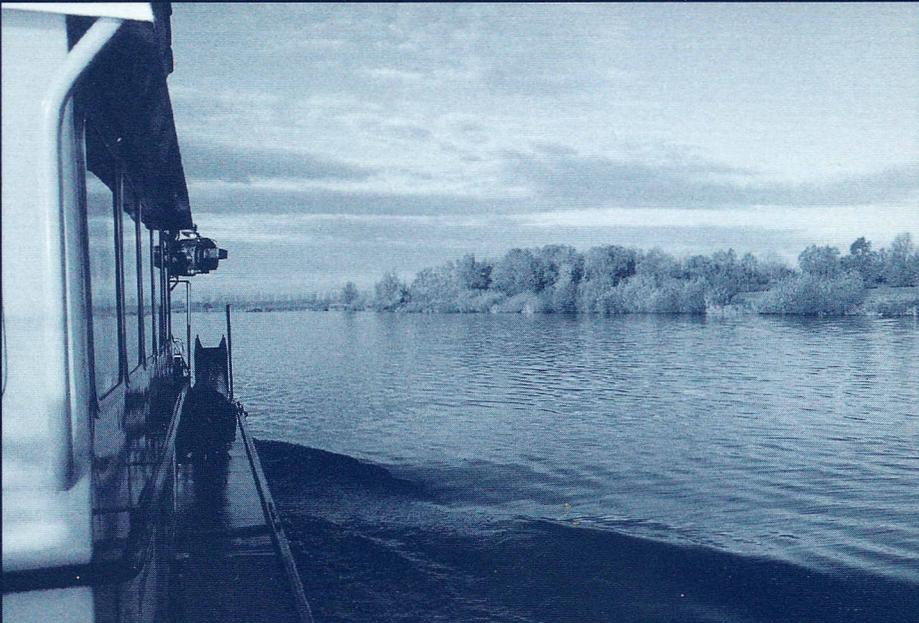


GEOLOGICA ULTRAIECTINA

Mededelingen van de
Faculteit Aardwetenschappen
Universiteit Utrecht

No. 163

**Geochemical behaviour of heavy metals
in a sedimentation area
of the rivers Rhine and Meuse**



Gerard van den Berg

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ISBN 90-5744-021-0

**Geochemical behaviour of heavy metals
in a sedimentation area
of the rivers Rhine and Meuse**

**Geochemisch gedrag van zware metalen in een
sedimentatiegebied van de rivieren Rijn en Maas**

(met een samenvatting in het Nederlands)

Proefschrift

ter verkrijging van de graad van doctor
aan de Universiteit Utrecht
op gezag van de Rector Magnificus, Prof. Dr. H.O. Voorma
ingevolge het besluit van het College voor Promoties
in het openbaar te verdedigen
op maandag 26 oktober 1998 des middags te 2.30 uur

door

Geert Arend van den Berg
geboren op 5 maart 1968, te Heerenveen

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The research described in this thesis was carried out at the Department of Geochemistry (Utrecht University). This study was partly supported by the Ministry of Transport, Public Works and Water Management, Directorate-General for Public Works and Water Management, Directorate IJsselmeergebied and the Ministry of Transport, Public Works and Water Management, Institute for Inland Water Management and Waste Water Treatment (RIZA).

Ter nagedachtenis aan mijn vader

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Summary

The Biesbosch, situated in the delta of the rivers Rhine and Meuse in The Netherlands, is considered an important freshwater tidal area, although the tidal amplitude has decreased as a result of the implementation of the Delta Works. Due to the decrease in flow rates since the closure of the area by sluices in 1970, the Biesbosch has developed into a semi-stagnant sedimentary basin, in which deposition of fine-grained highly contaminated calcareous sediments takes place. Dutch environmental policy aims at nature development in this area by increasing the number and area of wetlands to enlarge the intertidal area. To achieve a sustainable situation in which environmental and ecological factors are also considered, the long-term behaviour of contaminants and their ecotoxicological effects should be well recognised (*Chapter 1*). The behaviour and the bioavailability of heavy metals in (temporarily) waterlogged soils and sediments is strongly coupled to the variation and intensity of redox processes. The purpose of this study was to describe the redox chemistry and mobility of heavy metals of sediments and hydric soils in the Biesbosch, as well as their emission to the groundwater and surface water. The results of this study are also used to evaluate environmental quality criteria to assess potential metal toxicity of sediments.

Decalcification is considered as a potential chemical time bomb in contaminated soils, because loss of pH buffering results in release of toxic heavy metals (*Chapter 2*). Using fuzzy c-means clustering, six types of hydric soils were distinguished in the Biesbosch. Geochemical and hydrological analyses indicate that soils subject to periodic waterlogged conditions show the highest degree of decalcification. Oxidation of previously formed iron sulphides during periods of aeration, as well as increased CO₂-pressure in the soil during periods of saturation are the major contributors to decalcification of the organic-rich topsoil. In the studied hydric soils, decalcification rates on the order of 3 mg CaCO₃ per gram dry soil per year may be explained by these two processes. However, at only few locations in the Biesbosch complete decalcification has taken place and pH of the topsoil has dropped below 6.5. Considering the high heavy metal content of these wetlands, a further pH decrease is expected to result in a significant increase in the mobility of heavy metals.

Summary

Temporarily increased pore-water concentrations are also associated with fluctuations in groundwater level or periodic inundations. During a nine month period, January to September 1994, pore water was sampled with an *in situ* sampling technique (*Chapter 3*). Precipitation and dissolution of labile sulphides may account for fluctuations in pore-water concentrations of heavy metals. The presence of authigenic Zn- and Fe(II)-(mono)sulphides during periods of water saturation of the soil, i.e. reducing conditions, was demonstrated by electron microprobe analyses. Because these sulphide precipitates are strongly associated with root remnants, it is concluded that fresh highly degradable organic material is probably an important intermediary in the sulphur cycling and, thus, in the behaviour of heavy metals in hydric soils. Oxidation of these labile sulphides may explain the increased Zn concentrations in the pore water during periods with low groundwater levels. Additionally, temporary mobilisation of Cu and Cd can be attributed to degradation of their host organic matter during periods with a high degree of biodegradation.

During two sampling campaigns, in November 1995 and June 1996, sediment cores were taken on four permanently submerged locations in tidal channels. Pore-water characteristics of these sediments provide insight into geochemical processes taking place in organic-rich freshwater sediments. During summer, pore-water profiles of redox-sensitive ions are generally characterised by steeper gradients at the sediment-water interface than during winter (*Chapter 4*). This temporal variation in pore-water chemistry reflects environmental and intrinsic changes of the sediment. These are related to a relatively large difference in temperature, in combination with increased supply of degradable organic matter, microbiological activity in the sediment, diffusion of solutes, mixing and reaction rates.

The pore-water concentration profiles of the sediment cores sampled in June 1996, were interpreted using a steady state one-dimensional reaction transport model that explicitly accounts for the organic matter degradation pathways and secondary redox reactions (*Chapter 5*). Measured pore-water profiles can be explained by the degradation of organic matter and the internal cycling of redox species. Methanogenesis is the major overall pathway for decomposition of organic matter in the sediments studied. The other oxic (oxic respiration), suboxic (denitrification, Mn(IV) and Fe(III) reduction) and anoxic (sulphate reduction) organic matter degradation pathways are limited to the top 3 centimetres of the sediments. Differences in profiles of redox-sensitive ions among the four locations are explained by large differences in the depth-integrated rates of organic matter degradation.

Summary

Solid-phase and pore-water profiles of heavy metals are discussed in *Chapter 6*. Supersaturation of the anoxic pore waters with respect to discrete heavy metal sulphides is explained by heterogeneity of the sediment and complexation with dissolved organic compounds. Distinct peaks in dissolved heavy metal concentrations in the pore water, measured immediately below the sediment-water interface, are attributed to degradation of organic matter and oxidation of sulphides. The resulting concentration gradients in the pore water indicate that diffusive upward fluxes of heavy metals from the sediment contribute to concentrations in the surface water. However, significant effects may be confined to locations characterised by slow displacement of the surface water. In addition, remobilisation of heavy metals as dissolved species to the surface water is negligible compared to the particulate-bound flux to the sediment.

Pore-water concentrations of heavy metals are strongly decreased by the presence of sulphides. In *Chapter 7*, it is shown that under oxic and suboxic conditions the amount of acid-volatile sulphide (AVS) may be too low to potentially bind all reactive metals, measured as simultaneously extracted metals (SEM). SEM/AVS ratios generally decrease with depth going from ratios higher than one in the surface sediments to ratios less than one at greater depths. Because the contaminated sediments studied contain relatively low levels of AVS, other solid phases, e.g. organic matter and oxyhydroxides, are expected to scavenge reactive heavy metals as well. The large vertical variation in AVS levels is attributed to sulphide oxidation in the (sub)oxic layer and sulphate reduction in the underlying anoxic sediment. An important implication of these findings is that SEM/AVS ratios in mixed homogenised sediment samples are generally not suited for the assessment of potential metal toxicity of sediments.

The effects of redox variation on the mobility of heavy metals were studied. It was demonstrated that fluctuating groundwater levels and periodic flooding significantly influence the redox chemistry of soils. On a smaller scale, changes in the intensity of redox processes were shown in permanently submerged sediments. This fluctuation in pore-water concentrations in sediments and hydric soils demonstrates that in dynamic depositional environments it is necessary to account for non-steady state to determine the exchange between sediments and groundwater or surface water.

Chapter 1

Development of the Biesbosch as a freshwater tidal area

Protection against flooding and interests of agriculture and industry originally were the primary focus of water management in The Netherlands. In the Third Policy Document on Water Management (Anonymous, 1990¹), integrated water management was introduced as a new strategy. Integrated water management intends to achieve a sustainable situation in which environmental and ecological factors are considered as well. In the Nature Policy Plan (Anonymous, 1990²) the Biesbosch, situated in the delta of the rivers Rhine and Meuse, is indicated as a core area in the network of important ecosystems in The Netherlands. Although most soils and sediments are characterised by high levels of contaminants, the Biesbosch may develop as a freshwater tidal area of national and international importance. This chapter provides a framework for the research described in this thesis. An overview is given of the historical and present development of the Biesbosch. Nature development goals are discussed in relation to the supply and deposition of contaminated sediments.

Geology and landscape development

The sediments in the Biesbosch are relatively young. The thickness of the Holocene sediment layer ranges approximately from 8 to 12 m and typically increases to the North. The Holocene sediments are subdivided in the Gorkum layer (mainly clayey humic perimarine deposits), the Dunkerque layer (mainly sandy marine deposits), and the Tiel layer (mainly sandy perimarine deposits). These three layers are part of the Westland formation. Thin peaty horizons (Hollandveen) and dark coloured organic-rich horizons within the Westland formation indicate transgression periods.

Chapter 1

The area has been subject to many floods in recent history. In its present shape, the Biesbosch was formed as a result of the 'St. Elizabeth's' flood (1421 AD). The breakthrough of the dikes surrounding the former Groote Waard led to the development of a large inland sea that was subject to tidal influence. New sediments were imported by the rivers Rhine and Meuse, mainly from the north-east.

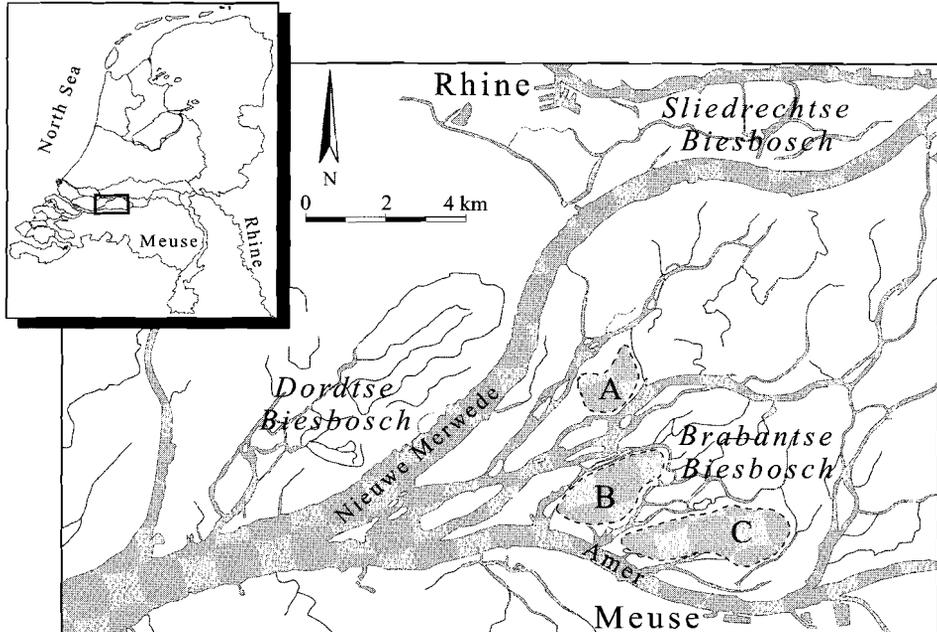


Figure 1.1. Map of the Biesbosch. The dotted areas (A, B, and C) represent the drinking-water storage reservoirs. The small map shows the location of the Biesbosch in the delta of the rivers Rhine and Meuse in The Netherlands.

Due to the construction of the Nieuwe Merwede (1864-1884), the Amer (1886-1908), and the westward proceeding estuary of the rivers Rhine and Meuse, the saltwater intrusion in the Biesbosch ceased to exist. The construction of the Nieuwe Merwede divided the area in the Brabantse, the Sliedrechtse, and the Dordtse Biesbosch (Fig. 1.1). Since the construction of the Nieuwe Merwede, the influence of

Development of the Biesbosch

the river Meuse is limited to the Brabantse Biesbosch. The Dordtse and Sliedrechtse Biesbosch are almost exclusively affected by the river Rhine. Because the tidal influence remained, a freshwater tidal area developed (Van der Meulen *et al.*, 1995), characterised by typical geomorphological freshwater tidal landscape units, i.e. open water, sand flats and sand bars, rough herbages, reed marshes, willow coppices, and pasture polders (Zonneveld, 1960). Their presence and development largely depends on gradients of flooding.

After implementation of the Delta Project, the civil engineering project to protect the Dutch coastline and delta against flooding, tidal fluctuations in the Biesbosch decreased considerably. As a result of the closure of Volkerak in 1969 and Haringvliet in 1970 by sluices, the tidal range was reduced from approximately 2 m to 0.6-0.8 m in the Sliedrechtse Biesbosch, and to 0.2-0.3 m in the Dordtse and Brabantse Biesbosch. At present, fluctuations in water levels in the Biesbosch are determined by water levels in the rivers Rhine and Meuse, mean water level in the North Sea, and tidal influence from sea (Janssen *et al.*, 1993). The rivers Rhine and Meuse have a direct connection to the North Sea via the Rotterdam harbour. Water is also released through the Haringvliet sluices at high discharge. Decreasing tidal fluctuation has invoked large-scale sedimentation in the former tidal gullies and erosion of dry shoals and mudflats in the Brabantse and Dordtse Biesbosch (Sevink *et al.*, 1993). Saris (1987) states that the tidal delta system is shaped into a lagoonal or lake system.

Vegetation type is strongly related to the degree of saturation of the soil and, therefore, depends primarily on inundation frequency and the depth of the groundwater level below surface (Patrick, 1994). Aeration of soils results in an increase of species adjusted to live in a relatively dry environment. Consequently, typical wetland plants disappear. As a result of the tidal changes in the Biesbosch due to the Delta Project, the vegetation type has changed dramatically, resulting in e.g. an explosive extension of stinging nettles and a quantitative as well as qualitative, decrease in reed (De Boois, 1982). The area of reed marshes in the Biesbosch has decreased from several hundreds of ha before 1970 to 30 ha nowadays. Remaining reed marshes are merely found on tidal flats. Higher altitude grounds are partly grassy, contain ditches and have a low bank. In the past, these areas were used as willow coppices. Nowadays, these areas are consistently being neglected and, as result, they turn into forests.

Present and future developments

Based on the presence and duration of water, terrestrial soils, aquatic sediments and semi-terrestrial soils are distinguished in the Biesbosch. Semi-terrestrial soils are characteristic for wetlands. Wetlands typically occur in topographic settings with collection of surface water collects and (or) seepage of groundwater, making the area wet for extended periods of time (Tiner, 1997). Wetlands are internationally considered a threatened biotope (Denny, 1994). The US Army Corps of Engineers and the US Environmental Protection Agency have jointly defined wetlands as 'those areas that are inundated or saturated by surface or groundwater at a frequency and duration sufficient to support, and that under normal circumstances do support, a prevalence of vegetation typically adapted for life in saturated soil conditions'. This definition indicates the three essential requirements for wetlands (Mitsch and Gosselink, 1993), i.e. wetlands are distinguished by the presence of water, have unique soils that differ from adjacent soils, and support vegetation adapted to the wet conditions (hydrophytes), and conversely are characterised by an absence of flooding-intolerant vegetation.

As discussed in the Fourth Policy Document on Water Management (Anonymous, 1997), environmental policy to restore free access of river water to floodplains in the delta of the rivers Rhine and Meuse in The Netherlands is aimed at improving ecological conditions by increasing the number and size of wetlands. According to the Ramsar convention on Wetlands, the southern part of the Biesbosch is recognised as an internationally important conservation wetland in this delta. A large part of the Biesbosch (7100 ha) was declared a national nature conservation area (National Park De Biesbosch) in 1994. In the Management and Equipment Plan (Overlegorgaan, 1992), the main goal for the National Park was formulated as 'the development of the current ecological and landscape quality of the Biesbosch as a freshwater tidal area'. A freshwater tidal area is a transition area between rivers and sea characterised by gentle differences in height.

In the Nature Policy Plan of The Netherlands nature development, defined by Hengeveld (1990) as 'the extension of possibilities of life for a certain amount of species by a local reduction of the anthropogenic influence', is mentioned as one of the major action points. Zonneveld (1993) states that the goal of nature development not only includes the protection of biota, but also the constitution of areas characterised by distinct abiotic natural processes. The goals for nature and landscape development in

the Biesbosch are formulated as 'sustainable maintenance, development, and enlargement of a connected freshwater tidal area as a natural connection between the catchment area of the rivers Rhine and Meuse and the North Sea, as well as the promotion of life opportunities for all organisms that belong in or are characteristic for a freshwater tidal area in The Netherlands' (Overlegorgaan, 1992).

Nature development in the Biesbosch strongly depends on the freshwater tidal character of the area and the presence of contaminated soils and sediments (Mes *et al.*, 1992). The lack of ecological coherency between the Sliedrechtse, Brabantse and Dordtse Biesbosch, the presence of polders in agricultural use, three large artificial drinking-water storage reservoirs, and waterways has divided the Biesbosch in small areas. The Management and Equipment Plan aims at the development of a large continuous freshwater tidal area by integrating enclaves and by removing parts of dikes surrounding polders (e.g. Mariapolder) to modify the current hydrological situation and to increase the amount of (temporarily) waterlogged soils. Several locations are intended for nature development in the Biesbosch (Coops *et al.*, 1994; Zingstra, 1997). Reed is intended to be the dominant plant species in these areas. Other species characteristic to freshwater tidal areas are expected to establish themselves.

Contaminated sediments are considered a large ecotoxicological risk to the aquatic environment (Burton, 1992). In the Evaluation Policy Document on Water Management (Anonymous, 1994), the Biesbosch is mentioned as one of the locations in The Netherlands characterised by the presence of highly contaminated sediments. According to Dutch environmental targets, a large part of the sediments in the Biesbosch waterways is classified as the most contaminated sludge type.

Before closure of the Haringvliet, sediments from the rivers Rhine and Meuse were transported mainly to the North Sea. In the tidal gullies in the Biesbosch, primarily accretion of sandy material took place. Since 1970 the Biesbosch has developed into a semi-stagnant sedimentation basin, characterised by flow rates lower than 0.1 m s^{-1} in the main waterways during average discharge of the rivers Rhine and Meuse. As a result, the Biesbosch currently behaves as a sink for fine-grained heavily contaminated sediments (Keukelaar and Van Berghem, 1991). Although the quality of surface water and suspended matter in the river Rhine has improved considerably (concentrations have decreased since the mid 1970s to levels comparable to those in the 1930s), concentrations in the river Meuse are still unsatisfactory (Van den Hark, 1995; Zwolsman, 1996; Van Eck *et al.*, 1997). Because deposition of contaminated

Meuse sediment continues, remediation of contaminated sediments in the Biesbosch does not immediately result in complete rehabilitation (Muilerman, 1991).

By extension of the intertidal area sediments are transported and deposited over a larger area. Because the presence of contaminants significantly affects ecological functioning of the Biesbosch (Gleichman Verheyen and Ma, 1989), Mes *et al.* (1992) and Borm and Huygens (1992) state that temporary isolation of polders and realisation of higher groundwater levels may be necessary before completely implementing nature development plans. Although Rhine and Meuse sediments are initially CaCO₃ rich, an additional problem resulting from periodic inundation may be decalcification. Although decalcification is of minor importance in polders in the Biesbosch (Van Driel and Schuurmans, 1991), wetlands may be subject to significant decalcification (Zonneveld, 1960; Hin *et al.*, 1995). Mobilisation of heavy metals as a result of a pH decrease of soils in the Biesbosch has been recognised by e.g. Dirksz *et al.* (1991), Winkels and Vink (1993), and Van Doornmalen *et al.* (1995).

Contaminant behaviour in relation to nature restoration

Although tidal influence has decreased considerably due to the implementation of the Delta Works, the Biesbosch may still be considered an important freshwater tidal area. By the decrease in flow rates since the closure of the area by sluices in 1970, the Biesbosch has developed into a semi-stagnant sedimentary basin characterised by deposition of fine-grained, highly contaminated, sediments. Dutch environmental policy aims at nature development by increasing the number and area of wetlands to enlarge the intertidal area in The Netherlands. Because integrated water management intends to achieve a sustainable situation in which environmental and ecological factors are also considered, the behaviour of contaminants and their ecotoxicological effects under changing hydrological conditions should be well recognised.

Therefore, studies were conducted, as reported in this thesis, aimed at describing dynamic (hydro)geochemical processes to determine the long-term and temporary mobilisation and fixation of heavy metals in contaminated sediments and hydric soils, as well as their emission to the groundwater and surface water in the Biesbosch. The results of this study are also used to evaluate environmental quality criteria to assess potential metal toxicity of sediments.

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Chapter 2

Decalcification of soils in wetlands subject to fluctuating hydrological conditions

G.A. van den Berg and J.P.G. Loch

Abstract - Decalcification is a major concern in contaminated soils that are subject to periodic waterlogged conditions, because loss of pH buffering may result in an increased mobility of heavy metals. Using fuzzy c-means clustering on the soil parameters CaCO_3 content, organic matter content, and $\text{pH}(\text{H}_2\text{O})$ in two layers of hydric soils from the Biesbosch, a wetland area in the Rhine-Meuse delta in The Netherlands, six types of soils could be distinguished. Soils subject to fluctuating hydrological conditions show the lowest CaCO_3 contents. Both oxidation of previously formed ironsulphides during periods of aeration and increased CO_2 pressures during periods of saturation of the soil contribute significantly to decalcification of the topsoil in the studied hydric soils. Currently, only at few locations in the Biesbosch complete decalcification and significant decrease of the pH of the topsoil has taken place.

Introduction

Environmental policy to restore free access of river water to floodplains in the delta of the rivers Rhine and Meuse in The Netherlands aims at improving ecological conditions by increasing the number and size of wetlands. The Biesbosch is an important conservation wetland area in this delta. It may be considered one of the largest freshwater tidal areas in Europe. In the Biesbosch several locations are intended for restoration of tidal flats.

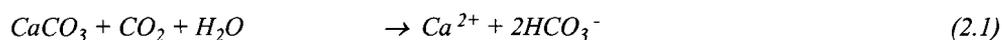
Hydric soils, normally present in wetlands, are soils that are wet long enough to periodically produce anaerobic conditions, thereby influencing the growth of plants (SSSA, 1997). As a result of fluctuating hydrological conditions, typical hydromorphic features can be distinguished in the hydric soil profile, e.g. Fe-(hydr)oxide mottles in a gley horizon, an organic topsoil, a reduced C-horizon at shallow depth or an unripened subsoil (Richardson, 1996). Hydric soils formed in freshwater and brackish marshes are generally characterised by fluctuating groundwater levels and periodic inundations, and have the FAO-classification Fluvisol.

One of the main geochemical processes resulting from fluctuating hydrological conditions in soils is decalcification, which has been identified as one of the first indicators of weathering in freshly reclaimed alluvial soils (Pons and Zonneveld, 1965). The Biesbosch has been recognised as an area subject to decalcification (e.g. Zonneveld, 1960; Dirksz *et al.*, 1990; Hin *et al.*, 1995). Decalcification was described in relation with sediment ripening, surface elevation, sedimentation rate, and soil drainage. Because the buffering capacity of a soil decreases as result of CaCO_3 dissolution, complete decalcification may result in acidification of the pore water. When pore-water pH decreases below certain levels, the mobility of heavy metals may increase rapidly as a result of an enhanced competition for exchange sites by Al and protons, dissolution of Mn- and Fe-(hydr)oxides which may act as strong adsorbents for heavy metals, and dissolution of sulphides which are often associated with heavy metals in reduced environments (Bourg and Loch, 1995). Consequently, bioavailability of heavy metals increases and quality criteria may be exceeded. Because decalcification and subsequent remobilisation of contaminants are relatively slow processes in calcareous soils, decalcification may be considered as a chemical time bomb (Stigliani, 1988).

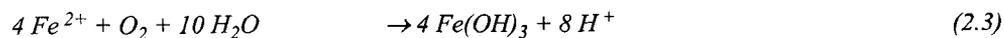
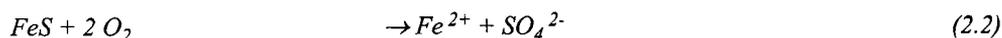
Two main causes for decalcification of the top layer of hydric soils are oxidation of ironsulphides under aerobic conditions (low tide, low river level, non-

flooded) and increased CO₂ pressure due to inhibition of CO₂ escape to the atmosphere during waterlogged conditions. It is important to notice that these processes take place during two different periods. Decalcification is further enhanced by acidifying components in rain and, in case of vegetation removal, cation uptake excess by vegetation (Van Breemen *et al.*, 1983).

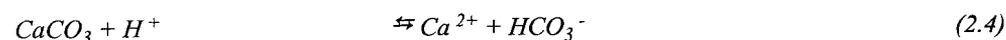
CO₂ is produced in the soil as a result of mineralisation of organic matter, e.g. methanogenesis, and root activity. Saturated conditions will inhibit the escape of CO₂ to the atmosphere. Under these conditions, dissolution of calcite is favoured, because CO₂ is a weak acid (reaction 2.1).



Effects of pyrite oxidation on acidification have long been recognised in e.g. acid mine drainage sites, acid sulphate soils (Van Breemen, 1976), salt marshes, and estuarine sediments (Luther *et al.*, 1982). In addition, mobilisation of heavy metals may be expected (Kerner and Wallmann, 1992). However, in freshwater systems, the formation of pyrite is probably not favoured and reduced sulphur may be present mainly as monosulphides (e.g. mackinawite) or non-crystalline sulphides. The process of oxidation of FeS by oxygen may be schematised in two steps (reactions 2.2 and 2.3).



For each FeS molecule oxidised 2 protons are produced. As shown by these reactions, the assumption that oxidation of sulphides leads to proton production is not correct. It is the oxidation of reduced Fe and subsequent precipitation of Fe(III)-hydroxides that leads to proton production. In calcareous soils the pH decrease is buffered by dissolution of calcite (reaction 2.4).



The presence of vegetation may stimulate decalcification of the soil. The rhizosphere is the soil compartment most subject to decalcification. Both living roots

and micro-organisms are sources of CO₂ and dead roots are a source of easily decomposable organic matter (Fischer *et al.*, 1989). Decomposition of root material will, therefore, result in a rapid decrease in redox potential, resulting in the formation of sulphides if sulphate-containing pore water is present.

The purpose of this investigation is to determine the relationship between soil conditions and decalcification in the Biesbosch. From fuzzy c-means clustering in combination with non-linear mapping the soil types showing the most intense decalcification are derived. A quantification is made of the contribution of chemical processes involved in decalcification. Furthermore, decalcification rates in hydric soils are calculated.

Materials and methods

Area description

In the Biesbosch, we distinguish artificially drained soils, which are situated mainly in polders, hydric soils subject to inundation and fluctuating groundwater levels, and aquatic sediments. According to the FAO-soil classification system (FAO, 1988) the soils are classified as calcareous Fluvisols. Both the aquatic sediments and soils in the Biesbosch are strongly contaminated by heavy metals, reflecting the serious metal pollution history of the rivers Rhine and Meuse. The soils in the Biesbosch may be constituted of either Meuse derived or Rhine derived parent material. Furthermore, soils present in a large area in the Biesbosch are constituted of both Meuse and Rhine derived parent material.

The former polder Plattehoek (Fig. 2.1), a part of the Biesbosch that has been subject to periodic inundations and fluctuating groundwater levels since the breakthrough of the surrounding dike in 1966, is used as a natural example to study the long-term effects of soil processes. Hydrological and geochemical data obtained for this area (Wolters and Vos, 1995; Van den Berg *et al.*, 1998/*Chapter 3*) enable assessment of realistic decalcification rates in hydric soils of the Biesbosch. Parent material in this former polder is largely Rhine sediment.

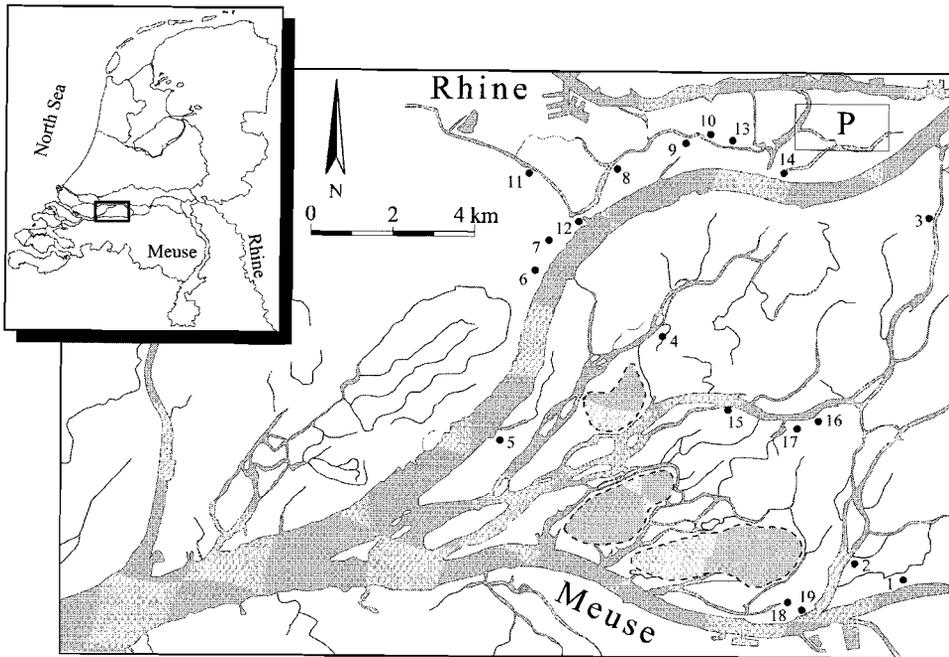


Figure 2.1. Sampling locations in the study area. The small scale map presents The Netherlands, the rivers Rhine and Meuse and the Biesbosch (P is the former polder Plattehoek).

Collection of soil samples

Sampling was carried out at 19 wetland locations in the Biesbosch (Fig. 2.1) in May and June 1995, using 'Edelman' auger equipment. Depending on the location, the number of sampling points per location varied between one and seven. The total number of cores was 78. For each sampling point, the visual soil characteristics were described. The topsoil (0-10 cm) and subsoil (10-20 cm) were sampled independently. In the former polder Plattehoek sampling of pore water and solid phase took place at three sites during the period January to October 1994. Hydrological data, i.e. groundwater tables, inundation frequencies, vertical and horizontal flow, precipitation and evapotranspiration, were collected simultaneously (Wolters and Vos, 1995).

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Soil parameter analysis

Individual soil samples were analysed for different soil parameters. Organic matter was determined according to Walkley and Black (Walkley, 1947), CaCO_3 with the Scheibler method (Williams, 1948), and $\text{pH}(\text{H}_2\text{O})$ was measured potentiometrically in a 1:2.5 mixture of soil and distilled water. Moisture content was determined after freeze-drying of soil samples. In addition, homogenised bulk samples of the topsoil and subsoil were made for each location. The bulk samples (19 topsoil and 19 subsoil samples) were digested in concentrated HClO_4 , HNO_3 , and HF in Teflon vessels at 90°C and finally dissolved in 1 M HCl. Concentrations of heavy metals (Zn, Cd, Cu, Pb, and Ni) as well as major elements in the acid solution were determined by inductively coupled plasma atomic emission spectrometry (Perkin Elmer Optima 3000). The methods of pore-water and solid-phase collection, analysis and the analytical results for the Plattehoek are described by Van den Berg *et al.* (1998/Chapter 3).

Statistical methods

Multivariate classification techniques are well suited to distinguish groups when considerable compositional overlap may occur. The fuzzy c-means clustering method may be used to classify a dataset into a number of homogeneous groups without *a priori* knowledge of the partitioning. Especially in the case of few samples this method is more robust than ordinary c-means clustering. In the fuzzy c-means clustering method the similarity between samples is expressed in a continuous function (membership) between zero (completely different from the cluster) and one (identical to the cluster), thus allowing for overlap between clusters (Vriend *et al.*, 1988). The memberships sum up to one per sample. Intermediate samples are recognised by significant memberships to more than one cluster. This allows for some flexibility during interpretation of a multivariate data set. In this study, a sample is attributed to a certain cluster if the highest membership is at least 1.5 times the next highest membership.

Bezdek (1981) gives two functionals (the partition coefficient F and the classification entropy H) for determining the appropriate number of clusters in a data set. As these are often inconclusive, the number of clusters is also chosen on the basis of (hydro)geochemical interpretability with the aid of non-linear mapping. Non-linear

mapping provides a two-dimensional image of a multidimensional data cloud, whereby the distortion of the intersamples is kept to a minimum. Opposite to fuzzy c-means clustering non-linear mapping assumes no grouping of data in advance. If both techniques show similar data groupings, it is likely that these are meaningful.

Results and discussion

Contamination grade

The studied hydric soils contain high levels of contaminants. The range of heavy metal contents in the topsoil (0-10 cm) and subsoil (10-20 cm) of the studied hydric soil profiles in the study area is given in Table 2.1.

Table 2.1. Heavy metal contents in the topsoil (0-10 cm) and subsoil (10-20 cm) of the studied hydric soils in the Biesbosch.

	Min. conc.	Max. conc.	Average conc.	St. deviation
	(mg kg ⁻¹ dry soil)			
<i>Topsoil</i>				
Zn	420	2341	1593	566
Pb	56	572	347	152
Cu	61	607	226	123
Cd	0.7	11.4	5.6	2.9
Cr	133	664	328	139
Ni	45	107	81	17
<i>Subsoil</i>				
Zn	469	2907	1786	666
Pb	60	749	459	175
Cu	67	563	265	130
Cd	0.7	11.9	6.4	2.5
Cr	141	923	406	214
Ni	52	120	83	20

Hydric soil characterisation

In Fig. 2.2 soil characteristics are given of a profile typical for hydric soils in the Biesbosch. The described core was collected at location 14 and consists of Rhine derived sediments. The sampling location may be characterised as an embanked basin. The groundwater table at this location fluctuates between 0 and 40 cm below the surface. As most wetlands in the Biesbosch, this location is characterised by small-scale geomorphological differences. Vegetation is dominated by low reed and grass. Soil colour, texture and other soil features can be used to predict the presence of specific soil constituents, which may in turn be characteristic for the redox conditions in the soil. Due to the presence of banks surrounding the lower wetland environments, inundation of the soil surface and active sedimentation only take place during periods of extremely high river water levels.

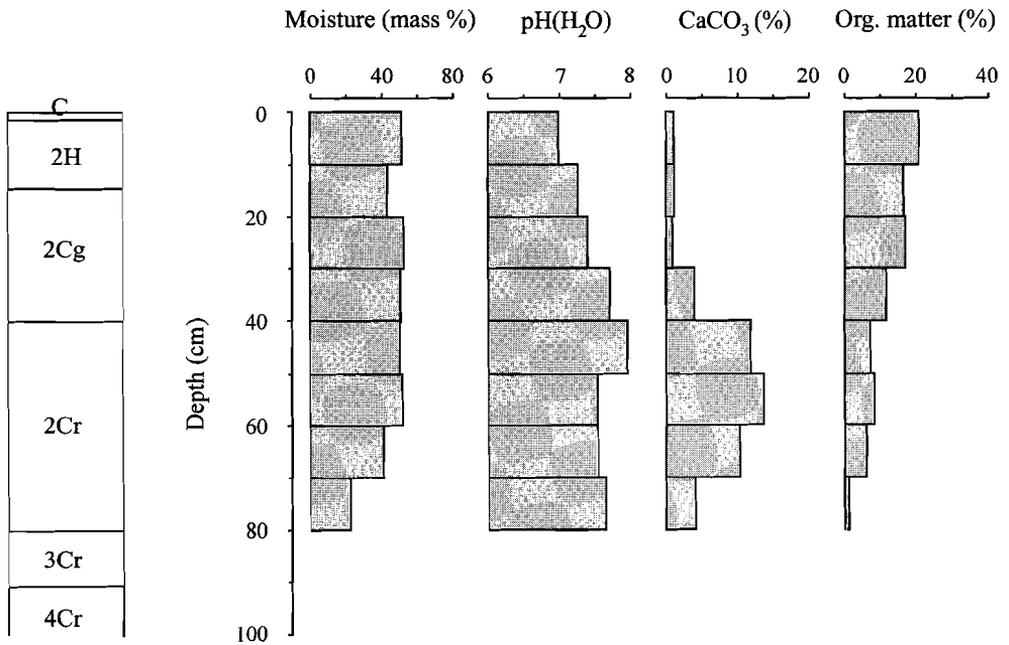


Figure 2.2. Characterisation of a hydric soil profile typical for the study area (location 14). Horizon designation according to FAO (1988).

Decalcification of soils in wetlands

This Fluvisol (Fig. 2.2) is characterised by a H-Cg-Cr profile and low CaCO₃ content in the top 40 cm. By sedimentation and development of a vegetation cover a high content of organic matter is built up in the surface layer. As the sedimentation rate decreases, ripening of the surface layer and, consequently, the mineralisation rate of the organic matter increases. The soil has an organic-rich top layer consisting mainly of vegetation debris. The profile is divided in five horizons:

The thin *C horizon* on top consists of heavy clay deposited mainly during the 1994 and 1995 winter inundations, when extremely high water levels caused flooding of many floodplains and adjacent land along the rivers Rhine and Meuse. This layer has a thickness of about 1 cm. It was not sampled separately.

The *2H horizon* is an organic-rich, semi-permanently anaerobic layer, containing a large amount of root tissue, supported by grey sulphide spots. The formation of the sulphide spots is related to anaerobic degradation of fresh reactive organic material (Van den Berg *et al.*, 1998/*Chapter 3*). This layer is almost completely decalcified.

The *2Cg horizon* is a mineral layer of half-ripened moderately heavy clay, containing a relatively large amount of plant tissue. This layer has characteristics of semi-permanent anaerobic conditions as well. The presence of reddish brown (5 YR 4/6) concretions and spots on aggregate surfaces indicates gley conditions and movement of iron in the pore water. Such oxides may be specifically enriched in heavy metals (Hiller and Brümmer, 1995). As a consequence of the increasing anaerobic conditions, the amount of Fe-(hydr)oxide spots as well as the colour chroma of these spots decrease with depth. This horizon is almost completely decalcified, but no significant decrease of pH(H₂O) is measured.

The *2Cr horizon* is a unripened moderately heavy clay containing significantly less organic material than the above horizons. It does not contain Fe-(hydr)oxide spots. In the top of this horizon grey sulphide spots (N 4/0) are present, indicating local anoxic environments. Deeper in the horizon the amount of these spots increases gradually. Below a depth of 70 cm the soil is homogeneously grey (7,5 Y 4/1), indicating continuous reductive conditions. This horizon contains sandy layers. The abundance of these layers increases with depth. At the high CaCO₃ levels in this horizon, significant decalcification is unlikely. The lower CaCO₃ content of the more sandy part of this horizon may be related to the lower initial CaCO₃ content of sandy material (Hin *et al.*, 1995).

The 3Cr horizon has a sandy texture. This horizon has not been sampled separately. The 4Cr horizon is the base layer. Due to spatial variability, this horizon may be either a peat layer or a very heavy dark brown clay rich layer (10 YR 3/4).

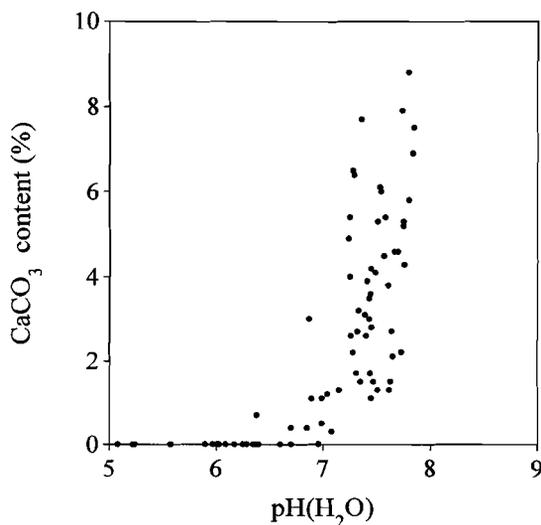


Figure 2.3. Plot of CaCO₃ content vs. pH(H₂O) in hydric soils in the study area.

Buffering capacity

The root zone of hydric soils is highly subject to decalcification. Consequently, the pH is generally lower in this zone relative to deeper layers. To determine the buffering capacities of hydric soils in the Biesbosch, both the topsoil (0-10 cm) and the subsoil (10-20 cm) was sampled at 19 locations. In Fig. 2.3, measured CaCO₃ contents are plotted vs. pH(H₂O). In calcareous soils, pH is dependent on pCO₂ in the soil. CaCO₃ is an efficient buffer in the neutral to basic pH range (pH > 6.5; Van Breemen *et al.*, 1996), as is also shown in Fig. 2.3 for the studied soil samples. The carbonate particle size distribution may have an influence on the pH. As long as carbonates are present in sufficiently fine particles or as coatings, they will provide pH buffering. However, in the clay fraction, a significant amount of CaCO₃ may be present in aggregates, and, therefore, be less available for reaction with acidifying components. Complete

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decalcification of the soil results in a pH decrease. However, in the study area pH(H₂O) never decreases to values below 5 in completely decalcified soil layers. This suggests that the pH is buffered by other soil phases, e.g. silicates and exchange sites (e.g. Schwertmann *et al.*, 1987).

Table 2.2. Overview of the calculated composition of the cluster centres (all concentrations on dry weight basis).

	A	B	C	D	E	F
<i>Topsoil</i>						
pH(H ₂ O)	5.46	6.39	6.53	7.36	7.39	7.64
Org. matter (%)	26.4	39.2	17.9	20.2	17.2	13.3
CaCO ₃ (%)	0.21	0.71	0.35	4.96	2.37	5.42
<i>Subsoil</i>						
pH(H ₂ O)	5.33	6.91	6.64	7.21	7.68	7.76
Org. matter (%)	18.2	19.0	13.5	23.2	11.8	11.5
CaCO ₃ (%)	0.22	1.24	0.35	1.41	3.69	5.53
<i>Parent material</i>						
Meuse	0	1	14	0	8	2
Rhine	0	4	2	9	6	10
Meuse and Rhine	6	1	1	0	8	1
no. of profiles	6	6	17	9	22	13

Soil types

Applying fuzzy c-means clustering on the data set using six parameters, i.e. CaCO₃ content, organic matter content and pH(H₂O) in topsoil (0-10 cm) and subsoil (10-20 cm), a six cluster model seemed sufficient to describe the variation in the study area. The obtained cluster centres are given in Table 2.2. The consistency of the partitioning is supported by the values for the F and H functionals, as well as by non-linear mapping plots. Four of the distinguished clusters (B, C, D, and F) show dominance of either Rhine (locations 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14) or Meuse (locations 1, 2, 3, 18, and 19) sediment as parent material. Cluster E includes a comparable number of soil profiles from both types of parent material. According to the soil map of Dirksz *et*

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al. (1990) the soil at locations 4, 15, 16, and 17 is constituted of mixed sediments. Four soil profiles have significant memberships to cluster E and F. One soil profile has significant memberships to cluster C and E.

Between the distinguished clusters the soils appear to differ in surface elevation and groundwater level, vegetation type, groundwater fluctuations, and sedimentation. With decreasing altitude hydric soils are likely to become more clayey, and thus lower in primary carbonate (Hin *et al.*, 1995). It should be noted that soil characteristics influence vegetation in an area for a great deal (e.g. De Boois, 1982). The development of reed marshes is specifically influenced by saturation of the soil and tidal fluctuation. The following groups of hydric soil were distinguished by clustering (the difference in elevation between low and high altitude soils is on the order of 1 m at maximum):

- A* Low altitude soils characterised by fluctuating ground water levels, which commonly reach the surface. The sampled profile consists of an organic horizon. The topsoil and subsoil are deficient in CaCO_3 ($< 0.5\% \text{CaCO}_3$). This has resulted in a significant pH decrease. The vegetation consists mainly of grasses.
- B* Low altitude soils characterised by fluctuating groundwater levels. The sampled profile consists of an organic horizon. The topsoil and subsoil are low in CaCO_3 ($0.5\text{-}2\% \text{CaCO}_3$). This has not resulted in a significant pH decrease. Vegetation consists mainly of reed marshes.
- C* Soils characterised by high groundwater levels. The sampled profile consists of borderline organic/mineral horizons. The topsoil and subsoil are deficient in CaCO_3 . This has, however, not resulted in a decrease of $\text{pH}(\text{H}_2\text{O})$. The vegetation mainly consists of grasses. At some locations reed is present, but its density is much less than on soils of cluster B.
- D* Low altitude soils, rich in CaCO_3 ($> 2\% \text{CaCO}_3$). A lower CaCO_3 contents is measured in the subsoil than in the topsoil. This may be related to active sedimentation. Due to the continuous supply of high carbonate sediments, CaCO_3 content and $\text{pH}(\text{H}_2\text{O})$ in the topsoil remain at a high level. The vegetation mainly consists of reed. The sampled profile consists of an organic horizon. The locations are depressions, having a low surrounding bank.
- E* High altitude soils characterised by a high CaCO_3 content and a relatively high pH. The vegetation consists of reed, willows, and stinging nettles. The sampled profile consists of a mineral horizon.

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F High altitude soils characterised by high CaCO_3 content and $\text{pH}(\text{H}_2\text{O})$. These locations include banks and willow coppices. The sampled profile consists of a mineral horizon having relatively low organic matter content.

From fuzzy c-means clustering it may be concluded that soils characterised by the lowest CaCO_3 contents, belong to clusters A, B and C. These soils are subject to large fluctuation of the groundwater and have relatively high organic matter content. Because groundwater levels are above surface for long periods of time, anaerobic conditions may be expected in the topsoil. For most clusters the characteristics of topsoil samples and subsoil samples are similar. Only in cluster D they are significantly different.

Decalcification potential of hydric soils

The former polder Plattehoek has strong similarity to the soils in clusters A, B, and C. At this location, the effects of long-term fluctuating hydrological conditions on decalcification have been measured *in situ*. Based on surface level and hydrology, the area may be divided into different regions.

Site A1 is a depression, characterised by a relatively unripened soil. During periods of weeks to months inundation water remains on the surface, resulting in a completely saturated soil, which may be related to the low permeability. This is clearly reflected by dissolved concentrations of chloride. Mean chloride concentration in the sampled pore water (5.6 mmol l^{-1}) at this site is significantly higher than in the adjacent surface water (2.4 mmol l^{-1}), suggesting strong evapotranspiration (Van den Berg and Loch, 1995). During the period June to early August 1994 the groundwater table at site A1 dropped and the top 50 cm of the soil became unsaturated. Fig. 2.4 shows the depth of the groundwater table during the sampling period. At two more elevated sites (A2 and A3), characterised by more ripened soils, pore-water chloride concentrations are similar to that in the surface water, indicating more rapid infiltration following inundation.

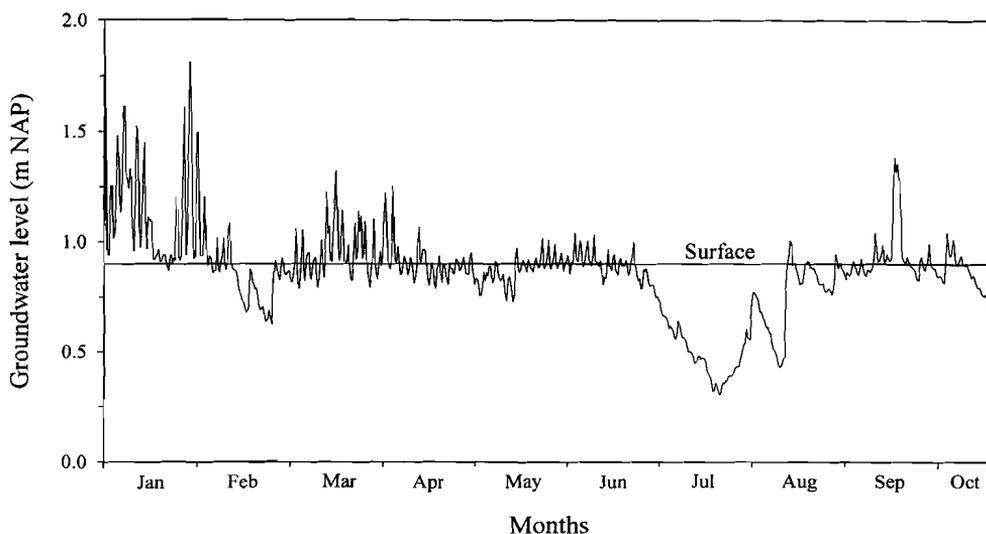


Figure 2.4. Fluctuation of the groundwater table at site A1 (Plattehoek) during the sampling period (0 m NAP is mean Dutch sea water level). Modified after Wolters and Vos (1995).

CaCO_3 contents of different size fractions in freshly deposited Rhine and Meuse sediments were estimated by Hin *et al.* (1995). Using the distribution of CaCO_3 among the different grain size fractions in freshly deposited sediments, the initial CaCO_3 content of the soils at the sampling sites can be estimated. We recognise that it is not possible to obtain more than a rough estimation of the initial lime content of the samples, because carbonate contents are variable in the various size fractions. The low initial CaCO_3 content of the clay fraction (3 % in Rhine sediment and 2 % in Meuse sediment) in comparison with the coarser fractions (Rhine sediment: 14 % in the 2-16 μm fraction, 12 % in the 16-63 μm fraction and 7 % in the >63 μm fraction; Meuse sediment: 5 % in the 2-16 μm fraction, 2.5 % in the 16-63 μm fraction and 1 % in the >63 μm fraction) may be related to decalcification during deposition (Van der Sluijs, 1970). According to the Dutch soil texture classification (De Bakker and Schelling, 1989) the soil at site A1 is a moderately heavy clay. At this texture, the initial CaCO_3 content was calculated to be 9-10 % on a dry weight basis. As the present CaCO_3 content in the microbial active zone (the upper 20 cm of the soil profile) is approximately 1 % (Table 3.1), it is concluded that this zone has been subject to intense decalcification. Relative to site A1, a less pronounced decalcification is

measured at the sites A2 and A3. The soil at sites A2 and A3 is a light clay. At these sites, the CaCO_3 content in the top 20 cm of the soil has decreased to approximately 6-7 % (at this texture the initial CaCO_3 was calculated to be 9-10 % as well).

Sulphide oxidation takes place in the top layer, which contains a high amount of highly degradable organic matter, mainly in the form of decaying plant roots. For calculation of the decalcification rate by oxidation of iron sulphides, it is assumed that the maximum acid-volatile sulphide (AVS) concentration at site A1 is $7 \mu\text{mol g}^{-1}$ dry soil (Table 3.1). In addition, it is assumed that all AVS is present as (amorphous) FeS. Although the soil has low permeability, it is assumed that during aerobic conditions in the upper 20 cm of the soil complete oxidation of all previously formed FeS takes place. Using the measured groundwater tables during the sampling period (Fig. 2.4), we distinguish one period per year during which this layer is completely aerated. It should be noted that the intensity of decalcification due to sulphide oxidation may vary depending on the length of the saturated period, as this determines the amount of sulphide formed in the sediment. Using reactions 2.2 to 2.4 it is estimated that complete oxidation of $7 \mu\text{mol FeS}$ results in dissolution of $14 \mu\text{mol CaCO}_3$. Consequently, the decalcification rate due to sulphide oxidation at site A1 is estimated at $1.4 \text{ mg CaCO}_3 \text{ g}^{-1} \text{ dry soil yr}^{-1}$.

During saturated conditions, calcite solubility is determined mainly by soil temperature and CO_2 pressure in the soil. As a result of high concentrations of nutrients and soil organic matter a large quantity of carbon dioxide is produced in hydric soils. The amount of decalcification by CO_2 production in the soil is estimated from the mean alkalinity of the pore water. The presence of a sandy layer in the subsoil facilitates natural drainage and leaching of acid-neutralising components. Assuming that, at the pH values measured in the studied soils, alkalinity equals the bicarbonate concentration, the amount of bicarbonate leached from the topsoil can be computed by

$$L_v = Q_v \cdot [\text{HCO}_3^-] \quad (2.5)$$

in which L_v is the amount of bicarbonate vertically leached (in $\text{mol yr}^{-1} \text{ ha}^{-1}$), Q_v is the downward vertical flux of pore water at site A1 ($1.62 \cdot 10^3 \text{ m}^3 \text{ yr}^{-1} \text{ ha}^{-1}$), $[\text{HCO}_3^-]$ is the mean dissolved bicarbonate concentration in the biologically active zone (24 mol m^{-3}) during the period of saturation of the soil (Van den Berg and Loch, 1995). From Fig. 2.4, the length of this period is estimated at approximately 10 months of the year. The microbial active zone in the studied soils was estimated at 20 cm. Decalcification due

to increased CO₂ pressure takes place only during saturated conditions. Using these values, it is calculated that the amount of bicarbonate annually leached is $3.88 \cdot 10^4$ mol HCO₃⁻ ha⁻¹.

Reaction 2.1 shows that one half of the bicarbonate in the pore water originates from dissolution of CaCO₃. Thus, the amount of CaCO₃ dissolved annually is approximately 970 g CaCO₃ m⁻³. Using the average measured porosity of 0.77 in the microbial active zone, which is comparable to porosities in similar unripened hydric soil profiles, an annual decalcification rate of 1.6 mg CaCO₃ g⁻¹ dry soil is calculated due to increased CO₂ pressure during periods of saturation of the soil at site A1.

These calculations show that decalcification due to sulphide oxidation during aerobic conditions and increased CO₂ pressure by saturation of the soil may be of equal importance at the studied location. In the 28 years since the breakthrough of the surrounding dike (1966-1994), approximately 8.4 mg CaCO₃ g⁻¹ dry soil may have been dissolved in the top 20 cm of the soil by these two processes at site A1. This equals 8.4 % CaCO₃ on a dry weight basis, which agrees well with the estimated amount of decalcification, based on the difference between initial and present CaCO₃ content in the top 20 cm of the soil at this site (on the order of 8-9 % CaCO₃). However, it should be noted that we implicitly assume the present hydrological and geochemical conditions and the absence of active sedimentation. In addition, as a result of heterogeneous distribution of reactive organic matter, groundwater levels, and AVS in hydric soils within the study area, a considerable spatial variation in decalcification rates may be expected.

Conclusions

Hydric soils in the Biesbosch, a freshwater tidally influenced wetland area in the Rhine-Meuse delta in The Netherlands, are subject to significant decalcification. Using fuzzy c-means clustering, applied to soil parameters, it is concluded that organic-rich soils subject to periods of saturation, show significant decalcification. Calculations with data on AVS, alkalinity, and downward water flux, show that two processes may fully explain estimated decalcification rates in these types of hydric soils. During saturated conditions in the organic-rich topsoil, increased CO₂ pressure stimulates decalcification. As a result of aeration of part of the soil, i.e. during periods of low groundwater levels and low inundation frequencies, oxidation of previously formed

amorphous iron sulphides may take place, resulting in production of protons. A decalcification rate on the order of 3 mg CaCO₃ per gram dry soil per year is calculated by summing the effects of these two processes. It is suggested that at low CaCO₃ contents, the pH is buffered by other soil phases. Considering the high heavy metal contents of the sediments studied, a further pH decrease may result in a significant increase in the mobility and bioavailability of heavy metals.

Acknowledgement - This project was carried out with financial support of the Ministry of Transport, Public Works and Water Management, Directorate-General for Public Works and Water Management, Directorate IJsselmeergebied. Hydrological data were supplied by H. Wolters. We thank S.P. Vriend for help with statistical interpretation of the dataset and C.H. van der Weijden for many useful comments on the manuscript.

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Chapter 3

Effect of fluctuating hydrological conditions on the mobility of heavy metals in soils of a freshwater estuary in The Netherlands

G.A. van den Berg, J.P.G. Loch, and H.J. Winkels

Abstract - The objective of this study was to measure the mobility of heavy metals in freshwater estuary soils that are seasonally inundated and to characterise the distribution of sulphide precipitates in these soils. Precipitation and dissolution of labile sulphides may account for changing pore water concentrations of heavy metals in freshwater wetland soils that are subject to temporary flooding or fluctuating groundwater levels. The presence of authigenic zinc- and iron-(mono)sulphide in this type of soils during periods with a high groundwater level was demonstrated by electron microprobe analyses. Because sulphide precipitates are strongly associated with root remnants, fresh soil organic material may be an important intermediary in the sulphur cycling and, consequently, in the behaviour of heavy metals in these freshwater soils. Oxidation of labile sulphides may be partly responsible for the increased zinc and sulphate concentrations in the pore water during periods with low groundwater levels. Heavy metals may also be mobilised by degradation of their host phase organic matter during periods with high biodegradation.

This chapter has been published in Water, Air, and Soil Pollution 102: 377-388 (1998).

Introduction

In freshwater wetlands, periodic inundations or fluctuating groundwater levels lead to changing redox conditions in the soil. Changing redox conditions are the result of differences in oxygen supply to the soil (Patrick and Henderson, 1980; Ransom and Smeck, 1986).

A range of oxidising agents is involved in the mineralisation of organic matter (Berner, 1981). Decomposition of organic matter may lead to the production of hydrogen sulphide by reduction of sulphate. The organic matter input determines the relative importance of sulphate reduction and methanogenesis for mineralisation of the organic matter in freshwater soils and sediments (Capone and Kiene, 1988). Soils generally have an aggregated structure, causing a heterogeneous distribution of redox conditions. Local sulphide precipitates may be present in microsites, where more anaerobic conditions prevail (Fischer *et al.*, 1989; Zausig *et al.*, 1993). The importance of sulphide precipitation in controlling heavy metal concentrations in the pore water of freshwater sediments and soils is dependent on the heavy metal content and the amount of sulphate reduction. Although heavy metal sulphides should be precipitated preferentially to iron sulphides due to their lower solubility product, this is mostly not observed under natural conditions. Heavy metals in sediments are usually co-precipitated with the more abundant iron sulphides (Huerta-Diaz and Morse, 1992). Immobilisation of heavy metals in the soil column by (co-)precipitation and adsorption reduces its leaching to the ground water and loss to the surface water. Precipitation of sulphides is an important factor decreasing the bioavailability and, consequently, toxicity of heavy metals (Di Toro *et al.*, 1990; Ankley *et al.*, 1991).

Fluctuations in redox conditions influence mineralisation of organic matter and affect the mobility of metals in the soil. In soils that are subject to fluctuating water levels, precipitation and dissolution of sulphides is supposed to occur (Hordijk *et al.*, 1989; Howard and Evans, 1993). In soils that are subject to seasonal variation of the water table, changes in equilibrium are expected during a year. Because of slow kinetics in the establishment of new equilibria, during changes in hydrology a nonequilibrium is present in the soil with minimum sorption and precipitation, which may result in higher heavy metal concentrations (Palsma and Loch, 1991). Alternating reduction and oxidation of iron may lead to the process of ferrollysis, resulting in net proton production (Brinkman, 1969/1970). In addition, oxidation of sulphides

promotes decalcification and acidification of soils (Van Breemen *et al.*, 1983; Ritsema and Groeninger, 1993).

The objectives of this study were to (1) investigate the mobility of heavy metals in freshwater soils that are seasonally inundated, by measuring seasonal changes in pore-water concentrations and (2) to characterise the distribution of heavy metal precipitates in these soils. Precipitates may be indicative for the bioavailability of heavy metals in polluted soils that are subject to fluctuating hydrological conditions. Results of this study will be used for nature development projects in the Dutch estuary of the rivers Rhine and Meuse.

Materials and methods

Study area

The Biesbosch is part of the freshwater estuary basin of the rivers Rhine and Meuse in The Netherlands. Tidal influences have decreased considerably due to closure of the estuary by a dam in 1970. The soils of the Biesbosch have been severely contaminated by heavy metals in the past. The study area (the Plattehoek polder, Fig. 2.1) has been subject to seasonal inundations since collapse of the surrounding dike in 1966. It has since been considered a wetland. The soils at this location consist mainly of freshwater tidal sediments underlain by clays and sands and are classified as calcareous Fluvisols according to the FAO soil classification system. The soils are clayey, contain high levels of heavy metals and are subject to alternate reduction and oxidation.

Three different sites were chosen for the investigation. All are vegetated during the major part of the year by reed (*Phragmites australis*). Sampling took place monthly during the period January to September 1994. Site A1 (height 0.90 m above mean sea level) was inundated during 25 % of the sampling period, although water remains on the surface much longer. Site A2 (height 1.05 m above mean sea level) was inundated during 14 % of the sampling period and site A3 (height 1.00 m above mean sea level) was inundated during 17 % of the sampling period. Inundation especially occurred during winter and spring (see also *Chapter 2*). During the summer months groundwater levels dropped. From mid August on, groundwater levels started to rise again. During the sampling period the groundwater levels fluctuated between 60 and 0 cm below the surface at site A1, between 95 and 0 cm at site A2 and between 85 and 0 cm at site A3

(Wolters and Vos, 1995). According to the Dutch textural soil classification (De Bakker and Schelling, 1989) the soil at site A1 is a moderately heavy clay and at sites A2 and A3 a light clay.

Sampling and analysis

The soil has been analysed for different soil properties at the depth intervals 10-20 cm and 30-40 cm. Organic C was determined according to Walkley and Black (Walkley, 1947), CaCO₃ with the Scheibler method (Williams, 1948), and amorphous Fe-(hydr)oxide by an oxalate extraction (McKeague and Day, 1966). pH(H₂O) was measured potentiometrically in a 1:2.5 mixture of soil and distilled water. Dry soil material was extracted in a mixture of concentrated HClO₄, HNO₃, HF, and finally dissolved in HCl. Zn, Pb and Cu concentrations in the acid solution were analysed by inductively coupled plasma atomic emission spectrometry (Perkin Elmer Optima 3000 ICP-AES). Cd was determined by Zeeman atomic absorption spectrometry (Perkin Elmer 4100ZL Z-AAS). Acid-volatile sulphide (AVS) contents were determined according to Henneke *et al.* (1991). This method is based on acidification of the sample to form H₂S which is subsequently collected in a base solution. The sulphide concentrations in the basic solution were measured polarographically with an EG&G Princeton Applied Research model 384B polarograph with a static mercury drop (model 303A).

Pore water was sampled *in situ* to avoid problems arising from spatial variability, sample oxidation, temperature change and degassing effects (Carignan *et al.*, 1985; Suarez, 1986). Sampling occurred monthly. The sampler was a modified version of the one described by Oenema (1988) and consisted of a PVC plate containing three open spaces (10 x 20 x 2 cm) at three depth intervals (30-40 cm; 50-60 cm; 70-80 cm) from which pore water was sampled. Both sides of the 2 cm wide sampling space were covered by a biologically inert acrylic copolymer membrane filter (Versapor-450; Gelman Sciences) with a 0.45 µm pore size. The sampler remained in the soil permanently. The compartments were initially filled with filtered (0.2 µm) de-oxygenated Biesbosch surface water and refilled immediately after sampling to prevent the compartments from oxygen penetration. From Fick's second law, the equilibration time of the solution in the compartments was calculated to be one month. To enable filling and water sampling the compartments were equipped with Tygon tubes (0.8 mm

inside diameter). Pore-water samples were withdrawn from the tubes using polypropylene syringes. During the experiment also the surface water was sampled monthly. The pH of pore water and surface water was determined immediately after collection to minimise degassing effects. Surface- and pore-water samples were acidified with concentrated HNO₃ and analysed for total dissolved concentrations of Fe, Mn, Ca, and Zn by ICP-AES technique and for Cd, Cu, and Pb by Z-AAS technique. Total alkalinity was determined by Gran alkalinity titration. Sulphate and nitrate concentrations were measured by ion chromatography with a Dionex QIC analyser.

Thin sections of soil profiles from the depth intervals 10-20 cm and 30-40 cm were made to study the morphology of sulphide precipitates in the soil. These thin sections were studied using a JEOL JXA-8600 electron microscope. The electron beam has a spot size of approximately 1 µm. Elemental levels were determined using Wavelength Dispersive Spectrometry (WDS) for Fe, Cu, Zn, Cd, Pb, As, and S, and Energy Dispersive Spectrometry (EDS) for Si, Al, Ca, K, and P.

Results and discussion

Characterisation of the solid phase

The soils at the three study sites are characterised by measuring different soil properties (Table 3.1). The soils are contaminated by high levels of heavy metals. At site A1 the organic matter content in the top soil is relatively high. At all sites, especially site A1, the CaCO₃ content in the upper layer is lower than in the deeper layer. This might be an indication of decalcification (discussion in *Chapter 2*).

AVS levels were only measured in April. However, levels are expected to change seasonally in the soils studied as a result of changing water levels. For the purpose of this study only an indication of AVS levels was sought. The relationship between sulphides and organic matter in these soils will be discussed later. Of the measured AVS levels in these soils, some are high enough to bind significant amounts of the heavy metals in the solid phase. It is, however, well known that adsorption on ironsulphides, particulate organic substances, Mn- and Fe-(hydr)oxides, carbonates and clay minerals may contribute to the binding of heavy metals in such environments as well (Wallmann *et al.*, 1993).

Table 3.1. Characterisation of the soil (contents on dry soil basis).

	Depth	pH(H ₂ O)	CaCO ₃	OrgC	amFe	AVS	Zn	Cu	Pb	Cd
	(cm)	(-)	———	(%)	———	($\mu\text{mol g}^{-1}$)	———	(mg kg ⁻¹)	———	———
A1	10-20	7.2	1.0	14.4	0.9	7.1	1140	214	529	9.7
A1	30-40	7.8	5.6	3.1	1.3	4.7	485	71	208	1.8
A2	10-20	7.9	6.8	3.2	0.7	1.4	420	55	215	1.8
A2	30-40	8.3	9.2	1.0	0.7	1.0	165	30	88	0.4
A3	10-20	7.8	6.1	3.1	0.8	< 0.5	470	59	246	2.2
A3	30-40	8.2	8.3	1.4	0.7	< 0.5	210	35	111	0.8

Fluctuations in pore-water composition

Fluctuations in pore-water concentrations of alkalinity and the redox sensitive ions Fe²⁺, Mn²⁺ and sulphate for site A3, with intermediate surface elevation, are shown in Fig. 3.1. The other two sites give comparable results. The gap in concentrations in the month of July for the 30-40 cm layer is caused by undersaturation of the soil pores resulting from a lower groundwater table. Redox potential (Eh) measurements (not shown) indicate that the soil system changes from an anaerobic situation during winter and spring to a more aerobic situation during summer and again to an anaerobic situation during fall. We believe, however, that by measuring pore-water concentrations a better estimation can be given of the actual processes that take place, i.e. dissolution and precipitation of Mn- and Fe-(hydr)oxides and sulphate reduction to sulphide. By knowing these processes, a better estimation can be given of the mobility of heavy metals. Eh measurements will only provide information of the processes that may take place.

From January to May reductive dissolution of Mn- and Fe-(hydr)oxides resulted in increasing concentrations of Mn²⁺ and Fe²⁺ in the pore water. The absence of pore-water sulphate indicates that sulphate reduction took place in these soils during that period.

In June and July the groundwater table dropped, resulting in oxygen penetration into the soil. The effects of decreasing groundwater table are first measured in the pore-water concentrations in the 30-40 cm layer. Oxidation of labile sulphides results in pore-water sulphate concentrations higher than those in the surface water (Table

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3.2). Precipitation of Mn- and Fe-(hydr)oxides results in a strong decrease in pore-water Mn^{2+} and Fe^{2+} concentrations. The decrease of alkalinity during summer months can be explained by oxidation of sulphides, oxidation of pore-water Mn^{2+} and Fe^{2+} and precipitation of $CaCO_3$. Pore-water pH decreases from 7.3 to 6.9 (data not shown) due to proton production by a combination of these oxidation processes. During summer months a large amount of fresh organic matter is produced in soils.

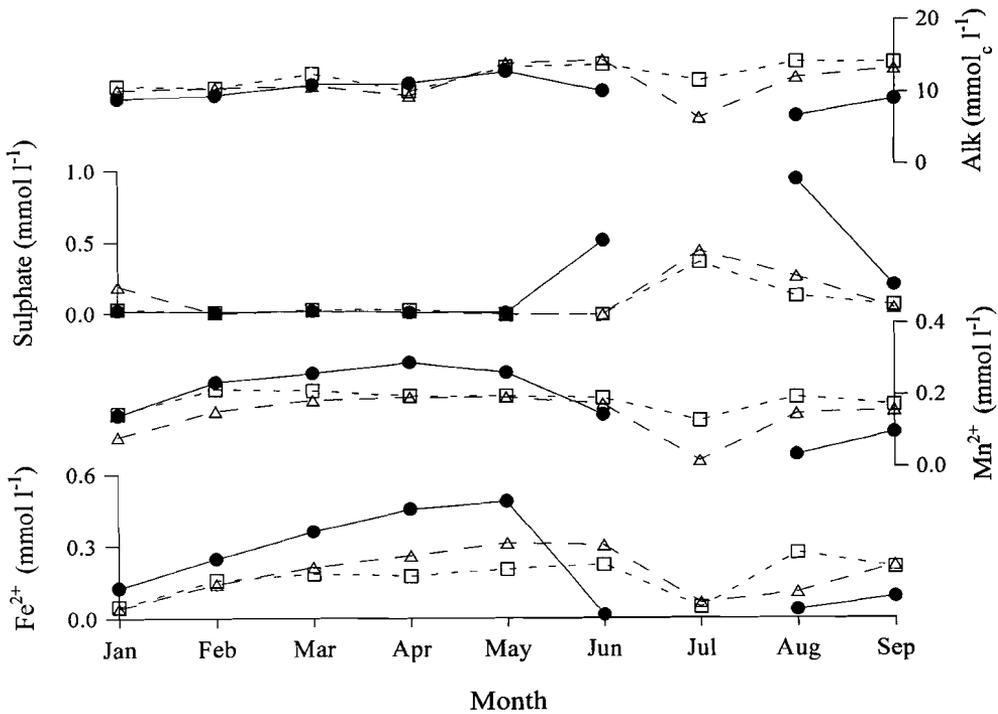


Figure 3.1. Pore-water fluctuations of Fe^{2+} , Mn^{2+} , sulphate, and alkalinity (● 30-40 cm depth; △ 50-60 cm depth; □ 70-80 cm depth) at site A3.

In August and September the groundwater table rose again resulting in anaerobic biodegradation of this fresh, highly reactive organic matter. This is reflected by an increase in pore-water Mn^{2+} and Fe^{2+} concentrations, pH and alkalinity and a decrease in sulphate concentration. Nitrate was absent in all pore-water samples.

Table 3.2. Characterisation of the monthly sampled surface water.

	Unit	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Alk.	mmol _c l ⁻¹	3.4	3.9	3.8	3.9	4.0	4.2	3.5	3.3	4.5
Sulphate	mmol l ⁻¹	0.36	0.57	0.42	0.41	0.42	0.34	0.44	0.67	0.38
Nitrate	μmol l ⁻¹	0.11	0.13	0.14	0.11	0.03	0.01	0.02	0.03	0.09
Fe	μmol l ⁻¹	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Mn	μmol l ⁻¹	1	1	1	2	3	4	2	2	7
Zn	μmol l ⁻¹	1.8	< 0.2	1.1	< 0.2	< 0.2	1.1	1.1	0.9	1.3
Cu	μmol l ⁻¹	0.09	0.05	0.35	< 0.02	0.05	0.06	0.05	0.15	< 0.02
Pb	nmol l ⁻¹	11	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Cd	nmol l ⁻¹	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2

It should be noted that during winter and spring the highest Mn and Fe pore-water concentrations are measured in the 30-40 cm layer. A difference in redox conditions may be related to the presence of a vegetation cover. Degradation of easily decomposable organic plant material in the top layer of the soil leads to the consumption of any dissolved oxygen present which causes the anaerobic conditions in the upper layer.

The behaviour of heavy metals in these soils and seasonal fluctuations in their pore-water concentrations during the sampling period may be explained by the fluctuations in groundwater levels. Monthly measured pore-water concentrations of Zn, Cu, Pb and Cd are shown in Fig. 3.2 (data from site A3). Fig. 3.2 shows that the highest pore-water concentrations of heavy metals are measured during summer months. Although most Cd concentrations fall below the detection limit (2 nmol l⁻¹ Cd), a clear peak in pore-water concentrations is measured in August. Cu also shows a peak in August, suggesting that the behaviour of Cd and Cu is similar. The peak in Pb concentrations only consists of one data point slightly higher than the detection limit (10 nmol l⁻¹ Pb), and is, therefore, not significant. During August maximum biodegradation of fresh, highly reactive organic matter takes place and adsorbed metals on this host phase are expected to be simultaneously released to the pore water. Comparable to results of Palsma and Loch (1991), a nonequilibrium may exist during that period, resulting in high pore-water concentrations.

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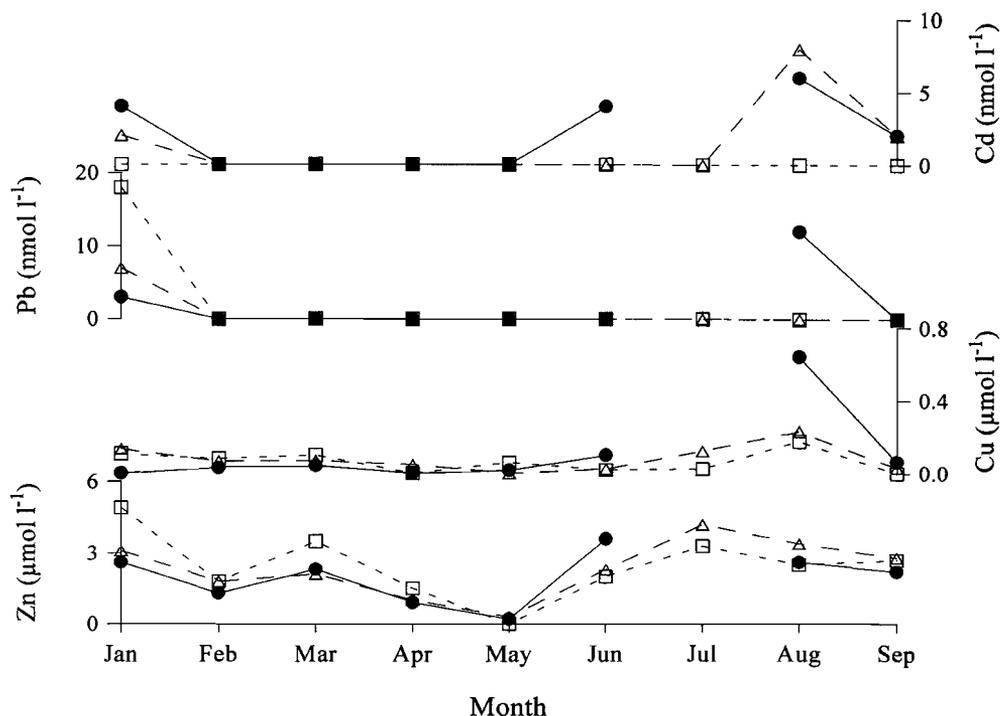


Figure 3.2. Pore-water fluctuations of Zn, Cu, Pb, and Cd (● 30-40 cm depth; △ 50-60 cm depth; □ 70-80 cm depth) at site A3.

Dissolved Zn concentrations increase during the summer months as well, but Zn concentrations show a peak in July, when the most aerobic conditions are present in the soil due to the low groundwater level. Therefore, the mobility of Zn during the summer months may be explained partly by oxidation of labile sulphides. As will be shown later, a strong correlation of Zn and sulphide is found in the solid phase under anaerobic conditions. In the 30-40 cm layer pore-water concentrations of Cd and Cu start to increase as well during June, which may indicate that these metals are also precipitated partly by sulphides in this layer. The reason for the decrease in pore-water Zn concentrations from January to May is still unclear, but may be related to a nonequilibrium situation during this period. In May the lowest Zn concentrations are measured. Pore-water concentration peaks during this period (peaks during January and March) correlate with concentration peaks in the inundating surface water (Table 3.2). The lower Zn concentrations in the 30-40 cm layer relative to deeper layers

during major part of the sampling period may be related to the higher amounts of organic matter and sulphides in this layer.

Evidence for sulphide precipitation

Using electron microprobe technique, the presence of sulphide precipitates was demonstrated at site A1. Heavy metal sulphide precipitates were observed in the layer 10-20 cm. These sulphides have a molar ratio Zn/S of almost one. Precipitates of other metal sulphides are hardly detectable by this method. Only traces of As, Cd, Pb and Cu have coprecipitated with the ZnS (molar ratio metal/Zn < 0.02). At greater depth (30-40 cm) the presence of almost discrete Fe-(mono)sulphides having a molar ratio Fe/S of nearly one, was demonstrated. Minor amounts of As were detected in these sulphides. The sensitivity of this method depends on the length of the scanning time and the measuring method (WDS, EDS). Detection limits for different elements vary between 600 mg kg⁻¹ for Cd, Fe, As and S, 800 mg kg⁻¹ for Zn and Cu and 1400 mg kg⁻¹ for Pb. At sites A2 and A3 no evidence of sulphides was found, although small amounts of available sulphides were probably present during part of the year, given the low sulphate concentrations in the pore water. Depending on the spot size of the electron beam, the grain size needed for a reliable measurement must be at least 3 to 5 µm. At sites A2 and A3 sulphides may be present more diffusely in the soil matrix relative to site A1.

The observed sulphide precipitates are all associated with the presence of vascular cell structures in the soil (Fig. 3.3). As the original structure of the roots is preserved, the observed sulphides may be considered as substitution substances in decaying roots. This kind of substitution (formation of pseudomorphs) has been described by Kooistra (1978) for salt marsh sediments.

The presence of sulphides substituting cell structures, indicates *in situ* formation during anaerobic degradation of the organic matter. In this system, sulphides are formed by diffusion of sulphate to the decaying organic matter and by decomposition of proteins in reed roots, which take up sulphate from the soil during growth (Raiswell *et al.*, 1993). Precipitation of metal sulphides in the plant remnants may be related to the presence of Fe-(hydr)oxide precipitates on the root surfaces, as described by Otte *et al.* (1989). When organic plant material is mineralised, the Fe-(hydr)oxides dissolve and sorbed heavy metals are liberated to be subsequently precipitated as sulphides. In microsites in the organic matter the sulphides may be protected against oxidation.

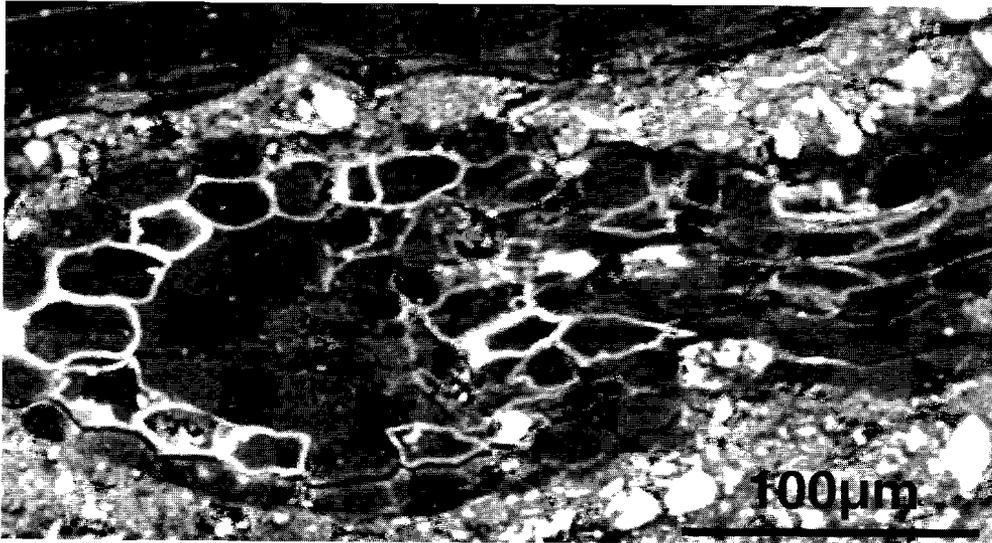


Figure 3.3. Backscatter image of sulphide precipitates. At the location of former cell walls sulphide precipitates are visible.

The association between sulphides, in the form of pyrite framboids, and vascular plant structures has also been observed by Marnette *et al.* (1993) in freshwater systems, and by Oenema (1990) and Feijtel *et al.* (1988) in salt marshes. Authigenically formed pyrite can also be preserved in geological materials where it has replaced vegetal matter, preserving its original cell structure (Kirchner, 1985). Frizzo *et al.* (1991) observed pyrite and monosulphides covering cell walls in estuarine sediments, but did not detect heavy metals in the sulphides. Norrish *et al.* (1986) described organic matter as a substrate for ZnS precipitation. The presence of framboidal Zn sulphides in heavily polluted estuarine sediments was reported by Luther *et al.* (1980). The absence of heavy metal sulphides in most studies is thought to be the result of low levels of heavy metals.

Phosphates, which may have formed under anaerobic conditions in a similar way, were observed. Phosphate precipitates, with a molar ratio P/Fe in the range 0.15-0.34, also correlate with vascular plant structures during this study. Locally, root remnants containing precipitates of Fe-(hydr)oxides or Fe-carbonates were observed, which also points at the heterogeneity of the soil system.

Conclusions

Fresh organic matter plays an important role in the geochemical cycling of seasonally flooded freshwater estuary soils. The increase in mobility of heavy metals during the summer months is thought to be the result of two different processes. A temporary increase in copper and cadmium concentrations in the pore water was observed during the period, when organic matter degradation rate is highest. Heavy metals associated with organic matter may be mobilised to the pore water by this process. Pore-water concentrations of heavy metals in this type of soils may also be influenced by the precipitation and dissolution of sulphide minerals. Anaerobic decomposition of organic matter by sulphate reduction during rising groundwater table in the autumn months may provide sulphide ions. The actual presence of Zn sulphide precipitates has been observed in root remnants. These sulphides probably substitute organic matter during mineralisation under reducing conditions. During the summer months, with dropping groundwater levels, oxygen supply to the soil is increased, and measured concentrations of heavy metals increase rapidly.

Acknowledgement - M. van Alphen and P.J. Kleingeld assisted in soil and pore-water collection. Valuable technical and editorial comments on the manuscript were provided by C.H. van der Weijden and P.R. van der Linde. The project was carried out on behalf and with financial support of the Ministry of Transport, Public Works and Water Management, Directorate-General for Public Works and Water Management, Directorate IJsselmeergebied. This chapter has been published as contribution 961006 of the Netherlands Research School of Sedimentary Geology.

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Chapter 4

Temporal variation in pore-water characteristics of recent sediments in the river Meuse, The Netherlands

G.A. van den Berg, J.P.G. Loch, L.M. van der Heijdt, and J.J.G. Zwolsman

Abstract - Pore-water characteristics may be influenced by variation in surface water chemistry and processes taking place in the sediment after deposition. The seasonal fluctuations in surface water concentrations in a recent sedimentation area of the river Meuse, The Netherlands, do not significantly influence the behaviour of most solutes in the underlying sediments. Pore-water concentration profiles of these freshwater sediments are mainly determined by internal, biogeochemical, processes. During summer, pore-water profiles of redox-sensitive ions are characterised by steeper gradients at the sediment-water interface than during winter, which reflects environmental and intrinsic changes in the sediments. These changes are related to a relatively large difference in temperature of the bottom water, presumably in combination with changes in degradation of organic matter, microbiological activity in the sediment, diffusion of solutes, mixing and reaction rates. This study demonstrates that it is necessary to account for non-steady state situations in dynamic depositional environments.

This chapter has been submitted for publication.

Introduction

Recent sedimentation basins in delta areas are commonly characterised by a relatively high input of reactive organic matter (OM), in combination with highly dynamic conditions. Pore water is recognised as the most sensitive phase to study effects of dynamic processes in sediments (Adams, 1994). If sampling takes place at high resolution, pore-water characteristics provide insight into (bio)geochemical processes in sediments and interactions between sediments and bottom water (Gaillard *et al.*, 1989, Santschi *et al.*, 1990). Temporal, often seasonal, variation in concentrations of pore-water solutes can be attributed to fluctuations in surface water chemistry and processes taking place in the sediment after deposition (Berner, 1980). Fluctuations in surface water concentrations are attributed to changes in the degree of oxygenation due to periodic stratification of the water column (Balistrieri *et al.*, 1992; Hines *et al.*, 1997), river discharge (Van der Weijden and Middelburg, 1989) and primary production (Zwolsman, 1994). Pore-water composition may be used to evaluate effects of diagenetic reactions on the distribution of redox-sensitive ions, trace metals and nutrients (Elderfield *et al.*, 1981).

The purpose of this research is to investigate temporal variation in pore-water profiles of nutrients and redox-related elements in recent sediments of the river Meuse, The Netherlands, and to relate this variation to differences in environmental conditions during summer and winter (e.g. temperature and surface water composition).

Sampling and analysis

Site description

The Biesbosch is a wetland, situated in the delta of the rivers Rhine and Meuse in the western part of The Netherlands (Fig. 4.1). The study area is almost exclusively flushed by the river Meuse, except for its north-western part, where Rhine water occasionally intrudes. Tidal influences in the Biesbosch have decreased considerably after 1970, when the former Rhine-Meuse estuary was closed off from the North Sea by a dam. Today, the Biesbosch is a freshwater tidal basin with a modest tidal range (some 20 to 30 cm in the study area). Due to the low current velocities, the former tidal channels are silting up. Both the sediments and soils in the Biesbosch are strongly

contaminated by heavy metals, reflecting the serious metal pollution history of the rivers Meuse and Rhine (Van Eck *et al.*, 1997).

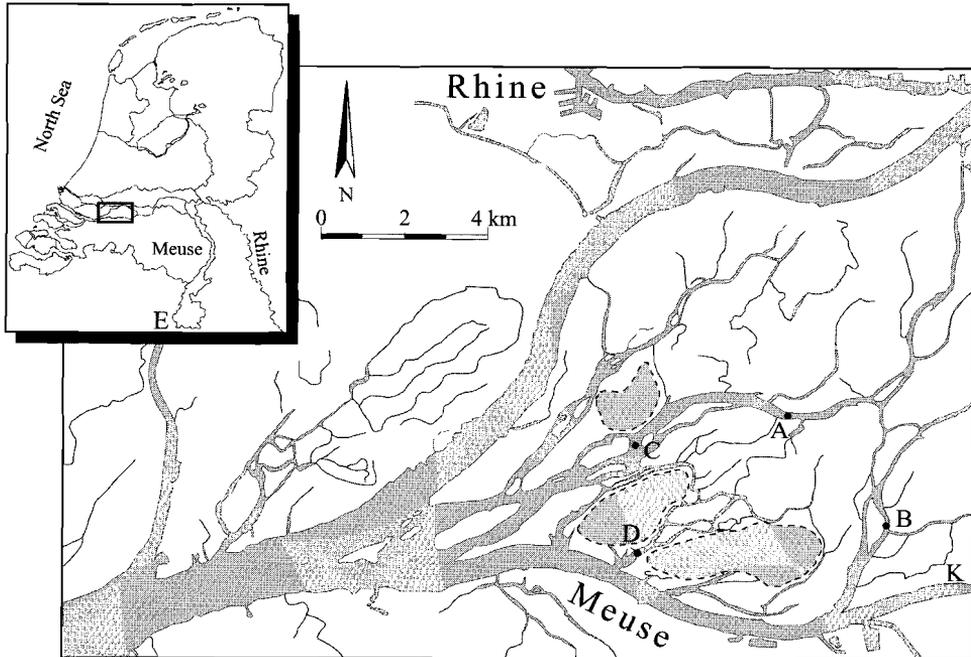


Figure 4.1. Map of the sampling locations in the Biesbosch. The small map shows The Netherlands and the study area (E is Eijsden; K is Keizersveer).

Sample collection and handling

At four permanently submerged locations in the Biesbosch (Fig. 4.1), sediment cores were collected in Plexiglas tubes with an inner diameter of 15 cm and a length of 60 cm. Mean depth of the water column at the locations A, B, C, and D is 1.4, 2.0, 4.2, and 3.3 m respectively. Sampling took place manually by SCUBA divers in November 1995 and June 1996. Bottom water remained on the sediment cores in the tubes in order to prevent oxidation of the sediment. Collected bottom water was analysed on board for temperature, dissolved oxygen, pH, and salinity with a sensor system. Pore-

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water pH was measured on board with a MI-410/MI-415 pH micro-electrode (Microelectrode INC.) equipped with a micromanipulator. To avoid disturbance of the sediment, pH measurements were conducted in a second core similar to the one used for pore-water and solid-phase extraction. The collected cores were stored at 4°C.

Within 48 hours after collection, the top 7-10 cm of the sediment cores were sectioned into 0.5- or 1.0-cm slices. Laboratory sampling took place under strictly anaerobic conditions in a nitrogen-filled glove box. Pore water was extracted by pressure filtration, according to the method described by De Lange (1992), and collected in High Density Polyethylene bottles. Part of the pore water was acidified with concentrated HNO₃ suprapur (1 ml HNO₃ per 50 ml pore water). Sediment and non-acidified pore-water samples were kept at 4°C under a nitrogen atmosphere until extraction and analysis. All materials (bottles, filters and filtration blocks) were acid-cleaned prior to use.

Sediment analysis

Freeze-dried sediment samples were digested in a mixture of concentrated HClO₄, HNO₃, and HF and finally dissolved in 1 M HCl. Total elemental concentrations (Ca, Al, Mn, Fe, S, and P) in the acid solution were determined by inductively coupled plasma atomic emission spectrometry (Perkin Elmer Optima 3000). Quality of the analyses was tested by simultaneously analysing international standard sediments. CaCO₃ was calculated from the elemental Ca content, assuming all Ca to be present as CaCO₃. Accuracy is within 5 % of the tabulated concentrations for all elements of interest. Measurement of organic C (OrgC) was made with a CNS analyser (Carlo Erba Strumentazione nitrogen analyzer 1500). Inorganic carbon was removed before analysis by shaking the sediment sample in 1 M HCl. Moisture content of the sediment samples, necessary to calculate porosity, was determined by measuring the weight loss after freeze drying.

Collected pore water was analysed for concentrations of major elements (Mn, Fe, S, Ca, Ba, and P) by ICP-AES. Ammonium was determined by autoanalyzer (Technicon TRAACS 800) in November 1995 and spectrophotometrically according to the Berthelot method (Solorzano, 1969) in June 1996. Sulphate, nitrate and chloride were measured in non-acidified pore water by ion-chromatography (Dionex QIC analyser). Alkalinity was determined with the Gran plot method after titration with 0.01 M HCl (Stumm and Morgan, 1996).

Temporal variation in pore-water characteristics

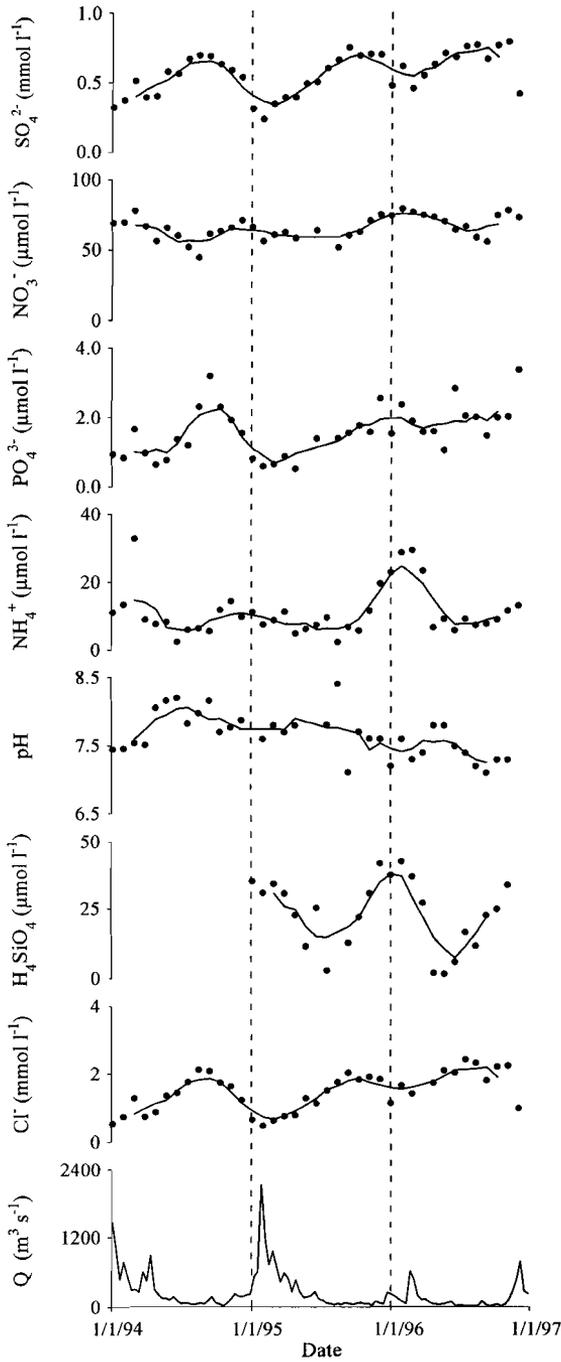


Figure 4.2.

Variation in solute concentrations in the river Meuse during the period 1994-1996. Data obtained from the DONAR data base system (Kroos and Oberweis, 1995). Discharge of the river Meuse is measured daily at Eijsden, concentrations are measured monthly at Keizersveer. The trend lines in the concentration profiles are calculated by moving average through five sampling points.

Dissolved organic carbon (DOC) was measured by the high-temperature catalytic oxidation method (Shimadzu Total Organic Carbon Analyzer TOC-500) after pre-treatment with phosphoric acid to remove inorganic carbon.

Results and discussion

Surface water fluctuations

The river Meuse is a river with a pluvial regime. Depending on river discharge, surface water concentrations of solutes are expected to fluctuate. Fig. 4.2 shows that during relatively dry periods and low river discharge (summer months), concentrations of especially chloride, phosphate, and sulphate in the river Meuse are higher than during wet periods and relatively high river discharge (winter months). Additionally, a significant difference in temperature of the bottom water (approximately 8°C during winter and 22°C during summer) was measured during the sampling campaigns. Due to the relatively small depth of the water column in the study area, temperature in the upper layer of the underlying sediments varies similarly to that in the bottom water.

Solid-phase characteristics

Deriving temporal effects from pore-water concentrations in sediment cores collected at various occasions is meaningful only when differences in solid-phase characteristics are insignificant. Sediment characteristics (OrgC, CaCO₃, porosity, Al, Mn, Fe, S, and P) of the studied cores are given in Fig. 4.3 to 4.6. At the locations B, C and D, sediment cores roughly have similar characteristics at the two occasions. Increased OrgC contents during summer may be the result of input of fresh algal material. Apparent temporal differences in porosity and Al content throughout the sampled sediment cores at location A (Fig. 4.3) are most likely related to spatial heterogeneity, which may be caused by variation in the input of sandy material. Differences in Al contents are also reflected in the solid-phase profiles of OrgC, CaCO₃, Mn, Fe, S and P. Because pore-water characteristics at location A can not be compared without taking changes in the solid phase into account, these are not discussed in this chapter.

Temporal variation in pore-water characteristics

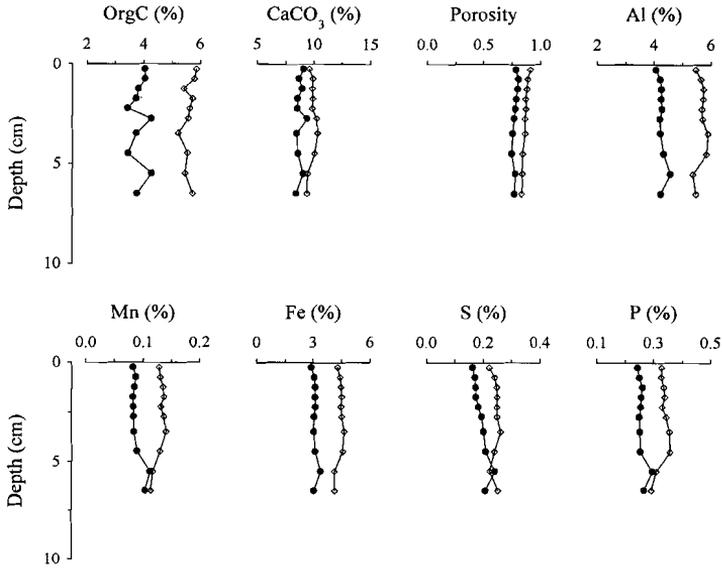


Figure 4.3. Solid-phase characteristics at location A (black dots represent concentrations in November 1995; open diamonds represent concentrations in June 1996).

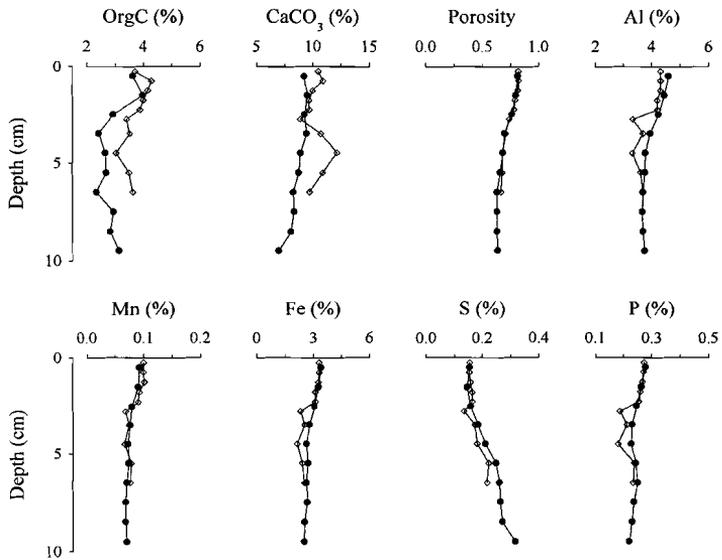


Figure 4.4. Solid-phase characteristics at location B (black dots represent concentrations in November 1995; open diamonds represent concentrations in June 1996).

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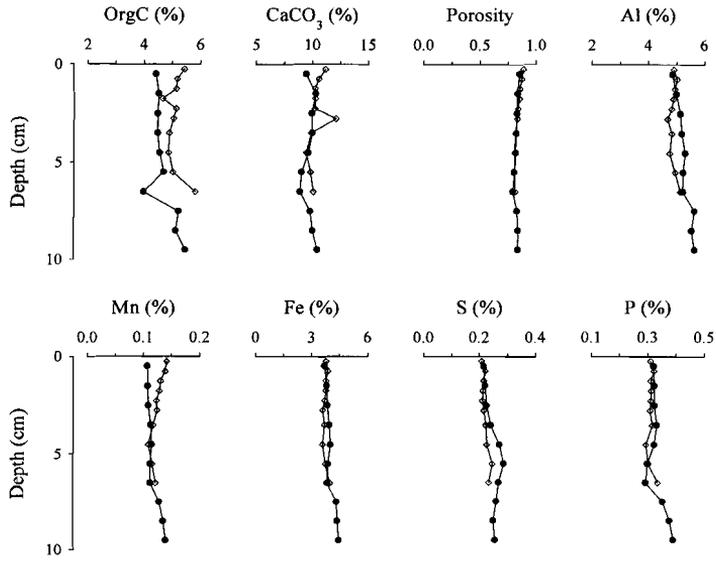


Figure 4.5. Solid-phase characteristics at location C (black dots represent concentrations in November 1995; open diamonds represent concentrations in June 1996).

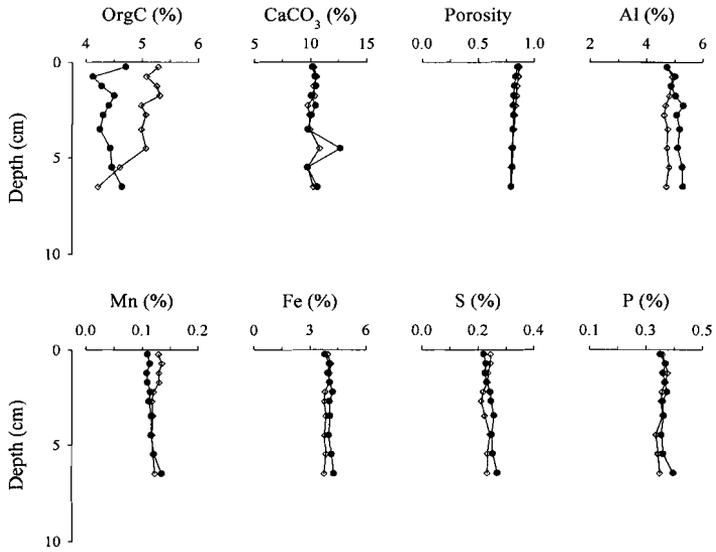


Figure 4.6. Solid-phase characteristics at location D (black dots represent concentrations in November 1995; open diamonds represent concentrations in June 1996).

Temporal variation in pore-water characteristics

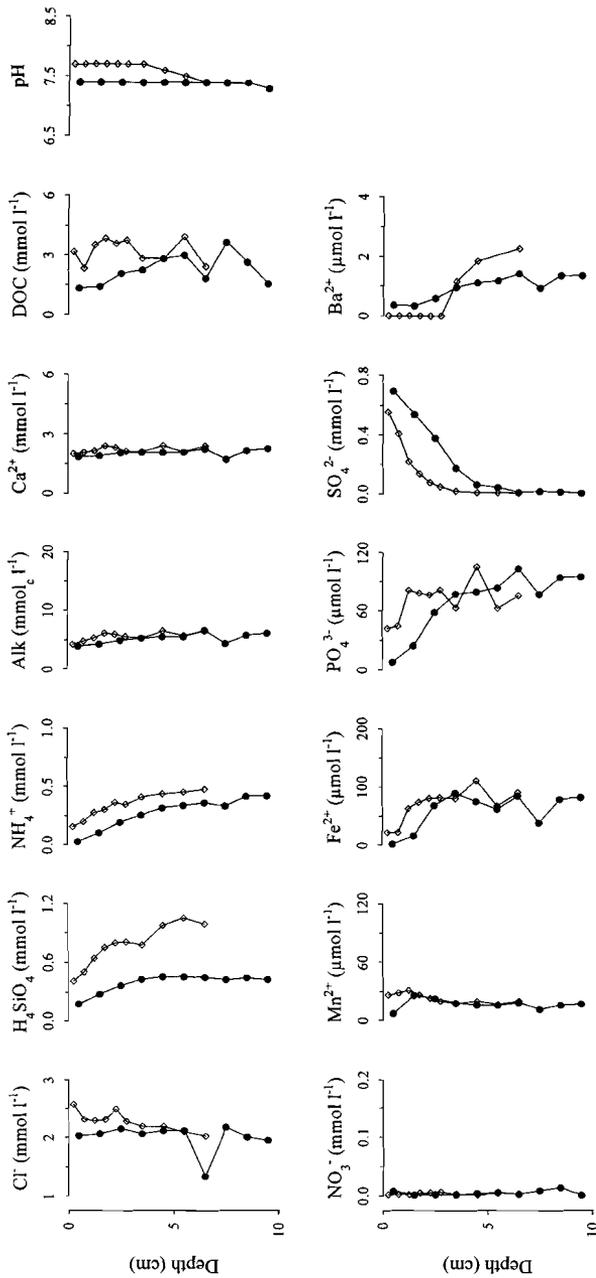


Figure 4.7. Pore-water characteristics at location B (black dots represent concentrations in November 1995; open diamonds represent concentrations in June 1996).

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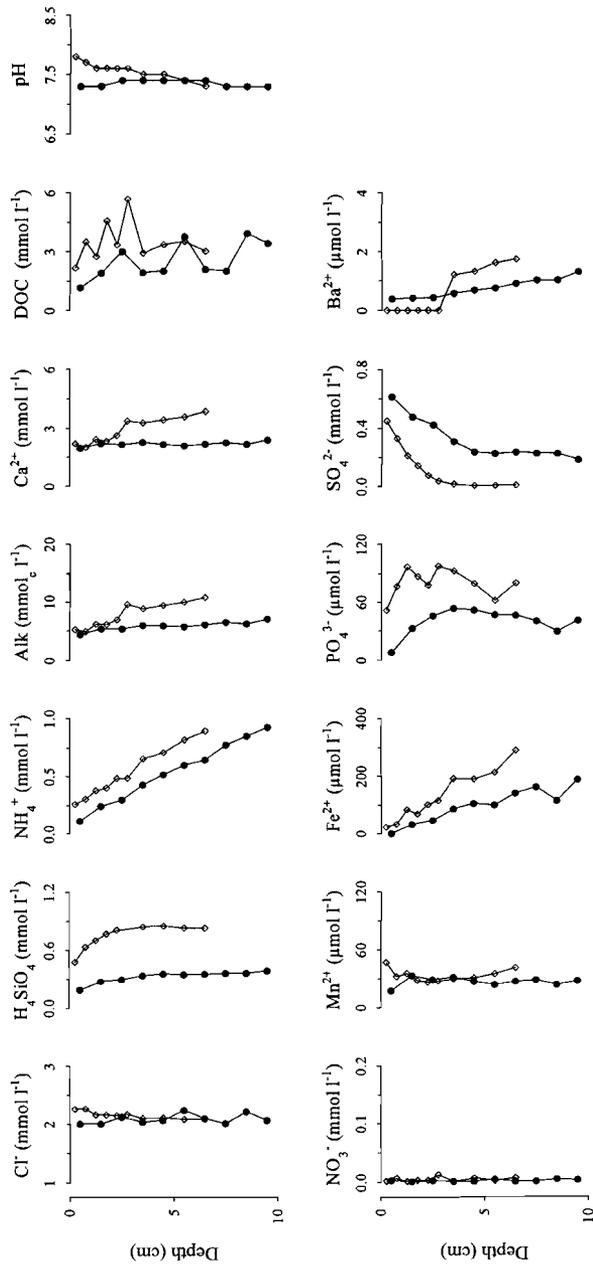


Figure 4.8. Pore-water characteristics at location C (black dots represent concentrations in November 1995; open diamonds represent concentrations in June 1996).

Temporal variation in pore-water characteristics

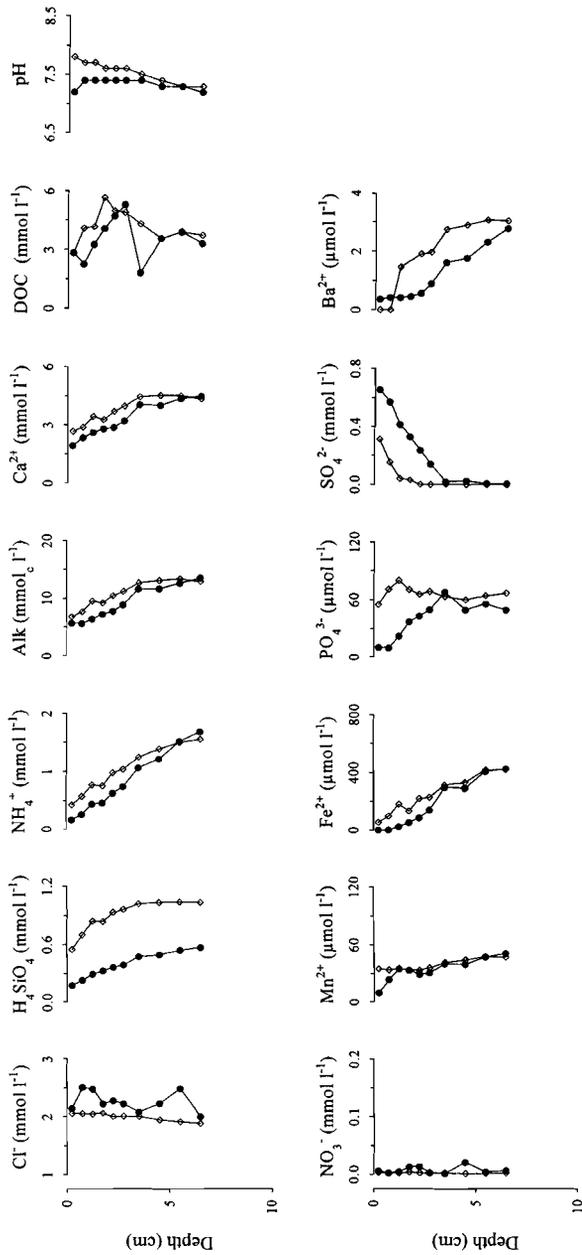


Figure 4.9. Pore-water characteristics at location D (black dots represent concentrations in November 1995; open diamonds represent concentrations in June 1996).

Geochemical processes in the sediments

Measured pore-water concentration profiles at locations B, C, and D are shown in Fig. 4.7 to 4.9 (note the different scales on the x-axes). Degradation of OM is the main biogeochemical process taking place in sediments after deposition. Pore water concentration profiles of redox-sensitive ions demonstrate the effects of degradation of OM. Degradation of OM results in a decrease of the redox potential with depth in the sediment. This is indicated by a slight decrease in the pore-water pH, the presence of reduced solutes, resulting from suboxic degradation of OM (Mn^{2+} and Fe^{2+}), and the absence of nitrate in the pore water. Secondary redox reactions, like oxidation of reduced pore-water and solid-phase species, and other postdepositional processes, like precipitation-dissolution and adsorption-desorption, also influence these changes in pore-water concentrations with depth.

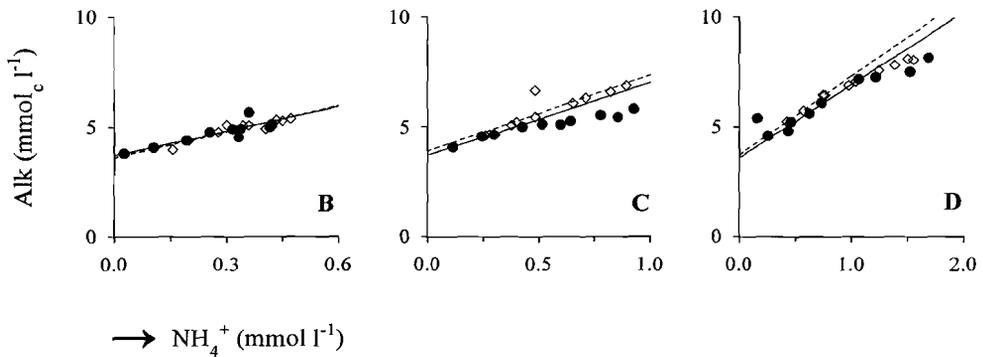


Figure 4.10. Plots of Δ Alkalinity (corrected for CaCO_3 dissolution) versus ΔNH_4^+ at the locations B, C, and D (black dots represent concentrations in November 1995; open diamonds represent concentrations in June 1996). Also plotted are ideal regression lines (continuous line for November 1995 and discontinuous line for June 1996).

The presence of ammonium in the pore water is predominantly related to degradation of N-bearing organic substrates (e.g. amino acids). Similarly, alkalinity production is recognised as a sensitive indicator of the extent of early diagenetic processes in sediments. However, in the sediments studied, alkalinity profiles are significantly affected by dissolution of CaCO_3 , especially in the cores at the locations

C and D. After subtraction of the amount of alkalinity produced by CaCO_3 dissolution, based on the increase in Ca^{2+} with depth, ΔAlk (= pore-water alkalinity - surface-water alkalinity) is almost linearly correlated with ΔNH_4^+ (Fig. 4.10). Regression lines have slopes in the range 3.3-4.0, both in winter and summer. Because these values are lower than the average C/N ratio of 7.2 for suspended matter in the study area (*Chapter 5*), N-rich organic substrates are probably predominantly degraded. The absence of complete linearity between ΔAlk (corrected for CaCO_3 dissolution) and ΔNH_4^+ , especially at larger depth (Fig. 4.10), suggests that alkalinity is additionally removed from solution by other secondary reactions taking place under anoxic conditions, such as precipitation of Mn(II)- and Fe(II)-carbonates (Postma, 1977, 1981).

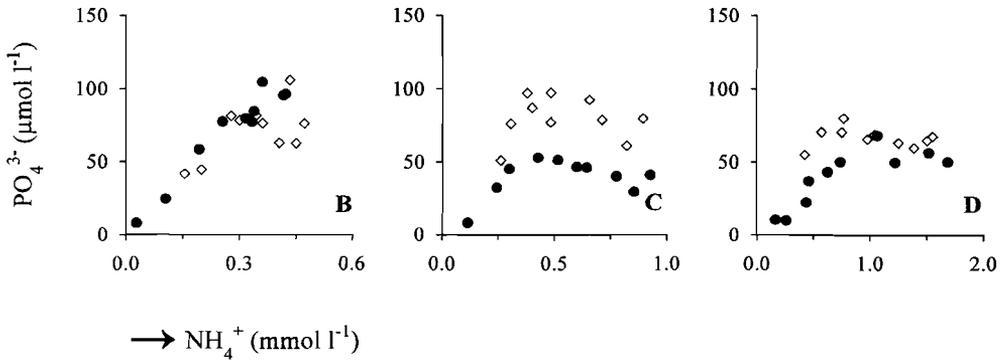


Figure 4.11. Plots of ΔPO_4^{3-} versus ΔNH_4^+ at the locations B, C, and D (black dots represent concentrations in November 1995; open diamonds represent concentrations in June 1996).

In addition to production of dissolved phosphate by degradation of organic-P compounds, Fe(III) reduction results in the release of associated phosphate to the pore water (Lazzaretti *et al.*, 1992; Sundby *et al.*, 1992). Comparison of the pore-water concentration profiles of Fe^{2+} and PO_4^{3-} (Fig. 4.7 to 4.9) suggests a strong relationship between Fe(III) reduction and PO_4^{3-} production in the sediments studied. Therefore, ratio's between ΔNH_4^+ and ΔPO_4^{3-} in the pore water can not be used to calculate N/P ratios of organic matter in the sediment. A poor relationship is shown between ΔPO_4^{3-} and ΔNH_4^+ (Fig. 4.11). Phosphate profiles in the pore water show a more or less distinct maximum, and a decrease to an asymptotic value with depth (Fig. 4.7 to 4.9).

This indicates a removal of dissolved phosphate from the pore water under anoxic conditions (Emerson and Widmer, 1978). It should be noted that total P was measured in the pore water. Except for orthophosphate, this consists of dissolved organic P and polyphosphates. The latter two are, however, generally of minor importance in such sediments.

The shapes of the Mn^{2+} pore-water concentration profiles are comparable. Below the sediment-water interface, a maximum in the pore-water concentration of Mn^{2+} is observed. Deeper in the sediment, Mn^{2+} concentrations in the pore water decrease to an asymptotic value (Fig. 4.7 and 4.8). Speciation calculations with MINTEQA2 (U.S. EPA, 1991) indicate that MnCO_3 may to a large extent control this pore-water concentration. Equilibria involving Mn minerals are generally reached faster than those involving Fe minerals (Davison, 1993). Consequently, the gradual increase in pore-water Fe^{2+} with depth (Fig. 4.7 to 4.9), even below the zone of sulphate reduction, may be explained by heterogeneity of the sediment and slow rates of dissolution of Fe(III)-(hydr)oxides and formation of Fe(II)-minerals (Wersin *et al.*, 1991; Postma, 1993). Supersaturation of the pore water with respect to reduced Fe(II)-minerals, such as FeCO_3 and $\text{Fe}_3(\text{PO}_4)_2$, also favours a non-equilibrium behaviour of Fe in the sediments studied. This may also explain why Fe^{2+} concentration profiles in the pore water show significant variation between the sampling locations.

Sulphate reduction theoretically takes place when all other terminal electron acceptors are exhausted, although significant overlap exists between redox zones in the sediments studied (discussion in Chapter 5). Concentration profiles of sulphate in the pore water are spatially comparable. Sulphate concentrations decrease to zero within the upper sediment layer as is also observed in a sedimentation basin of the river Rhine (Paalman, 1997). We do not have a reasonable explanation for the exceptional behaviour of sulphate in the winter core at location C. Sulphate reduction influences the stability of barite (BaSO_4) in sediments (Van Os *et al.*, 1991). As a result of reduction of sulphate, barite dissolves. The depths at which Ba^{2+} concentrations in the pore water increase, clearly represent the depths at which sulphate reduction takes place (Fig. 4.7 to 4.9). Similar observations were made in brackish sediments of the Scheldt estuary (Zwolsman and Van Eck, 1993). The presence of methanogenesis in the sediments studied is indicated by the continuous production of NH_4^+ with depth, even below the zone of sulphate reduction.

Temporal fluctuation in pore-water concentration profiles

Temporal fluctuation in surface water concentrations may influence the chemical characteristics of the underlying sediment. A conservative parameter illustrative for the influence of surface water composition on pore-water concentrations in the sediments studied is chloride. Chloride concentrations in the surface water increase during summer due to the low discharge of the river Meuse (Fig. 4.2). This is reflected by the variation in pore-water chloride concentration. Near the sediment-water interface, chloride concentrations are significantly higher during summer than during winter, especially in the sediment cores at the locations B and C (Fig. 4.7 and 4.8).

Surface water concentrations of dissolved silica (H_4SiO_4) in the river Meuse show a clear seasonal variation (Fig. 4.2), as was also observed by Van der Weijden and Middelburg (1989) for the river Rhine. The cycle of dissolved silica in aquatic systems is strongly coupled to the biological activity in the surface water and dissolution of biogenic silica in freshwater sediments (Calvert, 1983). The increased concentrations of dissolved silica in the pore water relative to those in the surface water is a reflection of this recycling of silica. Dissolved silica concentrations in the pore water increase with depth and reach an asymptotic concentration at a depth of a few cm. The higher asymptotic concentrations of dissolved silica in the pore water during summer (approximately $1.0 \text{ mmol l}^{-1} \text{ H}_4\text{SiO}_4$), compared to those during winter (approximately $0.4 \text{ mmol l}^{-1} \text{ H}_4\text{SiO}_4$), reflect increased dissolution of freshwater diatoms.

Although the water column is completely aerobic throughout the year, pore-water concentration profiles of redox-sensitive ions indicate that reduced conditions are present immediately below the sediment-water interface during summer and winter. A temporal change in these pore-water concentration profiles suggests differences in OM degradation rates. These changes include a steeper Fe^{2+} concentration gradient at the sediment-water interface during summer. This agrees well with an upward shift of the peak in the Mn^{2+} concentration profiles. Additionally, during summer, sulphate concentrations in the pore water show a significantly larger negative gradient at the sediment-water interface. This is also reflected in acid-volatile sulphide (AVS) profiles (Van den Berg *et al.*, 1998¹/Chapter 7). AVS is present closer to the sediment-water interface, because sulphate reduction takes place closer to the sediment-water interface during summer.

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Significant changes in pore-water concentration gradients can be linked predominantly to the large difference in temperature (some 14°C between the sampling periods) of the bottom water and upper sediment layer, which may be reflected by changes in OM degradation rates, metabolic activity in the sediment, diffusivity of pore-water solutes, and reaction and bioturbation rates. Temporal changes in the amount of OM degradation in the sediments studied is also indicated by concentration profiles of DOC in the pore water. Dissolved organic matter (DOM) is produced by incomplete mineralisation of OM (Orem *et al.*, 1986). Relatively high DOC concentrations (1-6 mmol l⁻¹ DOC) are present in the pore water in comparison to the bottom water concentration (0.3 mmol l⁻¹ DOC). The higher pore-water concentration profiles of DOC during summer at all locations, especially in the top 3-4 cm (Fig. 4.7 to 4.9), indicate an increased degradation of OM. The variation in DOC concentrations, however, suggests that measurements may be subject to a relatively large error.

The effects of changes in temperature on the intensities of (bio)geochemical processes in sediments are also described for e.g. near-shore sedimentary coastal areas (Klump and Martens, 1989), salt-marshes (Kostka and Luther, 1995), and lakes (Holdren and Armstrong, 1986). Temperature effects in periodically saturated environments, like salt marshes and wetlands, may be outweighed by short-term effects like episodic inundations (Van den Berg *et al.*, 1998²/Chapter 3) and plant growth (Oenema, 1988; Hines *et al.*, 1989). In such dynamic environments, variation in the intensity of (bio)geochemical processes may significantly affect the behaviour and bioavailability of e.g. nutrients and heavy metals in sediments, and their interactions between sediments and surface- and groundwater (Carignan and Lean, 1991; Sherman *et al.*, 1994). Consequently, this study shows that in dynamic depositional environments, fluxes of solutes, e.g. nutrients and heavy metals, between the sediment and the surface water are not calculated properly when assuming steady state.

Conclusions

This study shows that temporal dynamics may affect pore-water concentration profiles in freshwater sediments. Except for chloride, the effects of temporal variation in surface water concentrations on the pore-water characteristics are negligible in the sediments studied. Significant changes in pore-water concentration profiles can be

linked predominantly to the difference in temperature, which may be reflected by e.g. changes in OM degradation rates, metabolic activity in the sediment, diffusivity of pore-water solutes, and reaction and bioturbation rates. During summer, pore-water profiles of redox-sensitive ions are generally characterised by steeper gradients at the sediment-water interface than during winter. Consequently, this study shows that in dynamic depositional environments it is necessary to account for non-steady-state conditions to determine fluxes of e.g. nutrients and heavy metals between the sediment and the surface water.

Acknowledgement - We thank C.H. van der Weijden for many useful comments on the manuscript. The assistance of Pieter Kleingeld, Gijs Nobbe and Mark van Alphen during sampling and in the laboratory is greatly appreciated. This project was carried out with financial support of the Ministry of Transport, Public Works and Water Management, Institute for Inland Water Management and Waste Water Treatment (RIZA).

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Chapter 5

Redox processes in recent sediments of the river Meuse, The Netherlands

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Abstract - Pore-water concentrations of inorganic solutes were measured at four locations in a recent sedimentation area of the river Meuse in The Netherlands. The pore-water concentration profiles were interpreted using the steady state one-dimensional reaction/transport model STEADYSED1. This model explicitly accounts for the organic matter degradation pathways and secondary redox reactions. Results show that the model reproduces the measured pore-water profiles of redox species reasonably well, although significant divergence is observed for pH. The latter is due to the absence of pH buffering by CaCO_3 in the model. At all locations, methanogenesis is the major pathway of organic matter degradation below 3 cm from the sediment-water interface. However, organic matter degradation rates by methanogenesis may be overestimated, because methane ebullition is not included. Differences in profiles of redox-sensitive ions among the four locations are explained by differences in depositional conditions, in particular the sediment accumulation rate, supply of organic matter, and macrofaunal activity.

This chapter has been submitted for publication.

Introduction

Pore-water distributions of redox-sensitive ions provide considerable information about pathways and rates of organic matter (OM) degradation, and the intensities of physical, chemical and biological processes in sediments (Berner, 1980; Santschi *et al.*, 1990). The relative contributions of the microbial pathways of OM mineralisation depend on the flux of OM to the sediment, the biological reactivity of the OM, the availability of electron acceptors, the kinetics of secondary reactions as well as the physical transport rates. High deposition fluxes of degradable OM in many freshwater systems result in compressed redox zones, with sulphate reduction occurring within the upper few centimetres of the sediments (Wersin *et al.*, 1991). Because of the limited supply of sulphate, methanogenesis may be an important pathway of OM degradation in freshwater sediments (Capone and Kiene, 1988).

Sediments are important sources or sinks of heavy metals in aquatic systems (e.g. Gaillard *et al.*, 1986; Calmano *et al.*, 1993). Because the behaviour of heavy metals in sediments is to a large extent controlled by the redox cycles of the major biogeochemical elements (Shaw *et al.*, 1990), the latter need to be quantified in order to provide a rational basis for managing contaminated water systems (Förstner *et al.*, 1994). Reactive transport models, e.g. Rabouille and Gaillard (1991), Dhakar and Burdige (1996), Soetaert *et al.* (1996), and Van Cappellen and Wang (1996), have been developed to identify environmental and biogeochemical factors controlling the chemical dynamics of sediments and to predict the behaviour and speciation of redox-sensitive ions. These models were primarily developed to quantify processes in marine systems. The latter model was also tested on freshwater systems (Van Cappellen and Wang, 1995).

The purpose of this research is to study redox processes in organic-rich freshwater sediments. Pore-water concentration profiles of redox-sensitive ions were measured from sediment cores, taken in a recent sedimentation area of the river Meuse in The Netherlands. To distinguish between chemical, biological and physical processes in order to show the relative importance and magnitude of redox cycles, the one-dimensional reaction/transport model STEADYSED1 (Van Cappellen and Wang, 1996) was used to simulate concentration profiles. This model explicitly accounts for the oxic, suboxic and anoxic OM degradation pathways, and it incorporates the secondary reactions involving the byproducts of OM biodegradation.

Sampling and analysis

Study area

The Biesbosch is a wetland, situated in the delta of the rivers Rhine and Meuse in the western part of The Netherlands (Fig. 4.1). The study area is almost exclusively flushed by the river Meuse, except for its north-western part, where Rhine water occasionally intrudes. Tidal influences in the Biesbosch have decreased considerably after 1970, when the former Rhine-Meuse estuary was closed off from the North Sea by a dam. Today, the Biesbosch is a freshwater tidal basin with a modest tidal range (20-30 cm in the study area). Due to the low current velocities, the former tidal channels are silting up. Both the sediments and soils in the Biesbosch are strongly contaminated by heavy metals, reflecting the serious metal pollution history of the rivers Meuse and Rhine (Van Eck *et al.*, 1997).

Sample collection and handling

At four permanently submerged locations in the Biesbosch (Fig. 4.1), sediment cores were collected in Plexiglas tubes with an inner diameter of 15 cm and a length of 60 cm. Mean water depth at the locations A, B, C, and D is 1.4, 2.0, 4.2, and 3.3 m respectively. Sampling took place manually by SCUBA divers. In this paper only the results of the sampling campaign in June are discussed. Bottom water remained on the sediment in the tubes to prevent oxidation of the sediment. Pore-water pH was measured on board with a MI-410/MI-415 pH micro-electrode (Microelectrode INC.) equipped with a micromanipulator. To avoid disturbance of the sediment, pH measurements were conducted in a second core similar to the one used for pore-water and solid-phase extractions. The collected cores were stored at 4°C. Bottom water was sampled at the same locations at 0.5 m above the sediment-water interface (Table 5.1). Collected bottom water was filtered through a 0.45 µm membrane filter (Sartorius). Suspended matter was collected by continuous flow-through centrifugation.

Within 48 h after collection, the top 7 cm of the sediment cores were sectioned into 0.5- or 1.0-cm slices. Laboratory sampling took place under strictly anaerobic conditions in a nitrogen-filled glove box. Pore water was extracted by pressure filtration, according to the method described by De Lange (1992), and collected in High Density Polyethylene bottles. Part of the pore water was acidified with

concentrated suprapur HNO₃ (1 ml HNO₃ per 50 ml pore water). Sediment and non-acidified pore-water samples were kept at 4°C under a nitrogen atmosphere until extraction and analysis. All materials (bottles, filters, and filtration blocks) were acid-cleaned prior to use.

Table 5.1. Characteristics of the bottom water, collected in June 1996 at a depth of 50 cm above the sediment-water interface.

	Unit	Range	Mean value
Temperature	°C	21.1-22.4	21.7
Salinity	‰	0.25-0.27	0.26
pH	-	7.6-8.6	8.0
Cl ⁻	mmol l ⁻¹	2.02-2.21	2.14
O ₂	mmol l ⁻¹	0.24-0.55	0.36
NO ₃ ⁻	mmol l ⁻¹	0.15-0.25	0.21
Mn ²⁺	μmol l ⁻¹	< 0.05	< 0.05
Fe ²⁺	μmol l ⁻¹	< 0.11	< 0.11
SO ₄ ²⁻	mmol l ⁻¹	0.65-0.69	0.67
Alkalinity	mmol _c l ⁻¹	3.64-3.87	3.80
NH ₄ ⁺	mmol l ⁻¹	< 0.01	< 0.01

Sediment and pore-water analysis

Freeze-dried sediment samples were digested in a mixture of concentrated HClO₄, HNO₃ and HF and finally dissolved in 1 M HCl. Elemental concentrations in the acid solution were determined by inductively coupled plasma atomic emission spectrometer (Perkin Elmer Optima 3000). The quality of the analyses was tested by simultaneously extracting and analysing international standard sediments. Accuracy was within 5 % of the tabulated concentrations for all elements of interest. Measurement of organic C (C_{org}) and total N (N_{tot}) contents in sediment and suspended matter was made with a CNS analyser (Carlo Erba Strumentazione nitrogen analyzer 1500). Inorganic carbon was removed before analysis by shaking the sediment sample in 1 M HCl. ²¹⁰Pb activity was measured indirectly by alpha-spectrometry of its daughter product ²¹⁰Po on dried sediment samples from location C. Moisture content of the sediment samples,

necessary to calculate porosity, was determined by measuring the weight loss after freeze drying.

Collected bottom waters were analysed on board for temperature, dissolved oxygen, pH, and salinity. Shipboard measurements took place with a sensor system. Pore waters and bottom waters were analysed for concentrations of major elements (e.g. Mn, Fe, and Ca) by ICP-AES. Ammonium was determined spectrophotometrically by means of a modified Berthelot reaction (Solorzano, 1969). Sulphate, nitrate and chloride were measured in non acidified surface and pore water by ion-chromatography (Dionex QIC analyser). Alkalinity was determined by the Gran plot method after titration with 0.01 M HCl (Stumm and Morgan, 1996).

Early diagenetic model

Model description

The multicomponent reaction/transport model STEADYSED1 (Van Cappellen and Wang, 1996) includes kinetic expressions describing decomposition of OM via oxic respiration, denitrification, Mn(IV) reduction, Fe(III) reduction, sulphate reduction, and methanogenesis. Solutes may participate in secondary redox reactions, adsorb on sediment particles or precipitate as authigenic solid phases, like (hydr)oxides, Mn- and Fe-carbonates, and sulphides. The model includes solute transport by molecular diffusion, pore-water irrigation, particle mixing, and advective sediment burial. The most important assumption of the model is that geochemical conditions in sediments are at steady-state.

Model parameters are divided into site-specific (environmental) parameters and reaction-specific parameters (Wang and Van Cappellen, 1996). The depositional environment is characterised by site-specific parameters, which include sediment accumulation rate, bottom-water chemistry, particulate deposition fluxes, intensities of particle mixing and irrigation, and physical characteristics such as temperature, porosity and particle densities. The chemical transformation processes in the sediment are described by reaction-specific parameters, which include reaction rate coefficients, apparent equilibrium constants, surface-site densities and limiting concentrations of electron acceptors. Secondary redox reactions are described by bimolecular reaction rate laws. Precipitation and dissolution rates are assumed to depend linearly on the

degree of saturation of the pore water with respect to the minerals. The mass conservation equations are solved numerically by finite difference.

Critical parameters in the computation are a set of limiting concentrations for the terminal electron acceptors of the respiratory pathways. These concentrations account for the effects of substrate limitation, inhibition, and competition (Rabouille and Gaillard, 1991; Van Cappellen and Gaillard, 1996). Respiratory transformation rates are based on a modified Monod formulation (see Van Cappellen and Wang, 1996 for further details).

Table 5.2. List of input parameter values.

	Unit	A	B	C	D
Temperature	°C	21.7	21.7	21.7	21.7
Salinity	‰	0.26	0.26	0.26	0.26
Deposition rate	cm yr ⁻¹	6	0.3	1	5
Porosity	-	0.86	0.73	0.83	0.83
Particle density	g cm ⁻³	2.4	2.4	2.4	2.4
Particle-mixing coefficient	cm ² yr ⁻¹	195	15	42	168
Depth of mixed layer	cm	15	15	15	15
C degradation rate at x=0	μmol cm ⁻³ yr ⁻¹	600	150	150	950
Depth-attenuation coefficient	cm ⁻¹	0.15	0.32	0.15	0.25
Molar C:N:P ratio	-	20:1.6:1	20:1.6:1	20:1.6:1	20:1.6:1
Flux MnO ₂	μmol cm ⁻² yr ⁻¹	60	3	10	50
Flux Fe(OH) ₃	μmol cm ⁻² yr ⁻¹	800	40	134	670
<i>Bottom water</i>					
pH	-	8.0	8.0	8.0	8.0
[O ₂]	mmol l ⁻¹	0.36	0.36	0.36	0.36
[NO ₃ ⁻]	mmol l ⁻¹	0.21	0.21	0.21	0.21
[Mn ²⁺]	μmol l ⁻¹	0	0	0	0
[Fe ²⁺]	μmol l ⁻¹	0	0	0	0
[SO ₄ ²⁻]	mmol l ⁻¹	0.67	0.67	0.67	0.67
Alkalinity	mmol _c l ⁻¹	3.8	3.8	3.8	3.8
[NH ₄ ⁺]	mmol l ⁻¹	0.2	0.1	0.2	0.2
[CH ₄]	mmol l ⁻¹	0	0	0	0

Pore-water modelling approach

Predicted profiles of solute concentrations are calculated by STEADYSED1 using the parameters listed in Table 5.2. The actual fitting parameters are the deposition rate, OM degradation rate and ammonium concentration in bottom water. Fluxes of reactive Mn- and Fe-(hydr)oxides to the sediment are based on measured deposition rates and solid-phase levels of Fe and Mn at the sediment-water interface. It is further assumed that 40 % of the Fe flux to the sediment consists of reactive Fe(III)-(oxyhydr)oxides and the total Mn flux consists of reactive Mn(IV)-oxide (Van den Berg and Loch, 1995). The remainder of the Fe flux is incorporated in the mineral structure of e.g. clay minerals and relatively unreactive oxides.

Solute transport within the top layer of the sediment takes place by advection, molecular diffusion, and mixing. The effects of infiltration are not considered. In many freshwater sediments, especially in dynamic tidal systems, bioturbation dominates transport in the top layer of the sediment, unless anoxic or suboxic conditions prevail in the bottom water. The intensity of biological mixing is influenced by the bottom-water oxygenation and the supply rate of detrital matter. In the top 15 cm of the core at location C, a constant ^{210}Pb activity is measured, which indicates that this layer is most likely subject to intense mixing. A constant (biological) mixing coefficient (D_{mix}) in the top 15 cm of the sediment is assigned to each location. It is assumed that below this depth no significant mixing takes place. Values of the mixing coefficient are calculated using the empirical equation of Tromp *et al.* (1995), which correlates the amount of (biological) mixing in sediments accumulating in oxic bottom water with the deposition rate

$$\log D_{\text{bio}} = 1.63 + 0.85 \log \omega \quad (5.1)$$

in which D_{bio} is the (biological) mixing coefficient (in $\text{cm}^2 \text{yr}^{-1}$) and ω is the deposition rate (in cm yr^{-1}). The deposition rates reported in Table 5.2 agree well with those based on sedimentation fluxes in the study area (RIZA, pers. comm.). It is important to notice that the measured pore-water profiles can be reproduced satisfactorily without taking additional physical mixing of the solid phase into account. This apparently negligible influence of physical mixing may reflect the relatively low surface area of open water (minimal wave impact) and low current velocities ($< 0.1 \text{ m s}^{-1}$) in the study area. Although irrigation may significantly lower pore-water concentrations of solutes, even

at very low abundance (Aller, 1980), in this study measured concentration profiles can be reproduced satisfactorily without including the effects of irrigation.

Because the sediments at the four locations have a similar origin (river Meuse suspended matter), spatial variability in intrinsic properties of sedimentary phases is neglected. Most chemical and kinetic constants are taken from Wang and Van Cappellen (1996). The limiting concentration for sulphate reduction was set to $0.03 \text{ mmol l}^{-1} \text{ SO}_4^{2-}$, based on experimental results of Lovley and Klug (1986) in freshwater sediments. The other limiting values ($20 \text{ } \mu\text{mol l}^{-1} \text{ O}_2$, $2 \text{ } \mu\text{mol l}^{-1} \text{ NO}_3^-$, $16 \text{ } \mu\text{mol g}^{-1} \text{ MnO}_2$ and $65 \text{ } \mu\text{mol g}^{-1} \text{ Fe(OH)}_3$) are from Wang and Van Cappellen (1996).

Results and discussion

Bottom-water characteristics

The characteristics of the bottom water are given in Table 5.1. Most parameter values fall into a narrow range. Relatively large variation in O_2 concentrations and pH may be explained by increased phytoplankton activity during daytime (sampling took place in the productive period). As input to the model the mean values are used, although we recognise the effects of diurnal variation, which may potentially effect benthic primary production in the uppermost millimetres of the sediment. Because bottom water concentrations used as boundary conditions in the model were measured 0.5 m above the sediment surface, these might in certain cases not reflect the actual concentrations at the sediment-water interface. Molar C/N ratios of the suspended matter are in the range 6.8-7.8, which are values typical of planktonic biomass (Tyson, 1995).

Sediment characteristics

The top 10 cm of the sediments are characterised by an olive brown layer near the sediment-water interface with a thickness of a few millimetres, underlain by an olive black layer. At location B the olive black layer transforms into a black layer at a depth of 7-8 cm, which extends throughout the core. Absence of a well developed reddish-brown layer may point to limited penetration of oxygen into the sediment and anaerobic conditions close to the sediment-water interface. The observed variation in sediment colour can be interpreted as a change in the predominance from ferric

Redox processes in sediments

oxyhydroxides to ferrous monosulphides. The characteristics of the sampled sediment cores are given in Table 6.2 (*Chapter 6*) and shown in Fig. 4.3 to 4.6 (*Chapter 4*). The relatively low standard deviations imply that solid phase levels of e.g. OrgC, CaCO₃, Fe, and Mn are almost constant with depth.

Pore-water profiles of redox-sensitive ions are strongly affected by the degradability of the OM. An indication of the degradability and, hence, the extent of mineralisation is given by the C/N ratio. Molar C_{org}/N_{tot} ratios in the top 7 cm of the sediment are on the order of 12.5±0.4 at location A, 13.6±0.9 at location B, 12.4±0.3 at location C and 12.4±0.5 at location D. The C/N ratio of the OM in the suspended matter in the study area (mean ratio of 7.2) is significantly lower than in the sediments. This indicates that freshly deposited OM is actively biodegraded in the upper centimetres of the sediment. Thus, as expected, highly labile OM is being supplied to the sediments.

Pore-water profiles

Measured and modelled pore-water profiles are shown in Fig. 5.1 to 5.4 (note the different scales in the figures). Concentrations in the bottom water are plotted at zero depth. At all locations anaerobic conditions are present directly below the sediment-water interface. Pore-water pH decreases from 8.0 near the sediment-water interface to 7.0-7.5 in the deeper sediment due to production of CO₂. As can be seen in the figures, STEADYSED1 overpredicts the decrease in pH in the sediments studied. This is because the current version of the model does not include CaCO₃(s) as a species. The sediments studied have CaCO₃ contents in the range 7.0-12.7 % at all depths. Thus, it is likely that CaCO₃ dissolution buffers the pH decrease in the upper sediment (Boudreau, 1987; Wang and Van Cappellen, 1996). Alkalinity increases with depth at all locations, but significant differences in the maximum values reached within 10 cm below the sediment-water interface are measured. In the sediments studied, the production of alkalinity is not only affected by OM degradation and secondary redox reactions, but also significantly by dissolution of CaCO₃. In Fig. 5.1 to 5.4, the modelled curves fit well to those alkalinity profiles which have been corrected for the effect of alkalinity production by CaCO₃ dissolution. This alkalinity production is calculated from measured Ca²⁺ pore-water concentrations ($\Delta\text{Alk} = 2 \cdot \Delta[\text{Ca}^{2+}]$).

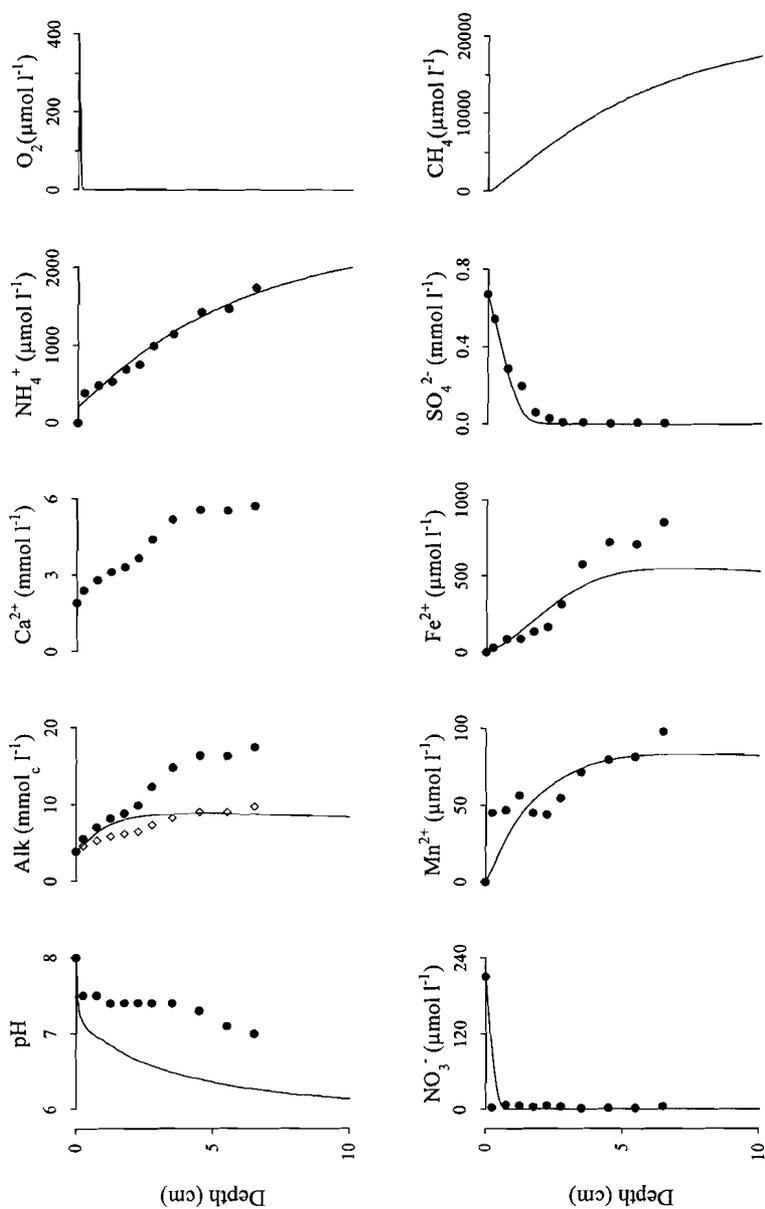


Figure 5.1. Measured concentrations in the pore water (black dots) and modelled concentration profiles (straight line) at location A (open diamonds represent corrected alkalinity).

Redox processes in sediments

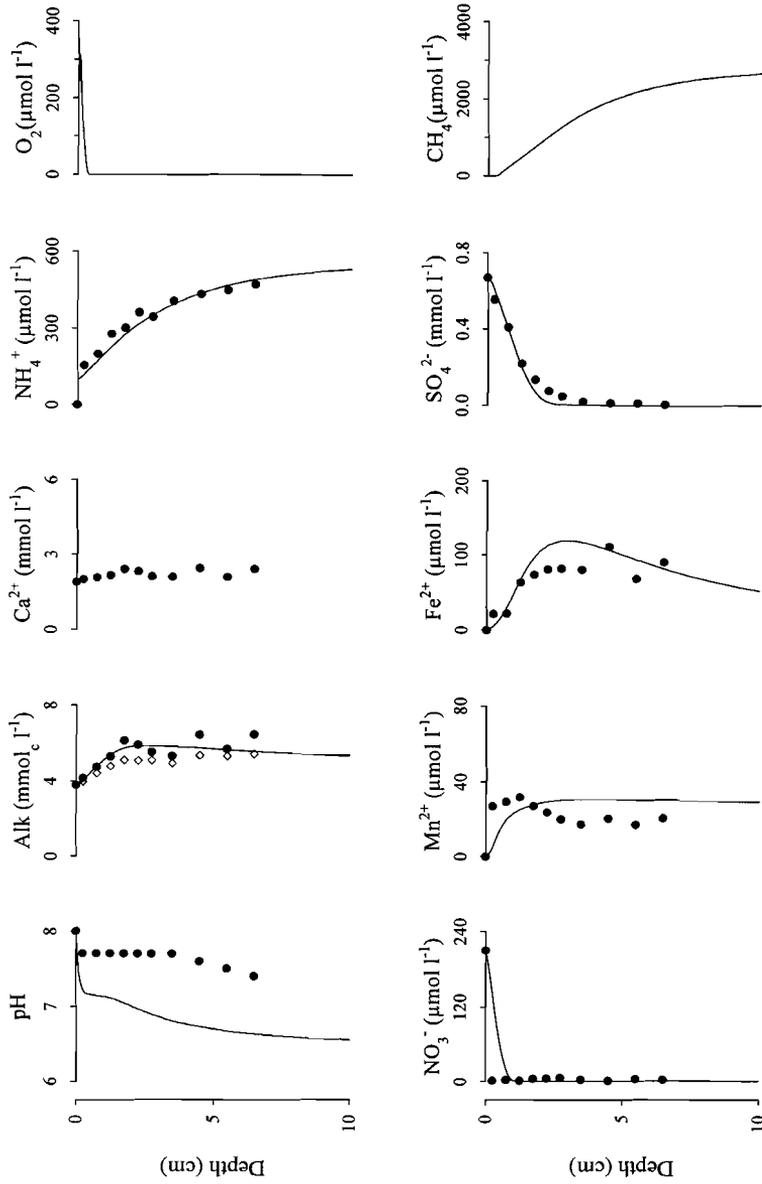


Figure 5.2. Measured concentrations in the pore water (black dots) and modelled concentration profiles (straight line) at location B (open diamonds represent corrected alkalinity).

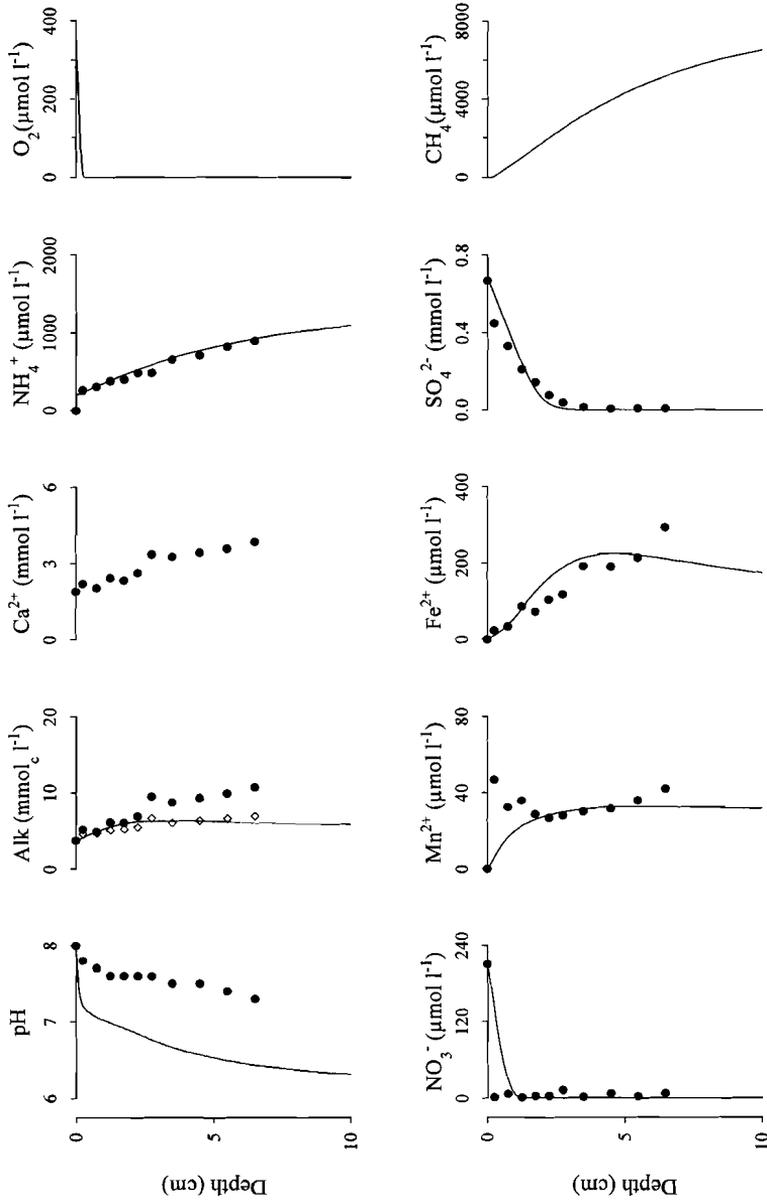


Figure 5.3. Measured concentrations in the pore water (black dots) and modelled concentration profiles (straight line) at location C (open diamonds represent corrected alkalinity).

Redox processes in sediments

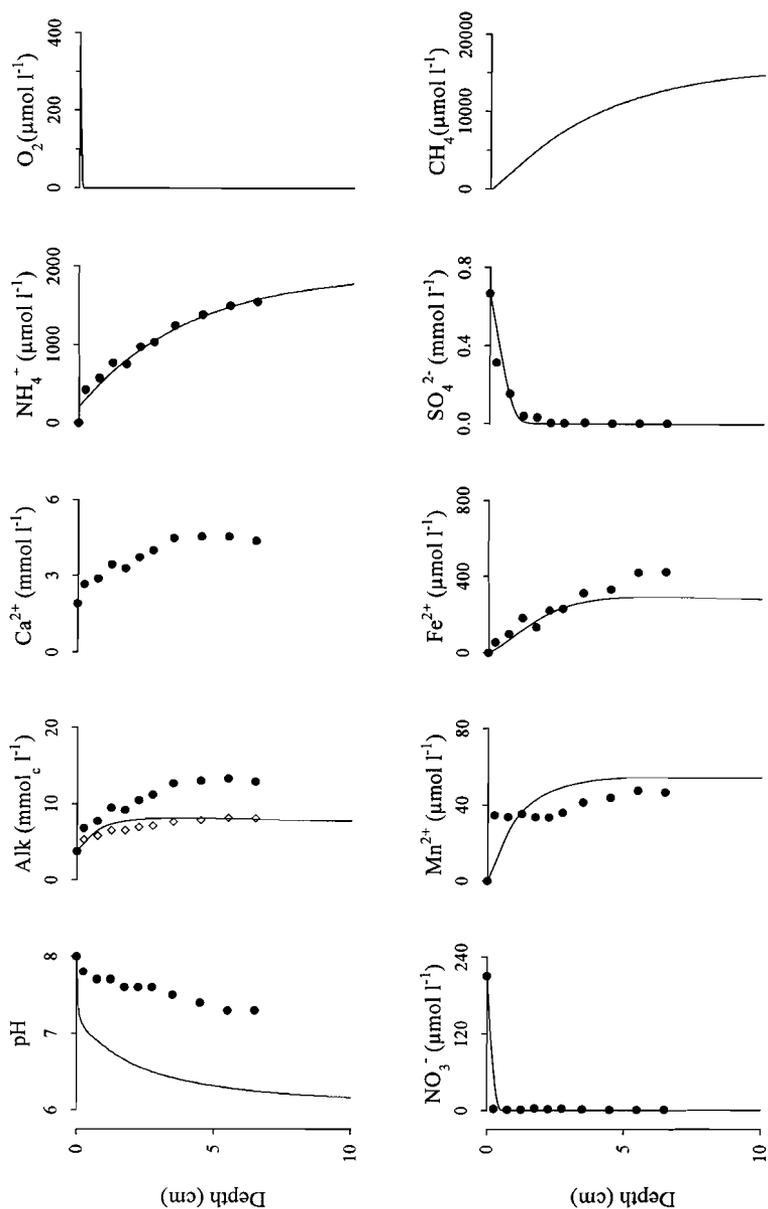


Figure 5.4. Measured concentrations in the pore water (black dots) and modelled concentration profiles (straight line) at location D (open diamonds represent corrected alkalinity).

Production of ammonium results from the degradation of N-bearing OM substrates (e.g. amino acids) and is, therefore, used as a measure for the overall OM degradation rate. Pore-water ammonium profiles show a typical increase with depth. The slope of the curves decreases with depth indicating a decrease in the OM degradation rate. The maximum concentration of the ammonium profile increases in the order $B < C < A \approx D$ (Fig. 5.1 to 5.4), indicating variation in the degradation rate of OM and in transport rates (mixing and accumulation). Slow transport and most degradation at depth in the sediment favour high concentrations of ammonium. The expected variation in OM degradation rates is in keeping with the model results. In Table 5.3 the calculated values for OM degradation rates at the sediment-water interface and depth-attenuation coefficients (coefficients for the first-order rate of change of organic matter degradation with depth) for each location are given.

Table 5.3. Depth-integrated rates of OM degradation within the top 10 cm of the sampled sediment cores. The percentage of each pathway to the total OM degradation rate is also shown.

Pathway	A	B	C	D	A	B	C	D
	$(\mu\text{mol cm}^{-2} \text{yr}^{-1})$				(%)			
O ₂	90	52	39	122	2.9	11.5	5.0	3.5
NO ₃	315	84	125	360	10.1	18.5	16.0	10.4
Mn(IV)	3	< 1	< 1	4	0.1	< 0.1	< 0.1	0.1
Fe(III)	212	19	38	177	6.8	4.2	4.9	5.1
SO ₄	390	102	140	462	12.5	22.5	17.9	13.3
Methanogenesis	2117	196	439	2338	67.7	43.3	56.2	67.5
Total	3127	453	781	3463				

The model simulations can be used to compare the importance of reactions controlling the pore-water concentrations of redox-sensitive ions in the sediment cores. Although oxygen-concentration profiles were not actually measured, the model results confirm that aerobic conditions are limited to the upper millimetres of the sediment cores (2 mm at location A and D, 4 mm at location C, and 5 mm at location B), as inferred from the absence of a well developed reddish-brown surface layer and the distribution of redox-sensitive pore-water species. Oxygen consumption is due to aerobic respiration in addition to oxidation of reduced solid-phase (adsorbed Fe(II),

adsorbed Mn(II), and FeS) and pore-water constituents (Fe^{2+} , Mn^{2+} , NH_4^+ , H_2S , HS^- , and CH_4). Therefore, presence of oxygen in the top few millimetres of the sediment may significantly decrease the flux of reduced pore-water constituents to the bottom water. Calculations with STEADYSED1 predict that in the studied sediments oxygen reduction takes place mainly as a result of oxidation of reduced pore-water constituents. Aerobic degradation of OM only accounts for a relatively small amount of total oxygen reduction (6.6 % at location A, 16.9 % at location B, 8.1 % at location C, and 9.2 % at location D). Oxidation of upward diffusing methane is the main oxygen-consuming process (89 % of total oxygen consumption at location A, 34 % at location B, 61 % at location C, and 88 % at location D).

Measured profiles suggest that nitrate is completely reduced within 1 cm below the sediment-water interface. This agrees fairly well with the model results given the fact that the measurements may be somewhat unreliable, because nitrate in non-acidified pore water is sensitive to reduction during storage.

Table 5.3 shows that the amount of microbial Mn(IV) reduction is negligible compared to the other respiratory pathways in the sediments studied. The shape of the Mn^{2+} pore-water profiles and the asymptotic values are comparable at all locations. Calculations of the saturation state with MINTEQA2 (U.S. EPA, 1991) show that the anoxic pore waters are saturated with respect to rhodochrosite (MnCO_3) below a depth of 2 cm. Thus, MnCO_3 may potentially control the pore-water concentrations of Mn^{2+} in these sediments. The sharp increase in dissolved Mn^{2+} , observed in the top 2 cm of cores B, C, and D, cannot be reproduced satisfactorily with STEADYSED1. This may be related to e.g. the presence of a diffusive boundary layer. Vertical separation between pore-water build-up of Mn^{2+} and Fe^{2+} may be caused primarily by oxidation of dissolved Fe^{2+} by MnO_2 (Postma, 1985; Wang and Van Cappellen, 1996). Calculations suggest that this is the main pathway of Mn reduction in the studied sediments, as it accounts for more than 90 % of all Mn(IV) reduction.

Microbial Fe(III) reduction accounts for less than 10 % of total degradation of OM in the studied sediments (Table 5.3). The depth at which the vertical colour transition is observed agrees well with the depth below which Fe^{2+} is present in the pore water. Significant differences are observed in Fe^{2+} concentrations between locations. The gradual increase in pore-water Fe^{2+} with depth may be explained by slow rates of dissolution of Fe(III)-(hydr)oxides and formation of Fe(II) solid phases (Wersin *et al.*, 1991; Postma, 1993). However, STEADYSED1 only includes reactive $\text{Fe}(\text{OH})_3$ as a Fe-(hydr)oxide species, which may be an oversimplification. FeS was

chosen as the only reduced Fe-sulphur species in the model, because FeS generally controls pore-water Fe concentrations in sulphidic freshwater sediments, rather than the thermodynamically more stable pyrite (Boudreau and Canfield, 1988). Because there is an excess of Fe²⁺ liberation over HS⁻ production, siderite (FeCO₃) as well as FeS control pore-water Fe²⁺ concentrations in the anoxic layer.

Respiratory sulphate reduction ideally takes place when all other electron acceptors are exhausted, but in the sediments studied significant overlap occurs between the zones of microbial Fe(III) reduction and sulphate reduction (Fig. 5.5), as will be discussed later. The pore-water sulphate profiles show a rapid decrease to zero concentration within 4 cm at all locations. The model calculations indicate that a small amount (0.5-2.2 %) of total sulphate reduction is due to the oxidation of upward-diffusing methane.

In the freshwater sediments studied, the supply of external oxidising agents, especially nitrate and sulphate, is limited and methanogenesis is the dominant process of OM degradation beyond 3 cm below the sediment-water interface at all locations (Fig. 5.5). Calculated concentration profiles (Fig. 5.1 to 5.4) show that methane is effectively oxidised in the aerobic layer at the sediment-water interface, where methane concentrations are close to zero. In addition, methane diffusing upwards may become a source of carbon for sulphate-reducing bacteria at the sulphate/methane interface (Devol, 1983; Iversen and Jørgensen, 1985). Calculations show that the amount of methane oxidised by oxygen is much larger (100-500 times) than the amount oxidised by sulphate. It should be noticed that in all cores studied the methane concentrations in the pore water exceed the solubility limit (approx. 1600 μmol l⁻¹ CH₄ at 1 atmosphere). As a consequence of methane accumulation in the pore water, concentration gradients increase and CH₄ oxidation rates are higher than they would be when the solubility limit would have been included. Methane release through bubbles (Martens and Klump, 1980) results in limited oxidation, because the zone of methane oxidation is passed by. Because methane ebullition is not included in the model, the contribution of methane oxidation to oxygen demand may consequently be overestimated (Martens *et al.*, in press). Hence, the contribution of the other oxidants is underestimated, and the results in Table 5.3 may only be indicative.

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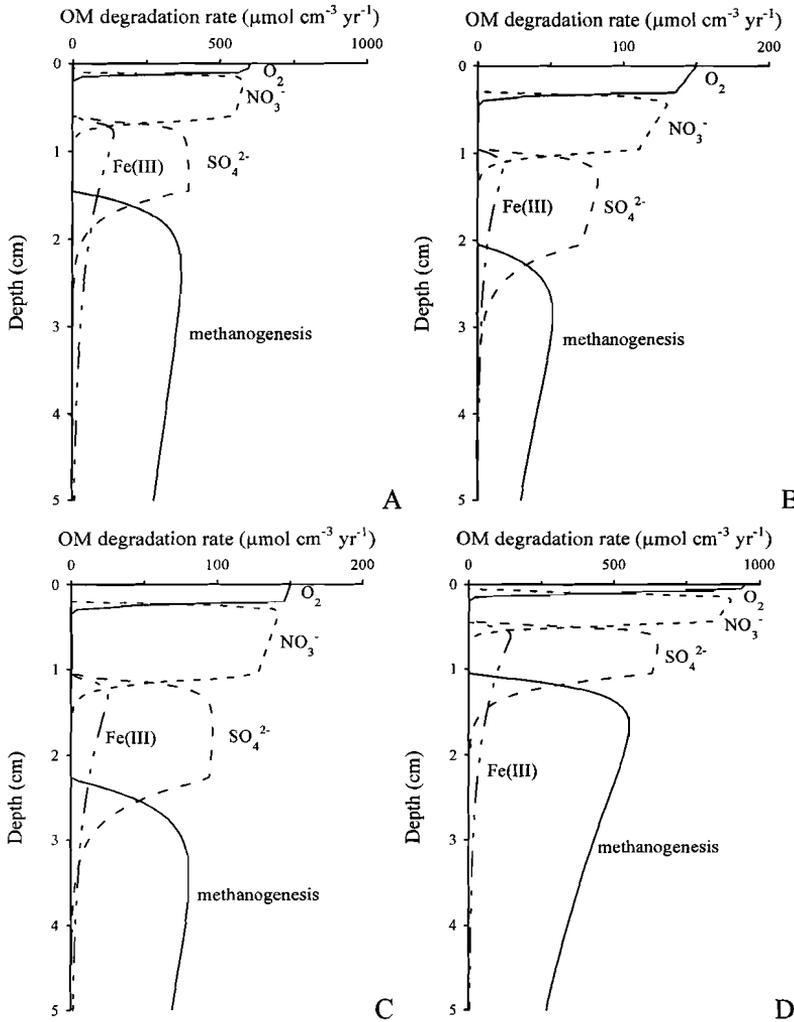


Figure 5.5. OM degradation rates of the relevant electron acceptors in the top 5 cm of the sediment at the four locations studied. OM degradation rates coupled to Mn(IV) reduction are not shown, because the role of dissimilatory Mn(IV) reduction seems negligible compared to the other degradation pathways (Table 5.3). Note the different rates on the x-axis.

Organic matter degradation pathways

By fitting STEADYSED1 to the measured pore-water concentration profiles, the rate distributions of the OM degradation pathways are calculated (Fig. 5.5). The calculated depth distributions of microbially-mediated electron transfer reactions within the sediment are roughly in accordance with their corresponding redox potentials (Stumm and Morgan, 1996) and correspond to that observed in marine systems (Froelich *et al.*, 1979). However, the model predicts considerable vertical overlap between the degradation pathways. This overlap reflects the high mixing intensities of the sediments in combination with limiting values of the respiratory electron acceptors (Wang and Van Cappellen, 1996). Additionally, in a one-dimensional modelling approach, as used in this study, considerable overlap may result from lateral heterogeneity of the sediment, as proposed by Brandes and Devol (1995) and Wang and Van Cappellen (1996) and the presence of a wide range of mineral reactivities (Postma and Jakobsen, 1996).

Depth-integrated rates of OM degradation are given in Table 5.3. Rates differ between locations, reflecting primarily the rate of supply of reactive OM. Table 5.3 shows that methanogenesis is the most important OM degradation process in the studied sediments. The relative importance of methanogenesis increases with overall rate of OM degradation (on the order $B < C < A \approx D$). However, supersaturation of the pore water with respect to methane suggests that OM degradation rates by methanogenesis may be overestimated. The importance of the suboxic pathways decreases with the overall OM degradation rate. The extent of CaCO_3 dissolution in the sediments studied, as indicated by the Ca^{2+} pore-water concentration profiles (Fig. 5.1 to 5.4), increases with integrated rates of O_2 reduction and methanogenesis (Table 5.3), which are the main producers of CO_2 driving the CaCO_3 dissolution reaction. This correlation supports the internal consistency of the predicted integrated rates of O_2 reduction and methanogenesis.

Conclusions

Early diagenetic processes in organic-rich freshwater sediments can be described quantitatively with the general diagenetic reaction/transport model STEADYSED1. The application of this model was successful and shows the generality of this

approach, although incorporation of other processes, especially CaCO₃ dissolution/precipitation and methane bubble formation and ebullition may improve the application in such sediments. Pore-water profiles can be explained by the degradation of OM and the internal cycling of redox species. The main pathway for OM degradation in the sediments studied is methanogenesis. The other oxidative pathways (O₂, NO₃⁻, Mn(IV), Fe(III), and SO₄²⁻ reduction) are limited to the top 3 cm of the sediments. Model results show that oxygen consumption takes place mainly by methane oxidation, and only to a limited extent by aerobic respiration. Oxidation of dissolved Fe²⁺ by MnO₂ seems the main pathway of Mn reduction in the sediments studied. The differences in the pore-water profiles of redox-sensitive ions at the sites studied are mainly the result of large differences in the depth-integrated rates of OM degradation.

Acknowledgement - We thank P. Van Cappellen (Georgia Institute of Technology) for his interest in this work and for his useful comments on an earlier version of the manuscript. The manuscript has also benefited from comments of C.H. van der Weijden. The assistance of Pieter Kleingeld, Gijs Nobbe and Mark van Alphen during sampling and in the laboratory is greatly appreciated. This project was carried out with financial support of the Ministry of Transport, Public Works and Water Management, Institute for Inland Water Management and Waste Water Treatment (RIZA).

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Chapter 6

Mobilisation of heavy metals in contaminated sediments in the river Meuse, The Netherlands

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Abstract - Due to seasonal variation in bottom-water temperature and degradation of organic matter, the depths of the redox boundaries fluctuate in sediments of the river Meuse. This is reflected by a non-steady state behaviour of heavy metals in the surface sediments. Because relatively low levels of acid-volatile sulphides are measured, other solid phases, especially organic matter, are expected to bind heavy metals to a large extent. Furthermore, heterogeneity of the sediment and complexation with dissolved organic compounds may explain supersaturation of the anoxic pore waters with respect to (discrete) heavy metal sulphides. In most sediments studied, a distinct peak in dissolved concentrations of heavy metals is measured immediately below the sediment-water interface. This concentration peak may be attributed to degradation of organic matter and oxidation of sulphides. Dissolved concentration gradients indicate that upward diffusion of heavy metals from the sediment can contribute to concentrations in the surface water, although significant effects may be confined to specific locations. In addition, the release of heavy metals as dissolved species to the surface water is negligible compared to particulate-bound fluxes of heavy metals to the sediment.

This chapter is based on Water Science and Technology 37: 39-46 (1998).

Introduction

Particle-water interactions influence the mobilisation and bioavailability of heavy metals in aquatic sediment systems (Hong *et al.*, 1995; Hamilton-Taylor and Davison, 1995). Because the behaviour of heavy metals in sediments is strongly dependent on redox gradients, pore-water concentrations of heavy metals can not be described properly by depth-independent equilibrium partitioning coefficients between solid phase and pore water, as suggested by Van der Kooy *et al.* (1991). Effects of diagenetic processes on the remobilisation of heavy metals in sediments have been studied extensively, mainly in marine and brackish water systems (Shaw *et al.*, 1990; Zwolsman and Van Eck, 1993). The studies in freshwater sediments are limited primarily to acidified lakes and rivers (e.g. Carignan and Nriagu, 1985; Davis and Galloway, 1993).

As a result of redox gradients in sediments, a gradual vertical change in solid phases controlling the solubility of heavy metals is observed. Secondary processes, directly or indirectly influenced by the primary diagenetic redox reactions, driven by degradation of organic matter (OM), may result in postdepositional remobilisation of heavy metals (Williams, 1992). Secondary processes in sediments include e.g. complexation of metals with dissolved organic and inorganic ligands, modification of surface properties of adsorptive particles, and formation and dissolution of metal precipitates (Kersten and Förstner, 1995). Heavy metal concentrations in pore water commonly decrease with depth, suggesting a source near the sediment-water interface and a removal process deeper in the sediment (Gaillard *et al.*, 1986; Walton-Day *et al.*, 1990). In the oxic and suboxic sediment layers, adsorption of heavy metals to sedimentary organic matter and oxyhydroxide surfaces is the main process controlling pore-water concentrations of heavy metals (Tessier *et al.*, 1993). Mn- and Fe-(hydr)oxides and OM may be present as coatings on minerals (Horowitz and Elrick, 1987; Tessier *et al.*, 1996), thus changing the adsorptive properties of mineral surfaces (Davis, 1984). Adsorption capacity for cationic heavy metals, e.g. Zn, Cd, Ni, Cu, and Pb, commonly decreases with pH (Benjamin and Leckie, 1981), resulting in an increased solubility of these heavy metals with depth in the oxic and suboxic layers (Bourg, 1983). Besides OM degradation, dissolution of (hydr)oxides promotes release of heavy metals to the pore water. Sulphides are recognised as important scavengers for heavy metals in anoxic sediments, thus reducing their bioavailability (Di Toro *et al.*, 1992; Van den Berg *et al.*, 1998¹/Chapter 7). However, heavy metals remobilised

by decomposition of OM near the sediment-water interface, may initially be scavenged by Mn- and Fe-(hydr)oxides rather than by sulphides (McKee *et al.*, 1989).

Describing heterogeneous dynamic sediments as equilibrium systems may not be realistic. Seasonal fluctuation in temperature, sedimentation rates and primary production of biomass may result in temporal variation in pore-water concentrations (Song and Müller, 1995). Pore-water concentrations are generally considered to be the most sensitive parameters of environmental change (Adams, 1994), serving as useful indicators of the solid phases controlling the fate of heavy metals in sediments. Sequential extraction techniques are not suitable to predict the solid phases controlling pore-water concentrations of heavy metals in (partly) anaerobic sediments, because they lack specificity for the extraction of particular sulphide phases (Wallmann *et al.*, 1993).

The purpose of this work was to study the redox chemistry, reflecting the diagenetic reactions near the sediment-water interface, and the resulting pore-water profiles of Zn, Cd, Ni, Cu, and Pb in recent (contaminated) sediments of the Meuse river in The Netherlands. Temporal changes were studied by comparing pore-water characteristics in November 1995 and June 1996. Pore-water data will be used to estimate the amount of remobilisation and the potential effect of upward diffusion from the sediment on dissolved concentrations of heavy metals in the surface water.

Materials and methods

Site description

The Biesbosch is a wetland, situated in the delta of the rivers Rhine and Meuse in the western part of The Netherlands. Tidal influences in the Biesbosch have decreased considerably after 1970, when the former Rhine-Meuse estuary was largely closed off from the North Sea by a dam. Today, the Biesbosch is a freshwater tidal basin with a modest tidal range (some 20 to 30 cm in the study area). The study area is almost exclusively flushed by the river Meuse, except for its north-western part, where Rhine water occasionally intrudes. Due to the low current velocities in the former tidal channels, these are silting up. Sediments and soils in the Biesbosch are strongly contaminated by heavy metals, reflecting the serious metal pollution history of the rivers Meuse and Rhine (Van Eck *et al.*, 1997).

Sample collection and handling

At four permanently submerged locations in the Biesbosch (Fig. 4.1), sediment cores were collected in Plexiglas tubes with an inner diameter of 15 cm and a length of 60 cm. Sampling took place manually by SCUBA divers in November 1995 and June 1996. Pore-water pH was measured on board with a MI-410/MI-415 pH micro-electrode (Microelectrode INC.) equipped with a micromanipulator. To avoid disturbance of the sediment, pH measurements were conducted in a core different from the one used for pore water and solid phase extraction. Bottom water remained on the sediment cores in the tubes to prevent oxidation of the sediment. The collected cores were stored at 4°C. Bottom water was sampled at the same locations at 0.5 m above the sediment-water interface in June 1996. Collected bottom water was filtered through a 0.45 µm membrane filter (Sartorius) and analysed on board for temperature, oxygen, pH and salinity. Suspended matter was collected by continuous flow-through centrifugation.

Within 48 h after collection, the top 7-10 cm of the sediment cores were sectioned into 0.5- or 1.0-cm slices. Laboratory subsampling took place under strictly anaerobic conditions in a nitrogen-filled glove box to prevent oxidation of reduced compounds (Förstner and Salomons, 1980). Pore water was sampled by pressure filtration, according to the method described by De Lange (1992), and collected in High Density Polyethylene bottles. Part of the pore water was acidified immediately with concentrated suprapur HNO₃ (1 ml HNO₃ per 50 ml pore water). All used materials (bottles, filters and filtration blocks) were acid cleaned prior to their use.

Sediment analysis

Freeze-dried sediment samples were digested in a mixture of concentrated HClO₄, HNO₃ and HF, and finally dissolved in 1 M HCl. Elemental concentrations in the acid solution were determined by inductively coupled plasma atomic emission spectrometry (Perkin Elmer Optima 3000). The quality of the analyses was tested by simultaneously extracting and analysing international standard sediments. Accuracy is within 5 % of the tabulated concentrations for all elements of interest. Moisture content of the sediment samples, necessary to calculate concentrations on a dry weight basis, was determined by measuring the weight loss after freeze drying. Measurement of organic C (OrgC) contents in sediment and suspended matter was made with a CNS analyser

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(Carlo Erba Strumentazione nitrogen analyzer 1500). Inorganic carbon was removed before analysis by shaking the sediment sample in 1 M HCl. Sectioned sediment samples were analysed for acid-volatile sulphide (AVS), according to the method described by Henneke *et al.* (1991) with slight modification for this purpose. About 1 g of wet sediment was weighed exactly and used for extraction of AVS. As proposed by Cornwell and Morse (1987), sediment samples were acidified during 1 h using a 10-ml 6 M HCl solution at room temperature to form H₂S which was subsequently collected in a 1 M NaOH solution. The sulphide concentration in the NaOH solution was measured with an EG and G Princeton Applied Research model 384 B polarograph with a static mercury drop (EG and G Parc model 303A) using square wave voltammetry. Duplicate extractions and analyses of AVS showed that, using the described method, the results are well reproducible.

Collected pore water and bottom water was analysed for concentrations of major elements by ICP-AES. Zn was measured by flame atomic adsorption spectrometry (Perkin Elmer 4000) using deuterium background correction. Cd, Pb, and Cu concentrations were measured with hydride graphite furnace AAS (Perkin Elmer Z3030/HGA600/AS60) using Zeeman background correction. Matrix modifiers (ammonium phosphate/magnesium nitrate for Cd and Pb) were used to correct for matrix effects. The detection limits for the heavy metals of concern were 3.0 µg l⁻¹ Zn, 0.03 µg l⁻¹ Cd, 0.2 µg l⁻¹ Pb, 0.8 µg l⁻¹ Cu, and 1.8 µg l⁻¹ Ni. Concentrations of sulphate, nitrate, and chloride were determined in non-acidified bottom and pore water by ion-chromatography (Dionex QIC analyser). Dissolved organic carbon (DOC) concentrations were measured by high-temperature catalytic oxidation (Shimadzu Total Organic Carbon Analyzer TOC-500) after pretreatment with phosphoric acid to remove inorganic carbon.

Results and discussion

Solid phase composition

Sediments in the study area contain high levels of heavy metals (Tables 6.1 and 6.2). The observed good correlation with OrgC (Fig. 6.1) does not imply that organic matter is the active adsorptive phase for heavy metals, given the linear correlation of OrgC with Al, Fe, and Mn. The latter may be due to the presence of OM and oxides in the finest fraction as well as formation of organic and oxide coatings on clay minerals. Based on differences in Al contents, spatial and vertical variation in metal contents in the sediments can be attributed mainly to variation in grain size. At the locations B, C, and D, sediment cores have similar solid phase characteristics at the two occasions sampling took place (see also *Chapter 4*). The observed temporal differences at location A are most likely related to spatial heterogeneity. Because pore-water characteristics at location A can not be compared without taking changes in the solid-phase into account, these are not discussed in this chapter.

Table 6.1. Characteristics of the sediment cores sampled in November 1995 (weighted averages and standard deviations are given).

	Depth (cm)	OrgC	CaCO ₃	Al (%)	Fe	Mn
A	0-7	3.9 ± 0.3	8.7 ± 0.3	4.3 ± 0.1	3.1 ± 0.1	0.09 ± 0.01
B	0-10	3.0 ± 0.5	8.7 ± 0.8	4.0 ± 0.3	2.8 ± 0.3	0.08 ± 0.01
C	0-10	4.7 ± 0.4	9.8 ± 0.5	5.3 ± 0.3	4.0 ± 0.3	0.12 ± 0.01
D	0-7	4.4 ± 0.2	10.5 ± 0.8	5.1 ± 0.2	4.1 ± 0.1	0.12 ± 0.01
	Depth (cm)	Zn	Cd	Pb (mg kg ⁻¹)	Ni	Cu
A	0-7	803 ± 58	8.2 ± 0.9	121 ± 11	39 ± 5	60 ± 5
B	0-10	824 ± 96	10.2 ± 1.5	122 ± 19	39 ± 8	50 ± 7
C	0-10	1053 ± 79	11.3 ± 0.9	159 ± 15	50 ± 4	80 ± 7
D	0-7	968 ± 46	9.5 ± 0.5	139 ± 7	48 ± 8	75 ± 4

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Table 6.2. Characteristics of the sediment cores sampled in June 1996 (weighted averages and standard deviation are given)

	Depth (cm)	OrgC	CaCO ₃	Al (%)	Fe	Mn
A	0-7	5.6 ± 0.2	9.8 ± 0.3	5.7 ± 0.2	4.4 ± 0.2	0.13 ± 0.01
B	0-7	3.6 ± 0.4	10.4 ± 0.9	3.8 ± 0.4	2.7 ± 0.5	0.08 ± 0.01
C	0-7	5.1 ± 0.3	10.3 ± 0.8	4.9 ± 0.1	3.8 ± 0.1	0.12 ± 0.01
D	0-7	4.9 ± 0.3	10.2 ± 0.4	4.8 ± 0.1	3.9 ± 0.1	0.12 ± 0.01

	Depth (cm)	Zn	Cd	Pb (mg kg ⁻¹)	Ni	Cu
A	0-7	1083 ± 30	< 17*	232 ± 13	56 ± 2	105 ± 4
B	0-7	684 ± 82	< 17*	129 ± 23	32 ± 4	58 ± 9
C	0-7	960 ± 27	< 17*	189 ± 7	48 ± 2	86 ± 3
D	0-7	881 ± 27	< 17*	165 ± 7	47 ± 2	83 ± 2

* Detection limit for Cd is 17 mg kg⁻¹

Table 6.3. Characteristics of the suspended matter, sampled in June 1996 (concentrations of suspended matter are 9 mg l⁻¹ on location A, 28 mg l⁻¹ on location B, 18 mg l⁻¹ on location C and 23 mg l⁻¹ on location D).

	OrgC	CaCO ₃	Al (%)	Fe	Mn
A	7.5	11.0	6.2	4.8	0.28
B	9.0	10.0	5.9	4.8	0.36
C	8.2	10.0	5.9	4.5	0.31
D	9.4	9.9	5.0	4.4	0.37

	Zn	Cd	Pb (mg kg ⁻¹)	Ni	Cu
A	1266	< 17*	281	64	122
B	1315	< 17*	267	64	118
C	1198	< 17*	253	64	107
D	1061	< 17*	218	55	93

* Detection limit for Cd is 17 mg kg⁻¹

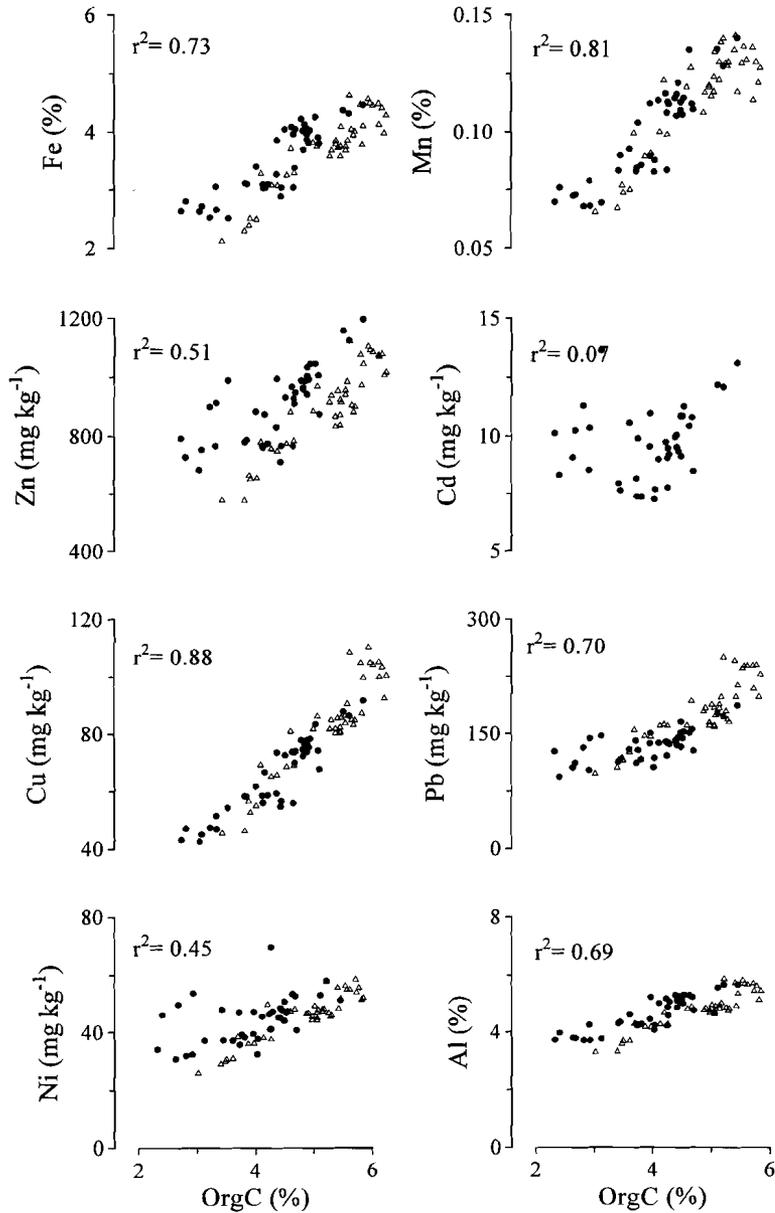


Figure 6.1. Scatter plots of solid phase metal contents versus OrgC content in the sediments at the locations A, B, C and D (black dots represent samples taken in November 1995; open triangles represent samples taken in June 1996). Cd concentration in June 1996 fall below detection limit.

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The composition of the suspended matter (Table 6.3) is almost constant throughout the study area. Only at location D lower concentrations of heavy metals are measured, which may be related to variation in grain size, based on differences in Al content. Differences in OrgC and metal content of collected suspended matter and sediments may be explained by either a preferential deposition of the more coarsed-grained particles (Van der Kooij *et al.*, 1991) or addition of sandy eroded bank material. The suspended matter is, however, strongly enriched in Mn with respect to the underlying surface sediments, even after normalisation by Al or OrgC. This may be explained by cycling of Mn between the sediment and the bottom water (Davison, 1993).

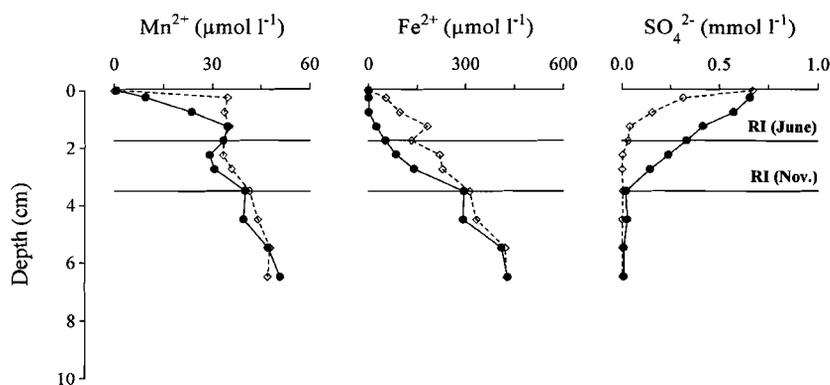


Figure 6.2. Profiles of redox sensitive ions at location D and the depth of the sulphate-sulphide redox interface (RI) during winter and summer (black dots represent samples taken in November 1995; open diamonds represent samples taken in June 1996).

General redox chemistry

In Fig. 6.2, pore-water concentrations of Mn^{2+} , Fe^{2+} and SO_4^{2-} are shown for location D. The other locations show similar pore-water concentration profiles (see *Chapter 4*). Within the surface sediments, steeper gradients of these redox sensitive ions are measured during summer (represented by samples taken in June 1996) than during winter (represented by samples taken in November 1995). As is clearly illustrated by the sulphate profile (Fig. 6.2), the (sub)oxic-anoxic redox interface (RI) is situated

closer to the sediment-water interface during summer. Temporal differences in redox conditions in the sediment can be explained by variation in degradation of OM and by temperature changes, both of which influence rates of redox reactions (microbial catalysis), mixing, and transport of solutes.

A shift of Mn(III,IV) and Fe(III) solid phases, mainly Mn- and Fe-(hydr)oxides, to Mn(II) and Fe(II) solid phases (e.g. MnCO_3 , FeCO_3 and FeS) may be expected with depth as a result of redox processes taking place in the sediment. Calculations with MINTEQA2 (U.S. EPA, 1991) show that the anoxic pore water is saturated with respect to MnCO_3 and FeCO_3 . As a result of mixing of the sediment (e.g. bioturbation and physical mixing), Fe^{2+} and Mn^{2+} in the pore water and Mn(II)- and Fe(II)-minerals may be oxidised and re-precipitated as (coatings of) amorphous Mn(III, IV)- and Fe(III)-(hydr)oxides, especially near the sediment-water interface. Due to the highly adsorptive surface properties of secondary (hydr)oxides, these may act as effective scavengers of heavy metals.

Distribution of heavy metals in the pore water

Pore water concentration profiles of Zn, Cd, Pb, Ni, and Cu, as well as AVS profiles are shown in Fig. 6.3 to 6.5 for the locations B, C, and D. Both in winter and summer, (slightly) increased heavy metal concentrations in the pore water are measured directly below the sediment-water interface in most cores (except for location D, summer core). These concentration peaks may be explained by degradation of organic (partly biogenic) compounds, which have concentrated metals during previous biological uptake and by binding to particle surface sites (Sigg, 1985). However, it should be noted that the observed surface peaks often consist only of one or few data points. Sampling with high-resolution techniques (e.g. Zhang *et al.*, 1995) may give more detail. Deeper in the profile, increased metal concentrations may be caused by reduction of Mn(III, IV)- and Fe(III)-(hydr)oxides or oxidation of metal sulphides. These solid phases may act as effective scavengers for heavy metals in sediments.

In freshwater sediments, reduced S formed mainly by reduction of pore-water sulphate, is predominantly present as inorganic S in the form of AVS. Although pyrite is the most stable sulphide mineral, its formation in freshwater sediments is subject to controversy (Rickard *et al.*, 1995). Davison *et al.* (1985) conclude that pyrite formation is stimulated in freshwater sediments with either low turnover of OM or periodic input of oxygen. Furthermore, laboratory experiments show that pyritisation of unoxidised

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iron monosulphide does not occur (Wilkin and Barnes, 1996). Therefore, we assume that conversion of FeS to pyrite does not play an important role in freshwater sediments, which are permanently submerged.

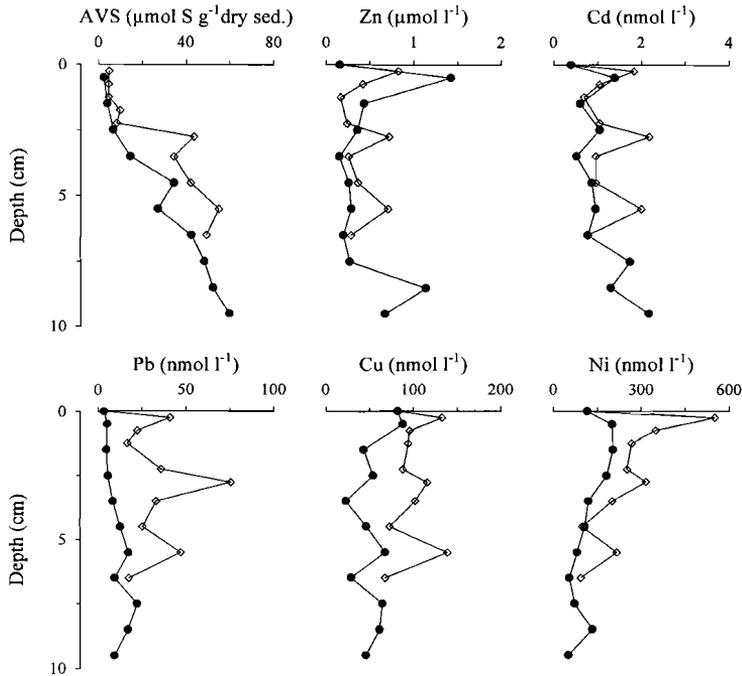


Figure 6.3. Profiles of AVS in the solid phase and heavy metals in the pore water at location B (black dots represent samples taken in November 1995; open diamonds represent samples taken in June 1996).

Thermodynamic equilibrium calculations are often employed to investigate solubility and speciation of heavy metals in sulphide bearing sediments. In the studied sediments, characterised by circumneutral conditions (pH 7-8), the stability field of FeS overlaps with that of FeCO₃. As a result, Fe²⁺ concentrations in pore water are controlled by equilibrium with both FeCO₃ and FeS, according to equations 6.1 and 6.2.

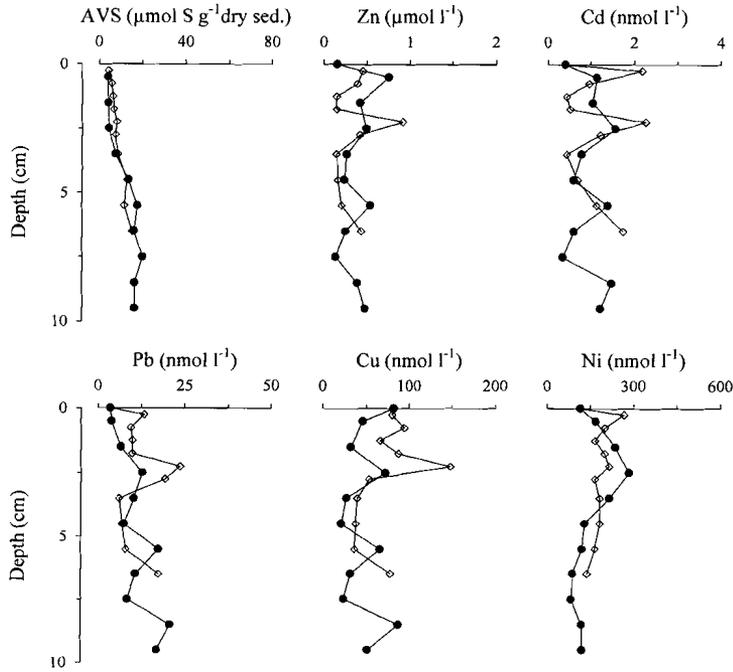


Figure 6.4. Profiles of AVS in the solid phase and heavy metals in the pore water at location C (black dots represent samples taken in November 1995; open diamonds represent samples taken in June 1996).



Consequently, dissolved sulphide is only dependent on the bicarbonate concentration. Assuming the activity coefficients of HS^- and HCO_3^- are approximately equal, the dissolved sulphide concentration can be calculated as

$$[\text{HS}^-] = K_{6.1}/K_{6.2} \cdot [\text{HCO}_3^-] \quad (6.3)$$

in which $K_{6.1}$ and $K_{6.2}$ are the equilibrium constants of the reactions 6.1 and 6.2. In the measured pH range, it is valid to assume that titration alkalinity equals $[\text{HCO}_3^-]$. HS^- concentrations calculated with equation 6.3, are on the order of $10^{-5} \text{ mol l}^{-1}$. These relatively low dissolved sulphide concentrations can be explained by high concentrations of dissolved Fe^{2+} (Carignan and Nriagu, 1985).

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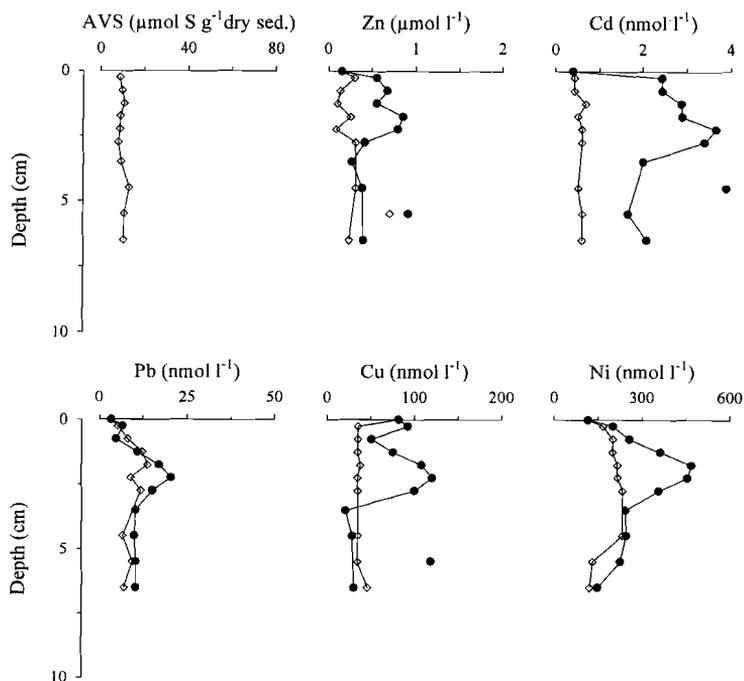


Figure 6.5. Profiles of AVS in the solid phase and heavy metals in the pore water at location D (black dots represent samples taken in November 1995; open diamonds represent samples taken in June 1996).

Equilibrium calculation with MINTEQ-A2, based solely on inorganic speciation, indicate that the anoxic pore waters are supersaturated with respect to crystalline sphalerite (ZnS), greenockite (CdS), millerite (NiS), galena (PbS) and covellite (CuS) during both periods at all locations. Saturation indices (S.I.) decrease roughly in the order CuS (S.I. ≈ 8) > PbS (S.I. ≈ 5) > ZnS (S.I. ≈ 3) \approx CdS (S.I. ≈ 3) > NiS (S.I. ≈ 2). Thus, pore-water concentrations of the respective heavy metals are significantly higher than would be predicted from their sulphide solubility. However, calculated saturation indices provide no direct evidence for the formation of sulphides, because e.g. kinetic factors are not included. The calculations assume an equilibrium between solid phase and pore water. Nonequilibrium may be expected in dynamic natural sediments. It should also be taken into account that the solubility of (sulphide) minerals may vary significantly between crystalline and amorphous forms (Davison, 1991). Moreover, coprecipitation of heavy metals with FeS implies supersaturation of

the pore water with respect to discrete sulphide precipitates (Davies-Colley *et al.*, 1985). Although the formation of discrete heavy metal sulphides has been demonstrated in various environments (Luther *et al.*, 1980; Lee and Kittrick, 1984; Van den Berg *et al.*, 1998²/Chapter 3), a strong association of heavy metals with iron-sulphides is generally observed (Davison *et al.*, 1992; Morse and Arakaki, 1993; Morse, 1994).

Complexation of heavy metals with dissolved organic matter (DOM), formed as a result of incomplete mineralisation of OM (Orem *et al.*, 1986), may explain the discrepancies between the pore-water concentrations of heavy metals and equilibrium concentrations based solely on inorganic speciation. Stability of organic metal complexes increases according to the Irving-Williams series (Turner *et al.*, 1981; Tipping and Hurley, 1992). Because Cu and Pb form the most stable complexes with both particulate OM and dissolved organic (sulphur) compounds (Boulègue *et al.*, 1982; Giblin *et al.*, 1986), the high supersaturation of the anoxic pore water with respect to CuS and PbS in the sediments may be an indication for intense organic complexation. A relatively high DOC concentration (1-6 mmol l⁻¹ DOC) is present in the pore water relative to the overlying water column (0.3 mmol l⁻¹ DOC). Additionally, compositional changes in DOM are expected to change the stability of organic metal complexes (Krom and Sholkovitz, 1977).

The measured pore-water profiles of heavy metals (Fig. 6.3 to 6.5) show some temporal changes. Most significant changes are measured at location D. During winter, distinct dissolved concentration peaks of heavy metal are measured in the top 3 cm of the sediment. These concentration peaks are absent during summer, resulting in more or less flat pore-water profiles with depth. The absence of a concentration peak during summer may be related to the nearly constant AVS levels throughout the profile, both in the suboxic and anoxic zone. The overall presence of AVS suggests intensive mixing of the sediment at this location. As described in Chapter 5, the amount of mixing in the sediments is related to the deposition rate, which differs between location B (0.3 cm yr⁻¹), C (1 cm yr⁻¹), and D (5 cm yr⁻¹). Unfortunately, during winter no AVS profile was measured at this location. However, the presence of peaks of dissolved concentration of heavy metals during winter suggests that, during this period, the amount of bioturbation is less than during summer.

Fluxes of heavy metals across the sediment-water interface

The sediment-water interface is characterised by the presence of highly degradable OM and reactive (hydr)oxides, which can be rapidly broken down or transformed into new phases (*Chapter 5*). Heavy metals may be released into solution or captured in the surface layer, making this a local source or sink of heavy metals. Remobilisation of heavy metals and exchange between sediments and the overlying water column may potentially influence concentrations in the surface water.

Although dissolved concentration peaks at the sediment-water interface are not well developed in most sediment cores, an indication of the diffusive flux of solutes to the bottom water may be given by applying Fick's first law to the measured data

$$J_s = \phi \cdot D_s \cdot \frac{dc}{dz} \quad (6.4)$$

in which J_s is the diffusive flux from sediment to bottom water (in $\text{mol m}^{-2} \text{yr}^{-1}$), ϕ is the porosity, D_s is the molecular diffusion coefficient in the sediment (in $\text{m}^2 \text{yr}^{-1}$) and dc/dz is the concentration gradient between the pore water and the water column (in mol m^{-4}), z being positive downward. Average dissolved bottom-water concentrations of 155 nmol l^{-1} Zn, 0.4 nmol l^{-1} Cd, 3.4 nmol l^{-1} Pb, 116 nmol l^{-1} Ni, and 82 nmol l^{-1} Cu were used in these calculations (as measured in June 1996).

After correction of the molecular diffusion coefficient for tortuosity effects, according to Ullmann and Aller (1982), equation 6.4 is rewritten as

$$J_s = D_0 \cdot \phi^3 \cdot \frac{dc}{dz} \quad (6.5)$$

in which D_0 is the molecular diffusion coefficient in water. Temperature dependency of the diffusion coefficient of free metal ions is calculated with the Stokes-Einstein relation (Li and Gregory, 1974).

The potential importance of the diffusive flux on the cycling of heavy metals is calculated by comparing the upward diffusion of heavy metals with particulate fluxes of heavy metals to the sediment. The particle-bound flux is estimated as the mass sedimentation rate times the total metal concentration in the incoming sediment particles, according to

$$J_p = -w \cdot d \cdot (1-f) \cdot c_{spm} \quad (6.6)$$

in which J_p is the particulate flux of heavy metals to the sediment (in $\text{mol m}^{-2} \text{yr}^{-1}$), w is the deposition rate (in m yr^{-1}), d is the density of the dry solids ($2.5 \cdot 10^6 \text{ g m}^{-3}$), f is the porosity of the top layer (0.9) and c_{spm} is the concentration of the heavy metal in the suspended matter (in mol g^{-1}), as given in Table 6.3. Deposition rates at the locations studied are similar to those used in *Chapter 5*. The ratio between diffusive and particle bound flux indicates the fraction of deposited heavy metals that is remobilised in the sediment. In Table 6.4 average values for remobilisation are given. By calculating average values, it is assumed that the sediment characteristics of the locations B, C, and D represent the average sediment composition in the study area. Except for Ni in June 1996, only a relatively small amount of the particulate flux of heavy metals to the sediment (< 2 %) is remobilised as dissolved species.

The contribution of diffusion of heavy metals from the sediment to the bottom-water concentration is also given in Table 6.4. Individual contributions on each location are calculated by

$$\text{Contribution (\%)} = 100 \cdot (J_s \cdot A) / (q \cdot C_w) \quad (6.7)$$

where J_s is the calculated dissolved flux at the sediment-water interface, A is the surface area of the study area covered with water (8.5 km^2 ; Van der Meulen *et al.*, 1995), q is the flow rate of the overlying water (in $\text{m}^3 \text{yr}^{-1}$), and C_w is the dissolved heavy metal concentration in the bottom water (in mol m^{-3}). A mean flow rate ($9.5 \cdot 10^8 \text{ m}^3 \text{yr}^{-1}$; Sonneveldt, 1993) and concentration in the bottom water is assumed in these calculations. However, because the Meuse is a river with a pluvial regime, both the concentrations in the surface water and the flow rate fluctuate with discharge. Table 6.4 shows that diffusion of solutes from the sediment may contribute significantly to dissolved concentrations in the surface water. During summer, the calculated contribution of diffusion of heavy metal from the sediment to bottom-water concentrations is somewhat higher, but only Pb shows a significant increase.

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Table 6.4. Calculated diffusive fluxes (J_s) to the bottom water, degree of remobilisation and potential contribution to concentrations in the bottom water (average values for the sampling locations B, C, and D are given).

	Unit	Zn	Cd	Ni	Cu	Pb
<i>November 1995</i>						
J_s	$10^{-5} \text{ mol m}^{-2} \text{ yr}^{-1}$	115.7	0.3	10.7	- 0.5	0.4
Remobilisation	%	1.1	0.6	1.9	< 0	0.1
Contribution	%	6.7	7.1	0.8	< 0	0.7
<i>June 1996</i>						
J_s	$10^{-5} \text{ mol m}^{-2} \text{ yr}^{-1}$	176.8	0.5	94.7	- 1.1	9.9
Remobilisation	%	1.7	1.0	16.5	< 0	1.5
Contribution	%	10.2	12.2	7.3	< 0	26.3

There are some serious drawbacks in these flux calculations. The use of equation 6.5 for determination of fluxes is valid only, when steady state prevails (so net sorption is absent). Due to the presence of (hydr)oxides, the (sub)oxic zone of the sediment can function as a (temporary) adsorbing layer for heavy metals that are transported upwards. Although the sum of inorganic and organic complexed heavy metals in the pore water is measured, fluxes have been calculated with the diffusion coefficients of free metal ions. However, diffusion coefficients of organically complexed metals may be 10 to 100 times lower than those of free metal ions (Elderfield, 1981). On the other hand, fluxes to the bottom water may be significantly increased by bioturbation, bioirrigation (Boatman and Devol, 1995), and resuspension as a result of wave action and shipping activities. Especially in organic-rich sediments, bioturbation should be taken into account. The effects of bioturbation can be described similar to those of molecular diffusion, and may significantly increase the calculated fluxes to the bottom water in the sediments studied (see *Chapter 5*). The effect of wind is probably insignificant in the study area, because of the small water surface. Equation 6.7 assumes that heavy metals released from the sediment, are not sorbed by suspended matter. Therefore, the actual contribution of diffusion from the sediment to dissolved concentrations in the surface water is probably much lower than those reported in Table 6.4. Considering the various factors which limit contribution, significant effects on dissolved concentrations in the surface water are expected to be significant only in isolated tidal channels where displacement of the water takes place slowly.

Conclusions

In recent contaminated sediments in the river Meuse, The Netherlands, the behaviour of heavy metals is influenced by adsorption-desorption and precipitation-dissolution processes. Increased pore water concentrations of heavy metals are observed directly below the sediment-water interface. This results in diffusion of dissolved heavy metals from the sediment to the overlying water column. However, the relative contribution of diffusive fluxes to dissolved concentrations of heavy metals in the surface water may be significant only at locations where displacement of the surface water takes place slowly. In addition, the diffusive flux of heavy metals remobilised as dissolved ions is small compared to the flux of particulate-bound heavy metals to the sediment. In the anoxic sediment layer, association of heavy metals with sulphides is expected. Supersaturation with respect to sulphide minerals, especially for Cu and Pb, may be explained by organic complexation. Non-steady state is induced by temporal changes in the degradation of organic matter and temperature, resulting in variation in the intensity of diagenetic processes in the sediment.

Acknowledgement - This project was carried out with financial support of the Ministry of Transport, Public Works and Water Management, Institute for Inland Water Management and Waste Water Treatment (RIZA). The assistance of Pieter Kleingeld, Gijs Nobbe and Mark van Alphen during sampling and in the laboratory is greatly appreciated. Part of this chapter has been published as contribution 980007 of the Netherlands Research School of Sedimentary Geology.

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Chapter 7

Vertical distribution of acid-volatile sulphide and simultaneously extracted metals in a recent sedimentation area of the river Meuse in The Netherlands

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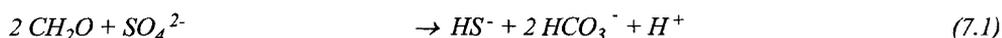
Abstract - The bioavailability of heavy metals in sediments may be strongly decreased by the presence of AVS (acid-volatile sulphide). In contaminated freshwater sediments, however, AVS levels may not be sufficiently high to scavenge all reactive heavy metals. In different seasons, the vertical distribution of AVS and SEM (simultaneously extracted metals) was studied in sediment cores of a recent sedimentation area of the river Meuse. In the suboxic layer of the sediments, the amount of AVS is always too low to bind all reactive metals as sulphides ($SEM/AVS > 1$). SEM/AVS decreases with depth in the sediments, going from ratios higher than one in the surface sediments to ratios on the order of one or even less than one at greater depths. This large vertical variation in AVS levels is attributed to diagenetic processes i.e., sulphide oxidation in the suboxic top layer and sulphate reduction in the underlying anoxic sediment layer. The depth of the boundary between the suboxic and the anoxic layer changes seasonally. An important implication of these findings is that SEM/AVS ratios in mixed homogenised sediment samples are generally not suited for the assessment of potential metal toxicity of sediments.

This chapter has been published in Environmental Toxicology and Chemistry 17: 758-763 (1998).

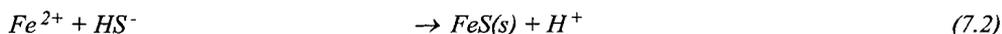
Introduction

The (bio-)availability of contaminants in sediments is influenced by the extent of their sorption and (co-)precipitation with the solid phase. Pore-water composition is considered as a useful indicator to predict the toxicity of sediments, although the exact pathway of uptake of contaminants by aquatic organisms is not yet well known (Swartz *et al.*, 1985). Because fast reliable measurements of pore-water concentrations are not possible without serious laboratory precautions, sediment quality criteria in The Netherlands are based on solid-phase contents and partition coefficients between the solid phase and the pore water (Van der Kooij *et al.*, 1991). In this equilibrium partitioning model a constant partition coefficient is assumed with depth in the sediment.

The most efficient fixation of heavy metals in sediments takes place by association with sulphide, which is produced by sulphate reduction. A useful parameter for assessing sulphate-reducing conditions in the sediment is the pore-water sulphate concentration. A simplified scheme for the oxidation of organic matter by sulphate-reducing bacteria is given by



Pore-water sulphide may precipitate with Fe^{2+} ions that are released to the pore water by reduction of Fe-(hydr)oxides

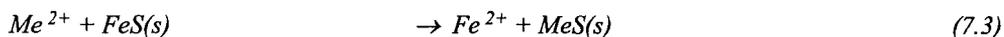


AVS (acid-volatile sulphide), pyrite (FeS_2) and organic sulphur (e.g., carbon-bound sulphur and sulphate esters) are recognised as sulphide phases in sediments. AVS includes amorphous iron monosulphides (FeS), crystalline mackinawite and pyrrhotite (FeS), greigite (Fe_3S_4), as well as sulphides of other metals, like ZnS , CdS , etc.

Although AVS is a metastable reduced sulphur form, it may be important for studying heavy metal toxicity in sediments. FeS is a reactive pool of solid-phase sulphide that can adsorb and coprecipitate divalent trace metals having sulphide solubility products smaller than FeS (Morse *et al.*, 1987; Di Toro *et al.*, 1992; Morse and Arakaki, 1993). Thus, in sulphidic environments, heavy metals can compete with or displace Fe(II) from previously formed iron(mono)sulphides to form metal sulphide precipitates.

Vertical distribution of AVS and SEM

Di Toro *et al.* (1990) have proposed the following reaction for the formation of heavy metal sulphides in anoxic sediments, in which Me is the divalent heavy metal

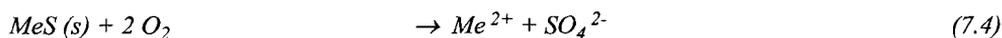


The toxicity of (freshwater) sediments has been studied intensively with respect to heavy metals. Di Toro *et al.* (1992) conclude that in most anoxic marine and freshwater sediments AVS is the controlling sediment property for metal bioavailability. Based on laboratory toxicity experiments, these authors introduced the ratio of SEM (simultaneously extracted metals) to AVS as a useful tool for predicting sediment toxicity. It should be mentioned that AVS and SEM are both operationally defined parameters. AVS is defined as the amount of sulphides released during cold acid extraction and SEM is defined as the sum of trace metals (usually Zn, Cd, Pb, Cu, and Ni) liberated during AVS extraction. When the ratio of the molar concentrations of SEM to AVS is smaller than one, there is no acute toxicity for aquatic organisms. The sediment is considered potentially toxic when the ratio SEM to AVS exceeds one. Actual toxicity may vary depending on the sensitivity of the organism (Hare *et al.*, 1994).

Various studies show that AVS is not the sole partitioning phase for predicting the acute toxicity, especially for Cu, which is strongly associated with sediment organic matter (Ankley *et al.*, 1993). The concurrent release of sulphide (AVS) and metals (SEM) during extraction with HCl cannot be considered as evidence that those particular metals were bound by sulphide in the sediment solely (Allen *et al.*, 1993). Although Huerta-Diaz *et al.* (1993) have presented experiments to measure the quantity of heavy metals associated with AVS in sediments, selective extraction techniques are still absent. The association of heavy metals with sulphide precipitates can also be shown using electron microprobe techniques (Lee and Kittrick, 1984; Van den Berg *et al.*, 1998/*Chapter 3*). To account for the amount of SEM and AVS in the sediment, it is recommended to use absolute differences between SEM and AVS, as opposed to ratios, as a basis to predict likely metal bioavailability (Ankley *et al.*, 1996²; Hansen *et al.*, 1996).

Because vertical and temporal (seasonal) variation in AVS concentrations make it difficult to decide what AVS concentration should be used in evaluating the toxicity of metals in natural sediments (Di Toro *et al.*, 1990; Ankley *et al.*, 1991), it has been proposed to develop sampling guidance that specifically addresses the issue of

temporal and spatial variations of AVS in sediments (Ankley *et al.*, 1996¹). Organic matter degradation by different oxidators results in various redox zones in the sediment. A distinction between an oxic layer (oxygen reduction), a suboxic layer (nitrate, manganese, and iron reduction), and an anoxic layer (sulphate reduction and methanogenesis) is usually made (Froelich *et al.*, 1979; Berner, 1981). In freshwater sediments, these zones generally occur on a millimetre to centimetre scale. These diagenetic processes highly influence the vertical distribution of sulphides in the sediment. Because rates of organic matter degradation are highly temperature dependent, during summer months usually a higher sulphate reduction rate is measured in freshwater sediments, which influences the production of AVS and the thickness of the redox layers. Leonard *et al.* (1993) have shown that variations in AVS concentrations in lake sediments are directly correlated with temperature of the overlying lake water. Large fluctuations in sediment AVS concentrations have also been measured in lakes with a seasonally anoxic hypolimnion (Howard and Evans, 1993). Mixing of the sediment by bioturbation and resuspension may result in oxidation of AVS, thus increasing the bioavailability of associated metals (Di Toro *et al.*, 1996; Peterson *et al.*, 1996)



The objective of this study was to examine the vertical distribution and temporal variation of AVS and SEM levels in recent (contaminated) freshwater sediments of the river Meuse. Our general aim was to demonstrate that diagenetic processes can lead to season- and depth-dependent distributions of the SEM/AVS ratio in (contaminated) sediments. Because our research has been accomplished in a recent sedimentation area, the role of pyrite and organic sulphur, which may be important as long-term sinks for sulphur in sediments, has not been considered in this study.

Materials and methods

The study area

The Biesbosch is a major wetland area, situated in the delta of the rivers Rhine and Meuse in the western part of The Netherlands (Fig. 4.1). Tidal influences in the

Vertical distribution of AVS and SEM

Biesbosch have decreased considerably after 1970, when the former Rhine-Meuse estuary was closed off from the North Sea by a dam. Today, the Biesbosch is a freshwater tidal basin with a very modest tidal range (some 20-30 cm in the study area). The study area is almost exclusively flushed by the river Meuse, except for its north-western part, where Rhine water occasionally intrudes. Due to the very low current velocities in the former tidal channels, these are actively silting up since 1970. Both the aquatic sediments and soils in the Biesbosch are strongly contaminated by heavy metals, reflecting the serious metal pollution history of the river Meuse (Hoogeveen, 1995). The water column, with a depth between 2 and 4 m, remains aerobic throughout the year.

Sample collection and handling

At four permanently submerged locations in the Biesbosch (Fig. 4.1), sediment cores were collected in Plexiglas tubes with an inner diameter of 15 cm. Sampling took place manually by SCUBA divers in November 1995 and June 1996. Surface water remained on the sediment cores in the tubes to prevent oxidation of the sediment. The cores were immediately stored at 4°C. Sediment and bottom water temperature was approximately 8°C in November 1995 and 20°C in June 1996.

Within 48 h after collection, the top 10 cm (in November) and the top 7 cm (in June) of sediment cores from two locations (B and C) were sectioned into 0.5- or 1.0-cm slices. Laboratory subsampling took place under strictly anaerobic conditions in a nitrogen-filled glove box to prevent sulphides from oxidation. Pore water was extracted by pressure filtration, according to the method described by De Lange (1992). The pore water was collected in High Density Polyethylene bottles. On each location, one homogenised mixed sediment sample was taken of the top 10 cm of a separate core. Sediment samples were kept at 4°C under a nitrogen atmosphere until extraction and analysis. Extraction of AVS and SEM took place within 24 h after subsampling.

Sediment analysis

Both the mixed and the sectioned sediment samples were analysed for SEM and AVS concentrations. The moisture content of the sediment samples, necessary to calculate AVS and SEM concentrations on a dry weight basis, was determined by measuring the

weight loss after freeze drying. About 1 g of wet sediment was weighed exactly and used for extraction of AVS and SEM. AVS concentrations were determined according to the method described by Henneke *et al.* (1991) with slight modification for this purpose. As proposed by Cornwell and Morse (1987), the sediment samples were acidified during 1 h using a 10-ml 6 M HCl solution at room temperature to form H₂S that was subsequently collected in a 1 M NaOH solution. The sulphide concentration in the NaOH solution was measured polarographically with an EG and G Princeton Applied Research model 384 B polarograph with a static mercury drop (EG and G Parc model 303A) using square-wave voltammetry (SWV). The acidified sediment suspension in the reaction flask was filtered through 0.45- μ m cellulose acetate filters (Sartorius) for measurement of SEM. Concentrations of Zn, Cd, Cu, Pb, and Ni in the filtrates were analysed with an inductively coupled plasma atomic emission spectrometer (Perkin Elmer Optima 3000). Duplicate extractions and analyses of SEM and AVS showed that, using the described method, the results are well reproducible. In order to study the effects of extractant acidity on AVS and SEM measurements, the four mixed samples from the cores taken in November 1995 were extracted with both a 1 M and a 6 M HCl solution.

Freeze-dried sediment samples were digested in a mixture of concentrated HClO₄, HNO₃ and HF in Teflon vessels and finally dissolved in a 1 M HCl solution. Total concentrations of major elements (Ca, Fe, Mn, Al, and total S) and heavy metals (Zn, Cd, Cu, Pb, and Ni) in the acid solution were determined by ICP-AES similar to the SEM measurements. The accuracy of the solid-phase extractions and analyses was validated by measuring three international standard sediments containing high levels of heavy metals (PACS-1, MAG-1, and GXR-1). Organic carbon was determined on a Carlo Erba Strumentazione nitrogen analyzer 1500. Inorganic carbon was removed before analysis by shaking the sediment sample in 1 M HCl. Collected pore water was analysed for sulphate using a Dionex QIC analyzer. CaCO₃ content was calculated from the Ca content of the solid-phase samples.

Results and discussion

Characterisation of the solid phase

The chemical characteristics of the sediments at the four sampling locations in the Biesbosch are presented in Table 7.1. The Al and Fe concentrations are typical of fine-grained sediments (silt and clay) in The Netherlands. The sediments contain high levels of heavy metals, especially Zn. Differences in sediment characteristics between the two sampling periods are relatively minor for locations A,C, and D, but larger for location B. During June 1996, the sediment at location B is relatively low in Al and Fe, indicating it is not so rich in clay, probably due to an increased contribution of sand. This dilution effect also explains the relatively low concentrations of heavy metals in the sediment at this time, as will be discussed later.

Table 7.1. Characteristics of the homogenised samples from the top 10 cm of sediment cores taken in November 1995 and June 1996.

	CaCO ₃	OrgC	Fe	Mn	Al	TotS	Zn	Cd	Cu	Pb	Ni
	————— (%) —————			—————			————— (µg g ⁻¹) —————				
<i>November</i>											
A	8.6	3.8	3.1	0.09	4.4	0.24	860	10	64	127	43
B	8.6	3.3	3.5	0.09	4.6	0.34	1247	15	75	173	44
C	9.7	4.5	4.0	0.11	5.4	0.26	1059	12	79	158	48
D	10.3	4.3	4.2	0.12	5.2	0.26	1014	10	82	143	49
<i>June</i>											
A	8.7	3.4	2.8	0.09	4.3	0.18	692	< 17*	63	140	39
B	7.9	2.9	2.2	0.06	3.4	0.18	699	< 17*	44	115	29
C	10.5	5.2	4.0	0.13	5.1	0.24	1044	< 17*	94	199	52
D	11.1	5.2	4.1	0.14	5.0	0.25	994	< 17*	92	181	50

* Detection limit for Cd is 17 mg kg⁻¹

AVS and SEM in mixed homogenised samples

The influence of extractant acidity on AVS and SEM measurements has been studied by extracting with both a 1 M HCl and a 6 M HCl solution. Using a 1 M HCl solution, similar amounts of Zn, Cd, and Pb, somewhat lower amounts of Ni, but significantly lower amounts of Cu are extracted compared to a 6 M HCl solution (Table 7.2). Therefore, it is concluded that Cu and Ni are partly bound to other sediment phases than Zn, Cd, and Pb (see also Cooper and Morse, 1998). The behaviour of Cu is often influenced by its great affinity for organic matter. Comparison of the total metal analyses and the SEM fractions showed that 90 to 100 % of total contents of Zn, Cd, Pb, and Cu are extracted using a 6 M HCl solution, which indicates that these heavy metals are almost completely bound in reactive phases in the sediment. However, only 50 % of the total content of Ni is extracted in 6 M HCl, which may be explained by incorporation of Ni in the mineral structure of, for example, clay minerals. The major part (85-90 %) of SEM consists of reactive Zn (Tables 7.2 and 7.3).

Extractions with both a 1 M HCl and a 6 M HCl solution show that AVS levels are well reproducible (Table 7.2). Because the extractions with a 1 M HCl solution were performed 1 to 2 d later than those with 6 M HCl, the slightly lower quantities of 1 M HCl extractable AVS in the cores from location C and D may be explained by partial oxidation of the sediment during storage.

Table 7.2. Concentrations of AVS and SEM in homogenised samples from the top 10 cm of four sediment cores taken in November 1995 (extractions performed with 1 M and 6 M HCl, concentrations in units per dry sediment).

	HCl	AVS	Zn	Cd	Pb	Ni	Cu	SEM	SEM/AVS
	(M)					($\mu\text{mol g}^{-1}$)			(-)
A	1	18.0	12.1	0.08	0.6	0.2	0.6	13.6	0.8
A	6	17.9	11.9	0.08	0.6	0.3	0.9	13.7	0.8
B	1	51.7	18.5	0.13	0.9	0.3	0.3	20.1	0.4
B	6	52.5	18.9	0.13	0.9	0.4	1.1	21.5	0.4
C	1	7.4	14.9	0.10	0.8	0.3	1.0	17.0	2.3
C	6	8.8	15.1	0.10	0.8	0.4	1.2	17.5	2.0
D	1	8.3	14.1	0.09	0.7	0.3	0.9	16.0	1.9
D	6	10.3	14.3	0.09	0.7	0.4	1.1	16.6	1.6

Vertical distribution of AVS and SEM

Table 7.3. Concentrations of AVS and SEM in homogenised samples from the top 10 cm of four sediment cores taken in June 1996 (concentrations in dry sediment).

	AVS	Zn	Cd	Pb	Ni	Cu	SEM	SEM/AVS
				($\mu\text{mol g}^{-1}$)			(-)	
A	9.5	8.9	< 0.15*	0.6	0.3	0.8	10.5	1.1
B	28.6	9.5	< 0.15*	0.5	0.3	0.6	10.9	0.4
C	9.1	13.2	< 0.15*	0.8	0.4	1.1	15.6	1.7
D	7.2	12.5	< 0.15*	0.8	0.4	1.1	14.7	2.0

* Detection limit for Cd is $0.15 \mu\text{mol g}^{-1}$

From Tables 7.2 and 7.3, it can be concluded that the SEM concentrations are relatively constant throughout the study area (within a factor of two), whereas the AVS concentrations can be extremely variable. The quantity and distribution of AVS in sediments depend upon a large number of variables, including carbon input rate, sediment burial rate, sulphate diffusion rate, biological and physical sediment mixing, and sediment temperature (Morse *et al.*, 1987). The relatively high AVS concentrations observed at location B might be related to the lower sedimentation rate at this location compared to the other sampling locations (similar to Matisoff and Holdren, 1995). Differences in AVS and SEM concentrations between November 1995 (Table 7.2) and June 1996 (Table 7.3) at locations A and B are not thought to be related to seasonal changes in sediment temperature or organic matter input, because the AVS and SEM concentrations at the other two locations (C and D) do not show such seasonal differences. Spatial heterogeneity of the sediment may be a better explanation for these differences in AVS concentration, as confirmed by the variation in solid-phase characteristics of core B (Table 7.1). It is important to notice that, although SEM and AVS levels are different, SEM/AVS ratios are comparable at these locations during both sampling periods. Also the ratios at locations C and D are not considered to be different significantly during both sampling periods.

From these mixed, homogenised, samples, it should be concluded that, according to the criteria by Di Toro *et al.* (1992), the sediments from the locations C and D are potentially toxic to aquatic organisms, and the sediment from location B is non toxic. The sediment from location A has a SEM/AVS ratio on the order of one. Less seriously contaminated freshwater sediments from The Netherlands studied by

Van den Hoop *et al.* (1997) generally contain abundant AVS to bind all reactive heavy metals.

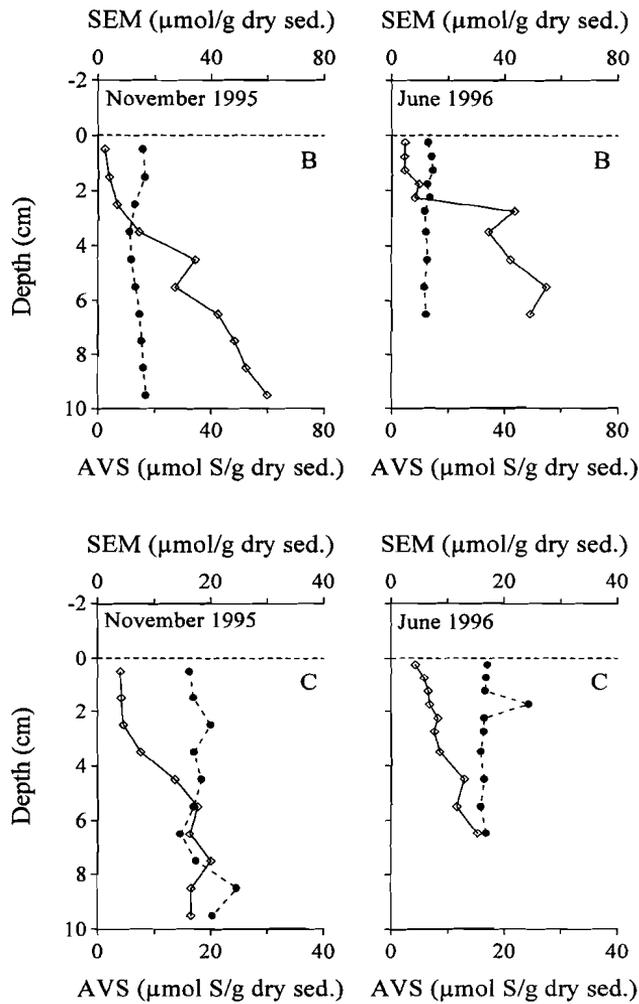


Figure 7.1. Depth profiles of SEM (black dots) and AVS (open diamonds) concentrations at locations B and C during November 1995 and June 1996 (note the different concentration scales). The dotted line represents the sediment-water interface.

Vertical distribution of AVS and SEM

Vertical and temporal variability in AVS and SEM concentrations

To study the vertical variability of AVS and SEM in the sediments, cores from the locations B (SEM/AVS < 1) and C (SEM/AVS > 1) were sectioned into small intervals. Because, contrary to the homogenised cores of these locations, the general characteristics of the sediment in the cores sampled for sectioning in November 1995 and June 1996 are similar, the AVS and SEM profiles can be compared between both periods. The vertical profiles of AVS and SEM in the sediments at locations B and C are shown in Fig. 7.1. Although the SEM contents are relatively constant, both with depth and with time, the AVS concentration increases dramatically below the top few centimetres in both profiles, where the sulphate reduction zone begins (Fig. 7.2). The increasing AVS concentration of the sediments with depth can be explained by *in situ* production of AVS during sulphate reduction.

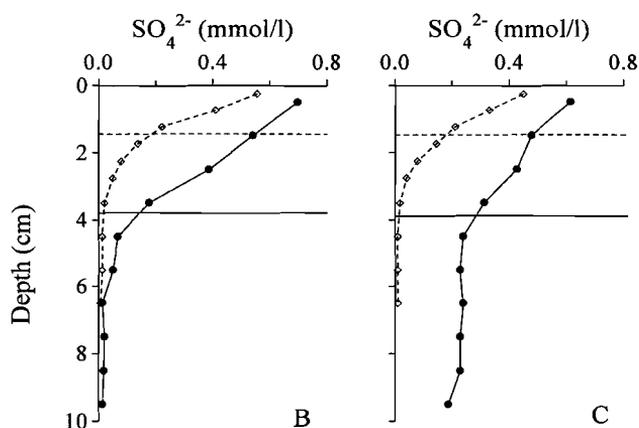


Figure 7.2. Depth profiles of pore-water sulphate concentrations at locations B and C during November 1995 (black dots) and June 1996 (open diamonds). The boundary between the suboxic and the anoxic layer, defined as the depth where the pore-water sulphate concentration gradient changes is indicated in the profiles (continuous line for November 1995; dotted line for June 1996).

The vertical variability of AVS in the sediments is very likely to influence their potential toxicity with respect to heavy metals. In the sediment cores studied, the

SEM/AVS ratios decrease from values greater than one (potentially toxic) in the surface sediments to values on the order of one (location C) or even lower than one (location B) at greater depth. The increase in AVS concentrations with depth may lead to erroneous conclusions as to the potential toxicity of the surface sediments. This is clearly illustrated by the AVS and SEM profiles of location B, featuring SEM/AVS ratios greater than one in the top few centimetres (Fig. 7.1), whereas the mixed sediment samples (0-10 cm) from location B have SEM/AVS ratios much smaller than one (Tables 7.2 and 7.3). Obviously, SEM/AVS ratios for mixed sediment samples (0-10 cm) fail to indicate the potential toxicity of the top few centimetres of the sediments, where (sub-)oxic conditions prevail. Moreover, SEM/AVS ratios give no indication of the absolute excess of metals over the sulphide-bound quantity. Additional binding phases may keep the pore-water concentrations at a low level (Leonard *et al.*, 1996). Therefore, conventional methods based on measured pore-water concentrations (directly measured or calculated from solid-phase composition and partition coefficients) may give a more reliable indication of bioavailability and potential toxicity of heavy metals in suboxic sediments.

Seasonal influence on the build-up of AVS is obvious in the profiles at location B and to a lesser extent at location C. During summer, high sediment temperature in combination with a larger amount of freshly deposited, highly degradable, organic matter results in more reducing conditions. As a result, the boundary between the suboxic and the anoxic layer moves upward (Fig. 7.2). This results in AVS build-up closer to the sediment-water interface, as shown clearly for the sediment cores from location B (Fig. 7.1). However, maximum AVS concentrations are comparable during both periods at locations B and C, because sulphate diffusion does not affect the sediment layer deeper than approximately 6 cm (Fig. 7.2). The seasonal change in AVS formation in the sediment reflects a non-equilibrium situation that may affect the heavy metal concentrations in the pore water. Therefore, it is doubtful that the pore-water heavy metal concentrations in the studied sediments are governed by their respective sulphide precipitates (in the presence of AVS).

Conclusions

Although SEM concentrations are independent of sediment depth in the studied cores, AVS levels increase dramatically with increasing depth due to sulphate reduction.

Vertical distribution of AVS and SEM

Because sulphate reduction is prohibited in the top few centimetres of the sediment where (sub-)oxic conditions prevail, AVS levels in the surface sediment are generally too low to bind all reactive heavy metals. Similar results may be expected in other (contaminated) sediments that are overlain by an oxic water column. Due to the increase in AVS concentrations with increasing sediment depth, it is obvious that SEM/AVS ratios of homogenised sediment samples (e.g. 0-10 cm) are not suited to assess the potential heavy metal toxicity in the surface sediments. Moreover, seasonal changes in sediment temperature and organic matter input influence the depth of the suboxic anoxic boundary, which leads to a nonequilibrium situation, possibly affecting pore-water metal concentrations. Because the presence of a large number of organisms is restricted to the surface layer (Bongers and Van de Haar, 1990) and assuming that only the dissolved species of metal ions are bioavailable, it is recommended that pore-water concentrations of heavy metals in surface sediments be either measured directly (posing serious sampling and analytical problems), or estimated indirectly from solid-phase composition and partition coefficients.

Acknowledgement - This project was carried out on behalf of and with financial support of the Ministry of Transport, Public Works and Water Management, Institute for Inland Water Management and Waste Water Treatment. The authors thank Suzan Buijckx for carrying out part of the experiments. This chapter has been published as contribution 970145 of the Netherlands Research School of Sedimentary Geology.

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Samenvatting

Het onderzoek dat beschreven wordt in dit proefschrift is uitgevoerd aan water- en bodemonsters afkomstig uit de Biesbosch. De Biesbosch is gelegen in de delta van de Rijn en Maas en behoort tot de ecologische hoofdstructuur van Nederland. Internationaal wordt de Biesbosch erkend als een belangrijk zoetwatergetijdengebied. De bouw van de Haringvlietdam in 1970 heeft grote gevolgen gehad voor de waterhuishouding in de Biesbosch. Hierdoor is een groot deel van het oorspronkelijk getijdenkarakter verloren gegaan.

Gebaseerd op hydrologische verschillen kan een aantal bodemtypen worden onderscheiden; 'droge' landbodems, landbodems die periodiek onder water staan (bijvoorbeeld in buitendijkse gebieden), en waterbodems. Door de toevoer van verontreinigingen met de Rijn en Maas is een grote hoeveelheid vervuild slib afgezet in de Biesbosch, zowel in de buitendijkse gebieden als in de waterwegen. Deze verontreinigingen vormen een groot probleem bij politieke besluiten omtrent de inrichting van de Biesbosch.

Dit proefschrift geeft een overzicht van de aanwezigheid en het gedrag van zware metalen, waaronder zink, koper, cadmium, lood en nikkel, in de verschillende bodems in de Biesbosch. Daarnaast wordt aandacht geschonken aan de gevolgen van natuurontwikkeling voor de mobiliteit van zware metalen. In bodems die geheel of gedeeltelijk verzadigd zijn met water, is de oxidatietoestand (redox-potentiaal) één van de belangrijkste parameters die het gedrag van zware metalen beïnvloedt.

Door de geologische opbouw van het achterland van de Rijn en Maas is het afgezette slib in de Biesbosch initieel kalkhoudend. Omdat kalk een bufferende werking heeft op de zuurgraad (pH), kan een bodem als gevolg van ontkalking in een relatief korte periode verzuren. Verlaging van de pH kan leiden tot een verhoogde biobeschikbaarheid en een versnelde uitspoeling van zware metalen. Omdat deze processen in een kort tijdsbestek kunnen plaatsvinden, wordt ontkalking beschouwd als een 'chemische tijdbom'. In *Hoofdstuk 2* wordt beschreven dat bodems die periodiek verzadigd zijn (hydic soils) de grootste mate van ontkalking vertonen. Periodieke verzadiging kan het gevolg zijn van tijdelijke overstroming (inundatie) en van fluctuaties in de grondwaterstand. Ontkalking in dergelijke bodems wordt voor een

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belangrijk deel beïnvloed door twee geochemische processen; oxidatie van ijzersulfiden en verhoging van de CO₂ druk in de bodem. Oxidatie vindt plaats gedurende perioden waarin de bodem onverzadigd, en dus zuurstofhoudend, is. Tijdens perioden waarin de bodem verzadigd is, wordt de CO₂ druk in de bodem verhoogd. Deze hangt sterk af van de afbraak van organisch stof en de snelheid van CO₂ diffusie. Als gevolg hiervan verschuift het kalkevenwicht. Op slechts een beperkt aantal locaties in de Biesbosch heeft ontkalking inmiddels geleid tot een volledig ontkalkte bodem.

De samenstelling van het poriewater is een goede indicator voor relatief kortdurende processen in bodems. In *Hoofdstuk 3* worden de effecten van periodieke verzadiging op concentraties aan zware metalen in bodems besproken. Gedurende perioden met lage grondwaterstanden, waardoor een groot deel van de bodem onverzadigd is, worden verhoogde concentraties aan zware metalen in het poriewater gemeten. Dit wordt veroorzaakt door oxidatie van sulfideneerslagen en versnelde afbraak van organisch stof. Zowel sulfiden als organisch stof zijn sterk geassocieerd met zware metalen in verontreinigde bodems. Met behulp van electronenmicroscopie is aangetoond dat Zn en Fe *in situ* neerslagen vormen met sulfide. Omdat deze neerslagen gesitueerd zijn in de celstructuur van afgestorven plantenwortels, wordt geconcludeerd dat reactief organisch materiaal het gedrag van zware metalen in dit type bodems sterk beïnvloed.

In *Hoofdstuk 4* wordt een beeld gegeven van de seizoensvariatie in de geochemische processen die plaatsvinden in waterbodems in de Biesbosch. In dit hoofdstuk wordt aangetoond dat fluctuaties in de (geo)chemische samenstelling van het poriewater voornamelijk wordt beïnvloed door interne processen in de waterbodem en in mindere mate door variatie in het oppervlaktewater. De gemeten verschillen hangen sterk samen met fluctuaties in de temperatuur van het oppervlaktewater en de bovenste laag van de waterbodem. Tijdens de zomer vindt verhoogde afbraak van organisch stof plaats. De hogere temperatuur gedurende deze periode biedt betere levensomstandigheden voor bacteriën. Deze zijn verantwoordelijk voor een groot deel van de redox-processen in bodems. Daarnaast verlopen chemische reacties sneller en vinden transportprocessen sneller plaats.

Om de geochemische processen in de bestudeerde waterbodems te kunnen kwantificeren is de gemeten data gemodelleerd. In *Hoofdstuk 5* wordt een beschrijving gegeven van het toegepaste model. In dit model wordt rekening gehouden met (bio)geochemische reacties en transportprocessen. Methanogenese, waarbij organisch stof wordt omgezet in onder andere methaan, is het belangrijkste proces in de

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waterbodems in de Biesbosch. De andere afbraakprocessen zijn slechts van belang in de bovenste centimeters van de waterbodem. Er kan een onderscheid worden gemaakt tussen verschillende locaties op grond van verschillen in de afbraakbaarheid van organisch stof, die sterk afhangt van de afzettingssomstandigheden.

De afbraakprocessen van organisch stof beïnvloeden het gedrag van zware metalen in waterbodems sterk (*Hoofdstuk 6*). Omdat zware metalen in zwevend slib geassocieerd zijn met organisch stof en (hydr)oxiden leidt afbraak van organisch stof tot mobilisatie van zware metalen en tot verhoogde concentraties in het poriewater. Op enkele centimeters onder het sediment-water grensvlak dalen deze concentraties. Dit hangt samen met de vorming van sulfiden. Uit berekeningen volgt dat ook binding aan opgeloste organische bestanddelen het gedrag van zware metalen in waterbodems sterk beïnvloedt. Op grond van opgeloste concentraties aan zware metalen in het poriewater en oppervlaktewater wordt geconcludeerd dat diffusie van zware metalen vanuit de waterbodem slechts ten dele kan bijdragen aan de kwaliteit van het oppervlaktewater.

Door het beleid zijn normen opgesteld voor kwaliteit van bodem, oppervlakte- en grondwater in Nederland. In de huidige normstelling zijn de normen voor waterbodems en periodiek verzadigde bodems gebaseerd op die in droge landbodems. Omdat sulfiden een belangrijke rol spelen in het gedrag van zware metalen in waterbodems wordt internationaal getracht deze te kwantificeren. In *Hoofdstuk 7* wordt beschreven dat de verhouding tussen het gehalte aan reactieve zware metalen (SEM) en sulfiden (AVS) een eenvoudige methode is om snel de potentiële toxiciteit van bodems te voorspellen. In het geval dat deze verhouding kleiner is dan één, kunnen alle zware metalen vastgelegd en geïmmobiliseerd worden. Als echter de verhouding groter is dan één dan is de waterbodem mogelijk toxisch voor organismen en is nader onderzoek noodzakelijk, bijvoorbeeld met bio-assays. In de bestudeerde waterbodems in de Biesbosch varieert de SEM:AVS verhouding sterk met de diepte. Door de aanwezigheid van oxidatoren vindt in de bovenste centimeters van de waterbodem oxidatie van sulfiden plaats. Daarom wordt aanbevolen om geen mengmonsters van de bovenste 10-20 cm te gebruiken voor de bepaling van de (potentiële) toxiciteit aan de hand van SEM:AVS verhoudingen.

Dit onderzoek toont aan dat wisselende waterhuishouding in bodems als gevolg van tijdelijke overstromingen en fluctuerende grondwaterstanden grote variatie in redox-omstandigheden veroorzaakt. Dit heeft grote effecten, wanneer droge (polder)gronden in het kader van natuurontwikkeling periodiek verzadigd worden. Omdat waterbodems

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permanent verzadigd zijn, wordt daar een minder grote seizoensvariatie gemeten. Een belangrijke conclusie van dit onderzoek is dat in dynamische bodem/watersystemen veranderingen plaatsvinden in de intensiteit van (hydro-)geochemische processen. Met deze veranderingen moet rekening worden gehouden bij de planning en uitvoering van natuurontwikkelingsprojecten.

Dankwoord

Voor de totstandkoming van dit proefschrift ben ik een groot aantal mensen dank verschuldigd. Ten eerste mijn promotor, Prof. Dr. Van der Weijden, die mij de mogelijkheid bood om te promoveren op een zeer interessant en breed onderwerp.

Mijn co-promotor Guus Loch is onmisbaar gebleken bij de uitvoering en de afronding van mijn promotie-onderzoek. Jouw grote inzet blijkt onder andere uit het feit dat je mede-auteur bent bij alle hoofdstukken. Vele uren heb ik met jou gediscussieerd over de interpretatie van onderzoeksresultaten. Hierbij bleek dat door jouw bodemkundige achtergrond vaak nieuwe aspecten werden toegevoegd aan de manier waarop binnen de geochemie naar processen in waterbodems wordt gekeken.

Direct na mijn afstuderen werd de mogelijkheid geboden om te beginnen aan een project waarin de gevolgen van het slechten van dijken op de mobiliteit van zware metalen in de vaak verontreinigde poldergronden werd onderzocht. Dit project werd uitgevoerd in samenwerking met medewerkers van Rijkswaterstaat directie IJsselmeergebied (Henk Wolters en Eddie Vos), de vakgroep Fysische Geografie en Bodemkunde van de UvA (onder leiding van Prof. Dr. J. Sevink) en de vakgroep oecologie & oecotoxicologie van de VU (onder leiding van Dr. J. Rozema). Deze samenwerking heeft geleid tot een aantal onderzoeksrapporten die zijn verschenen als Flevobericht. Door dit project heb ik nieuwe inzichten gekregen in de samenhang tussen fysische, chemische en biologische processen die plaatsvinden in (natte) bodems. Speciaal wil ik in dit verband Jos Vink en Herman Winkels (beiden RWS directie IJsselmeergebied, later RIZA) bedanken. Laatstgenoemde fungeerde als projectleider en is medeauteur van Hoofdstuk 3. In de begeleidingscommissie zaten verder Jan Willem van Berghem (RWS directie Zuid-Holland) en Henk Zingstra (Overlegorgaan Nationaal Park “De Biesbosch”). Voor de bereikbaarheid van de monsterlocaties in de Biesbosch, ijs en weder dienende, wil ik de medewerkers van Staatsbosbeheer van harte bedanken.

Hierna verlegde de aandacht van onderzoek zich naar verontreinigde waterbodems. Hoewel het project bescheiden begon, is het uiteindelijk toch de basis gebleken voor dit proefschrift. Ik wil Bertie van der Heijdt en Gertjan Zwolsman bedanken voor het getoonde vertrouwen. Jullie grote inzet is terug te vinden in de hoofdstukken 4 tot en met 7 van dit proefschrift. Voor de monstercampagnes in de

Biesbosch wil ik de bemanning van de Nes onder leiding van schipper D.C. Aarnoutse (RWS, directie Zuid Holland) bedanken voor alle inspanningen.

Op de faculteit Aardwetenschappen wil ik een aantal mensen in het bijzonder noemen. Pieter Kleingeld, liefhebber van waadpakken en redoxelectroden, is onmisbaar gebleken bij het oplossen van allerlei technische problemen, zowel in het veld als in het lab. Marc van Alphen en Gijs Nobbe voor hulp bij experimenten en analyses. Denk daarnaast ook nog eens aan het tillen van gasflessen in het veld, het plaatsen van memocellen in de (zware) klei en het zoeken naar monsterlocaties in het riet. De medewerkers van het AGL wil ik bedanken voor de vele analyses die ze ten behoeve van mijn onderzoek hebben uitgevoerd. Daarnaast wil ik mijn kamergenoot Thomas Keijzer bedanken voor zijn interesse in mijn onderzoek en zijn planten.

Jeroen de Graaff, Jasper Griffioen, Ralf Haese, Hans Hage, Niels Hartog, Ronald Jonckbloedt, Sieger van der Laan, Gert de Lange, Peter van der Linde, Dorinda van der Linden, Dineke van de Meent, Gerben Mol, Ivar Nijenhuis, Hilde Passier, Peter Pruyzers, Gert-Jan Reichart, Arrian Rutten, Patrick van Santvoort, Sjoerd Schenau, Arthur Schmidt, Hendrik-Jan Visser, Simon Vriend, Helen de Waard, Berend Wilkens en Mariëtte Wolters wil ik bedanken voor de prettige tijd die ik heb gehad bij Geochemie.

Daarnaast wil ik nog Marcel Hoefs, Dick Schipper en Arjen van der Weijden noemen. Als leden van ons geochemisch clubje (bijna omgedoopt in IT-clubje) zorgden zij voor de broodnodige (muzikale) ontspanning tijdens en na werktijd.

Als laatste wil ik graag mijn familie bedanken voor alle steun en interesse in de afgelopen jaren. Als laatste bedank ik natuurlijk Jolanda. Jouw vertrouwen heeft mij gesterkt in mijn keuze om langer op de universiteit te blijven en dit proefschrift af te ronden.

Gerard

Curriculum Vitae

Gerard van den Berg werd geboren op 5 maart 1968 in Heerenveen. Aan de Rijksscholengemeenschap te Heerenveen werd de middelbare school doorlopen. Het VWO diploma werd behaald in 1986. Na een jaar opleiding Chemische Technologie aan de Universiteit Twente, startte hij in 1987 met de studie Geologie aan de Universiteit Utrecht. In 1988 werd het propaedeutisch examen behaald. Tijdens de doctoraalstudie heeft hij in opdracht van Rijkswaterstaat een studie verricht naar de inrichting van depots voor opslag van baggerspecie. Zijn afstudeeronderzoek had als onderwerp transport van opgeloste stoffen in kwetsbare zandgronden. Gedurende de periode januari tot juni 1993 bezocht hij het Institution för Miljö och Energisystem aan de Universiteit van Lund in Zweden. Hier werd onderzoek uitgevoerd naar droge depositie van aerosolen in natuurlijke watersystemen. In augustus 1993 behaalde hij het doctoraalexamen Geochemie met als specialisatie Exogene Geochemie. Hierna werd hij aangesteld als toegevoegd onderzoeker bij de vakgroep Geochemie waar hij het gedrag van zware metalen in periodiek verzadigde bodems en waterbodems bestudeerde. Gedurende deze periode werd ook dit proefschrift geschreven. Sinds juli 1998 is hij werkzaam bij het Rijksinstituut voor Integraal Zoetwaterbeheer en Afvalwaterbehandeling (RIZA), afdeling Transport van Water, Stoffen en Slib.