Multi-level effects of sulphur–iron interactions in freshwater wetlands in The Netherlands

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Abstract

Although sulphur deposition rates in Europe have considerably decreased over the last decades, sulphate concentrations in freshwater wetlands are still high, as a result of drainage, nitrate pollution, and increased sulphur loads in rivers. High sulphur fluxes may cause sulphide toxicity and eutrophication, and strongly interfere with the biogeochemical cycling of iron and phosphorus. In the present study the ecotoxicological interactions between sulphur, phosphate, iron, and trace metals in freshwater wetlands are reviewed.

Keywords: Ecotoxicology, Iron, Sulphur pollution, Toxicity, Wetlands

1. Introduction

Within the stimulation program system-oriented ecotoxicological research the present study focused, amongst others, on the ecotoxicological interactions between metals, in particular iron, and sulphide. These interactions can be rather complex, since many factors may influence the bioavailability, and therefore the toxicity, of natural toxicants such as iron and sulphide. The main factors involved and their interactions, which were assessed in the present study, are presented in Fig. 1 and will be discussed in the following sections.

2. Sulphur pollution in freshwater wetlands

Pollution of wetlands poses a serious threat to wetland ecosystem structure and functioning (Mitsch and Gosselink, 2000; Lamers et al., 2002). Although sulphur pollution of minerotrophic freshwater wetlands has received less international attention than that of other ecosystem types, it can lead to severe deterioration of these wetlands too (Holmer and Storkholm, 2001). Sulphur pollution has various origins, the main sources being agriculture (fertilizers), atmospheric deposition as a result of combustion of fossil fuels and industrial waste, and acid mine drainage (Schlesinger, 1997).

In the present study the latter (acid mine drainage) is not involved.

Although the atmospheric deposition of sulphur compounds in Europe has strongly decreased over the last decades, sulphate concentrations in freshwater wetlands have increased from 200 to 500 µmol/L and even higher as a result of input of sulphate-enriched river water and mobilization from recent or geological pyrite deposits due to drainage (Lamers et al., 2002; Zak et al., 2006). There are three major effects of sulphur pollution: acidification as a result of atmospheric SOx deposition and the combined effect of desiccation and FeSx oxidation (Schlesinger, 1997; Lamers et al., 2002), increased mobilization of phosphate from within the system, without external input (Patrick and Khalid, 1974; Boström et al., 1982; Roelofs, 1991; Lamers et al., 1998; Smolders et al., 2006), and sulphide toxicity.

In addition to the above sources of sulphur pollution, there is another possible source, which has often been overlooked. When nitrate-polluted groundwater passes through soil layers...
that are rich in iron sulphides, nitrate can be used in the chemolithoautotrophic oxidation of iron sulphides (Brunet Garcia-Gil, 1996; Molénat et al., 2001; Haaijer et al., 2006; Van der Welle, 2007). This may lead to the redistribution of sulphur along the hydrological pathway, which may lead to the (negative) effects described above downstream. Especially in freshwater wetlands with marine sediments in the subsoil, (often containing high concentrations of iron–sulphides) situated in heavily fertilized agricultural areas, this process may be the main source of sulphate.

3. Sulphide toxicity

As mentioned above, sulphur pollution can lead to severe sulphide toxicity, especially in peatlands, because oxygen supply is low as a result of wet conditions and decomposition. Sulphide is a naturally occurring compound that can be toxic to several species at levels as low as 10 µmol/L, while concentrations up to 3000 µmol/L have been measured in Dutch freshwater wetlands (Geurts et al., 2004). Sulphide is in particular toxic to aquatic macrofauna (Wang and Chapman, 1999), and aquatic macrophytes (Koch et al., 1990; Smolders et al., 1995a; Armstrong et al., 1996; Lamers et al., 1998; Van der Welle et al., 2006).

One way for plants to deal with sulphide is by detoxification. Plants have the ability to leak oxygen from their roots, which oxidizes the sulphide in the rhizosphere and thus detoxifies it (Van der Welle et al., 2007a). However, when plants are growing in a permanently anaerobic environment, this mechanism may not be very useful, since the sediment consumes oxygen faster along the roots than the plant can supply it to the apical parts, where growth and nutrient uptake predominantly take place. Many plant species growing in anaerobic environments therefore have adaptations to prevent oxygen loss along most of their roots (Armstrong, 1979; Armstrong et al., 1996; Končalová, 1990; Colmer et al., 1998; Connell et al., 1999). Van der Welle et al. (2007a) describe how the difference in radial oxygen loss between Caltha palustris and Juncus effusus results in large differences in sulphide concentrations in the porewater, despite equal addition of sulphide and overall equal conditions.

4. Iron–sulphur interactions and their effects on wetland plants

In addition to biological processes, there are also chemical processes that can result in the detoxification of sulphides. Sulphide toxicity can be regulated by the formation of highly insoluble metal sulphides like iron sulphides (FeS, FeS2 or pyrite) or metal–sulphide complexes (Chapman et al., 1998; Huerta-Díaz et al., 1998; Morse and Luther, 1999; Wang and Chapman 1999; Van der Welle et al., 2006, 2007a,b), thereby reducing the toxicity of both sulphide and metals. In areas where iron-rich groundwater is discharged, free sulphide concentrations are usually very low, as a result of iron–sulphide precipitation.

Although it seems a one-way beneficial process, the mutual detoxification of iron and sulphide by the formation of iron sulphides is a delicate equilibrium (Van der Welle et al., 2007a,b), since iron itself can be toxic as well (Wheeler et al., 1985; Snowden and Wheeler, 1993; Lucassen et al., 2000; Kamal et al., 2004). Fig. 2 shows the interacting effects of iron and sulphide on the growth of the common wetland species C. palustris. From this figure it appears that the sulphide toxicity may shift to iron toxicity when a surplus of iron is supplied. Iron toxicity causes all kinds of unfavourable effects in aquatic macrophytes, such as slower growth, smaller leaves, leaf die-back, formation of necrotic leaf spots, root flaccidity and the formation of root precipitates (Snowden and Wheeler, 1993; Lucassen et al., 2000). Van der Welle et al. (2006, 2007a,b) showed that in a gradient of both iron and sulphide, plant growth is hampered by both substances and is optimal when there is just enough iron present to detoxify all of the sulphide (Fig. 2). This indicates that iron is much more toxic than had previously been thought. Iron addition is experimentally used to combat eutrophication and sulphide toxicity (Boers et al., 1994; Smolders et al., 1995b; Geurts, unpublished data). Studies by Van der Welle et al. (2007a,b) indicate that this measure should be used with caution, since iron addition may not only have beneficial effects.

In addition to direct toxicity, iron can have indirect effects on plant growth, as iron binds to phosphate, which may lead to lower P availability (Boers et al., 1994; Smolders et al., 1995b). In phosphate-rich systems, high iron input can thus prevent eutrophication, which is probably the reason why the most
iron-rich nature reserves in heavily fertilized areas generally have the best developed vegetation (Lamers et al., 2006).

Since both iron and sulphide may be toxic to wetland plants, increased concentrations of either compound may lead to a shift in vegetation composition due to differing tolerance of plant species. In addition, a recent study by Van der Welle et al. (2007b) showed that there may be another, indirect effect of iron and sulphide on vegetation composition. Due to sulphur–iron interactions, interspecific competition between the two aquatic macrophytes Elodea nuttallii and Stratiotes aloides was altered, favouring the first species at increased iron availability. As a result, growth of S. aloides was strongly reduced at iron concentrations which should not be toxic to the species, as they were found growing in the field under similar conditions at much higher iron concentrations (De Lyon and Roelofs, 1986; Smolders et al., 1996).

Finally, high sulphide concentrations may lead to sulphide-induced iron deficiency. Since iron preferentially binds to sulphide, high sulphide loads under low iron conditions will lead to depletion. Iron is an essential nutrient for plant growth, which is, inter alia, used for the synthesis of chlorophyll and as a metal component in redox reactions in enzymes or as a bridging element between enzymes and substrate (Marshner, 1995). Strong immobilization of iron by iron–sulphide precipitation may lead to iron deficiency in wetland plants (Smolders et al., 1996; Lucassen et al., 2004), which has been found to decrease photosynthetic activity even before chlorophyll concentrations showed a significant decrease (Van der Welle et al., 2007a).

5. Implications for the conservation of polluted wetlands

Studies have made it clear that sulphur pollution poses a serious threat to freshwater wetlands, especially when they are poor in iron (Roelofs, 1991; Smolders et al., 1995a; Lamers et al., 1998; Holmer and Storkholm, 2001; Zak et al., 2006; Van der Welle et al., 2007b). Although sulphide can immobilize iron and other metals, this potentially beneficial effect cannot counteract the negative effects of the component itself, such as toxicity and eutrophication.

In addition, it has been made clear that iron addition is not an easy way to combat eutrophication and sulphide toxicity. Iron addition can have serious implications when not carefully carried out and may lead to unwanted shifts in vegetation composition as a result of toxicity and altered interspecific relations. In addition, iron consumption may be too high for a durable effect, especially in those wetlands receiving high fluxes of sulphate and/or phosphate in which the effect was shown too last only for one season (Boers et al., 1994; Smolders et al., 1995b). Therefore, sulphate pollution in freshwater wetlands should be tackled at the source by optimizing hydrological conditions and, if possible, by legislation.

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