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Effects of Groundwater Nitrate and Sulphate Enrichment on Groundwater-Fed Mires: a Case Study

G. van Dijk · J. Wolters · C. Fritz · H. de Mars · G. J. van Duinen · K. F. Ettwig · N. Straathof · A. P. Grootjans · A. J. P. Smolders

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Abstract Mires and peatlands in general are heavily influenced by anthropogenic stressors like acidification, eutrophication, desiccation and fragmentation. Groundwater-fed mires are, in contrast to rainwater-fed mires, often well protected against desiccation due to constant groundwater discharge. Groundwater-fed mires can however be influenced by groundwater pollution such as groundwater nitrate enrichment, a threat which has received minor attention in literature. The present case study demonstrates how groundwater nitrate enrichment can affect the biogeochemical functioning and vegetation composition of groundwater-fed mires through direct nitrogen enrichment and indirect

nitrate-induced sulphate mobilisation from geological deposits. Biogeochemical and ecohydrological analyses suggest that the Dutch groundwater-fed mire studied is influenced by different water sources (rainwater; groundwater of local and regional origin) with differing chemical compositions. The weakly buffered and nitrate-enriched groundwater leads, where it reaches the uppermost peat, to nitrogen enrichment, enhanced isotopic nitrogen signatures and altered the vegetation composition at the expense of characteristic species. Nitrate-induced sulphate mobilisation in the aquifer led to enhanced sulphate reduction, sulphide toxicity and elemental sulphur deposition in the mire. Despite

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sulphate reduction and nitrate enrichment, internal eutrophication did not play an important role, due to relatively low phosphorus concentrations and/or low iron-bound phosphorus of the peat soil. Future management of groundwater-fed mires in nitrate-polluted aquifers should include the reduction of nitrate leaching to the aquifer at the recharge areas by management and ecohydrological restoration measures on both a local and landscape scale.

Keywords Biogeochemistry · Eutrophication · Lignite deposits · Nitrate leaching · Sulphate mobilisation

1 Introduction

1.1 Mires Under Threat from Anthropogenic Influences

The functioning and biodiversity of mires are under threat by desiccation (due to drainage and conversion to agriculture), eutrophication, acidification and fragmentation (Joosten and Clarke 2002; Lamers et al. 2002b, 2015; van Diggelen et al. 2006). Especially when several of the aforementioned processes co-occur, they may result in increased peat decomposition and enhanced (internal) eutrophication leading to a loss of (bio-) diversity (Grootjans et al. 2006; Smolders et al. 2006; Hautier et al. 2009; Lamers et al. 2015). The functioning of mires and peatlands in general is to a large extent driven by the combination of hydrological and biogeochemical processes from a landscape scale down to microhabitat scale (Succow and Joosten 2001; Lamers et al. 2015). For groundwater-fed mires in particular, the factors groundwater discharge and chemical composition of the groundwater are major drivers. Whereas rainwater-fed mires often suffer from desiccation during periods with less precipitation or as a consequence of anthropogenic drainage, intact groundwater-fed mires are protected from desiccation due to constant groundwater discharge, which also generates a constant supply of minerals and nutrients (Succow and Joosten 2001). Changes in groundwater pressure and/or groundwater chemical composition can therefore directly affect the functioning of these systems. Several studies already demonstrated how hydrological and chemical alterations can affect the functioning of mires, for example by changing redox conditions (i.e. increased oxygen (O_2), sulphate (SO_4^{2-}) and nitrate (NO_3^-) concentrations) (De Mars and Wassen 1999;

Lamers et al. 2001, 2002a; DeLaune and Reddy 2008; Smolders et al. 2010; Cirkel et al. 2014) or changing groundwater levels (Holden et al. 2004; Grootjans et al. 2006; van Diggelen et al. 2006; Lamers et al. 2015).

Until now, the effects of groundwater NO_3^- enrichment on groundwater-fed systems have received relatively little attention in literature, in contrast to other forms of N enrichment such as aerial N deposition. Since the 1970s, however, elevated groundwater NO_3^- concentrations have become a growing global environmental problem in areas with aquifers influenced by NO_3^- leaching from agricultural fields (Thorburn et al. 2003; Rivett et al. 2008; Burow et al. 2010; Howden et al. 2011). Groundwater NO_3^- pollution mainly occurs in aquifers poor in labile organic material, such as sand or loess soils, where NO_3^- remains present on its flow path through the aquifer, due to the absence of organic material and consequent low denitrification rates (Smolders et al. 2010). NO_3^- often originates not only directly from leaching from agricultural soils (Di and Cameron 2002; Kirchmann et al. 2002; Beaudoin et al. 2005) but can also leach from non-agricultural soils like forest soils, which intercept aerial reactive N compounds originating from agricultural and industrial sources (Borken and Matzner 2004; Rothe and Mellert 2004; Gundersen et al. 2006). The intensity of NO_3^- leaching and groundwater NO_3^- pollution is only expected to increase in the future due to worldwide agricultural intensification (Di and Cameron 2002; Smolders et al. 2006; Shibata et al. 2017).

1.2 Influence of Groundwater NO_3^- Enrichment on Mires

Although many studies have focussed on the effects of enhanced N availability in oligotrophic (semi) aquatic systems like mires (Aerts et al. 1992, 1999; Bobbink et al. 1998; Lamers et al. 2000; Fritz et al. 2014; van den Elzen et al. 2018), increased N loading through NO_3^- -enriched groundwater has received less attention. Mires are partly buffered against increased nutrient loads (Lamers et al. 2000; Fritz et al. 2014), but a prolonged high N input may result in an increase of species adapted to more eutrophic conditions such as graminoids, rushes and trees like *Betula* and *Salix* at the cost of species characteristic for these systems (Verhoeven et al. 1996; Limpens et al. 2003, 2004; Tomassen et al. 2004; Fritz et al. 2012; Cusell et al. 2014; Lamers et al. 2015). Although enhanced N availability will affect a wide

range of mire types, groundwater-fed mires harbouring poor-fen vegetation that often comprise characteristic bog species are probably more prone to nitrogen enrichment and a resulting shift in species composition than rich fens (Kooijman 2012; Lamers et al. 2015).

NO_3^- , as a favourable electron acceptor, may increase anoxic decomposition rates of organic matter (Hartog et al. 2002; Rivett et al. 2008), and oxidise ferrous iron-bearing carbonates (Straub et al. 1996; Chaudhuri et al. 2001) and ferrous iron-bearing sulphides (Postma et al. 1991; Haaijer et al. 2007; Schwientek et al. 2008; Zhang et al. 2009; Korom et al. 2012). These processes can lead to SO_4^{2-} mobilisation from both sulphur-rich geological deposits in the aquifer and from sulphur in the peat material of the affected mire (Lucassen et al. 2004; Zhang et al. 2009). Consequential SO_4^{2-} availability in mires can stimulate SO_4^{2-} reduction and may lead to internal eutrophication due interference of sulphide (H_2S) with the iron–phosphorus (Fe–P) cycle leading to phosphate (PO_4^{2-}) mobilisation (Lamers et al. 1998; Lucassen et al. 2004; Smolders et al. 2006, 2010). Especially in combination with increased N availability, this NO_3^- -induced SO_4^{2-} and indirect PO_4^{2-} mobilisation may have an even stronger negative impact on the biodiversity in mires (Wassen et al. 2005; Fritz et al. 2012; Lamers et al. 2012, 2015).

Globally increasing groundwater NO_3^- concentrations lead to an urge to study the effects of groundwater NO_3^- enrichment on the functioning of groundwater-fed ecosystems and to define measures that could be taken to conserve and/or restore affected systems. Several studies report high groundwater NO_3^- levels in the Netherlands, well above the limit of 50 mg l^{-1} formulated in the European Nitrates Directive in 1991 (Council Directive 91/676/EEC, 1991) (Baumann et al. 2012; Fraters et al. 2016). Northwest European groundwater-fed systems, particularly the Dutch systems, are hereby heavily enriched with NO_3^- (De Mars et al. 2017). In the present paper, we assess in what way high groundwater NO_3^- concentrations and NO_3^- -mediated SO_4^{2-} mobilisation affect mire functioning (e.g.; plant community composition, peat conservation and nutrient sequestration). Using a case study of a groundwater-fed mire, in which we studied groundwater movement and biogeochemical parameters to unravel the functioning of the mire, we hypothesise the effects of groundwater NO_3^- enrichment to be both direct and indirect. Firstly, we hypothesise that where NO_3^- -enriched groundwater

influences the rhizosphere, it leads to direct N enrichment, alters the vegetation composition and leads to reduced presence of characteristic poor-fen and bog species. Secondly, we hypothesise that the potentially related, SO_4^{2-} enrichment leads to (internal) eutrophication and eventually a built-up of nutrients in the soil and vegetation.

2 Materials and Methods

2.1 Study Area

The study site is a groundwater-fed mire with a surface area of 15 ha, situated in the Dutch-protected nature area the Brunsummerheide ($50^\circ 55' 39.63'' \text{ N}$, $5^\circ 59' 50.73'' \text{ S}$) (Fig. 1a). It is a base-poor percolating mire with poor fen vegetation and some aspects of bog vegetation.

The mire is imbedded in small erosion valley incised in a Miocene fine sandy soil layer (grain size $< 300 \mu\text{M}$) (Heksenberg formation) with a thickness of up to 150 m deep, which is underlain by a thick impermeable clay layer (Formation of Rupel). The peat layer of the mire varies in thickness from several decimetres up to 3 m. Both the mineral base and the surface of the mire are sloping northwards (from South to North, 85 to 77 m above Amsterdam Ordnance Datum (AOD) ($\approx 1.15^\circ$) at the mire base and 85 to 80 m above AOD for the surface ($\approx 0.72^\circ$)). The surrounding sandy flanks are partly covered with pine forest (*Pinus*) and some small patches with deciduous trees (*Betula*). The area surrounding the mire is covered with heather, pine forest and urban areas. Two fault lines are present in the region, the Heerlerheide fault (about 2.5 km southwest of the mire) and the Feldebiss fault (about 0.5 km northeast of the mire). The presence of the impermeable Feldebiss fault in particular, influences the local hydrology of the area due to its low permeability (caused by smearing of clay layers) and provokes upwelling of groundwater (Swierstra 2008). The flow pattern of the regional groundwater is directed towards the northwest parallel of these fault lines. However, the presence of the draining headwaters of the Roode beek including the mire locally results in a northern flow direction. Within the Miocene sand layer, two brown coal deposits are present (Frimmersdorf and Morken) of which only fragments of the Morken occurs within the catchment area of the mire. Based on geological drill cores collected within the area in the past, the presence of these

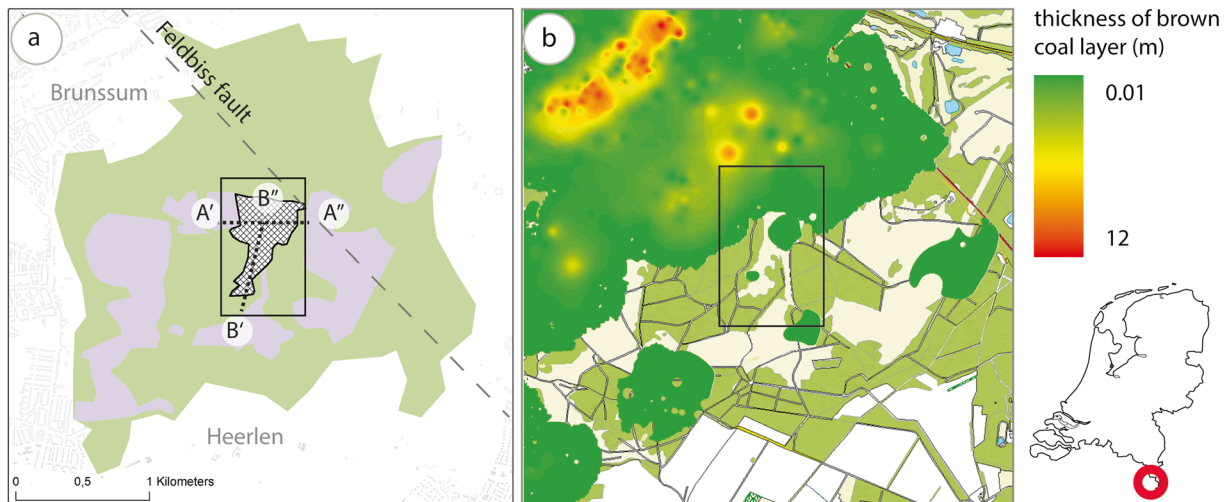


Fig. 1 **a** Map of the Brunsummerheide, with the study area shown in the centre (shaded in **a** and rectangle in **b**), and in the bottom right the location of the area within the Netherlands (red circle). Forest is shown in green and heathland in purple. The geological Feldbiss fault is shown as a broken line. In fine broken

lines, the two cross section transects of Fig. 2 (A'-A'' and B'-B'') are indicated. **b** An interpolation of the presence and thickness of lignite and marcasite containing brown coal layers in the underground is shown for the study area (data from TNO, 2013 (online DINOloket database))

fragmented marcasite containing lignite and deposits is proven (Fig. 1b) (Dubelaar and Menkovic 1998).

The combination of relatively large elevation gradients, presence of the impermeable fault nearby and the incision of the erosion valley led to the development of a discharge area with permanently wet conditions and peat formation. As the mire is fed by groundwater originating from a sandy aquifer poor in minerals, a weakly buffered percolation mire has developed with poor fen vegetation (Gorham 1955; Succow and Joosten 2001; van Dijk et al. 2012). The surplus of water from the mire is approximately 20 l s^{-1} and is drained by the Roode beek (Swierstra 2008). The peat layer consists of remains of rushes (*Juncus*) and peat mosses (*Sphagnum*) and contains several sand bands (varying in thickness and gravel content) indicating its spring-like origin as well as former wind- and/or water-mediated deposition of eroded material. The actual vegetation consists of a combination of oligotrophic and minerotrophic plant species including several *Sphagnum* species, *Narthecium ossifragum*, *Eriophorum angustifolium*, *Andromeda polifolia*, *Molinia caerulea*, *Juncus acutiflorus* and some juvenile Willow and Alder trees. In the northern part, *Sphagnum*-dominated peat is present with *Narthecium ossifragum* (community *Erico-Sphagnetum magellanici*; plant communities according to (Schaminée et al. 1995)), while further south, *Molinia caerulea* becomes more dominant (community *RG*

Molinia caerulea (*Oxycocco Sphagnetea*) and *RG Molinia caerulea* (*Scheuzerieta Sphagnetae*) (the distribution of a selection of species is presented in Results S2)).

2.2 Sampling

2.2.1 Surface Water, Pore Water and Groundwater

Surface water samples were collected in June and July of 2008 on 107 locations using polyethylene bottles. Anaerobic soil pore water samples were sampled with ceramic cups (5 cm, Eijkelkamp Agrisearch Equipment, Giesbeek, The Netherlands) connected via Teflon tubes to vacuum 60 ml syringes. On 11 locations in the mire, ceramic cups were placed in depth gradients (in total 34 ceramic cups, varying in depth from 5 cm to a maximum of 270 cm). Soil pore water samples were collected on five moments in time over a period of 10 months (June 2008–April 2009). In 2012 and 2013, additional groundwater samples were collected simultaneously with plant samples, for groundwater $\delta^{15}\text{N}-\text{NO}_3^-$ and plant tissue $\delta^{15}\text{N}$ analyses respectively. All water samples were transported to the laboratory under cool and dark conditions and stored at 4°C before analysis. H_2S concentrations were determined directly after sampling by fixing 10.5 ml pore water

with 10.5 ml H₂S anti-oxidant buffer, and using an Orion H₂S electrode and a Consort Ion meter (type C830). In August 2008, electrical conductivity (EC) measurements (indicating total dissolved ion content) were carried out in depth profiles (to a maximum depth of 200 cm) along four transects, with a WTW-Retch conductivity meter.

2.2.2 Hydrology

Groundwater levels were measured at eight locations with piezometers with 1-m filters installed at 1.5 m ($n = 5$) and at 5 m ($n = 3$) below the surface (see Fig. 2). Groundwater levels were automatically recorded by divers (TD Divers, Van Essen Instruments) (recordings were taken twice a day and corrected for local air pressure, from 2008 to 2014). The piezometers are part of an ecohydrological monitoring network of the Sigrano company and the Province of Limburg. Data are available from the DINO database (TNO, www.dinoloket.nl).

2.2.3 Vegetation

Vegetation samples of a selection of species (*Sphagnum fallax* ($n = 5$), *Molinia caerulea* ($n = 5$), *Calluna vulgaris* ($n = 3$), *Betula pendula* ($n = 6$)) and *Pinus sylvestris* ($n = 3$)) were collected from seven locations (when present) differing in groundwater influence to analyse tissue N and $\delta^{15}\text{N}$ content, in May 2013. For *Sphagnum fallax*, the upper 5 cm of the bryophyte (including *capitulum*) was collected, while for the other four plant species, only the 1-year-old leaves were collected.

2.2.4 Precipitation and N Deposition

To estimate the local aerial N deposition, precipitation collectors were placed for a period of 10 months (Aug–May in 2008–2009) and collected and sampled regularly. Precipitation samples were preserved by the addition of 1 ml of 1 M HgCl₂ prior to installation in the field. Precipitation collectors consisted of funnels (containing a mesh) attached to dark bottles which were located at nine locations (six in the forest and three on the mire, all randomly assigned). Precipitation samples were analysed as described below.

2.3 Chemical Analysis

2.3.1 Surface Water; Pore Water; Ground Water and Precipitation Samples

The pH was measured using a combined pH electrode with an Ag/AgCl internal reference, and alkalinity was measured by titration to pH 4.2 with 0.01 M HCl. Prior to elemental analyses, 10 ml of each sample was stored at 4 °C with 0.1 ml HNO₃⁻ to prevent metal precipitation. For the analyses of P, Ca, Mg, Fe, S, K and Al, inductively coupled plasma spectrophotometry (ICP-Optical Emission Spectrometer, Thermo Scientific iCAP 6000 Series ICP) was used. To determine NO₃⁻, NH₄⁺, PO₄²⁻, Na and Cl concentrations, 20 ml of each sample was stored at -20 °C and analysed colorimetrically with an AutoAnalyzer 3 system (Bran and Luebbe). Sodium and potassium were determined with a Technicon Flame Photometer IV Control (Technicon Corporation). For details on chemical analyses, see Van Dijk et al. (2015). The $\delta^{15}\text{N}$ -NO₃⁻ signature of groundwater samples was analysed at the NIOZ, Yerseke, the Netherlands, using an adaptation of the ammonia diffusion method described by Sigman et al. (1997).

2.3.2 Vegetation Analysis

Vegetation samples were oven dried at 70 °C for at least 48 h. Dried vegetation samples were ground using a mortar with liquid N and/or a MM 301 mixer mill (Retsch). Vegetation samples were rinsed with deionised water prior to drying to wash away N originating from atmospheric deposition that may have accumulated on leaves. Total element concentrations were determined by digesting 200 mg of dried (24 h, 70 °C) and homogenised sample in 4 ml concentrated HNO₃ (65%) and 1-ml H₂O₂ (30%) using an Ethos D microwave (Milestone microwave MLS 1200 Mega). Samples were analysed by ICP, as described above. Total N and C concentrations were measured with a CNS analyser (Model NA 1500; Carlo Erba Instruments, Milan, Italy). Vegetation $\delta^{15}\text{N}$ signature was measured with a Delta Plus isotope ratio mass spectrometer (IRMS) (Thermo Finnigan) that was coupled, through a ConFlo III interface (Thermo Finnigan), to a Flash EA 1110 Elemental Analyser (Thermo Finnigan).

Data Analysis Significant differences among groups were tested using one-way ANOVA tests. Data was

tested for normal distribution (Shapiro–Wilk tests and visual inspection of Q–Q plots). Not normally distributed data were tested for significant differences among groups using Kruskal–Wallis tests and Dunn’s post hoc tests. Normally distributed data were checked for equality of error variances using Levene’s tests. Significant differences among groups were assessed using one-way ANOVAs with Tukey post hoc tests for equal variances or using Welch tests and Games–Howell post hoc tests for non-equal variances. Correlation relationships in pore water concentrations were defined using Pearson correlation. All tests were carried out using SPSS Statistics for Windows (Version 24. IBM Corp. Armonk, NY, 2016).

3 Results

3.1 Ecohydrological Functioning

The studied mire was found to be influenced by weakly buffered groundwater (alkalinity usually $< 0.5 \text{ meq l}^{-1}$), originating from the sandy aquifer, throughout the year.

Along the edges of the mire, usually little evidence was found for seepage; however, closer to the runnels and in the centre of the mire, an average hydraulic head above the peat surface was recorded ($> 2\text{--}10 \text{ cm}$ above peat surface) indicating year-round seepage (Fig. 2). Due to the high hydrological resistance of the peat layer and large local variations in elevation, the hydraulic head in the surrounding sandy hills is higher than that under the mire. These two phenomena indicate an inflow of groundwater of both regional and local origins (Fig. 2).

As ion concentrations differ largely between regional groundwater and rainwater/groundwater of local origin, patterns of differing water composition could be observed; ranging from predominantly rainwater fed to predominantly regional groundwater fed and zones of mixing. These differences also enable a parameter like EC to be used as an indicator for distinction between water types. The edges of the mire, in the far south side (transect IV in Fig. 3c.) and in the northeastern part of the study area (east of transect I in Fig. 3c.), were mainly influenced by rainwater ($\text{EC} < 200 \mu\text{S cm}^{-1}$), based on EC measurements along four cross sections and a surface water survey (transects in Figs. 3 and 4a). More to the

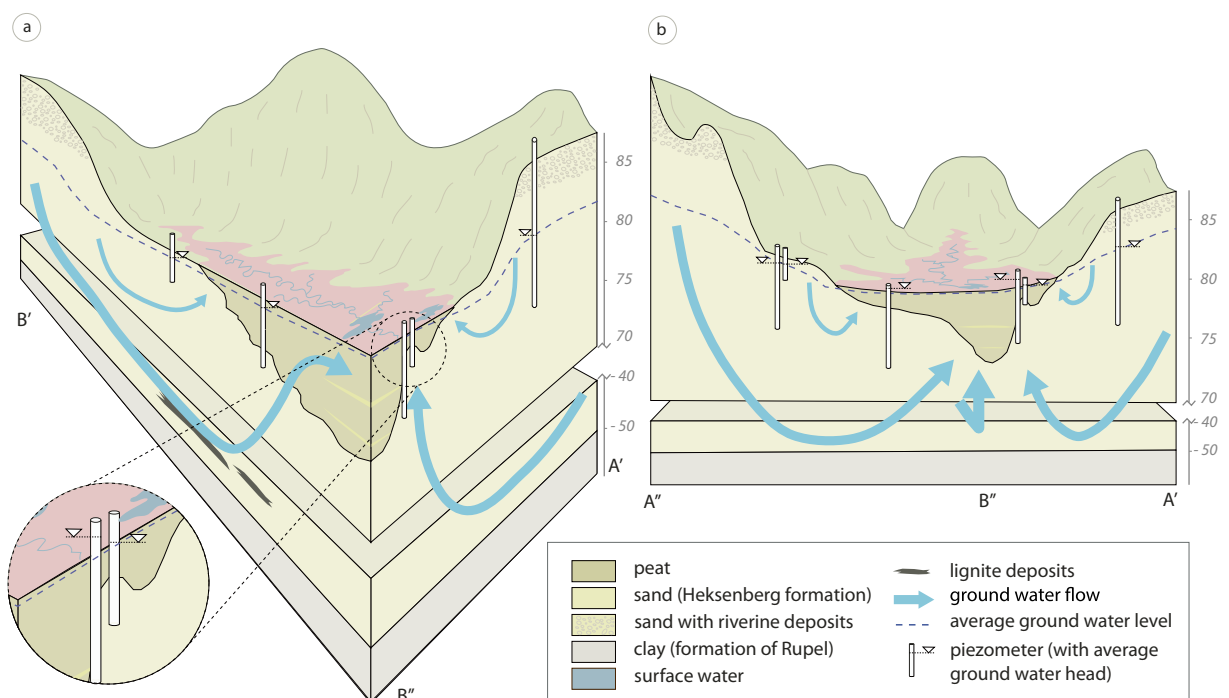


Fig. 2 Schematic overview and cross section of the study area with supposed flow of groundwater, within a south–north A'–A'' (a) and an east–west cross section B'–B'' (b) (In Fig. 1, the location of the cross sections is shown). Elevation, groundwater head and

soil profiles are based on field measurements, soil cores and interpolations. Piezometers are shown with average groundwater head. Dotted lines represent the average groundwater level. Scale in meters to Amsterdam Ordnance Datum

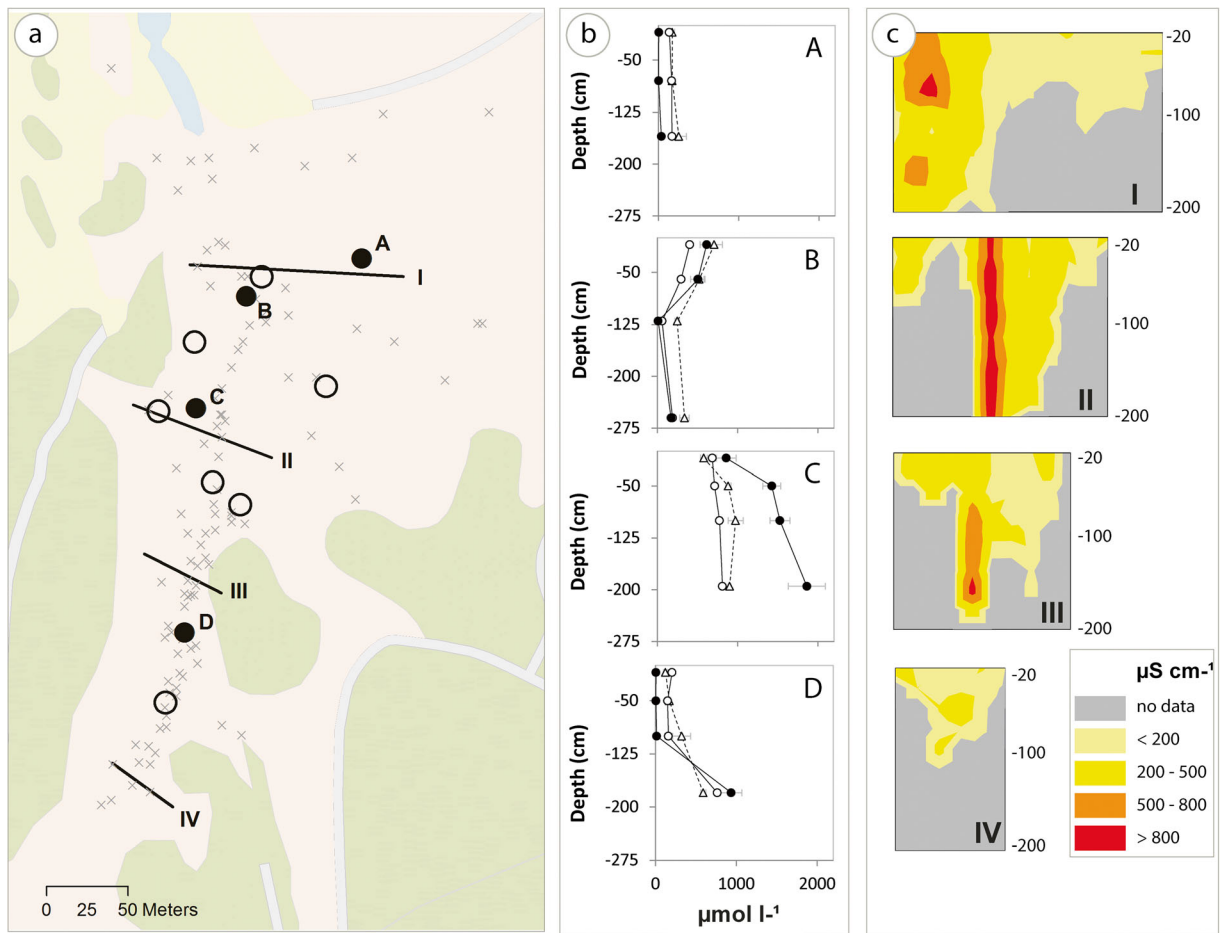


Fig. 3 a.) Location of the pore water depth profiles (open and filled circle, filled circles shown in b), EC transect shown as lines (transect I to IV, shown in c), surface water sampling locations shown with grey crosses. b.) average pore water concentrations

($t = 5$) of SO_4^{2-} (open circles), NO_3^- (filled circles) and chloride (open triangles) in depth profiles on 4 locations (A–D) in the mire. c.) Depth transects of EC ($\mu\text{S cm}^{-1}$) interpolated within the transects

centre of the mire and along several runnels, the influence of local origin and/or a mix of regional groundwater and rainwater was established (EC 200–750 $\mu\text{S cm}^{-1}$). The dominance of regional groundwater (EC 700–1000 $\mu\text{S cm}^{-1}$) was observed at a depth of 1–2 m in the peat profile in the southern (upstream) part of the mire (transect III in Fig. 3c). Upwelling (spring) of regional groundwater (EC 700–> 1000 $\mu\text{S cm}^{-1}$) was observed in the centre of the mire (at location C, middle of transect II in Fig. 3c.), with water rising from the underlying sandy aquifer up to the rhizosphere. At this location, a runnel starts which runs north (downstream) partly over and partly percolating through the upper part of the peat. Further to the north at the western side of transect I, this resulted in increased EC levels (up to 700–1000 $\mu\text{S cm}^{-1}$) in the upper section of the peat profile.

3.2 Biogeochemical Functioning—Groundwater Influence

Biogeochemical analyses of pore water and surface water samples showed similar patterns as found with EC measurements and groundwater level data (Figs. 3 and 4). On locations influenced by regional groundwater Ca^{2+} , concentrations were above 200 $\mu\text{mol l}^{-1}$ and Cl^- concentrations above 500 $\mu\text{mol l}^{-1}$ (Figs. 3b and 4b). In contrast, locations mainly influenced by local groundwater and/or a mix of regional groundwater and rainwater showed Cl^- concentrations of 200–500 $\mu\text{mol l}^{-1}$ and Ca^{2+} concentrations of 100–200 $\mu\text{mol l}^{-1}$, while Cl^- and Ca^{2+} concentrations were < 200 $\mu\text{mol l}^{-1}$ and < 100 $\mu\text{mol l}^{-1}$ respectively for locations mainly influenced by rainwater (\approx average 30 $\mu\text{mol l}^{-1}$ Ca^{2+}) (Figs.

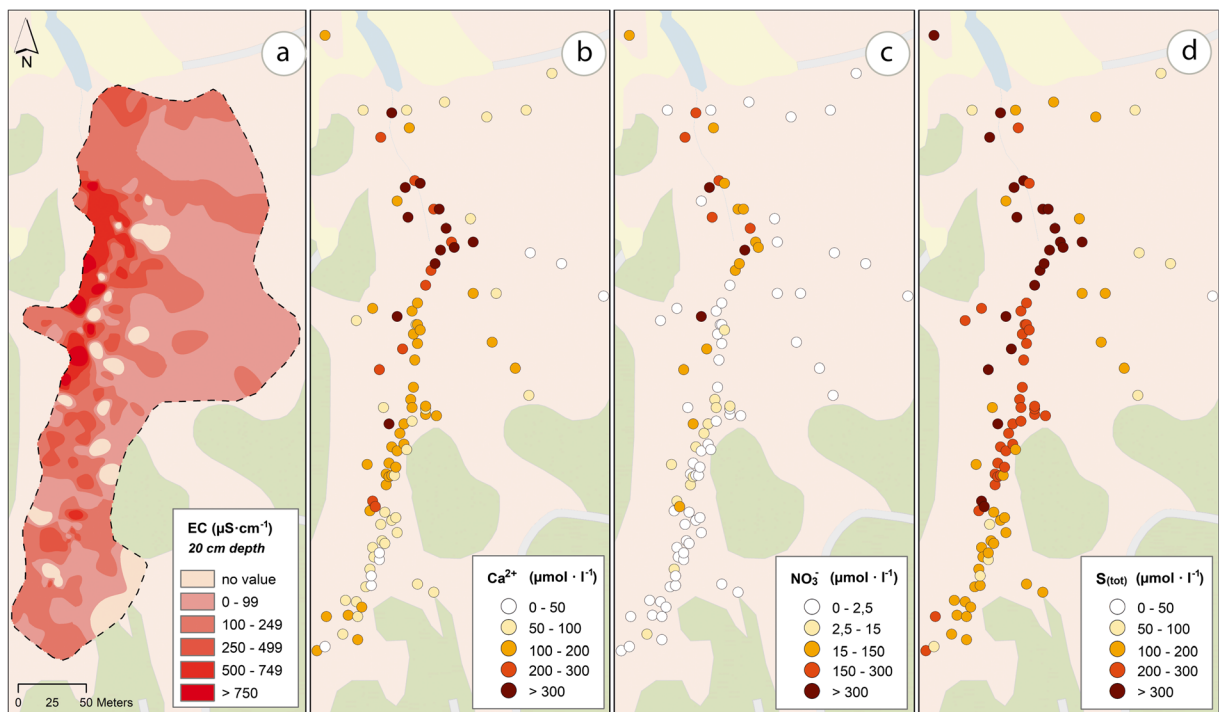


Fig. 4 **a** Surface covering interpolated image of EC ($\mu\text{S}\cdot\text{cm}^{-1}$) at 20 cm of depth in the soils. **b** Surface water calcium concentrations. **c** Surface water NO_3^- concentrations. **d** Surface water SO_4^{2-} concentrations

3b and 4b). Other parameters, including Na^+ , K^+ and pH, followed a similar pattern (see Results S1) and showed a significant positive correlation (R^2 0.6 to 0.88 $P < 0.001$) with concentrations of Ca^{2+} and Mg^{2+} indicating the common origin of these ions (most likely groundwater-originated).

3.3 Biogeochemical Variation and Nutrient Availability

Elements associated with groundwater (i.e. $\text{Ca}^{2+}+\text{Mg}^{2+}$) showed a significant positive correlation with NO_3^- concentrations (R^2 0.88, $P < 0.001$) and SO_4^{2-} concentrations (R^2 0.78, $P < 0.001$) in both the pore water and surface water samples (Fig. 5a), indicating the groundwater to be enriched by these ions. The mire is relatively poor in P with average values of 1.4 (max. 9) $\mu\text{mol}\cdot\text{l}^{-1}$ in surface water and values ranging from below the detection limit to 2.5 $\mu\text{mol}\cdot\text{l}^{-1}$ in the pore water samples. NO_3^- was the dominant form of N in both surface water and surprisingly also in pore water (see Results S1).

In the centre of the mire, especially in the northern part, remarkably high NO_3^- concentrations were observed in the surface water (up to $> 600\ \mu\text{mol}\cdot\text{l}^{-1}$

NO_3^-) (Fig. 3). On the mire flanks and in the southern upstream part, low pore water NO_3^- concentrations were observed in the top of the peat profile (i.e. depth profiles A and D in Fig. 3). Pore water NO_3^- concentrations were much higher on locations with regional groundwater influence (900–1800 $\mu\text{mol}\cdot\text{l}^{-1}$) in deeper soil layers (D in Fig. 3) or through the entire peat profile (from the bottom up to the rhizosphere) (C in Fig. 3). Pore water and surface water SO_4^{2-} concentrations showed a comparable pattern, although SO_4^{2-} concentrations also seemed to be higher on locations influenced by groundwater of local origin and/or a mix of regional groundwater and rainwater (Figs. 3b and 4d). For $\text{Ca}^{2+}+\text{Mg}^{2+}$ concentration below 500 $\mu\text{mol}\cdot\text{l}^{-1}$, NO_3^- concentrations were (very) low and steeply increased above this threshold (Fig. 5a, b). On some locations that were influenced by SO_4^{2-} rich and NO_3^- poor groundwater, SO_4^{2-} reduction and free H_2S were found in the pore water (from 25 $\mu\text{mol}\cdot\text{l}^{-1}$ H_2S in the rhizosphere up to 300 $\mu\text{mol}\cdot\text{l}^{-1}$ H_2S at a depth > 0.5 m). In some streams, yellowish elemental sulphur deposits were also found on dead organic matter (see Fig. 6).

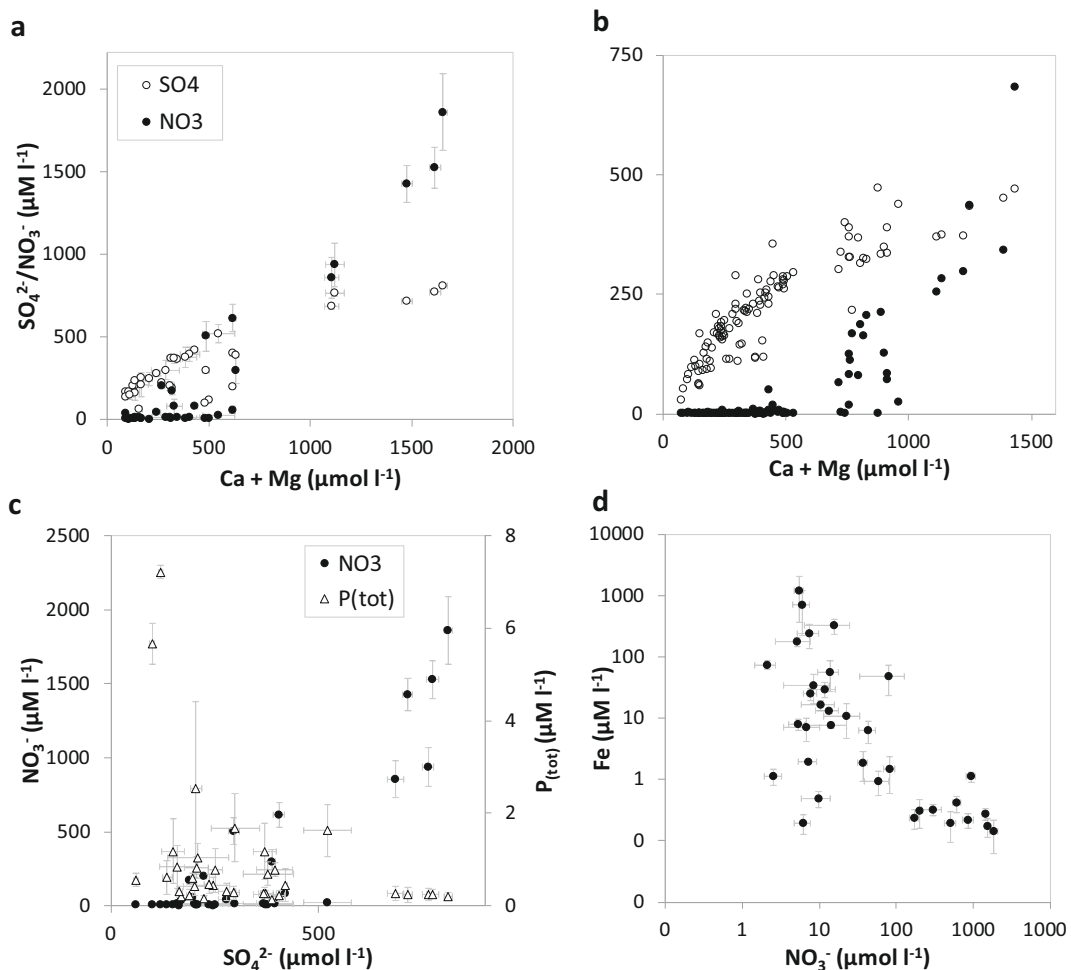


Fig. 5 SO_4^{2-} (open circles) and NO_3^- (closed circles) concentrations in the pore water (a) and the surface water (b) plotted against $\text{Ca}^{2+} + \text{Mg}^{2+}$ concentrations. Values are presented as means ($n = 5$) \pm SE for pore water samples, collected on 11 locations at several depths, while surface water samples are based on a single measurement on 107 locations. c Pore water NO_3^- (filled circles)

and $\text{P}_{(\text{tot})}$ (open triangles) concentrations plotted against SO_4^{2-} concentrations. d Pore water NO_3^- concentrations plotted against Fe concentrations, values are presented as means ($n = 5$) \pm SE. Note different scales on the axes, and in d axes are on a logarithmic scale

3.4 Effects of NO_3^- and SO_4^{2-} Enrichment on Species Distribution

Although we lack historic data on plant species composition and cannot present changes over time, we can compare plant species composition in different zones. The distribution of plant species and plant species composition correlated with zones with the influence of different sources of water, ranging from predominantly influenced by rainwater to vegetation patches predominantly influenced by regional groundwater. Zones with dominance of species like

Sphagnum magellanicum, *S. papillosum*, *Erica tetralix* and *Eriophorum vaginatum* were predominantly rainwater influenced. Zones with dominance of species like *S. fallax*, *S. flexuosum* and *Narthecium ossifragum* were predominantly influenced by groundwater from local origin or a mixture of this local groundwater with rainwater. On spots where NO_3^- -rich regional groundwater reached the surface, the dominant bryophyte species is *Sphagnum fallax* and plant species like *Juncus acutiflorus*, *J. effusus* and juvenile *Salix* sp. and *Alnus* sp. trees were more abundant.

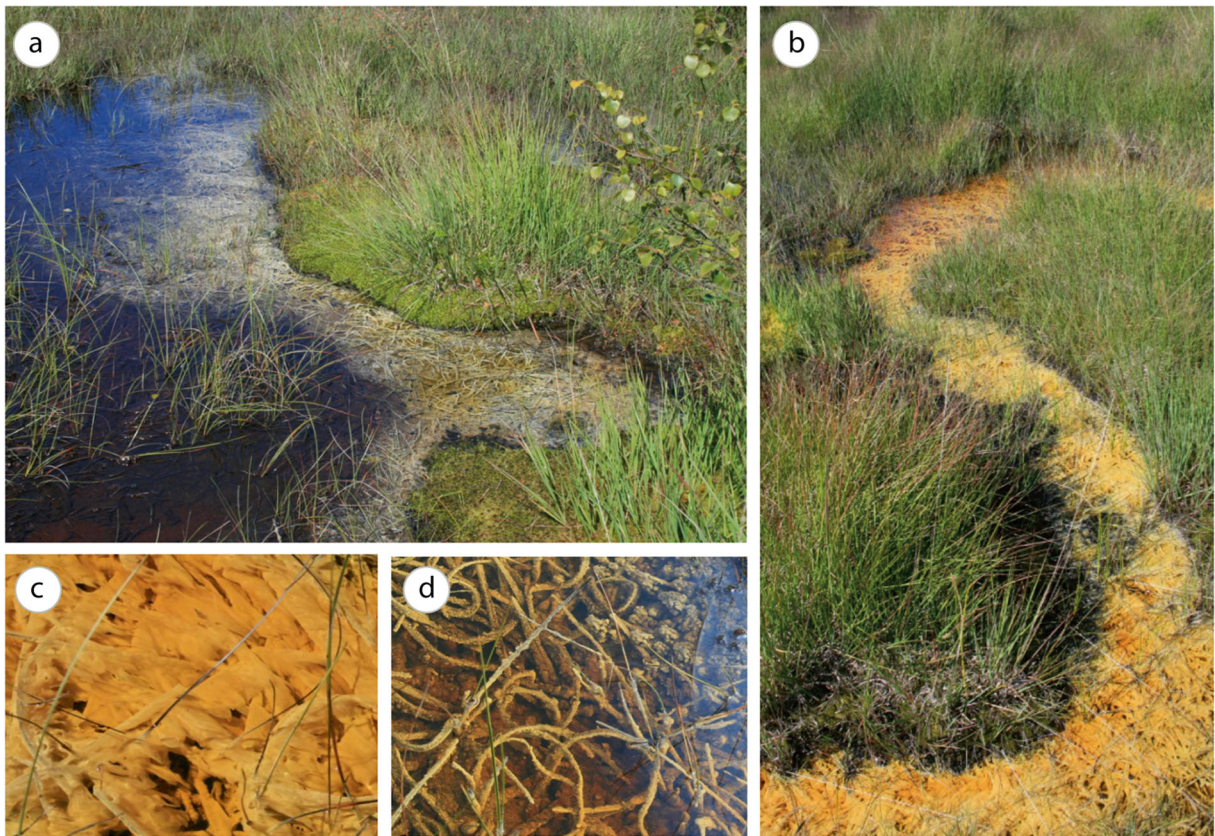


Fig. 6 Elemental S deposition on dead plant material on spots where sulphate rich groundwater seepage occurs (a) or in entire spring streams (b). In c and d, two close ups are presented. Photos by G. van Dijk

3.5 Groundwater Versus Aerial Nutrient Input

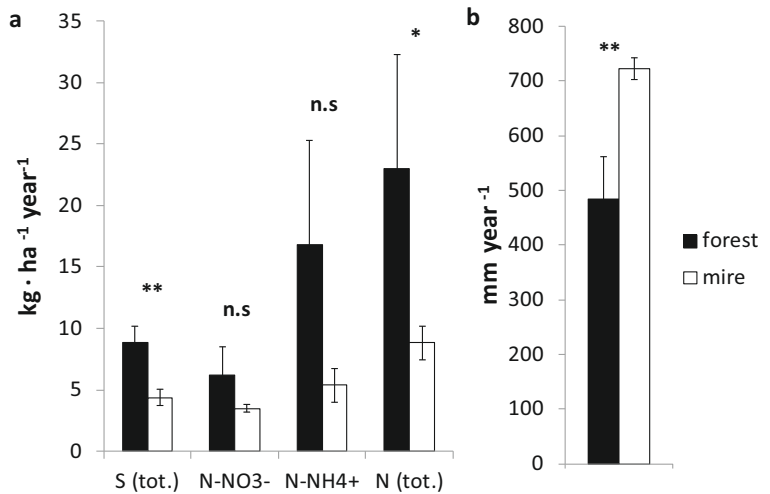
Regional groundwater was not the only source of N and S. Atmospheric deposition measurements in the present study area showed a significantly higher total N and total S deposition in the surrounding pine forest compared with the mire itself (Fig. 7a). Average total wet N deposition was $8.8 \text{ kg N ha}^{-1} \text{ year}^{-1}$ (40% NO_3^- , 60% NH_4^+) and total S deposition was $4.4 \text{ kg S ha}^{-1} \text{ year}^{-1}$ on the mire itself ($n = 3$), while in the surrounding pine forest ($n = 6$), the total average deposition of N and S was $23.0 \text{ kg N ha}^{-1} \text{ year}^{-1}$ (27% NO_3^- , 73% NH_4^+) and $8.9 \text{ kg S ha}^{-1} \text{ year}^{-1}$, respectively. Average precipitation which reached the soil surface was significantly lower (> 40%) in the forest than in the mire due to interception of rainwater by trees (Fig. 7).

When water samples are divided in groups based on the dominant water source, (1) rainwater, (2) groundwater of local origin or (3) groundwater of regional origin, a pattern (not significant, due to

low sample size) can be observed indicating that the $\delta^{15}\text{N}\text{-NO}_3$ signature of the regional groundwater, which is often richer in NO_3^- , is higher compared with the signature of the rainwater and local groundwater (Fig. 8).

$\delta^{15}\text{N}$ signature analyses of plant tissue of species occurring in zones with different water sources indicated that individuals grown on locations influenced by groundwater with high NO_3^- concentrations displayed higher $\delta^{15}\text{N}$ values (Fig. 8). $\delta^{15}\text{N}$ signatures seemed to differ between groups receiving water from different sources. Dividing the plant tissue analyses in three classes based on the water source by which they are influenced (RW: rainwater, LG: local groundwater and RG: regional groundwater) there was a trend of increased $\delta^{15}\text{N}$ signatures for species on locations influenced by NO_3^- -enriched regional groundwater, comparable with the trend observed in the groundwater itself (Fig. 8).

Fig. 7 **a** Total S and total N (both NO_3^- and NH_4^+) deposition and precipitation **b** on the mire itself (white bars, $n = 3$) and in the surrounding forest (black bars, $n = 6$). Values are presented as means \pm SE. Significant differences between groups are indicated with single ($P < 0.05$) and double asterisks ($P < 0.01$)



4 Discussion

This paper presents the results of a case study on the effects of NO_3^- -enriched groundwater on the functioning of a groundwater-fed mire. A clear zonation of water types, with specific chemical composition, was found. The upwelling groundwater was weakly buffered and the regional groundwater was rich in NO_3^- and SO_4^{2-} . Groundwater NO_3^- enrichment resulted in a direct N enrichment and altered the vegetation composition at the expense of characteristic poor fen species. Correlations between groundwater NO_3^- and SO_4^{2-} pointed to NO_3^- -induced SO_4^{2-} mobilisation in the aquifer leading to SO_4^{2-} enrichment and SO_4^{2-} reduction in the mire.

Despite NO_3^- -induced SO_4^{2-} mobilisation, no indirect NO_3^- -induced internal eutrophication was found, probably due to the P poor nature of the mire.

4.1 Functioning of the Groundwater-Fed Mire

The chemical composition of the ground and surface water indicates the influence of several (ground) water sources in the study area. Different parts of the mire are influenced by different water sources which led to contrasting biogeochemical conditions and vegetation assemblages. The boundaries of the mire showed to be predominantly influenced by rainwater and groundwater of local origin. However, the centre of the mire is

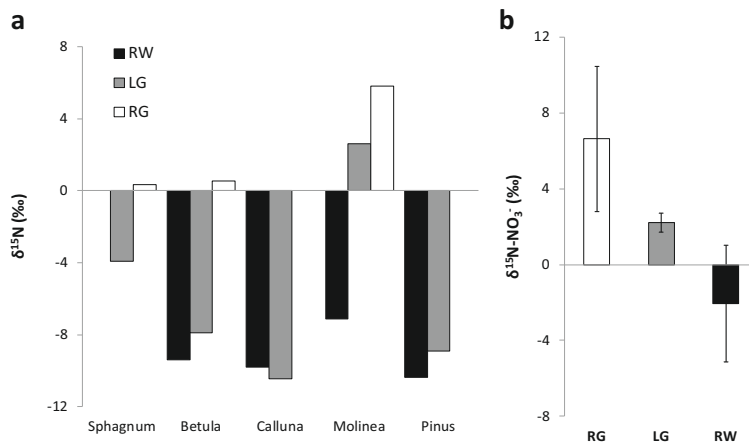


Fig. 8 **a** Plant tissue of $\delta^{15}\text{N}$ signatures for the different measured plant species. $\delta^{15}\text{N}$ signature of all species divided in different groups based on their location on the mire; no error bars are shown because some bars are based on only one measurement. **b.** $\delta^{15}\text{N}-\text{NO}_3^-$ signatures analyses of seven groundwater samples in the

study area divided in three groups based on major water source (RW sites with dominated rainwater influence (black bars), LG: sites with local groundwater influence (grey bars), RG: sites with locations with regional groundwater (white bars))

influenced by upwelling weakly buffered regional groundwater as indicated by stable water levels permanently above the surface and high concentrations of NO_3^- and cations.

4.2 Groundwater NO_3^- and SO_4^{2-} Enrichment—Potential Sources

An important driver in the functioning of the study area is the groundwater NO_3^- and SO_4^{2-} enrichment. Based on modelling results of (Swierstra 2008), the size of the catchment area is estimated to be around 275–300 ha which includes forest (50%), heathlands (25%) and agricultural and urban area (25%). Possible sources for groundwater NO_3^- enrichment could therefore be NO_3^- leaching from forests (indirect NO_3^- enrichment via atmospheric N deposition) (Dise and Wright 1995; Bobbink and Hettelingh 2011) and NO_3^- leaching from agricultural areas (originating from both inorganic fertilisers and manure). Sources for SO_4^{2-} enrichment can be similar although additional NO_3^- -mediated SO_4^{2-} mobilisation from sulphur rich geological deposits in the aquifer (lignite and marcasite deposits) could also play a role here (Smolders et al. 2010). Based on the data collected in the present study, the proportional contribution of different sources for NO_3^- and SO_4^{2-} cannot be established. Groundwater $\delta^{15}\text{N}$ - NO_3^- signatures are highest (more enriched in ^{15}N) on locations influenced by regional groundwater, lower in zones dominated by groundwater of local origin and lowest on predominantly rainwater fed locations. The higher isotope signature of regional ground water can be explained by the fact that most biological processes preferentially use ^{14}N . Denitrifying microorganisms, for instance, preferably use the lighter ^{14}N isotope, which leads to ^{15}N becoming more abundant in the remaining NO_3^- (Böttcher et al. 1990; Lehmann et al. 2003; Madigan and Jung 2009; Zhang et al. 2009, 2012). The correlation found between groundwater $\delta^{15}\text{N}$ - NO_3^- signature with the groundwater SO_4^{2-} concentration (R^2 0.59, $P < 0.05$) indicates that regional groundwater passes pyrite containing lignite deposits in the aquifer, where part of the NO_3^- in the groundwater can mediate denitrifying pyrite oxidation, resulting in isotopic fractionation of NO_3^- . The combination of strong indications for groundwater-mediated denitrifying pyrite oxidation and still continuous high NO_3^- levels does point to a high degree of NO_3^- enrichment of the regional groundwater.

Groundwater $\delta^{15}\text{N}$ - NO_3^- signature will of course also depend on the original NO_3^- source (Nestler et al. 2011). According to (Nestler et al. 2011) the $\delta^{15}\text{N}$ - NO_3^- signatures in the present study fall within the range of artificial fertiliser, soil N and atmospheric deposition, which excludes manure or sewage as origin. No clear distinction can however be made between artificial fertiliser, soil N and atmospheric N deposition, although atmospheric N deposition is usually characterised by lower $\delta^{15}\text{N}$ - NO_3^- values than those measured in groundwater NO_3^- . N deposition measured in this study showed higher deposition in the forest ($23.0 \text{ kg N ha}^{-1} \text{ year}^{-1}$) in comparison with the mire ($8.8 \text{ kg N ha}^{-1} \text{ year}^{-1}$) (Fig. 7), which can lead to NO_3^- leaching from the forest floor (with little organic matter) to the sandy aquifer (Dise et al. 1998; Gundersen et al. 1998, 2006; MacDonald et al. 2002; Borken and Matzner 2004). Lower aerial N deposition measured on the mire itself could be explained by the relatively small surface of the open mire situated in a depression that is imbedded by dense pine forest, which in turn intercepts aerial N deposition. Another source can be intensive agricultural land use which is well known to lead to NO_3^- leaching to the groundwater (Goulding 2000; Di and Cameron 2002; Smolders et al. 2010). NO_3^- and Cl concentrations of the regional groundwater are substantially higher compared with groundwater from local origin, which might indicate that N originating from aerial N deposition is probably only an additional source (Stites and Kraft 2001; Martin et al. 2004). Care should however be taken when comparing present atmospheric N deposition, as presented here, with groundwater N levels which originate from a much longer time span in which atmospheric N deposition levels were higher in the Netherlands. Therefore, one can conclude that groundwater NO_3^- enrichment in the study area is caused by a combination of (1) intensive use of fertilisers on the agricultural fields at the southeast side of the catchment area and (2) dense pine forest intercepting aerial nitrogen deposition (Fig. 9).

As for NO_3^- , similar sources can be listed for groundwater SO_4^{2-} enrichment. Higher S deposition was found in pine forest compared with the open mire itself (Fig. 7), indicating that leaching from forest soils in the catchment might be a possible source. And even more so for S, care should however be taken when comparing present atmospheric S deposition, as presented here, with groundwater S levels which originate from a much longer time span in which atmospheric S deposition

levels were much higher in the Netherlands. And agricultural activities are also known to lead to SO_4^{2-} leaching (due use of different forms of SO_4^{2-} -containing fertilisers). An important additional source for groundwater SO_4^{2-} enrichment can be the mobilisation of SO_4^{2-} from S bearing marcasite rich lignite deposits in the aquifer. In combination with high groundwater NO_3^- concentrations, this FeS_x deposits can be oxidised via NO_3^- reduction, leading to the mobilisation of SO_4^{2-} (Postma et al. 1991; Lucassen et al. 2004; Haaijer et al. 2007; Schwientek et al. 2008; Zhang et al. 2009; Smolders et al. 2010; Korom et al. 2012) (Fig. 9).

4.3 Groundwater NO_3^- Enrichment—Potential Effects on Ecosystem Functioning and Biodiversity

Groundwater NO_3^- concentrations found (800–2000 $\mu\text{mol l}^{-1}$ NO_3^- (50–125 mg l^{-1} NO_3^-)), exceed the maximum groundwater NO_3^- concentrations allowed by the EU-Nitrate directive (800 $\mu\text{mol l}^{-1}$ NO_3^- (50 mg l^{-1} NO_3^-)). These high groundwater NO_3^- concentrations can result in direct eutrophication and lead to an altered vegetation composition. $\delta^{15}\text{N}$

signatures of vascular plants, bryophytes and tree species were found to be higher on locations influenced by NO_3^- -enriched groundwater, indicating uptake of anthropogenic N and potential eutrophication on the longer term. *Sphagnum* mosses, being the dominant peat former in this system, can actively take up both NH_4^+ and NO_3^- , with particularly NH_4^+ being taken up very efficiently (Jauhiainen et al. 1998; Fritz et al. 2014). This ability prevents the dominance of vascular plants under ombrotrophic conditions (Van Breemen 1995; Lamers et al. 2000). However, when N loads exceed assimilation rates by *Sphagnum* growth, as in the present study with high total N fluxes through the centre of the mire due to constant influence of NO_3^- -enriched groundwater, this will lead to N saturation of *Sphagnum* mosses and upper peat layers. This N saturation of *Sphagnum* mosses leads to N becoming available for other species, leading to competitive advantage of faster growing species like graminoids and trees, at the expense of oligotrophic species (Lamers et al. 2000; Limpens et al. 2003; Tomassen et al. 2004). Based on maximum critical N loads (MCL), the aerial N deposition already is at its maximum limit or exceeds the MCL

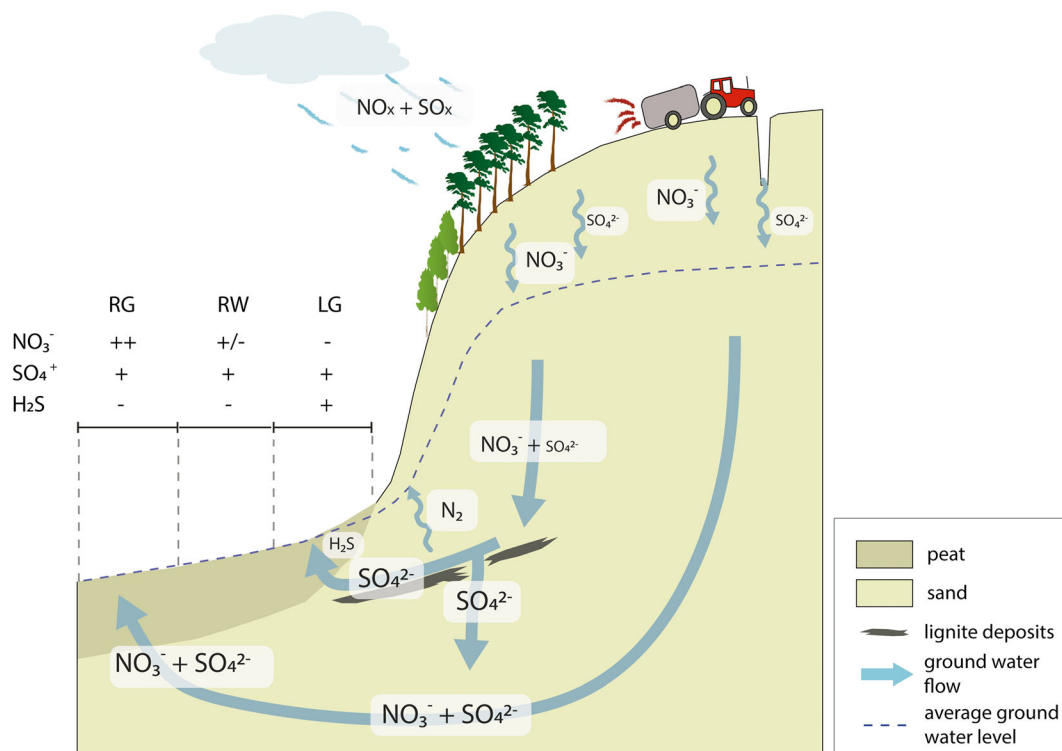


Fig. 9 Schematic overview of sources and processes influencing groundwater NO_3^- and SO_4^{2-} enrichment in the present study area, (RG: zone dominated by regional groundwater, RW: zone dominated by rainwater, LG: zone dominated by local groundwater)

for ombrotrophic bogs (MCL of $10 \text{ kg N ha}^{-1} \text{ year}^{-1}$, $8.8 \text{ kg N ha}^{-1} \text{ year}^{-1}$ in the study area) and coniferous forests (MCL of $20 \text{ kg N ha}^{-1} \text{ year}^{-1}$, $23 \text{ kg N ha}^{-1} \text{ year}^{-1}$ in the study area) (Bobbink and Hettelingh 2011). Additional N loading via NO_3^- -enriched groundwater (roughly estimated at $350\text{--}880 \text{ kg N year}^{-1}$ for the upwelling zone based on the presented data) will therefore definitely exceed the MCL for these habitats on locations influenced by NO_3^- -enriched groundwater. Besides being a nutrient, NO_3^- is a strong electron acceptor with the potential to influence redox processes in peatlands (Lamers et al. 2012). A detailed study on microbiological and biogeochemical processes along a depth profile in the study area did also indicate groundwater NO_3^- enrichment to influence C and N cycling via stimulation of anaerobic CH_4 oxidation by microorganisms within the peat profile (Zhu et al. 2012). Although relatively little is known about the effects of NO_3^- on organisms, high concentrations in the present study might have (toxic) effects, possibly via the denitrification intermediate nitrite. Literature reviews on the effects of NO_3^- concentrations on aquatic invertebrates in streams and springs mainly point to effects via biogeochemical processes and redox processes and little on direct toxicity (Camargo and Alonso 2006; Ferreira et al. 2006). Summarising, we can accept our hypothesis stating that NO_3^- -enriched groundwater, where it reaches the rhizosphere, leads to N enrichment and zones where NO_3^- -enriched groundwater reaches the rhizosphere the vegetation composition differs with fewer characteristic poor fen and bog species.

4.4 Groundwater SO_4^{2-} Enrichment—Potential Effects on Ecosystem Functioning and Biodiversity

Both NO_3^- and SO_4^{2-} are electron acceptors that can influence redox processes to a major extent, especially in wet soils rich in organic matter such as peatlands (Lamers et al. 2012). As expected, SO_4^{2-} reduction was only seen on locations with low NO_3^- concentrations, because NO_3^- reduction is thermodynamically more favourable than SO_4^{2-} reduction. This led to H_2S production within the rhizosphere on locations under the influence of relatively NO_3^- -poor and SO_4^{2-} -rich groundwater (Figs. 6 and 9). H_2S can be highly toxic for organisms (Lamers et al. 2013). Elemental S deposition, found on the same locations, probably resulted from the oxidation of groundwater H_2S after it reached

the surface. Little is known about the ecological effects of widespread permanent S deposits, but one can imagine that they might be toxic for aquatic invertebrates and will reduce food availability for these animals. Plants and bryophytes in the direct surrounding of S deposits were observed to be dead (pers. obs. G. van Dijk, see Fig. 6). However, it seems more likely that this is caused by the (temporal) presence of free H_2S (under the microbial mats (Fig. 6)). Apart from these direct effects of H_2S , the influx of SO_4^{2-} is known to cause enhanced decomposition of organic matter, decreased methane (CH_4) production (Pester et al. 2012; Hausmann et al. 2016) and mobilisation of internally bound P (internal eutrophication) (Lamers et al. 2001, 2002a; Smolders et al. 2006). No clear indications of internal eutrophication were found in the present study, as pore water P concentration showed no correlation with pore water SO_4^{2-} concentrations (Fig. 5c). In contrast to what was hypothesised, it can be concluded that although groundwater NO_3^- -induced groundwater SO_4^{2-} enrichment led to enhanced SO_4^{2-} reduction, sulphide toxicity and elemental S deposition, internal eutrophication does not seem to play an important role. This might also be the case because almost no P in this ecosystem is bound to iron-complexes that could easily be mobilised under enhanced SO_4^{2-} reduction.

4.5 Lessons for the Future—a Management Dilemma Between Groundwater Quantity and Groundwater Quality

The present paper stresses, as others did before (Bedford 1996; Grootjans et al. 2006; Lamers et al. 2015), the importance of interactions between biogeochemical processes and (eco-) hydrological processes for the functioning of ecosystems, especially for groundwater fed mires. Understanding the functioning of systems is important when aiming at restoration of these systems and mitigation of anthropogenic influences including targeting major threats and critical thresholds. The present paper showed the study area to be affected by weakly buffered NO_3^- -enriched groundwater, leading to NO_3^- -induced groundwater SO_4^{2-} enrichment, enhanced SO_4^{2-} reduction leading to sulphide toxicity but no internal eutrophication and direct N enrichment and different vegetation composition where NO_3^- -enriched groundwater reaches the rhizosphere. If the influence of groundwater NO_3^- and SO_4^{2-} enrichment remains locally confined, this might however even

generate a large heterogeneity of habitats and biodiversity on a landscape scale. The study area has a high biodiversity due to the presence of steep gradients, of both ecohydrological and biogeochemical conditions, ranging from oligotrophic and acidic conditions to mesotrophic and slightly buffered conditions (van Dijk et al. 2014). Especially the combination of different habitats along these gradients can result in suitable habitats for a large number of species (Wheeler and Proctor 2000; Verberk et al. 2006; van Kleef et al. 2012). As groundwater-fed mires are often small in size, these systems are probably not very resilient after facing a large scale impact of these biogeochemical stressors for a longer time.

Mitigating the effects of groundwater NO_3^- enrichment is not an easy task, however. One faces a management dilemma as direct reduction of regional groundwater influence enriched with NO_3^- would result in reduced water supply, leading to desiccation, enhanced decomposition and internal eutrophication. One option could be to increase the influence of local groundwater, poorer in NO_3^- , by removing forests in the catchment area. Transformation of the current pine forests in the catchment area (which cover has steeply increased during the twentieth century (Swierstra 2008)) into the more open heathland vegetation of more than a century ago will lead to a reduced interception of precipitation by at least 20% (Fig. 7) and a reduced interception of aerial N and S deposition. This will increase the relative influence of local NO_3^- poor groundwater over the NO_3^- rich regional groundwater.

However, a more sustainable option is the reduction of NO_3^- leaching in the groundwater recharge areas. Measures to reduce the leaching of NO_3^- from agricultural soils might include the reduction of N applications to soils to levels slightly below those expected to give optimum yield, or enhance the N use efficiency and a range of counter measures (such as catch crops) (Kirchmann et al. 2002; Shibata et al. 2017). However, reducing NO_3^- leaching from agricultural lands provokes conflicts of interests and faces political and practical difficulties. Even though it may take up to a few decades before the results of a decreased NO_3^- leakage to the regional groundwater are noticeable in the discharge area, this is the only long-term sustainable solution to protect groundwater-fed mires in the future.

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References

- Aerts, R., Wallen, B., & Malmer, N. (1992). Growth-limiting nutrients in Sphagnum-dominated bogs subject to low and high atmospheric nitrogen supply. *Journal of Ecology*, *80*, 131–140.
- Aerts, R., Verhoeven, J. T. A., & Whigham, D. F. (1999). Plant-mediated controls on nutrient cycling in temperate fens and bogs. *Ecology*, *80*, 2170–2181.
- Baumann, R. A., Hooijboer, A. E. J., Vrijhoef, A., et al. (2012). Agricultural practice and water quality in the Netherlands in the period 1992–2010. *Environmental Monitoring and Assessment*, *102*, 225–241.
- Beaudoin, N., Saad, J. K., Van Laethem, C., et al. (2005). Nitrate leaching in intensive agriculture in northern France: effect of farming practices, soils and crop rotations. *Agriculture, Ecosystems and Environment*, *111*, 292–310.
- Bedford, B. L. (1996). The need to define hydrologic equivalence at the landscape scale for freshwater wetland mitigation. *Ecological Applications*, *6*, 57–68.
- Bobbink, R., & Hettelingh, J.-P. (eds.) (2011). *Review and revision of empirical critical loads and dose-response relationships: Proceedings of an expert workshop, Noordwijkerhout, 23–25 June 2010*. Rijksinstituut voor Volksgezondheid en Milieu RIVM. Utrecht, The Netherlands
- Bobbink, R., Hornung, M., & Roelofs, J. G. M. (1998). The effects of air-borne nitrogen pollutants on species diversity in natural and semi-natural European vegetation. *Journal of Ecology*, *86*, 717–738.
- Borken, W., & Matzner, E. (2004). Nitrate leaching in forest soils: an analysis of long-term monitoring sites in Germany. *Journal of Plant Nutrition and Soil Science*, *167*, 277–283.
- Böttcher, J., Strebel, O., Voerkelius, S., & Schmidt, H.-L. (1990). Using isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy aquifer. *Journal of Hydrology*, *114*, 413–424.
- Burow, K. R., Nolan, B. T., Rupert, M. G., & Dubrovsky, N. M. (2010). Nitrate in groundwater of the United States, 1991–2003. *Environmental Science & Technology*, *44*, 4988–4997.
- Camargo, J. A., & Alonso, Á. (2006). Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: a global assessment. *Environment International*, *32*, 831–849.
- Chaudhuri, S. K., Lack, J. G., & Coates, J. D. (2001). Biogenic magnetite formation through anaerobic biooxidation of Fe (II). *Applied and Environmental Microbiology*, *67*, 2844–2848.
- Cirkel, D. G., Van Beek, C., Witte, J. P. M., & Van der Zee, S. (2014). Sulphate reduction and calcite precipitation in

- relation to internal eutrophication of groundwater fed alkaline fens. *Biogeochemistry*, 117, 375–393.
- Cusell, C., Kooijman, A., & Lamers, L. P. M. (2014). Nitrogen or phosphorus limitation in rich fens? - edaphic differences explain contrasting results in vegetation development after fertilization. *Plant and Soil*, 384, (1-2) 153–168. <https://doi.org/10.1007/s11104-014-2193-7>.
- De Mars, H., & Wassen, M. J. (1999). Redox potentials in relation to water levels in different mire types in the Netherlands and Poland. *Plant Ecology*, 140, 41–51.
- De Mars, H., van der Weijden, B., van Dijk, G., Smolders, A.J.P., Grootjans, A.P., Wolejko, L. (2017) Towards threshold values for nutrients; petrifying springs in South Limburg in northwest European context. Report OBN2016/210-HE, VBNE, Driebergen. <https://doi.org/10.13140/RG.2.2.34563.09763>.
- Reddy, K. R., Delaune, R. D. (2008). Biogeochemistry of wetlands: science and applications. CRC, Taylor and Francis Group, Boca Raton
- van den Elzen, E., van den Berg, L. J. L., van der Weijden, B., et al. (2018). Effects of airborne ammonium and nitrate pollution strongly differ in peat bogs, but symbiotic nitrogen fixation remains unaffected. *Science of the Total Environment*, 610–611, 732–740. <https://doi.org/10.1016/j.scitotenv.2017.08.102>.
- Di, H. J., & Cameron, K. C. (2002). Nitrate leaching in temperate agroecosystems: sources, factors and mitigating strategies. *Nutrient Cycling in Agroecosystems*, 64, 237–256.
- van Diggelen, R., Middleton, B., Bakker, J., et al. (2006). Fens and floodplains of the temperate zone: Present status, threats, conservation and restoration. *Applied Vegetation Science*, 9, 157–162.
- van Dijk, G., Smolders, A. J. P., Fritz, C., et al. (2012). Ecologische gradiënten op de helling in de Brunsummerheide. *De Levende Natuur*, 113, 174–179.
- van Dijk, G., van Kleef, H. H., van Duinen, G.-J. A., et al. (2014). De rijke watermacrofauna van het hellingveen op de Brunsummerheide. *Natuurhistorisch Maandblad*, 103, 293–298.
- van Dijk, G., Smolders, A. J. P., Loeb, R., et al. (2015). Salinization of coastal freshwater wetlands; effects of constant versus fluctuating salinity on sediment biogeochemistry. *Biogeochemistry*, 126, (1–2) 71–84. <https://doi.org/10.1007/s10533-015-0140-1>.
- Dise, N. B., & Wright, R. F. (1995). Nitrogen leaching from European forests in relation to nitrogen deposition. *Forest Ecology and Management*, 71, 153–161.
- Dise, N.B., Matzner, E. & Forsius, M., (1998). Evaluation of organic horizon C: N ratio as an indicator of nitrate leaching in conifer forests across Europe. *Environmental Pollution*, 102 (1), 453–456.
- Dubelaar, C., & Menkovic, A. (1998). Coring information database TNO. <http://www.dinoloket.nl>. Accessed 20 June 2018.
- Ferreira, V., Gulis, V., & Graça, M. A. S. (2006). Whole-stream nitrate addition affects litter decomposition and associated fungi but not invertebrates. *Oecologia*, 149, 718–729.
- Fraters, B., Hooijboer, A. E. J., Vrijhoef, A., et al (2016) Landbouwpraktijk en waterkwaliteit in Nederland; toestand (2012-2014) en trend (1992-2014): resultaten van de monitoring voor de Nitraatrichtlijn. RIVM Rapport 2016-0076, Bilthoven, the Netherlands
- Fritz, C., van Dijk, G., Smolders, A. J. P., et al. (2012). Nutrient additions in pristine Patagonian Sphagnum bog vegetation: can phosphorus addition alleviate (the effects of) increased nitrogen loads. *Plant Biology*, 14(3), 491–499. <https://doi.org/10.1111/j.1438-8677.2011.00527.x>.
- Fritz, C., Lamers, L. P. M., Riaz, M., et al. (2014). Sphagnum mosses - masters of efficient N-uptake while avoiding intoxication. *PLoS ONE*, 9(1), e79991. <https://doi.org/10.1371/journal.pone.0079991>.
- Gorham, E. (1955). On some factors affecting the chemical composition of Swedish fresh waters. *Geochimica et Cosmochimica Acta*, 7, 129–150.
- Goulding, K. (2000). Nitrate leaching from arable and horticultural land. *Soil Use and Management*, 16, 145–151.
- Grootjans, A. P., Adema, E. B., Bleuten, W., et al. (2006). Hydrological landscape settings of base-rich fen mires and fen meadows: an overview. *Applied Vegetation Science*, 9, 175–184.
- Gundersen, P., Callesen, I., & De Vries, W. (1998). Nitrate leaching in forest ecosystems is related to forest floor C/N ratios. *Environmental Pollution*, 102(1), 403–407.
- Gundersen, P., Schmidt, I. K., & Raulund-Rasmussen, K. (2006). Leaching of nitrate from temperate forests effects of air pollution and forest management. *Environmental Reviews*, 14, 1–57.
- Haaijer, S. C. M., Lamers, L. P. M., Smolders, A. J. P., et al. (2007). Iron sulfide and pyrite as potential electron donors for microbial nitrate reduction in freshwater wetlands. *Geomicrobiology Journal*, 24, 391–401.
- Hartog, N., Griffioen, J., & van der Weijden, C. H. (2002). Distribution and reactivity of O₂-reducing components in sediments from a layered aquifer. *Environmental Science & Technology*, 36, 2338–2344.
- Hausmann, B., Knorr, K.-H., Schreck, K., et al. (2016). Consortia of low-abundance bacteria drive sulfate reduction-dependent degradation of fermentation products in peat soil microcosms. *The ISME Journal*, 10, 2365.
- Hautier, Y., Niklaus, P. A., & Hector, A. (2009). Competition for light causes plant biodiversity loss after eutrophication. *Science*, 324(80), 636–638.
- Holden, J., Chapman, P. J., & Labadz, J. C. (2004). Artificial drainage of peatlands: Hydrological and hydrochemical process and wetland restoration. *Progress in Physical Geography*, 28, 95–123.
- Howden, N. J. K., Burt, T. P., Worrall, F., et al. (2011). Nitrate pollution in intensively farmed regions: what are the prospects for sustaining high-quality groundwater? *Water Resources Research*, 47. W00L02. <https://doi.org/10.1029/2011WR010843>.
- Jauhiainen, J., Wallén, B., & Malmer, N. (1998). Potential NH₄⁺ and NO₃⁻ uptake in seven Sphagnum species. *The New Phytologist*, 138, 287–293.
- Joosten, H., & Clarke, D. (2002). *Wise use of mires and peatlands*. International Mire Conservation Group / International Peat Society, Saarijärvi, Finland
- Kirchmann, H., Johnston, A. E. J., & Bergström, L. F. (2002). Possibilities for reducing nitrate leaching from agricultural land. *AMBIO A Journal of the Human Environment*, 31, 404–408.
- van Kleef, H. H., van Duinen, G.-J. A., Verberk, W. C. E. P., et al. (2012). Moorland pools as refugia for endangered species

- characteristic of raised bog gradients. *Journal for Nature Conservation*, 20, 255–263.
- Kooijman, A. M. (2012). Poor rich fen mosses': Atmospheric N-deposition and P-eutrophication in base-rich fens. *Lindbergia*, 35, 42–52.
- Korom, S. F., Schuh, W. M., Tesfay, T., & Spencer, E. J. (2012). Aquifer denitrification and in situ mesocosms: modeling electron donor contributions and measuring rates. *Journal of Hydrology*, 432, 112–126.
- Lamers, L. P. M., Tomassen, H. B. M., & Roelofs, J. G. M. (1998). Sulfate-induced eutrophication and phytotoxicity in freshwater wetlands. *Environmental Science & Technology*, 32, 199–205. <https://doi.org/10.1021/es970362f>.
- Lamers, L. P. M., Bobbink, R., & Roelofs, J. G. M. (2000). Natural nitrogen filter fails in polluted raised bogs. *Global Change Biology*, 6, 583–586.
- Lamers, L. P. M., Ten Dolle, G. E., Van Den Berg, S. T. G., et al. (2001). Differential responses of freshwater wetland soils to sulphate pollution. *Biogeochemistry*, 55, 87–101.
- Lamers, L. P. M., Falla, S., Samborska, E. M., et al. (2002a). Factors controlling the extent of eutrophication and toxicity in sulfate-polluted freshwater wetlands. *Limnology and Oceanography*, 47, 585–593.
- Lamers, L. P. M., Smolders, A. J. P., & Roelofs, J. G. M. (2002b). The restoration of fens in the Netherlands. *Hydrobiologia*, 478, 107–130.
- Lamers, L. P. M., Van Diggelen, J. M. H., Op Den Camp, H. J. M., et al. (2012). Microbial transformations of nitrogen, sulfur, and iron dictate vegetation composition in wetlands: a review. *Frontiers in Microbiology*, 3, 156.
- Lamers, L. P. M., Govers, L. L., Janssen, I. C. J. M., et al. (2013). Sulfide as a soil phytotoxin—a review. *Frontiers in Plant Science*, 4, 268.
- Lamers, L. P. M., Vile, M. A., Grootjans, A. P., et al. (2015). Ecological restoration of rich fens in Europe and North America: from trial and error to an evidence-based approach. *Biological Reviews of the Cambridge Philosophical Society*, 90, 182–203. <https://doi.org/10.1111/brv.12102>.
- Lehmann, M. F., Reichert, P., Bernasconi, S. M., et al. (2003). Modelling nitrogen and oxygen isotope fractionation during denitrification in a lacustrine redox-transition zone. *Geochimica et Cosmochimica Acta*, 67, 2529–2542.
- Limpens, J., Berendse, F., & Klees, H. (2003). N deposition affects N availability in interstitial water, growth of Sphagnum and invasion of vascular plants in bog vegetation. *The New Phytologist*, 157, 339–347.
- Limpens, J., Berendse, F., & Klees, H. (2004). How phosphorus availability affects the impact of nitrogen deposition on Sphagnum and vascular plants in bogs. *Ecosystems*, 7, 793–804.
- Lucassen, E., Smolders, A. J. P., van der Salm, A. L., & Roelofs, J. G. M. (2004). High groundwater nitrate concentrations inhibit eutrophication of sulphate-rich freshwater wetlands. *Biogeochemistry*, 67, 249–267.
- MacDonald, J. A., Dise, N. B., Matzner, E., et al. (2002). Nitrogen input together with ecosystem nitrogen enrichment predict nitrate leaching from European forests. *Global Change Biology*, 8, 1028–1033.
- Madigan, M. T., & Jung, D. O. (2009). An overview of purple bacteria: systematics, physiology, and habitats. In *The purple phototrophic bacteria* (pp. 1–15). Springer.
- Martin, C., Aquilina, L., Gascuel-Oudou, C., et al. (2004). Seasonal and interannual variations of nitrate and chloride in stream waters related to spatial and temporal patterns of groundwater concentrations in agricultural catchments. *Hydrological Processes*, 18, 1237–1254.
- Nestler, A., Berglund, M., Accoe, F., et al. (2011). Isotopes for improved management of nitrate pollution in aqueous resources: review of surface water field studies. *Environmental Science and Pollution Research*, 18, 519–533.
- Pester, M., Knorr, K.-H., Friedrich, M. W., et al. (2012). Sulfate-reducing microorganisms in wetlands—fameless actors in carbon cycling and climate change. *Frontiers in Microbiology*, 3, 72.
- Postma, D., Boesen, C., Kristiansen, H., & Larsen, F. (1991). Nitrate reduction in an unconfined sandy aquifer: Water chemistry, reduction processes, and geochemical modeling. *Water Resources Research*, 27, 2027–2045.
- Rivett, M. O., Buss, S. R., Morgan, P., et al. (2008). Nitrate attenuation in groundwater: a review of biogeochemical controlling processes. *Water Research*, 42, 4215–4232.
- Rothe, A., & Mellert, K. H. (2004). Effects of forest management on nitrate concentrations in seepage water of forests in southern Bavaria, Germany. *Water, Air, and Soil Pollution*, 156, 337–355.
- Schaminée, J. H. J., Weeda, E. J., Westhoff, V. (1995). *De vegetatie van Nederland. Deel 2: Plantengemeenschappen van wateren, moerassen en natte heiden*. Opulus, Uppsala.
- Schwientek, M., Einsiedl, F., Stichter, W., et al. (2008). Evidence for denitrification regulated by pyrite oxidation in a heterogeneous porous groundwater system. *Chemical Geology*, 255, 60–67.
- Shibata, H., Galloway, J. N., Leach, A. M., et al. (2017). Nitrogen footprints: regional realities and options to reduce nitrogen loss to the environment. *Ambio*, 46, 129–142.
- Sigman, D. M., Altabet, M. A., Michener, R., et al. (1997). Natural abundance-level measurement of the nitrogen isotopic composition of oceanic nitrate: an adaptation of the ammonia diffusion method. *Marine Chemistry*, 57, 227–242.
- Smolders, A. J. P., Lamers, L. P. M., Lucassen, E. C. H. E. T., et al. (2006). Internal eutrophication: How it works and what to do about it - a review. *Chemistry and Ecology*, 22, 93–111. <https://doi.org/10.1080/02757540600579730>.
- Smolders, A. J. P., Lucassen, E. C., Bobbink, R., et al. (2010). How nitrate leaching from agricultural lands provokes phosphate eutrophication in groundwater fed wetlands: the sulphur bridge. *Biogeochemistry*, 98, 1–7.
- Sites, W., & Kraft, G. J. (2001). Nitrate and chloride loading to groundwater from an irrigated north-central US sand-plain vegetable field. *Journal of Environmental Quality*, 30, 1176–1184.
- Straub, K. L., Benz, M., Schink, B., & Widdel, F. (1996). Anaerobic, nitrate-dependent microbial oxidation of ferrous iron. *Applied and Environmental Microbiology*, 62, 1458–1460.
- Succow, M., & Joosten, H. (2001). *Landschaftsökologische Moorkunde*. Stuttgart: Schweizerbart Science Publishers.
- Swierstra, W. (2008). *Passende beoordeling Sigrano Groeve, 9T3160/R004/WSW/Maas*. Maastricht: Eindrapportage, RH-DHV.

- Thorburn, P. J., Biggs, J. S., Weier, K. L., & Keating, B. A. (2003). Nitrate in groundwaters of intensive agricultural areas in coastal northeastern Australia. *Agriculture, Ecosystems and Environment*, *94*, 49–58.
- Tomassen, H. B. M., Smolders, A. J. P., Limpens, J., et al. (2004). Expansion of invasive species on ombrotrophic bogs: desiccation or high N deposition? *Journal of Applied Ecology*, *41*, 139–150.
- Van Breemen, N. (1995). How Sphagnum bogs down other plants. *Trends in Ecology & Evolution*, *10*, 270–275.
- Verberk, W., Van Duinen, G. A., Brock, A. M. T., et al. (2006). Importance of landscape heterogeneity for the conservation of aquatic macroinvertebrate diversity in bog landscapes. *Journal for Nature Conservation*, *14*, 78–90.
- Verhoeven, J. T. A., Koerselman, W., & Meuleman, A. F. M. (1996). Nitrogen-or phosphorus-limited growth in herbaceous, wet vegetation: relations with atmospheric inputs and management regimes. *Trends in Ecology & Evolution*, *11*, 494–497.
- Wassen, M. J., Venterink, H. O., Lapshina, E. D., & Tanneberger, F. (2005). Endangered plants persist under phosphorus limitation. *Nature*, *437*, 547.
- Wheeler, B. D., & Proctor, M. C. F. (2000). Ecological gradients, subdivisions and terminology of north-west European mires. *Journal of Ecology*, *88*, 187–203.
- Zhang, Y.-C., Slomp, C. P., Broers, H. P., et al. (2009). Denitrification coupled to pyrite oxidation and changes in groundwater quality in a shallow sandy aquifer. *Geochimica et Cosmochimica Acta*, *73*, 6716–6726.
- Zhang, Y.-C., Slomp, C. P., Broers, H. P., et al. (2012). Isotopic and microbiological signatures of pyrite-driven denitrification in a sandy aquifer. *Chemical Geology*, *300*, 123–132.
- Zhu, B., van Dijk, G., Fritz, C., et al. (2012). Anaerobic oxidization of methane in a minerotrophic peatland: Enrichment of nitrite-dependent methane-oxidizing bacteria. *Applied and Environmental Microbiology*, *78*. <https://doi.org/10.1128/AEM.02102-12>.

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