SYNTHESIS AND EMERGING IDEAS

How nitrate leaching from agricultural lands provokes phosphate eutrophication in groundwater fed wetlands: the sulphur bridge

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Abstract Increased phosphorus availability may provoke serious eutrophication problems in wetlands. Strong evidence indicates that sulphate induced mobilization of phosphate (internal eutrophication) has been responsible for a strong decline of the biodiversity in wetlands during the last decades. It is currently underestimated, however, that the wide spread leaching of nitrate from agricultural lands can indirectly provoke strong internal phosphate eutrophication in wetlands, via its interference with sulphur and iron biogeochemistry in the subsoil. Nitrate can mobilize sulphate from geological pyrite deposits by the oxidation of FeSₓ in the aquifer, leading to a decrease of nitrate and an increase of groundwater sulphate concentrations. Furthermore nitrate immobilizes iron in the subsoil by oxidizing reduced (dissolved) iron. Increased sulphate concentrations may provoke strong phosphate eutrophication in wetlands fed directly or indirectly (via surface water) with groundwater as sulphate strongly interferes with iron phosphorus chemistry and stimulates anaerobic decomposition of organic matter. Management of wetlands should therefore be approached at a broader scale which includes the landscape-scale management of groundwater systems. Leaching of nitrate to the groundwater, for instance, should not only receive attention for its potential effects on drinking water quality but above all because of the resulting large scale mobilization of sulphate from geological pyrite deposits and the immobilization of ferrous iron.

Keywords Nitrate · Sulphate · Eutrophication · Phosphorus · Groundwater · Wetland

Introduction

To understand abiotic conditions of an individual wetland, understanding of landscape-scale hydrological and biogeochemical processes may be essential (e.g. Bedford, 1996). Nowadays, human activities have major impacts on landscape properties that control wetland hydrology and water chemistry. Obviously, hydrological measures may affect groundwater flows and thereby the hydrology of wetlands. Next, excessive fertilization by agricultural activities...
may strongly affect wetland ecosystems. Nitrogen emissions in the surroundings, for instance, are well known to affect oligotrophic systems (such as moorland pools and raised bogs) by locally causing strongly increased atmospheric deposition rates of nitrogen (e.g. Bobbink et al. 1998). Next, nitrate losses from agricultural lands are considerable and nowadays contaminate groundwater worldwide.

Although in eutrophication research nitrogen has received most attention, phosphorus availability may be a main determinant for biodiversity in groundwater fed wetlands (e.g. Wassen et al. 2005). In the soil, however, phosphorus (P) is—in contrast to the rather mobile nitrate (NO$_3^-$)—quite immobile and vertical movement of phosphorus is assumed to be strongly restricted because of a high phosphorus fixation capacity in mineral soils (Heckrath et al. 1995; Sims et al. 1998). Although recent research revealed that leaching of phosphorus can occur from heavily fertilized agricultural lands (McDowell and Sharpley 2004), on the whole soluble P losses of <1 kg P ha$^{-1}$ yr$^{-1}$ are more common (Sims et al. 1998) and phosphate leaching to deeper groundwater is merely seen as a distinct possibility over a period of decades, depending on the degree of phosphate saturation of the subsoil (Behrendt and Boekhold 2006).

Although currently movement of phosphorus via aquifers does not play an important role in the eutrophication of groundwater fed surface waters, we will show that landscape-scale hydrological and biogeochemical processes can lead to increased phosphorus eutrophication of wetlands in an unexpected way. In essence, nitrate pollution of the groundwater can provoke strong phosphate eutrophication in groundwater fed wetlands, by its interference with sulphur and iron biogeochemistry. Through oxidation of iron sulphides (including pyrite), for instance, nitrate may extend its biogeochemical reach into the groundwater much further than its mere physical presence. A schematic representation of this mechanism, which is elaborated in this article, is presented in Fig. 1.

**Nitrate pollution**

In the past century the intensification of agricultural activities and the application of artificial fertilizers have caused a severely disturbed nitrogen balance in agricultural areas as the input of nitrogen by far exceeds the yield in these systems (e.g. Goodchild 1998; Iversen et al. 1998; Kirchmann et al. 2002; Fig. 1). Under aerobic soil conditions ammonia and ammonium ions are microbially transformed (nitrified) to nitrate. The adverse effects of high atmospheric nitrogen deposition in Western Europe (e.g. Bobbink et al. 1998) have resulted in governmental measures to decrease the loss of volatile ammonia from agricultural soils. Low emission application techniques (including manure injection) substantially reduced the ammonia emission but as a result, the leaching of nitrate to the groundwater further increased (Iversen et al. 1998).

Next, non agricultural sources, such as leaking sewage systems and home gardens (Wakida and Lerner 2005) and forests (e.g. Rothe and Mellert 2004; Gundersen et al. 2006), which catch atmospheric nitrogen deposition, may also significantly contribute to increased groundwater nitrate concentrations. In most parts of Europe, anthropogenic nitrogen deposition has led to increased nitrate leaching from forests. Pine forests have a high leaf area which is also maintained throughout the year, which leads to higher rates of N deposition from the atmosphere to the forest floor and to higher concentrations of nitrate in drainage water compared with broadleaved forests (Rothe and Mellert 2004).

World-wide, nitrate has become one of the common groundwater contaminants (e.g. Kool 1988;
Postma et al. 1991; Nolan et al. 1997; Goodchild 1998; Iversen et al. 1998; Kirchmann et al. 2002; Senn and Hemond 2002; Thorburn et al. 2003; Broers et al. 2004; Surridge et al. 2007). Obviously nitrate pollution plays an important role in surface water eutrophication (Iversen et al. 1998; Kirchmann et al. 2002). However, it also poses a serious risk for drinking water quality as infants under six months of age are susceptible to nitrate poisoning (Comly 1945; Fan and Steinberg 1996). The European standard for the maximum concentrations of nitrate in potable water is 50 mg L\(^{-1}\) (806 μmol L\(^{-1}\)). At present, this concentration is often exceeded in potable waters extracted from surface water or aquifers recharged by water from areas of agricultural activity.

In the Netherlands, for instance, the phreatic and shallow groundwater below infiltrating agricultural lands nowadays typically contains median nitrate concentrations as high as 2000 μmol l\(^{-1}\), with minimum and maximum values of 900 and 3300 μmol l\(^{-1}\) (Broers et al. 2004). The increase in deeper aquifers, however, is generally much less pronounced than would be expected from model studies. This phenomenon has been attributed to the consumption of nitrate due to microbially mediated nitrate reduction processes in the sub-soil.

### Nitrate reduction

The reduction capacity of the aquifer soils will determine the extent to which reduction of nitrate may take place. Sedimentary organic matter (SOM) is a relevant electron donor in aquifers (reaction 1) (e.g. Hill et al. 2000; Hartog et al. 2002). The remaining reactivity of SOM in ground water systems may differ greatly, but the residual SOM tends to become more stable (less degradable) during oxidation (Cowie and Hedges 1994; Hartog et al. 2002, 2004). Sediment oxygen exposure time is probably a key factor determining the remaining reactivity of the SOM in aquifer sediments (Hartog et al. 2005). Generally, in deeper aquifers SOM is present in low concentrations (0.01–0.02 wt. %). Next, it is also characterized by the absence of more labile compounds such as cellulose, indicating that SOM has degraded to a considerable extent from its biomass precursors and has become relatively inert (Hartog et al. 2004).

\[
\begin{align*}
\text{NO}_3^- + 1.25\text{CH}_2\text{O} & \rightarrow 0.5\text{N}_2 + \text{HCO}_3^- + 0.25\text{H}_2\text{CO}_3 + 0.5\text{H}_2\text{O} \quad (1)
\end{align*}
\]

Being a powerful electron acceptor, nitrate can also be reduced by ferrous iron and may therefore importantly influence iron cycling in natural systems. Ferrous iron (Straub et al. 1996) and ferrous iron bearing carbonates (such as siderite) and sulphides (such as pyrite) (Postma et al. 1991; Aravena and Robertson 1998; Pauwels et al. 1998; Moncaster et al. 2000; Lucassen et al. 2004; Haaijer et al. 2006, 2007; Burgin and Hamilton 2008) turn out to be important electron donors for denitrification in aquifer soils (reaction 2, 3, 4; Fig. 1). These reactions are all catalyzed by microorganisms which, withstanding a wide variety of environmental conditions, thrive in shallow and deep aquifers (e.g. Pauwels et al. 1998; Haaijer et al. 2006, 2007; Burgin and Hamilton 2008).

\[
\begin{align*}
2\text{NO}_3^- + 10\text{Fe}^{2+} + 24\text{H}_2\text{O} & \rightarrow 1\text{N}_2 + 10\text{Fe(OH)}_3 + 18\text{H}^+ \quad (2)
\end{align*}
\]

\[
\begin{align*}
\text{NO}_3^- + 5\text{FeCO}_3 + 7\text{H}_2\text{O} & \rightarrow 0.5\text{N}_2 + 5\text{FeOOH} + 4\text{H}_2\text{CO}_3 + 2\text{H}_2\text{O} \quad (3)
\end{align*}
\]

\[
\begin{align*}
30\text{NO}_3^- + 10\text{FeS}_2 + 10\text{H}_2\text{O} & \rightarrow 20\text{SO}_4^{2-} + 10\text{FeOOH} + 15\text{N}_2 + 10\text{H}^+ \quad (4)
\end{align*}
\]

As long as groundwater nitrate concentrations are high, ferrous iron levels tend to remain low because nitrate acts as a redox buffer, preventing the reduction of iron(III)oxides (Lucassen et al. 2004; Smolders et al. 2006a). Additionally, ferrous iron may be microbially oxidized by nitrate (Straub et al. 1996; Senn and Hemond 2002). High nitrate loads therefore strongly decrease groundwater iron concentrations (Fig. 2). An advantage of this process might be that P entering aquifers along with nitrate, can be bound to oxidized iron in aquifers, potentially reducing the supply of P to wetlands via groundwater.

The chemoautolithotrophic oxidation of iron sulphide deposits by nitrate, frequently leads to a concomitant increase of groundwater sulphate concentrations (Postma et al. 1991, 1998; Aravena and Robertson 1998; Moncaster et al. 2000; Broers and Van der Grift 2004; Broers et al. 2004; Van Beek et al. 2006). Although the reduction of nitrate by organic matter is thermodynamically favourable, iron
sulphide oxidation appears to be kinetically favoured in deeper aquifers, probably because of the different microbiological availability of iron sulphides (including amorphous pyrite) and organic matter (Postma et al. 1991; Wriedt and Rode 2006).

As a result of nitrate leaching, groundwater chemistry has changed profoundly in many parts of the world and is nowadays characterized by lower iron and much higher sulphate concentrations (Postma et al. 1991; Aravena and Robertson 1998; Hoffmann et al. 1998; Pauwels et al. 1998; Moncaster et al. 2000; Molenat et al. 2002; Broers and Van der Grift 2004). In the Pleistocene regions of the Netherlands, for instance, increased agricultural activities have led to a strongly increased leaching of nitrate and to a concomitant increase of the groundwater sulphate concentrations. Near the pumping station of Vierlingsbeek (in the province of Limburg, the Netherlands), sulphate concentrations have increased from 400 to 1450 µmol L⁻¹ between the 1960s and 2000, of which atmospheric sulphur deposition only contributes ±200 µmol L⁻¹. In the same time span groundwater nitrate concentrations have increased from hardly detectable to ±500 µmol L⁻¹ (Van Beek et al. 2006). Estimations reveal that at present up to 70% of the sulphate present in groundwater in the Netherlands is derived from nitrate induced pyrite oxidation resulting in mean groundwater sulphate concentrations of 833 µmol L⁻¹ (Van Beek et al. 2006). Before the 1950’s, groundwater sulphate concentrations in these regions were typically lower than 200 µmol L⁻¹ (STOM 1983).

Internal eutrophication

Under anaerobic conditions, the availability of alternative electron acceptors strongly affects the breakdown of organic matter. In addition to the availability of electron acceptors, (anaerobic) decomposition is obviously strongly regulated by the availability of degradable organic matter (Drever 1997). In wetlands the availability of reactive SOM will be much higher compared to (deeper) aquifers due to the constant input of plant litter. This means that nitrate and sulphate, supplied by groundwater enriched with these compounds, can strongly stimulate the decomposition of organic matter (e.g. Roden and Edmonds 1997; Holmer and Storkholm 2001; Smolders et al. 2006a).

Next, the increased input of sulphate and decreased input of iron in groundwater fed (semi-)aquatic ecosystems may also cause phosphate release due to the fact that sulphide (produced by sulphate reduction) interferes with the iron-phosphorus cycle (Fig. 1). The main product of sulphate reduction is dissolved sulphide. Sulphide may react with dissolved reduced iron and particulate iron (hydr)oxides. The products of the reaction between sulphide and iron are highly insoluble iron sulphide minerals while phosphate adsorbed to the iron (hydr)oxides or present as iron phosphates becomes mobilized (Sperber 1958; Caraco et al. 1989; Søndergaard et al. 1993; Roden and Edmonds 1997; Smolders et al. 2001; Smolders et al. 2006a).

Prolonged high sulphate loads to such sediments will ultimately result in sediments in which up to 80% of the iron can be bound to reduced sulphur (FeSₓ) (Smolders et al. 1995). As a consequence, the capacity of the sediment to retain P will greatly decrease (FeSₓ has far fewer sorption sites for P than have iron(hydr)oxides), which may result in a high mobility of P in the soils and thus in a strong eutrophication of such systems (Caraco et al. 1989; Søndergaard et al. 1993; Roden and Edmonds 1997;
Lamers et al. 1998; Wetzel 2001; Lamers et al. 2002; Smolders et al. 2006a). This may be enhanced by the decreased input of ferrous iron via the groundwater due to nitrate induced immobilization of iron. If sulphate reduction continues, toxic concentrations of hydrogen sulphide may accumulate in the sediment pore water and cause serious problems for rooted aquatic macrophytes by inducing sulphide toxicity and iron deficiency (Smolders and Roelofs 1996; Lamers et al. 2002; Smolders et al. 2006a). In extremely dry years desiccation of such sediments can lead to a strong acidification and mobilization of toxic metals, due to the oxidation of accumulated reduced sulphur to sulphuric acid (Lucassen et al. 2002; Smolders et al. 2006b).

In general, the classic iron cycle can explain the actual release of P from the sediment. In the oxygenated boundary layer between sediment and water layer, dissolved iron becomes oxidized and phosphate is effectively bound by iron(III)(hydr)oxides (Wetzel 2001; Smolders et al. 2006a). This mechanism explains the frequently found positive relation between the phosphate release to the water layer and the dissolved-P: dissolved-Fe ratios in sediment pore water (Caraco et al. 1989; Wetzel 2001; Smolders et al. 2001). Under sulphur-rich reducing conditions, however, this mechanism will no longer function as all dissolved ferrous iron is precipitated with sulphide as FeSₙ (Caraco et al. 1989; Smolders and Roelofs 1996; Wetzel 2001; Smolders et al. 2001). Furthermore, dissolved sulphide (and other reduced compounds) consume oxygen in the top sediment layer, thus decreasing the thickness of the oxidized boundary layer. This may greatly boost the release of dissolved phosphate from the sediment. Increased methane production rates under highly reductive conditions may further stimulate P release by ebullition, causing mixing of anaerobic phosphate rich sediment pore water with surface water, especially in organic sediments (Søndergaard et al. 1993; Wetzel 2001).

Geurts et al. (2008) recorded the aquatic vegetation and collected surface water, sediment pore water and sediment samples in 145 fen waters in the Netherlands, Ireland and Poland. In halve of these waters they found a decreased biodiversity and increased phosphate concentrations in the water layer which appeared to be SO₄²⁻-induced and especially occurred below certain threshold values for total sediment Fe:P (10 mol mol⁻¹). This suggests that especially sediments with a relatively low iron content and/or a high phosphorus content are prone to sulphate induced eutrophication.

**Conclusion**

Leaching of nitrate to the groundwater should receive much more attention for its potentially large scale mobilization of sulphate from geological pyrite deposits and the immobilization of ferrous iron. As nitrate is concomitantly stripped (denitrified to nitrogen gas and dinitrogen gas) from the groundwater, pyrite oxidation has been wrongfully promoted to be beneficial since it was assumed to act as a natural cleaning mechanism. It is still underestimated that during the last decades, sulphate induced eutrophication and sulphide toxicity have been responsible for the strong decline of the biodiversity in wetlands which are directly or indirectly (via surface water) fed by sulphate rich groundwater (e.g. Søndergaard et al. 1993; Roden and Edmonds 1997; Lamers et al. 2002; Smolders et al. 2006a).

Under low nutrient availability, plants will compete mainly for nutrients (Grime 1979) while under high nutrient availability, competition for light becomes the main factor, resulting in the dominance of a few high-yield species. Therefore, low concentrations of nutrients, P in particular, seem to be a prerequisite for long-term co-existence of plant species. Being a key nutrient limiting autotrophic growth in most wetlands, phosphorus availability has been proposed to be a main determinant for biodiversity (e.g. Janssens et al. 1998; Wassen et al. 2005) and increased phosphorus availability indeed provokes serious eutrophication problems in many wetlands. However, the reduction of nitrogen loads to the groundwater should be a major objective to tackle this problem. In this respect, measures to reduce the leaching of nitrate from agricultural soils are urgently needed. Such measures might include environmental indexing of fields, reduction of nitrogen gifts to soils to levels slightly below those expected to give optimum yield and a range of counter measures (such as catch crops) (see Kirchmann et al. 2002).

At present, nitrate pollution of groundwater might be one of the most serious environmental threats for wetlands. Understanding the spatial scales at which wetland processes operate, including hydrological and...
biogeochemical elements, are of utmost importance. Management of wetlands should therefore be approached at a broader scale which includes the landscape-scale management of groundwater systems, including aquifer geology. Knowledge on aquifer geology is highly important in order to be able to estimate the potential effects of nitrate leaching in different parts of the world. For instance, it is important to estimate how long it will take to oxidize the reduced sulphur present in the subsoil, given a certain nitrate load.

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