lamers, L.P.M., Tomassen, H.B.M., Roelofs, J.G.M., 1998. Sulfate-induced eutrophication and phytotoxicity in freshwater wetlands. *Environ. Sci. Technol.* 32, 199–205.
- Lamers, L.P.M., Falla, S.J., Samborska, E.M., Van Dulken, I.A.R., Van Hengstum, G., Roelofs, J.G.M., 2002. Factors controlling the extent of eutrophication and toxicity in sulfate-polluted freshwater wetlands. *Limnol. Oceanogr.* 47, 585–593.
- Lamers, L.P.M., Govers, L., Janssen, C.J.M., Geurts, J.M., Van der Welle, M.E.W., Van Katwijk, M., Van der Heide, T., Roelofs, J.G.M., Smolders, A.J.P., 2013. Sulfide as a soil phytotoxin—a review. *Front. Plant Sci.* 4, 268.
- Likens, G.E., Driscoll, C.T., Buso, D.C., Mitchell, M.J., Lovett, G.M., Bailey, S.W., Siccama, T.G., Reiners, W.A., Alewell, C., 2002. The biogeochemistry of sulfur at Hubbard Brook. *Biogeochemistry* 60, 235–315.
- Lowe, L.E., Bustin, R.M., 1985. Distribution of sulphur forms in six facies of peats of the Fraser River Delta. *Can. J. Soil Sci.* 65, 531–541.
- Lucassen, E.C.H.E.T., Smolders, A.J.P., Van de Crommenacker, J., Roelofs, J.G.M., 2004. Effects of stagnating sulfate-rich groundwater on the mobility of phosphate in freshwater wetlands: a field experiment. *Arch. Hydrobiol.* 160, 117–131.

- Meuleman, A.F.M., Beltman, B., Scheffer, R.A., 2004. Water pollution control by aquatic vegetation in treatment wetlands. *Wetl. Ecol. Manage.* 12, 459–471.
- Oenema, O., Postma, R., 2003. Managing sulphur in agroecosystems. In: Abrol, Y.P., Ahmad, A. (Eds.), *Sulphur in Plants*. Kluwer Academic Publishers, The Netherlands, pp. 45–70.
- Pedersen, M.L., Friberg, N., Skriver, J., Baattrup-Pedersen, A., Larsen, S., 2007. Restoration of Skjern river and its valley – short-term effects on river habitats, macrophytes and macroinvertebrates. *Ecol. Eng.* 30, 145–156.
- Penning, W.E., Genseberger, M., Uittenbogaard, R.E., Cornelisse, J.C., 2013. Quantifying measures to limit wind-driven resuspension of sediments for improvement of the ecological quality in some shallow Dutch lakes. *Hydrobiologia* 710, 279–295.
- Pons, L.J., 1992. Holocene peat formation in the lower parts of the Netherlands. In: Verhoeven, J.T.A. (Ed.), *Fens and Bogs in the Netherlands: Vegetation, History, Nutrient Dynamics and Conservation*. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 7–79.
- Post, V., Bloem, E., Ooteman, K., Slob, E., Groen, K., Groen, M., 2002. The use of CVES to map the subsurface salinity distribution: a case study from the Netherlands. In: 17th Salt Water Intrusion Meeting, Delft.
- Schothorst, C.J., 1977. Subsidence of low moor peat soils in the western Netherlands. *Geoderma* 17, 265–291.
- Smolders, A.J.P., Lamers, L.P.M., Den Hartog, C., Roelofs, J.G.M., 2003. Mechanisms involved in the decline of *Stratiotes aloides* L. in the Netherlands: sulfate as a key variable. *Hydrobiologia* 506 (509), 603–610.
- Smolders, A.J.P., Lamers, L.P.M., Lucassen, E.C.H.E.T., Roelofs, J.G.M., 2006. Internal eutrophication: how it works and what to do about it, a review. *Chem. Ecol.* 22, 93–111.
- Smolders, A.J.P., Van den Broek, T., Lucassen, E.C.H.E.T., Van der Welle, M.E.W., Zaanvoordijk, W.J., 2011. Monitoring proefsloten Lopikerwaard. BWARE rapport 2011.30 (in Dutch: monitoring experimental ditches in the Lopikerwaard).
- Specken, B., De Groot, J., 2010. Trends in waterkwaliteit in het beheersgebied van Amstel, Gooi en Vecht. *H₂O* 43 (4), 19–22 (in Dutch: Trends in water quality in the water district Amstel Gooij and Vecht).
- Toivonen, J., Österholm, P., Fröjdö, S., 2013. Hydrological processes behind annual and decadal-scale variations in the water quality of runoff in Finnish catchments with acid sulfate soils. *J. Hydrol.* 487, 60–69.
- Twisk, W., 2010. Interne eutrofiëring binnen Schieland en de Krimpenerwaard: verkennend onderzoek naar overeenkomsten en verschillen (in Dutch: internal eutrophication in Schieland and the Krimpenerwaard: a reconnaissance study. Internal Document Waterboard Schieland and the Krimpenerwaard).
- Van Beek, C.L., Van den Eertwegh, G.A.P.H., Van Schaik, F.H., Velthof, G.L., Oenema, O., 2004. The contribution of dairy farming on peat soil to N and P loading of surface water. *Nutr. Cycl. Agroecosyst.* 70, 85–95.
- Van Dam, H., 2009. Evaluatie basismetnet waterkwaliteit Hollands Noorderkwartier Trendanalyse hydrobiologie, temperatuur en waterchemie 1982–2007. AWN rapport 708, Amsterdam (in Dutch: evaluation of the standard monitoring network of the water board Holland Noorderkwartier, trend analysis of hydrobiology, temperature and water chemistry).
- Van den Akker, J.J.H., Hendriks, R.F.A., Hoving, I.E., Pleijter, M., 2010. Toepassing van onderwaterdrains in veenweidegebieden: effecten op maaiveldvaling, broeikasgasemissies en het water. *Landschap* 27, 136–149 (in Dutch: application of submerged drains in peat meadows: effects on subsidence).
- Van der Welle, M.E.W., Smolders, A.J.P., Op den Camp, H.J.M., Roelofs, J.G.M., Lamers, L.P.M., 2007. Biogeochemical interactions between iron and sulfate in freshwater wetlands and their implications for interspecific competition between aquatic macrophytes. *Freshwat. Biol.* 52, 434–447.
- Van Gerven, L.P.A., Van der Grift, B., Hendriks, R.F.A., Mulder, H.M., Van Tol-Leenders, T.P., 2011. Nutriëntenhuishouding in de bodem en het oppervlaktewater van de Krimpenerwaard. Bronnen, routes en sturingsmogelijkheden. Alterra rapport 2220 (in Dutch: nutrient dynamics in the soil and surface water of the Krimpenerwaard: sources, pathways and management options).
- Van Kempen, C., Griffioen J., 2011. Pyriet in de Nederlandse zeekeleigebieden, 1–2 m onder maaiveld. Deltares report 12029000, Delft, The Netherlands (in Dutch: pyrite in the Dutch marine clay areas, 1–2 m below the surface).
- Vermaat, J.E., Hellmann, F., 2010. Covariance in water- and nutrient budgets of Dutch peat polders: what governs nutrient retention? *Biogeochemistry* 99, 109–126.
- Vermaat, J.E., Harmsen, J., Hellmann, F.A., Van der Geest, H.G., De Klein, J.M., Kosten, S., Smolders, A.J.M., Verhoeven, J.T.A., 2012. Zwavedynamiek in het West-Nederlandse laagveengebied, met het oog op klimaatverandering. Report AE-12/01 Earth Sciences and Economics, VU University Amsterdam (in Dutch: Sulfur dynamics in the Western lowland peat areas of the Netherlands, with a view on climate change).
- Vermeulen, J., Hendriks, R.F.A., 1996. Bepaling van afbraaksnelheden van organische stof in laagveen. Ademhalingsmetingen aan ongestoorde veenmonsters in het laboratorium. Rapport 288, DLO-Staring Centrum, Wageningen (in Dutch: Determination of decomposition rates of organic matter in lowland peat: respiration measurements in undisturbed monoliths in the lab).
- Winiwarter, W., Haberl, H., Simpson, D., 1999. On the boundary between man-made and natural emissions: problems in defining European ecosystems. *J. Geophys. Res.: Atmos.* 104, 8153–8159.