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Changes in pore water chemistry of desiccating freshwater sediments with different sulphur contents

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Abstract

Especially in dry summers, such as 2003 in Europe, wetlands may become subject to desiccation and oxidation processes may affect sediment top layers. In this paper, we present the results of a study in which the development of the pore water chemistry (major ions, nitrate, ammonium, phosphate and some metals) was monitored during experimental desiccation of previously anaerobic freshwater sediments. Three sediments with different concentrations of oxidizable sulphur were compared. Sediments appeared to respond very differently to prolonged oxidation due to desiccation. It can be concluded that oxidizable sulphur pools play an important role in freshwater wetlands. Water level fluctuations may have beneficial effects in sediments of which the buffer capacity is large enough to prevent acidification as a result of oxidation of reduced sulphur compounds. Oxidation of such sediments will result in net nitrogen losses and a decrease of the phosphate availability. Desiccation of sediments with high oxidizable sulphur contents, however, might lead to reactions that resemble those observed in acid sulphate soils. Extreme acidification might occur resulting in the mobilisation of high concentrations of potentially toxic metals such as aluminium and zinc. Dissolution of oxidized iron at very low pH will also result in the release of previously adsorbed phosphate. In freshwater systems, high concentrations of reduced sulphur will especially accumulate in reductive and iron-rich sediments which are fed by sulphate-enriched groundwater and which almost never fall dry.

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1. Introduction

In anaerobic/reductive sediments, sulphate reduction results in the formation of sulphide which may be reoxidized, escape from the sediment as gaseous H_2S or be bound in the sediment as insoluble metal sulphides. Usually iron is quantitatively the most important metal by which sulphide is bound (Drever, 1997). Therefore, the concentration of sulphur accumulating in reductive sediments depends on the concentration of sulphur supplied and the concentration of iron available to bind sulphide. High sulphur accumulation rates are found in sediments which are influenced by

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water rich in both sulphate and iron (Postma, 1982; Dellwig et al., 2001; Lucasssen et al., 2002). In coastal regions, for instance, sediments commonly contain high concentration of FeS_x as seawater provides large concentrations of sulphate while terrestrial sources supply iron (Dellwig et al., 2001).

In general, sulphate levels tend to be much lower in freshwater environments. However, atmospheric deposition, contaminated surface water and groundwater (seepage) may form important sources of sulphur (Postma, 1982; Schuurkes, 1987; Ritsema et al., 1992; Roelofs, 1991; Smolders and Roelofs, 1993; Dellwig et al., 2001; Lucassen et al., 2004a). Atmospheric sulphate deposition rates have been very high in the second half of the last century (Roelofs, 1983, 1986; Schuurkes, 1987). In large parts of The Netherlands, ground water sulphate concentrations have shown a strong increase over the last decades. This increase can be explained by the oxidation of geological pyrite-rich formations in the subsoil owing to decreased groundwater levels and increased nitrate losses from agricultural lands and forests (Stuyfzand, 1993; Lamers et al., 1998, 2002; Lucassen et al., 2004a,b). In pyrite containing subsoil, denitrifying bacteria use nitrate to oxidize sulphides to sulphate (Stuyfzand, 1993; Aravena and Robertson, 1998). In many European countries, nitrate concentrations in groundwater have increased strongly due to losses from agricultural lands (Ruano Criado, 1996; Iversen et al., 1998). Lucasssen et al. (2002) showed that high concentrations of pyrite may accumulate in sediments of wetlands that are fed by sulphate and iron enriched groundwater.

In dry summers, such as 2003 in Europe, wetlands may become subject to desiccation and oxidation processes may affect sediment top layers. In general, temporary oxidation of reductive sediments might have beneficial effects. Oxidation of reduced iron, for instance, may increase the phosphate-binding capacity of sediments (Smolders et al., 1995a,b; Golez and Kyuma, 1997; Lamers et al., 1998; Lucassen et al., 2005). Next, oxidation of the top layer may stimulate nitrogen losses from the sediment by so-called coupled nitrification/denitrification reactions (D'Angelo and Reddy, 1993; Risgaard-Petersen and Jensen, 1997). On the other hand, if reduced sulphur concentrations are high, oxidation reactions may lead to a strong acidification of sediments and to a concomitant strong increase of (heavy) metal concentrations (Van Breemen, 1973; Harmsen and Van Breemen, 1975; Banks et al., 1997; Ludwig and Balkenhol, 2001; Lucasssen et al., 2002). After re-wetting of such sediments, the water layer may become acidic and remain so for a considerable time (Lucasssen et al., 2002). In such cases, metal toxicity may provoke lethal effects in fish and other fauna elements (Leuven, 1988).

In this paper, we present the results of a study in which the development of the pore water chemistry (major ions, nitrate, ammonium, phosphate and some metals) was monitored during experimental desiccation of previously anaerobic freshwater sediments. Three sediments with different concentrations of sulphur were compared.

2. Material and methods

2.1. Sediment types

Sediments were collected at three locations in The Netherlands. These locations were selected primarily for their total sulphur content of the sediment.

One sediment with total sulphur content of 0.002% consisted of sand and was collected from a location called "De Berendonck" (5°46′40″ E, 51°48′44″). The Berendonck is a large open water which has been created after sand extraction and is not influenced by sulphate-rich seepage. Another sediment consisted of clay from an ox-bow lake in the former flood plain of the river Waal located in the Ooypolder ("Oude Waal" 5°53′35″ E, 51°51′16″ N). This sediment had a total sulphur content of 0.033%. Finally a silty/loam, sulphur-rich sediment with a total sulphur content of 0.272%, was collected from a ditch in "De Bruuk" (5°57′45″ E, 51°47′10″ N). "De Bruuk" is a small nature reserve near the village of Groesbeek, which receives sulphur and iron-rich seepage (Smolders et al., 1995a,b).

2.2. Total oxidizable sulphur

Total oxidizable sulphur was determined by mixing 50 ml of fresh sediment with 450 ml of demineralised water and flushing the sediment in a 1-L cylinder with compressed air or with compressed nitrogen gas for 30 days. The dissolved sulphur concentrations were determined in filtered (0.45 μm) water at the end of