Long-term Metal Retention Processes in a Peat Bog: Field Studies, Data and Modelling

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Doctoral Thesis

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Abstract

The study was inspired by the need to assess long-term metal retention in municipal solid waste (MSW) landfills. The long-term processes in landfills are poorly known due to the relatively short time that such landfills have been in existence. Natural analogues where similar metal binding processes could be expected were therefore sought for.

The work described in this thesis aims to elucidate the long-term transport and attenuation processes involved in the retention of heavy metals in a peat bog, through field studies and modelling. The Oostriku peat bog (central Estonia) has been exposed to metal-rich groundwater discharge over a long period of time and was found to have accumulated high concentrations of Fe, other heavy metals (e.g. Pb, Cu, Zn, Mn), and As. It was characterised in detail with respect to metal depth distribution and main metal binding mechanisms (using an optimised Tessier extraction scheme).

The oxidation of metal sulphides in the surrounding carbonate bedrock was proposed to be a possible long-term source of heavy metals in the water emerging in a spring at the peat site. The water in the spring and peat pore-water was sampled and analysed. The dissolution sequence of the sulphide minerals and evolution of the water composition along a flowpath in the carbonate rock were modelled. Resulting aqueous phase concentration of major and minor elements are discussed in relation to governing geochemical processes. The simulated water composition was compared with that observed.

Retention of metals transported with water through the peat was assessed through modelling equilibrium sorption on solid organic matter and amorphous ferric oxyhydroxide by using a simplified quantitative modelling approach and independently obtained data. Dynamic evolution of metal sorption fronts along a peat profile over time was modelled to test metal-metal competition effects. A possible formation of ferric oxyhydroxide in the peat bog was also assessed with the model.
List of publications

This thesis is based on the following papers:


II. Syrovetnik K., Malmström M.E, Neretnieks I. Modelling of sulphide mineral oxidation as a source of heavy metals in the Oostriku peat bog, Estonia. 2005 (manuscript).

III. Syrovetnik K., Malmström M.E. Neretnieks I. Accumulation of heavy metals in the Oostriku peat bog: determination of binding processes by means of sequential extraction. 2005, (accepted for publication in Environmental Pollution).

# Table of contents

1. INTRODUCTION ......................................................................................................................... 1
   1.1 Background ........................................................................................................................... 1
   1.2 Aims and scope of the study ................................................................................................. 3
   1.3 Thesis in outline .................................................................................................................... 3

2. PEAT AND METAL RETENTION PROCESSES ............................................................... 5
   2.1 Peat formation and composition .......................................................................................... 5
   2.2 Metal transport processes ...................................................................................................... 10
   2.3 Metal retention processes ..................................................................................................... 12

3. OOSTRIKIU PEAT BOG CHARACTERISATION ............................................................ 16
   3.1 Location and description ....................................................................................................... 16
   3.2 Metal depth distribution in the peat .................................................................................... 19
   3.3 Metal distribution among geochemical phases in the peat ................................................ 23
   3.4 Spring and peat pore-water composition .......................................................................... 33
   3.5 Conclusions ......................................................................................................................... 35

4. OXIDATION OF SULPHIDE MINERALS IN THE SURROUNDING BEDROCK AS A POSSIBLE LONG-TERM SOURCE OF HEAVY METALS IN A PEAT BOG .......................................................................................................................... 37
   4.1. Conceptual model .............................................................................................................. 37
   4.2 Sequence of mineral-aqueous phase reactions in carbonate rock over time ....... 39
   4.3 Effluent evolution along a flowpath in the carbonate rock ............................................... 42
   4.4 Conclusions ......................................................................................................................... 48

5. RETENTION OF METALS IN A PEAT BOG ................................................................. 50
   5.1 Conceptual model ............................................................................................................... 50
5.2 Formation of ferric oxyhydroxide in the peat bog and other possible metal precipitation
5.3 Approach to modelling metal sorption in peat
5.4 Model performance of metal sorption in peat and the relative importance of different sorbents
5.5 Importance of metal-metal competition effect on Pb and Cu sorption in peat over time
5.6 Conclusions

6. DISCUSSIONS AND OVERALL CONCLUSIONS
REFERENCES
ACKNOWLEDGEMENTS
1. Introduction

1.1 Background

This study was initiated by the need to assess the long-term metal retention in municipal solid waste (MSW) deposits. The times of interest can range over hundreds to thousands of years. Processes over such long times cannot readily be studied by conventional laboratory methods. Natural analogues were therefore sought for, i.e. processes occurring over long periods of time and where similar metal binding processes can be expected.

Landfilling is the most frequently used method of disposing of municipal solid waste (MSW) and it remains the main means of MSW management in the world (Williams, 2005). MSW deposits contain a complex mixture of both organic and inorganic matter, and they have a high water contamination potential in terms of heavy metals (e.g. Bozkurt et al., 2000). The potential effects of organic matter on the mobility of heavy metals in landfills are significant. One important aspect of this is that organic matter may sorb and thereby attenuate metals that can later be released during the degradation of the organic matter. Very little of the original heavy metal content of a landfill is leached within the first decades after disposal, as most of the metals are sparingly insoluble in the anaerobic phase of degradation of organic matter and are thus retained in the solid phase (Bozkurt et al., 2000).

In the long term, after tens to several hundreds years, when the humic phase is reached in the landfill and the readily degradable organic matter has been transformed to compounds that are more stable to degradation such as humic substances, oxygen supplied to the landfill by diffusion or infiltrated with water may generate aerobic conditions as the degradation reactions become too slow to consume all the oxygen. The duration of this humic phase is expected to be very long, probably many thousands of years. During this time, the remaining heavy metals will either leach out of or be immobilised within the landfill through the precipitation of new mineral phases (such as ferric oxyhydroxide) or sorption on ferric oxyhydroxide and solid organic matter.
An understanding of the behaviour of heavy metals in landfills thus requires knowledge of the sorption and precipitation reactions in these environments. However, the long-term processes in landfills are poorly known due to the relatively short time during which such landfills have existed and this makes it difficult to assess the associated environmental risks. Such assessments are usually carried out with models that are based on observations from old landfills or similar environments, which can contribute valuable information with respect to the long-term behaviour.

In this context, peat-ecosystems have been suggested as valuable natural analogues to MSW landfills (Bozkurt et al., 2001). The analogy is based mainly on the similarity of processes involving organic matter, as peat is an organic deposit that is formed in-situ with the exclusion of atmospheric oxygen by water and where more organic matter is produced by vegetation than is being decomposed (Sjörs, 1980). Peatlands have formed over periods of hundreds and thousands of years (Grumpelt et al., 1991; Clymo, 1991) and the long-term processes can, thus, now be observed there.

The oxidation of sulphides by dissolved atmospheric oxygen in the groundwater leads to the dissolution of iron and heavy metals. These metals are transported with the groundwater and can accumulate at places of sharply changing physical-chemical conditions called geochemical barriers. Such geochemical barriers can also form in the peat ecosystems. The Oostriku peat bog located in central Estonia has accumulated high concentrations of Fe and heavy metals (Pb, Cu, Zn, Mn, As, etc) over a long time period. In addition to the rainwater supply, water that has percolated through the surrounding rock occurs as springs and upwellings over the peat area.

Studying such peat ecosystems which have been exposed to the discharge of metal-rich groundwater over a long period of time makes it possible to gain an insight into the long-term transport and attenuation processes involved in the retention of heavy metals. The information obtained can be used to develop a reactive transport model, which can hopefully provide a better understanding of how different metals are attenuated by different competitive processes over a long period of time.

Findings could be also useful for other purposes such as the attenuation of contaminant transport for the treatment of municipal and industrial wastes, or for the melioration of metal-containing mire effluents. Natural or constructed wetlands have recently received attention as passive treatment systems (Reed et al., 1988; Kwong et al., 1994; Mungur et
al., 1997; August et al., 2002) which use natural biogeochemical processes to remove contaminants from wastewaters. Several studies have established the potential of peat to capture dissolved metals (Hg, Cd, Zn, Fe, Pb, and Cu), nutrients, suspended solids, organic matter, oils, and odours from domestic and industrial effluents (MsLellan et al., 1987; Brown et al., 2000; Ringqvist et al., 2001).

The findings may also be of importance for catching radionuclides that could escape from deep geologic repositories (Bergström et al., 1999) in the event of failures in multiple barriers which are designed to protect the environment over hundreds and thousands of years. An effective geochemical enrichment factor for naturally occurring uranium could be as high as $5 \times 10^4$ in relation to peat (Owen et al., 1995).

1.2 Aims and scope of the study

The overall aim of the thesis is to describe the long-term transport and attenuation processes involved in the retention of heavy metals in a peat bog that has been exposed to groundwater discharge over a long period of time.

In order to achieve this aim, the peat site is characterized with respect to metal depth distribution and dominant binding mechanisms. The peat pore-water and the water emerging in a spring at the peat site have been analysed, and the water compositions are compared. The observed water composition is compared to what could be expected in waters that have flown through the surrounding bedrock over a long time. The oxidation of sulphide minerals in the bedrock is modelled as a possible long-term source of heavy metals in water entering the peat bog. The accumulation of metals by sorption and precipitation in the peat bog is modelled and compared to that found experimentally.

1.3 Thesis in outline

Chapter two gives an introduction to peat ecosystems, some indication of the different kinds of peat ecosystems, and describes transport and metal interaction processes. Chapter three presents the Oostriku peat bog site and describes experimentally determined field observations e.g. metal depth distribution and the main binding
mechanisms of metals in the peat, and the spring-water and peat pore-water compositions. This chapter also presents the methodology used for the chemical analysis of heavy metals in the peat by sequential extraction. The main outcomes of the field observations conclude chapter three.

Thereafter, the modelling of metal-rich groundwater composition is described in chapter four where the experimentally determined water composition is used to evaluate the model performance and it is compared with the predicted water composition. Modelling retention of heavy metals in the peat is described in the chapter five. Equilibrium sorption of metals on ferric oxyhydroxide and solid organic matter (humic substances) is modelled by a simplified quantitative model and by using independently obtained data. Modelled and experimentally obtained amounts of sorbed metals are compared. The dynamic evolution of metal sorption fronts along a peat profile over time is assessed in the model to test metal-metal competition effects on metal (e.g. Pb and Cu) sorption. Furthermore, the formation of ferric oxyhydroxide and the possible precipitation of other metals (e.g. Mn, Pb, and Cu) in the peat is assessed in the model by dynamic simulations. Finally, chapter six concludes the thesis work.
2. Peat and metal retention processes

2.1 Peat formation and composition

_Peat-ecosystems_

Peat is an organic deposit that has been formed during the last 10 000 to 12 000 years in-situ in waterlogged ecosystems where more organic matter is produced by the local vegetation growth than is being decomposed. In such ecosystems, sufficient surface or groundwater and/or ample precipitation are available, and water loss by evaporation or run-off is less than the water supply. The ecosystems are recognised as peat-forming systems where at least 30 cm of peat has accumulated. Natural potentially peat-forming ecosystems are called mires (active peatlands). Areas actually covered by peat, whether natural, drained or even drastically transformed by forestry, agriculture or peat cuttings are recognised as peatlands (Sjörs, 1980). Depending on environmental factors such as climate, local geology and hydrology, different types of peatlands are recognised (Grumpeltet and Deimann, 1991).

Three principal mechanisms of waterlogging are known (Clymo, 1991). First, water may percolate through rock or soil and emerge as springs or simply as upwellings over a large area. Water of this kind has a relatively high concentration of solutes, supporting luxuriant vegetation. By a second mechanism, water can be replenished from a catchment, for example near a small lake, and the surface of the vegetation mat falls and rises following droughts and rains. The third mechanism of waterlogging is a dynamically maintained, domed water table for which precipitation is the source of water.

Ombrotrophic peatlands or bogs have a water regime based on atmospheric precipitation and they are poor in most mineral nutrients. Peat bogs are convex (domed) in form, several meters above the mineral soil surface. Peat mosses (Sphagnums) are the main peat bog formers. Mineratrophic peatlands or fens are formed in contact with water that has earlier percolated through mineral soil and is rich in plant nutrients. Mineratrophic or fen peat is very heterogeneous. Reed, Carex and wood-rich peats are the main peat-formers. Peatlands where the ecological conditions of bogs and fens overlap are recognised as the transition type, moors.
**Peat formation**

The accumulation of peat involves an interaction between plant productivity, hydrology, and the processes of decay. Peat decay takes place mainly by aerobic and anaerobic microbial metabolism. If the readily degradable part of the peat is represented by the simple formula, CH₂O, the aerobic and anaerobic decay can be written respectively as follows:

\[
\begin{align*}
\text{CH}_2\text{O} + \text{O}_2 & \iff \text{CO}_2 + \text{H}_2\text{O} \quad \text{(R1)} \\
2 \text{CH}_2\text{O} & \iff \text{CH}_4 + \text{CO}_2 \quad \text{(R2)}
\end{align*}
\]

The most important agents of decay present in the peat are fungi and bacteria. Bacteria and other microorganisms mediate the oxidation reaction, and obtain energy for their metabolic needs from unstable products of decomposition. It is primarily the low-molecular dissolved organic compounds that can degrade completely to form carbon dioxide and water or methane. The remaining material is transformed to more stable compounds e.g. lignin or humic substances.

Peat formation processes can be described by looking at a peatland configuration (Figure 1) where four structural layers have been recognised (Clymo, 1991). “Acrotelm” is a term used for the largely oxygenated surface layer with high hydraulic conductivity and within which the water table fluctuates. The term “catotelm” is used for the underlying, saturated and mainly anoxic layer with low hydraulic conductivity. There are two layers within the acrotelm, the euphotic layer, and the aerobic layer, and within the catotelm, the collapse layer and the lower peat layer.
The euphotic layer (2-5 cm thickness) within the acrotelm is characterised by the growth of plants and photosynthesis. This layer is characterised by a low dry bulk density (10-20 g/dm$^3$) and a high void fraction (about 90% of the volume). The aerobic layer (10-50 cm thickness) is forming at the base of the euphotic layer where most of the plant material is dead and aerobic decay is the major process. Fungi, bacteria, invertebrate grazers, oxygen, and moisture allow aerobic decay. Most of the primary production of plant material is aerobically decomposed and only a minor fraction, less than 20%-wt, is accumulated as peat (Sjörs, 1980). The peat in the aerobic layer is still very porous and has a high hydraulic conductivity. The material that was once at the surface has been slowly covered by the continued growth of plants.

While more plant material grows and accumulates above the dead plants, the main structural elements lose their integrity and collapse under the weight of the overlying material forming the collapse layer (2-15 cm thickness). The dry bulk density increases (to about 100 g/dm$^3$), reducing both the void fraction and the hydraulic conductivity. The water level may be raised by capillary action to a maximum distance of 50 cm. Then, at the water table there is still some oxygen, and decay continues aerobically to a small distance below the water table.

The main source of oxygen is diffusion from the atmosphere, and the rate of diffusion of oxygen in water is approximately 10 000 times lower than in air (Sjörs, 1980). Continuing aerobic decay leads to the formation of anoxic conditions. The redox potential

Figure 1. Structural layers of a peatland (from Bozkurt et al., 2001).
decreases and anaerobic decay becomes the major process. Under reducing conditions, sulphides may be produced as a result of the oxidation of organic matter by sulphates. The peat in the anaerobic decay layer (> 100 cm thickness) is characterised by a high dry bulk density (≥100 g/dm³), low hydraulic conductivity and permanent water saturation. The anaerobic decay is much slower than the aerobic, and incomplete decomposition of organic matter leads to the accumulation of peat. Peat becomes amorphous and highly humified.

The functional layers do not coincide with the structural layers in peat, because of the seasonal water table fluctuation within the acrotelm. The water table responds rapidly to rainfall (Clymo, 1991). When the water table is low, during draught periods, the oxygen-rich layer of aerobic decay is shifted and includes also the collapse layer, and part of the anoxic layer.

**Chemical composition of peat**

The chemistry of peat is dependent on the chemical composition of mire plants and microorganisms, the soil water quality, and the secondary substances produced during decomposition processes (Bozkurt et al., 2001). The water content of fresh peat increases with increasing degree of decomposition and can be as high as 96 wt-% (Grumpelt and Deilmann, 1991). The solid fraction of the peat (Carex type) can be in the range of 7.5-15 wt-%. Organic matter comprises 86-99 wt-% under moderately decomposed peat conditions and the inorganic matter content varies between 1 and 15wt-% of the total dry weight (Bozkurt et al., 2001).

The main fraction of peat organic matter (dry weight) 36-59wt-% is lignin. The lignin concentration increases with increasing degree of decomposition. In excessively wet sediments, fungi that degrade lignin are not usually found. Lignin is incompletely utilised by microorganisms and increasing decomposition can lead to a conversion of lignin to humic substances (Stevenson, 1994). Modified lignins can be a major contribution to the humus of peat. The average content of humic substances determined in peats (Flaig, 1992; Hännien, 1992) can reach 30-40 %-wt. In normal aerobic soils, lignin can be broken down into low-molecular weight products prior to humus synthesis.
Carbohydrates comprise 10-31 wt-% of the total dry peat organic mass and their content decreases with increasing decomposition. Most of the sugars show the same trend with decomposition except for mannose, the concentration of which increases in the first thousand years. Uronic acids are in the range of 5-13 wt-%. The average content of peat “wax” (a mixture of true waxes, asphalt and resins) is about 5 wt-% and its proportion increases with increasing degree of decomposition.

The inorganic material of peat is almost non-volatile and leaves ash upon combustion (Bozkurt et al., 2001). Mineratrophic peatlands generally contain higher amounts (5.9-22.2 wt-%) of ash than ombrotrophic. The main elements are Si, Ca, Fe and Al and the others are Mg, K, P, Na, S, V, Ni, Pb, Mn and Cu derived mostly from groundwater and accumulated in the peat layers. About 20-50 wt-% of the ash content is metals. Secondary minerals, such as oxides of Al, Fe, and Mn, and sulphides, and other salts, make up the residual part of the inorganic material of peat. Decomposition of organic matter without the removal of an element can lead to a gradual increase in concentration with time. In such cases, the content of the element increases within a peat profile.

**Humic substances**

Humic substances are defined as a series of relatively high molecular weight, yellow to black coloured substances formed by secondary synthesis reactions by organic matter degradation involving microorganisms (Stevenson, 1994). Based on their solubility in alkali and acid, humic substances are divided into three main fractions: humic acids, fulvic acids, and humin. These substances cannot be regarded as distinctly different but rather as a continuum of compounds varying in molecular weight, carbon content, oxygen content, acidity and cation exchange capacity in the order: humin > humic acids > fulvic acids (Alloway, 1995).

Since humic substances are major constituents of peat organic matter, the behaviour of humic substances is significant in determining the peat characteristics (Takacs and Alberts, 1999). Humic substances have a strong ability to form metal complexes. They have a variety of functional groups, including carboxyl, phenolic hydroxyl, amino, carbonyl, ester and possibly quinone and methoxy groups. The oxygen-containing functional groups in humic substances are the most important for binding metals.
major metal binding sites are considered to be the carboxylic and phenolic group contents. These two groups contribute to the acidic nature of humic substances, with carboxylic being the more important.

The contents of the reactive groups change with the molecular weight of the humic substances (Stevenson, 1994). The molecular weight of humic substances varies from as low as a few hundred Da (g/mol) for fulvic acids to as high as several hundred thousand Da for humic acids (Stevenson, 1994). The molecular weight values of the humic substances studied by Peminova et al. (1997) were distributed as follows: aquatic fulvic acids < soil fulvic acids < sediment humic acids < soil humic acids < peat humic acids.

2.2 Metal transport processes

There are several mechanisms that may be responsible for metal transport in peat pore-water. In a stagnant peat, pore-water molecular diffusion may control the metal transport. The migration of metal species by molecular diffusion occurs as a result of a concentration gradient in accordance with Fick’s laws of diffusion. Dissolved metal species move from regions of high concentration to region of low concentration as a result of random molecular motion. Fick’s first law is used primarily for calculations involving steady-state systems in which the concentrations at any particular location do not change with time:

\[ J = -D \frac{dC}{dx} \]  

(Eq.1)

Fick’s second law applies to non-steady-state systems when the concentration changes with time:

\[ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} (D \frac{\partial C}{\partial x}) \]  

(Eq.2)

where \( J \) is the flux of material, i.e. is the mass of material moving across unit area in unit time (mol/m\(^2\)/s), \( C \) is the concentration in mass per unit volume (mol/m\(^3\)), \( D \) is the diffusion coefficient (m\(^2\)/s), and \( x \) is linear distance (m), \( t \) is time (s). The diffusion
coefficients of most species in aqueous solution are approximately $10^{-10}$ to $10^{-9}$ m$^2$/s (Drever, 1988). The rate of diffusion in peat pore-water is lower than it would be in pure water because the porosity of peat-soil is less than unity (e.i. part of the cross-sectional area is solid grains) and because of tortuosity effects. The minus sign in Ficks’ first law indicates that the flux is in the direction opposite to the concentration gradient.

At the water table, capillary action can to some extent promote metal transport. Due to capillary effects, water may rise to some distance above the water table carrying dissolved metals causing a capillary fringe. The rate at which the water rises by capillarity is relevant to evaporation.

Groundwater can also actively move through deep, decomposed peat (Hill and Siegel, 1991). In peat systems exposed to groundwater discharge, advection is the main mechanism controlling metal transport in pore water. The physical movement of the water in which dissolved metals are transported at the velocity of the water current is called advection. The advective flux rate is a product of the volumetric flow rate and the mean concentration. Under steady flow ($\partial Q/\partial t = 0$) and steady state ($\partial C/\partial t = 0$) conditions, the advective mass transport is constant with time:

$$J = uC = 1/A \cdot QC$$  (Eq.3)

If the flow rate or the concentration varies with time, then the advective mass transport also varies with time:

$$\partial C/\partial t = -1/A \cdot \partial (QC)/\partial x = u \cdot (-\partial C/\partial x)$$  (Eq.4)

where J is the flux of material, which is the mass of material per unit area unit time (mol/m$^2$/s), C is the concentration in mass per volume (mol/m$^3$), u is the mean flow velocity (m/s), Q is the volumetric flow rate (m$^3$/s), and A is the cross-sectional area (m$^2$). The following term $u \cdot (-\partial C/\partial x)$ is valid under steady state flow conditions, such that the mean velocity, $u = Q/A$, is constant.
2.3 Metal retention processes

Metals transported with water through the peat can be retarded as inorganic or organic complexes or compounds deposited onto solid matter with respect to the water velocity as a result of chemical, physical or biological processes. Adsorption and precipitation are the main processes responsible for the transfer of metals from the aqueous to the solid phase. These processes control the concentrations of metal ions and complexes in the peat pore solution. Retention of metals is affected by the properties of the peat and its environment e.g. conductivity, redox conditions, pH, and humus content.

Redox reactions

Peat is exposed to variations in oxidation-reduction (redox) conditions and this mainly affects elements as C, N, O, S, Fe and Mn, although As, Cu, Pb can also be affected (Alloway, 1995). Redox reactions are frequently slow, but they are catalysed by microorganisms, which are present over the range of pH and pE conditions (pH 3-10 and pE +12.7 to –6.0). Large positive values of pE favour the existence of oxidised species, and low or negative values of pE are associated with reduced species. Oxic soil conditions usually give values in the range mostly from pE 6.8 to 10.1. Anaerobic soils have values from pE +2 to –7. Frequently, the soil colours provide a good indication of the redox status. Red and brown colours indicate oxic conditions, blue-green and grey colours indicate anoxic soils.

Respiration by microorganisms, mesofauna and plant roots consume a relatively large amount of oxygen. If oxygen in a zone of peat becomes exhausted, as happens with waterlogging or compaction, microorganisms with anaerobic respiration predominate and elements (e.g. Mn and Fe) are reduced. Reduction of manganese oxides occurs at the same pE levels as nitrate reduction prior to the reduction of iron oxides to ferrous iron. When sufficiently negative pE levels have been reached (from –2.0 to –3.0), sulphate ions are reduced to sulphide and this can lead to precipitation of metal sulphides e.g. FeS₂, CuS, MnS, and ZnS. The reduction of carbon dioxide occurs almost simultaneously with the reduction of sulphates (Stumm and Morgan, 1996). With increasing pE and pH, oxidation of ferrous iron and precipitation of iron and manganese oxides occur.
**Iron and manganese oxides**

In freely drained oxic conditions, oxides of iron and manganese can precipitate from solution and occur as coatings on peat-soil particles, filling in voids, and concentric nodules. Iron is usually precipitated in the form of gelatinous ferric oxyhydroxide (5Fe$_2$O$_3$•9H$_2$O) initially and this gradually dehydrates to more stable forms, such as goethite (FeOOH). Hydrous iron oxide minerals tend to be the most abundant of all the oxides in soils. The common mineral forms of manganese oxides in soils are birnesite (MnO$_2$) and hollandite. Iron and manganese oxides play an important role in the chemical behaviour of metals. They can co-precipitate and adsorb cations including Co, Cr, Cu, Mn, Mo, Ni, V, and Zn from solution. In addition to being adsorbed on mineral surfaces, heavy metal ions can diffuse into oxide minerals and become adsorbed and fixed at positions within the mineral particles (Alloway, 1995).

**Co-precipitation**

Co-precipitation is defined as the simultaneous precipitation of a chemical agent in conjunction with other elements by any mechanism and at any rate (Alloway, 1995). The types of mixed solid commonly formed include clay minerals, iron and manganese oxides, and calcite in which isomorphous substitution has occurred.

**Cation exchange**

Most heavy metals exist mainly as cations in the soil solution, and their adsorption therefore depends on the density of negative charges on the solid surfaces. Negative charges on solid surfaces can be of two types: permanent charges independent of pH due to isomorphous substitution and pH-dependent charges on the edges of clay minerals, on humus substances and oxides. In order to maintain electroneutrality, the surface negative charge is balanced by an equal quantity of cations. Ion exchange occurs between the counter-ions balancing the surface charge on the solid surfaces and the ions in the solution. Ion exchange is reversible and stoichiometric, and there is in most cases selectivity or preference for one ion over another by the adsorbent.
Surface complexation

The adsorption reactions may be alternatively considered as complexation reactions with functional groups on the solid surfaces creating surface metals species analogous to the main aqueous species in pore solution (Alloway, 1995). Surface functional groups, including hydroxyl groups on the edges of hydrous oxides and carboxyl and phenolic groups on the surfaces of organic matter, react with metal species to form surface complexes. These surface complexes can be of two types: inner-sphere complexes and outer-sphere complexes. Inner sphere complexes result in the formation of a co-ordination bond between a surface ligand and a metal, and are also recognised as specific adsorption. The transition metal elements (Cu$^{2+}$, Zn$^{2+}$, Mn$^{2+}$, Fe$^{3+}$, and others) tend to favour this type of interaction and the bond is stronger. Metals that are most able to form hydroxy complexes are specifically sorbed to the greatest extent.

Essentially, a coordinate complex arises because the outer electron shell of the metal ion is not completely filled and can accept additional pairs of electrons from atoms that have a pair of electrons available for sharing. When only one electron pair is shared with a metal ion and a single coordinate bond is formed, this type of complex is called monodentate. Most metal ions can accept more than one pair of electrons and can form multidentate complexes where two or more coordinate positions of the metal ion are occupied by donor groups of a single surface ligand. If two bonds are formed, the complex is called bidentate. The formation of more than one bond between the metal and the organic molecule usually gives high stability to the complex. The stability sequence for some selected cations is in the order: Cu$^{2+}$ > Ni$^{2+}$ > Co$^{2+}$ > Zn$^{2+}$ > Fe$^{2+}$ > Mn$^{2+}$ (Stevenson, 1994).

An outer sphere complex has a purely electrostatic nature, and both the ligand and the metal retain their hydration spheres. The alkali and alkaline earth metals (Na$^+$, K$^+$, H$^+$, Ca$^{2+}$, and Mg$^{2+}$) tend to favour this ionic type of interaction in which the metal is held in an exchangeable form. The surface charge is a result of the ionisation of all the surface sites, mostly by proton exchange reactions.

Metal sorption occurs first at those sites that form the strongest complexes, e.g. coordinate linkages and ring structures on humic substances, and sorption at the weaker sites becomes increasingly important as the stronger sites become saturated. The pH range at which the maximum sorption of metals occurs depends on the acid-base
constants for the surface sites and on the strength of the surface complexation reaction described by a specific stability equilibrium constant (Schnoor, 1996).

Peat acidity

Acidity is an important chemical characteristic of peat. Internal processes that generate or consume the acidity within a peat system are the production of organic acids from the decomposition of vegetation, ion exchange attributed to the cation or anion uptake, change in redox conditions, mineral acidity (e.g. HNO$_3$, H$_2$SO$_4$), activity of sulphur-metabolising bacteria, and input of alkalinity (Urban et al., 1986). In general, the pH of peat pore water is in the range of 4.0 to 8.5, where the highest limit can be related to calcite equilibrium (Bozkurt et al., 2001).
3. Oostriku peat bog characterisation

3.1 Location and description

The Oostriku peat bog belongs to a protected mire complex, the Endla Nature Reserve, located in central Estonia (Figure 2), which covers ca. 8100 ha of the medium and best preserved mires.

![Map of Estonia](image)

*Figure 2 Protected mires in Estonia – Endla Nature Reserve location, marked as Endla-Oostriku (from Masing, 1997).*

The reserve is located in the transition climatic zone from the sub-maritime to the sub-continental part (Illomets, 1995). The mean temperature in February ranges from −3.5 to −7.0 °C and in July it ranges from 16.3 to 17.3 °C. The annual precipitation varies from 509 to 746 mm with a mean of 628 mm. The most abundant rains are from April to October, about 330-480 mm annually. The mean air humidity is high, and it varies from 82% in the western part to 70-72% in the continental part of Estonia.
Allikvee et al. (1988) have divided the Estonian mires into different districts and sub-districts according to the paludification intensity of the landscape, mire size and etc. The Endla Nature Reserve is a part of the district of large mosaic mires in the North Estonian Uplands, which consists of the central and marginal parts of the Pandivere upland, and the Vooremaa (drumlin land) area. In the central part, in the Pandivere uplands, mires are very rare, but the marginal part is highly poludified. The Nature Reserve belongs to the marginal part of the Pandivere upland (Figure 3).

The Pandivere Upland is a significant form in northern Estonia. The sedimentary cover of the upland consists mainly of Ordovician and Silurian carbonate rocks - limestone, marls and dolomites. The zones of tectonic dislocations, the frequent occurrences of fractures, and the limestone bedrock poor in clay have favoured the karst formation in this region. On the slope of the upland, due to Ca-rich water flowing out from the uplands, different fen types are rather common, which, when expanding, form ombrotrophic bog areas (Illomets, 1995).

![Figure 3: Endla mire complex location at a slope of the Pandivere Upland, central Estonia.](image)

The Oostriku peat bog is a part of a mineratrophic peatland, which in addition to rainwater receives groundwater. There are a number of springs in the western part of the Endla Reserve that vary in depth, regime and water quality, being fed by the karsts water from the upland. These springs form the Norra-Oostriku-Võllingi solution spring area,
about 30 km² in size, feeding a number of small streams. The Oostriku peat bog belongs to this area and it is located 0,5-km northern-east from the Punaraba bog massif (Figure 4). This area is influenced by forest drainage. There are ditches of forest drainage in the west and south of the Punaraba bog.

There is a spring called Värvallikas (coloured) located in the Oostriku peat bog area. The spring is 3-4 m in cross-sectional area and 0.9 m in depth with a groundwater discharge of 0.03 m³ per second. This Värvallikas spring is unique compared with the other springs in the Nature Reserve as well as in Estonia as it contains polymetallic elements in remarkably high concentrations for natural waters: Pb, Zn and Mo up to 300 µg/l, Cu 100 µg/l, and As 0.5 µg/l (Heinsalu et al., 1978).

Figure 4 The Oostriku peat site location in the Endla Nature Reserve marked as management zone around the Värvallikas spring (scale 1:50000 m).
Peat in the spring surroundings and mud at the bottom of the ditches is greatly enriched with various metals. Field studies at the Oostriku peat bog have been performed to analyse and compare the water emerging in the spring at the peat site and peat pore-water, and to characterise the peat site with respect to metal depth distribution and metal binding mechanisms (Papers I and III). The data obtained have been further used to perform modelling of metal long-term retention in a peat bog (Papers II and IV).

3.2 Metal depth distribution in the peat

To describe the metal distribution in Oostriku peat profiles, a field survey\(^1\) was carried out in the summer of 1999. Altogether, 38 peat samples were collected (sampling points 1-11; Figure 5) and analysed using different methods (Paper I). 29 samples of the peat were analysed for crystalline phases using X-ray diffractometry (DRON-3M, Fe-anode). Two peat samples (sampling point 3; Figure 3.4) were dated using radiocarbon dating (C-14). All the samples were analysed for Fe, As and a range of heavy metals (Cd, Cu, Mn, Ni, Pb and Zn).

Metal accumulation in the Oostriku peat bog was found to be localised to an area of about 10x10 m\(^2\) surrounding the spring at the peat site (Figure 5). Two zones of heavy metal accumulation were distinguished in the peat bog: Zone one closest to the spring at the peat site, characterized by a distance up to 15 m and described by Sampling points 1 and 3, and Zone two at a distance of 15-30 m from the spring, described by Sampling points 2, 4, and 5.

In Zone one, the uppermost peat layer contained poorly degraded peat and plant roots, and plant matter to a depth of 0-0.20 m from the surface. This layer was followed by a reddish-brown ochre layer (ferric oxyhydroxide accumulation) visible at a depth of 0.20-0.40 m. The lowest peat layer, without roots or ochre, occurred at a depth of 0.50-1.10 m and was underlain by limestone bedrock. The colour of the peat changed downwards from dark-brown to black. The partly water-saturated conditions in the peat changed to waterlogged conditions at a depth of 0.70-0.80 m, corresponding to the water table at the spring located in the peat bog area.

\(^1\) Field survey was carried out by Dr. E. Puura, Institute of Geology, Tartu University, Estonia.
X-ray diffraction analyses (1% detection limit) showed poorly crystalline goethite at depths of 0.10-0.50 m and traces of pyrite and gypsum at depths of 1.00-1.05 m. The peat age was $3,660 \pm 110$ years at a depth of 0.3 m, and $7,610 \pm 50$ years at a depth of 0.80 m (C-14 dating). Thus, the peat has been formed at a rate of about 0.10 mm per year.

Further from the spring in Zone two, the peat profile was found to be similar to the profile in Zone one, except that the ochre layer in Zone two was not as clearly evident as in Zone one.

Figure 5. Map of the Oostriku peat bog. Numbers and dotted lines mark the sampling points and zones, respectively. OV in the figure stands for forest at the peat site. Sampling points from 1 to 11 refer to metal peat depth distribution analysis (sampling in 1999), sampling points marked X refer to metal geochemical phases distribution analysis in the peat (sampling in 2001), and filled squares refer to the peat pore-water analysis (sampling in 2003). The insert shows the location of the field site within Estonia marked as Endla-Oostriku.
From an environmental point of view, the results of the chemical analysis of the heavy metals in the peat samples showed high amounts of As and especially Pb that exceeded by 20 and 50 times respectively the maximum permissible soil concentration values set by the Estonian National Legislation. At the same time, the amounts of these metals as well as Cu, Mn, and Zn varied by one to three orders of magnitude depending on the sampling depth (Paper I).

The metals were found to be distributed differently with depth in the peat, making it possible to divide them into three groups. Iron, As, and Mn (group one) showed their highest concentrations in the ochre layer of Zone one, where the concentration of Fe was up to 43% (Figure 6a). The profiles of As and Mn were found to be very similar to that of Fe. This tendency was also followed in Zone two (Figure 6b), but the concentrations were highest in the uppermost layer.

Lead and Cu (group two) showed the highest concentrations in the uppermost peat layer of Zone one, with Pb maximum values at 31 000 ppm and Cu at 340 ppm (Figure 6c). The concentrations of Pb varied by almost two orders of magnitude. In Zone two, the profiles of Pb and Cu were also similar (Figure 6d), but the lowest concentrations occurred in the ochre layer, and were similar in the uppermost and lowermost layers.

Cadmium, Ni and Zn (group three) showed insignificant differences in concentrations between the zones, except that there were somewhat higher Zn concentrations in the ochre layer of Zone 2 (Figure 6e,f).
Figure 6 Depth profiles of metals concentrations (dry weight) in the peat a) Fe, As, and Mn, Zone one; b) Fe, As, and Mn, Zone two; c) Cu and Pb, Zone one; d) Cu and Pb, Zone two; e) Ca, Ni, and Zn, Zone one; f) Cd, Ni, and Zn, Zone two.
3.3 Metal distribution among geochemical phases in the peat

In order to evaluate the main binding processes by which metals are retained in the peat, it is useful to know how the metals are distributed among the geochemical phases (binding agents) present. Sequential extraction of heavy metals from soils and sediments is a useful technique for determining the chemical forms of metals in soils (Miller et al., 1986).

Peat and ochre samples for the sequential leaching experiments (Paper III) were collected during the summer of 2001 in the vicinity of Sampling points 1 and 3 within Zone one (Figure 5, the sampling point is marked by x) where the highest accumulation of metals had been found. Metal concentration profiles in Zone two were found to be similar to the metal concentration profiles in Zone one, but the concentrations were generally lower than those observed in Zone one. Zone two was not therefore further assessed.

**Sequential extraction of metals from the peat**

The most widely used sequential extraction procedure is that proposed by Tessier et al. (1979), which has been applied to contaminated soils (Lo et al., 1998; Hall et al., 1999; Stalikas et al., 1999; Maiz et al., 2000; Balasoiu et al., 2001; Li et al., 2001) and has also been used for peat (Jones, 1987; Twardowska et al., 1999; Burba et al., 2001; Twardowska et al., 2003). In this procedure, appropriate chemical reagents are used to extract different metal forms selectively. The Tessier procedure is designed to differentiate between metals bound in exchangeable, carbonate, reducible (hydrinous Fe/Mn oxides) and oxidisable (sulphides and organic phases) forms and also residuals.

There is some uncertainty concerning the incomplete selectivity of reagents and the extent of post-extraction redistribution of leached metals among undissolved solid phases (Gomez-Ariza et al., 1999). Nevertheless, the results obtained from sequential extraction can be used at least qualitatively to understand the relative roles of binding agents and to evaluate the mechanisms involved (Yong et al., 1992; Lo et al., 1998).
The Oostriku peat has a high content of organic matter and a high content of iron, varying with depth from 15% to 40% by weight in the upper peat, and is highly contaminated with heavy metals (Fe, Pb, Zn, Mn, Cu, Ni, Cd) and As (Paper I). To avoid possible problems with the selectivity and re-adsorption, a version of the Tessier extraction scheme optimised for heavily polluted iron oxide-rich (>17%) sediments (Gomez-Ariza et al., 2000) was used to extract metals from the Oostriku peat. The extraction scheme used is given in Table 1. For the details of the sequential extraction procedure of heavy metals from the peat the reader is referred to Paper III.

*Table 1 Metal extraction scheme (0.5 g dry weight peat sample)*

<table>
<thead>
<tr>
<th>Step</th>
<th>Fraction name</th>
<th>Reagent, V (ml)</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>Water-soluble</td>
<td>Deionised water, 10 ml</td>
<td>20 °C, 2h-agitation</td>
</tr>
<tr>
<td>F2</td>
<td>Exchangeable/acid</td>
<td>1M NH₄OAc, 35 ml</td>
<td>pH 5, 20 °C, 5h-agitation</td>
</tr>
<tr>
<td>F3-1</td>
<td>Reducible</td>
<td>0.4M NH₂OH-HCl in 25% (v/v) HOAc, 20 ml</td>
<td>96 °C, 6h, Shaking every 30 min</td>
</tr>
<tr>
<td>F3-2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F4-1</td>
<td>Oxidiseable</td>
<td>0.02M HNO₃, 3 ml</td>
<td>pH 2, 85 °C, Shaking every 30 min</td>
</tr>
<tr>
<td>F4-2</td>
<td></td>
<td>30% H₂O₂, 5 ml</td>
<td>pH 2, 85 °C, 3h Shaking every 30 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Further, 30% H₂O₂, 3 ml</td>
<td>Cooling to room T °C, 30 min, 20 °C, Continuous agitation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.2M NH₄OAc in 20% HNO₃, 5 ml</td>
<td></td>
</tr>
<tr>
<td>F5</td>
<td>Residuals</td>
<td>7M HNO₃, 20 ml</td>
<td>30 min, 120 °C, 220 kPa Digestion in autoclave</td>
</tr>
</tbody>
</table>

1 All the reagents used in the extraction procedures were of analytical grade. Plastic containers and glassware was cleaned before use by soaking in 14% (v/v) HNO₃ for 24 hours and rinsing with distilled water.
**F1-Water-soluble fraction**

Metals extracted with water indicate water-soluble metals in the peat. These are accessible to plants for uptake by their roots.

**F2-Exchangeable/acid fraction**

Metals extracted with ammonium acetate adjusted to pH 5 occur in the ion exchangeable form or are specifically sorbed at the surface of a solid, e.g. ferric oxyhydroxide and/or organic matter, as well as metals bound to or in carbonates (if such are present), which are dissolved in the acid. Tessier et al. (1979) observed that the ammonium acetate leaches the specifically sorbed metals from the solid. Dissolution of iron oxide by the ammonium acetate was observed to be insignificant (Tessier et al., 1979; Gomez-Ariza et al., 2000), and to have no effect on the evaluation of the reducible fraction of metals.

Ammonium acetate at 1M-concentration was the preferred reagent, as the relatively high concentration and the metal-complexing power of the acetate prevented re-adsorption or precipitation of the released metal ions (Gomez-Ariza et al., 2000). Strong readsorption of Cu, As, and Pb, when using weak reactants such as 1M MgCl₂ and 1M NaOAc in the Tessier extraction scheme, has been reported for oxide-rich (> 13%) sediments (Gomez-Ariza et al., 1999).

**F3-Reducible fraction**

Metals expected in this fraction include those attached to amorphous oxides via precipitation or co-precipitation or incorporated by other means in oxides. Tessier et al. (1979) observed that the reducing reagent does not significantly leach solid organic matter. The labile organic fraction of metals is believed to have been removed already in the exchangeable/acid fraction prior to the reducing extraction in our study.

In our study, the concentration of the reagent used was ten times higher than the concentration used by Tessier et al. (1979). Only two repetitive extractions with fresh amounts of the reagent were used in our study to avoid attack of organic matter and due to time constraints. Such modifications were suggested by Gomez-Ariza et al. (2000) to improve the selectivity of the reagent in the treatment of oxide-rich sediments.
**F-4 Oxidisable fraction**

Metals released in this fraction are expected to include metals strongly bound to organic matter. Metals occurring as insoluble sulphides (if such are present) under reducing conditions would also be released in this fraction.

Hydrogen peroxide in an acidic medium, pH 2 (H_2O_2/HNO_3), is generally used to oxidise organic matter, but it is known to oxidise organic matter incompletely (Tessier et al., 1979). Instead of using a higher reagent volume to avoid saturation, repetitive extractions with fresh reagent were used by Gomez-Ariza et al. (2000) to improve the selectivity of the reagents. Two repetitive extractions with fresh amounts of the oxidising reagent were used in our study.

**F5-Residual fraction**

Metals released in the residual fraction include those incorporated in materials resistant to chemical degradation, such as refractory organic matter and undissolved amorphous oxides. Concentrated nitric acid (7M HNO_3) was used to dissolve residual material by digestion at 120 °C (220 kPa) in an autoclave.

**Total amounts**

Nitric acid digestion was used to obtain the total amounts in the sequential extraction of raw peat samples with a mass of 1 g (dry weight) with 7M HNO_3 in an autoclave at 120 °C (220 kPa). Nitric acid may not completely dissolve metals from aluminosilicate minerals (if such are present) and possibly not from poorly crystalline goethite, so that an underestimation of metals may be expected.

The focus of this study was not on contents of metals incorporated in “undissolvable” forms of silicates. Therefore, digestion in nitric acid, rather than lithium metaborate fusion was used to determine the residual fraction and totals, although this may have been insufficient to dissolve resistant silicates.
Comparison between total metal amounts extracted from the peat

The totals obtained (Paper I) from the samples collected at the sampling points 1 and 3 (Zone 1, Figure 5), the totals obtained by the digestion with concentrated nitric acid, and the totals summed from all five fractions of the sequential extraction (Paper III) are shown in Figure 7a-f to provide a comparison of the metal depth distribution in the peat between sampling occasions within the same zone of accumulation, but from different sampling points.

In general, the depth trends of the solid phase metal concentrations in the samples used for the sequential extraction were similar to those observed in sampling points 1 and 3. Consistent with previous results (Paper I), the ochre layer and the uppermost peat layer were found to be the main geochemical barriers accumulating the metals in the Oostriku peat. Similar absolute concentrations were observed for the individual elements from the different peat cores analysed (Figure 7).

One exception is at a depth of 0.21-0.42 m in the peat, where there was some difference in the Fe concentration between the profiles (Figure 7a). The lower Fe content from the nitric acid digestion (diamonds) compared with the previously obtained data (squares and circles) may indicate incomplete dissolution of Fe or it might be due to heterogeneity of the peat.

The lower Fe content from the sum of fractions (triangles) than from the nitric acid digestion (diamonds) is possibly associated with an underestimation of Fe in the sequential extraction procedure. This may indicate that the hydroxylamine hydrochloride acetic acid reagent, with two repetitive extractions and a concentration in the sequential extraction procedure ten times higher than that recommended by Tessier et al. (1979), was insufficient to completely dissolve the iron oxide at a content higher than 20 wt-% in the peat. For future analysis of the reducible fraction it would be valuable to test if an increased number of repetitive extractions would alter the results for Fe.

As mentioned previously, hydrogen peroxide in acidic medium (pH 2) is known to oxidise the organic matter incompletely (Tessier, 1979). In the sequential extraction procedure, two repetitive extractions with a fresh amount of the oxidising reagent were used to oxidise the organic matter in the peat to leach the bound metals. We have not tested whether organic matter is oxidised completely in these two repetitive extractions.
For future analysis of the oxidisable fraction it would be valuable to test if the increased number of repetitive extractions would alter the results.

The concentration of Zn at a depth of 0.80 m in sampling point 1 is out of the distribution range (Figure 7c), possibly due to the heterogeneity of the peat material. The concentrations of Ca at depths of 0.49-0.56 m and 0.70 m obtained with the nitric acid digestion are lower by a factor of two than the concentration obtained with the sequential extraction (Figure 7e), which is probably due to incomplete dissolution during the digestion.

In conclusion, the amount of Fe (Figure 7a) observed in the Oostriku peat was about 15-20 wt-% in the uppermost peat layer at a peat depth of 0.07-0.14 m, and increased to 30-40 wt-% in the ochre layer at a depth of 0.28-0.35 m. In the lower peat, at a depth of 0.49-0.70 m, it decreased to 5wt-%. Manganese and Zn (Figures 7b,c) showed their highest concentrations in the ochre layer (0.21-0.42 m), where the highest Fe concentration occurred. The concentration profiles of Mn and Zn were very similar to that of Fe.

Lead and Cu (Figures 7d,e), on the other hand, had their highest concentrations in the uppermost peat layer (0.07-0.14 m), above the ochre layer, and showed no tendency to increase with increasing Fe content in the peat. The amount of Pb was about 2.5-3%-wt in the uppermost peat, and decreased to very low values at depth. The maximum Cu concentration was two orders of magnitude lower than that of the Pb. In contrast to Pb, the Cu concentration increased with increasing depth below the ochre layer.

Figure 7f shows the Ca content as function of depth, as obtained with the nitric acid digestion. No analysis of Ca in the peat was made previously. The total Ca concentration in the peat varied between 1.5wt-% and 3wt-%.
Figure 7: Total metal concentration as a function of depth in the Oostriku peat. a) Fe; b) Zn; c) Mn; d) Pb; e) Cu; f) Ca. Triangles are the total sums of the sequential extraction steps and diamonds are the totals from nitric acid digestion. Circles and squares are the totals from Sampling point 1 and 3 (Figure 5) obtained experimentally in the field study during the summer 1999 (Paper I). The uppermost peat layer is 0 to 21 cm, the ochre layer is from 21 to 42 cm, and the lower peat layer is from 42 to 100 cm from the surface.
Applying the sequential extraction procedure for the leaching of metals from the peat, it was possible to differentiate between metals weakly associated with the peat and metals that are strongly bound to the peat. Weakly associated metals include metals bound in carbonates, exchangeable metals, and metals complexed at solid surfaces that are released in the exchangeable/acid fraction. The metals strongly bound in the peat include the metals incorporated into amorphous oxides and leached in the reducible fraction, the metals strongly bound to organic matter or in the form of metal sulphides (if such are present) and leached in the oxidisable fraction, the metals incorporated into crystalline mineral lattices, and the metals present in refractory unoxidised organic matter or undissolved amorphous iron oxide, and released in the residual fraction.

The metals addressed were Fe, Pb, Zn, Mn, Cu, and Ca. The use of the sequential extraction scheme by Tessier et al. (1979) for fractionating As has been criticised, as the leachability of As strongly depends on its oxidation state, and another method than the one employed here should be used for its speciation (Balasoiu et al., 2001). Thus, leaching data for As are not included in this study. Sequential extraction results for the metal distribution among the fractions are shown in Figure 8. In general, there was good agreement between duplicate determinations, and average values are used. For the total amounts of the metals see Figure 7.

Most of the Fe (80-90%) in the peat is present in the form of amorphous iron oxide (Figure 8a). The exchangeable/acid and organic fractions of Fe are negligible. Iron oxide is the dominating binding agent for Pb, Zn, and Mn (Figures 8b-d). The oxide fraction comprises 70% for Mn and 70%-90% for Pb. For Zn, the oxide fraction varies between 60% in the upper peat (uppermost peat and ochre layer) and 40% in the lower peat.

Minor fractions of Pb, Mn, and Zn in the peat occur as exchangeable/acid leachable, most probably associated with organic matter and iron oxide via surface complexation. For Pb and Mn in the peat, the exchangeable/acid fraction amounts to 10% to 30%. For Zn, the exchangeable/acid fraction is small in the upper peat, where it varies from 5% to 15%, but it becomes much larger, about 50%, in the lower peat, below the ochre layer (Figures 8b-d). The organic fractions of Pb, Mn, and Zn are negligible.
In contrast to the previously described metals, Cu, in addition to the oxide fraction, is found mainly in the organic fraction, while its exchangeable/acid fraction is negligible (Figure 8e). The oxide fraction comprises up to 50% of the Cu in the upper peat (uppermost peat and ochre layer), where the highest content of Fe occurs, below which it
decreases with increasing depth as the iron content decreases. The organic fraction of Cu increases from 15% to 60% with increasing depth below the ochre layer. Cu is thus the only metal found to be extensively bound to the organic matter in the peat in the presence of a high content of Fe (see also Figure 7e).

These results are consistent with observations of several other authors indicating that Cu forms very stable complexes with organic matter (Manunza et al., 1995; Logan et al., 1997; McKay et al., 1997; Lo et al., 1998, Lubal et al., 1998) and with the findings of Balasoiu et al., (2001), who observed that Cu is preferentially retained in organic matter. In samples with a high content of organic matter, Gomez-Ariza et al. (1999) observed re-adsorption of Cu from the previous reducing extraction step. Therefore, it is conceivable that in our experiments, Cu is redistributed to some extent during the extraction procedure, leading to an overestimation of the organic fraction of Cu and underestimating its oxide fraction.

Ca is mainly present (70-90%) in the exchangeable/acid fraction, with a contribution (about 20%) in the oxide fraction (Figure 8f). These results are interpreted as indicating that Ca is dominantly sorbed to the organic and oxide surfaces in the peat. Alternatively, the Ca may be present in the peat as carbonate. No crystalline carbonates were observed in the peat by X-ray diffraction (1% detection limit) in previous examinations (see Paper I). However, this cannot be expected at the low Ca contents and it does not exclude the presence of amorphous carbonate phases. If carbonates are present in the peat, metals associated with the carbonates (e.g. Pb, Zn) were released by application of the acid.

The residual fraction of Fe is considerable in the upper peat, which also has the highest content of Fe. This probably indicates incomplete dissolution of iron oxide by the reducing reagent. The residual fraction of Fe at a depth of 0.07-0.49 m comprises about 20%, but it is almost negligible at lower depths (Figure 8a). The residual fractions of Zn and Cu amount to 20%-40% in the upper peat, where Fe has its maximum concentration, probably due to metals associated with undissolved iron oxide (Figures 8c,e). Residual fractions of metals can also include metals associated with refractory organic matter. The residual fraction of Mn in the peat is 10%-15%, and it is evenly distributed with depth (Figure 8b). The residual fractions of Pb and Ca are negligible, indicating that these elements are absent in the refractory material (Figures 8d,f).
3.4 Spring and peat pore-water composition

The Oostriku peat bog is fed by waters percolating through surrounding carbonate bedrock and emerging as springs or upwellings over the peat site area. The water emerging in the Värvallikas spring at the peat site and the water from the river 3 km downstream with other springs feeding the stream were sampled during the summer of 1999 to determine the concentrations of heavy metals and perform pH measurements (Paper I).

It was hypothesised that the water feeding the peat from below has the same origin as the water emerging from the spring at the peat site. In order to test this hypothesis, the composition of peat pore water was analysed and compared to the composition of the spring water emerging at the site (Paper III). Three different peat cores were taken within Zone one, in the vicinity of sampling points 1 and 3 (marked as filled squares in Figure 5) in the autumn of 2003. Pore-water recovered from the peat by squeezing was used for the pH measurements and the determination of metal concentrations.

According to the results of the spring water analysis, the concentrations of Pb, Zn and Cu in the Värvallikas spring water (W1) were considerably higher than the background values (W2) in the area, but the concentrations of Fe, Mn and Ni were lower. Copper and Pb slightly exceed the drinking water standard (DWS) values, and the concentration of Zn was higher than the Estonian control value of Zn in groundwater (50 μg/l). The differences in concentration of metals in the water emerging in the spring at the peat site (W1) and 3 km downstream (W2) are given in Table 2. The spring water and the water in the ditches downstream were found to be slightly alkaline, pH 7.2-8.4.
Table 2  Concentrations of metals in the Värviallikas spring-water (W1) and in water 3-km downstream (W2) compared with chemical and indicator values in EU drinking water standard (DWS).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>DWS (μg/l)</td>
<td>200</td>
<td>10</td>
<td>5</td>
<td>2</td>
<td>50</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>W1 (μg/l)</td>
<td>130</td>
<td>&lt;5.0</td>
<td>&lt;0.1</td>
<td>3.0</td>
<td>120</td>
<td>&lt;1.0</td>
<td>12</td>
<td>98</td>
</tr>
<tr>
<td>W2 (μg/l)</td>
<td>210</td>
<td>&lt;5.0</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>330</td>
<td>4.0</td>
<td>1.0</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

The results of the peat pore-water analysis showed reasonable agreement with the results of the spring water analysis (Figure 9). The Ca and Zn concentrations in the peat pore-water agree within half an order of magnitude with the concentrations in the spring water, except for the Zn concentration in the pore water at very low peat depths (two values), where it was one and a half orders of magnitude higher than in the spring water.

There was a tendency for the concentrations of Fe, Pb, and Cu in the pore-water to increase with increasing peat depth. The Fe and Pb concentrations in the pore-water were up to one and a half orders of magnitude higher than the concentrations in the spring water. The Cu concentration in the pore-water was up to an order of magnitude higher than the Cu concentration in the spring water. Finally, the Mn concentration in the peat pore water was one and a half orders of magnitude lower than the concentration in the spring water. The pH in the pore-water extracts recovered from one of the peat cores was about 6.0.

Samples of pore-water recovered from the peat with a high Fe content in the solid were observed to have a reddish colour and centrifugation together with filtration did not removed this colour. This may indicate the presence of dissolved or colloidal iron in the extracts.

Sudov and Tibar, (1974a) in their 2-years observation carried out from 1971 to 1973 found no significant changes in the relative metal concentrations in the groundwater at several locations as well as the water emerging as the spring. The absolute concentrations of the elements were changing. Highest concentrations were measured during the winter and summer. A decrease in concentrations was observed during several days after rainfall due to dilution.
3.5 Conclusions

The distribution of metals with depth showed that the ochre layer (iron oxide accumulation) and the uppermost peat layer are the main natural geochemical barriers accumulating heavy metals in the Oostriku peat. In two-component systems (iron ochre and peat), As, Mn, and Zn were found to follow the trend of the Fe-ochre concentration with their highest concentrations in the ochre layer, while Pb and Cu were concentrated in the uppermost peat layer, above the ochre layer, and were not related to the Fe-ochre concentration.

The sequential extraction of metals from the peat indicated that Fe mostly occur in the peat as amorphous iron oxide, and that this iron oxide is the dominant binding agent for the metals Pb, Zn, and Mn. Copper was the only metal that is strongly bound to organic matter in an appreciable amount, although a considerable fraction of Cu is also bound to
the iron oxide. A fraction of the Ca, Pb, Zn, and Mn was found to be relatively weakly bound in the peat, probably being sorbed on the iron oxide and/or solid organic matter.

The water emerging from the spring was found to contain heavy metals in considerable concentrations. Although the concentrations of the heavy metals in the spring water at the Oostriku peat site were only slightly above the environmental standards, the long-term infiltration of metal-containing water into the peat, the precipitation of ferric oxyhydroxide under sharply changing physical-chemical conditions and the adsorption of heavy metals onto both organic matter and ferric oxyhydroxide could lead to extremely high concentrations of the metals in the peat. The peat pore-water analysis results showed reasonably good agreement for most metals with the results of the spring-water analysis, supporting the hypothesis that the water feeding the peat from below has the same origin as the water emerging at the peat site.

The experimental results of the field studies at the Oostriku peat bog are used further for evaluation of models describing the accumulation of heavy metals in the peat (Papers II and IV).
4. Oxidation of sulphide minerals in the surrounding bedrock as a possible long-term source of heavy metals in a peat bog

The source of heavy metals in the peat was considered to an oxidative dissolution of metal sulphides in upstream carbonate rock (for details see Paper II). The oxidation of metal sulphides was hypothesised to be the source of heavy metals in the water emerging in the spring at the peat site and the water entering the peat from below. The metal accumulation in the peat in this case may have had duration of many thousands of years.

To model the oxidative dissolution of metal sulphides in the carbonate rock, dynamic simulations were performed. The dissolution of the sulphide minerals along a flowpath in the carbonate rock was modelled (Section 4.2) where the water composition has evolved over time, as the mineral composition of the rock changed due to different chemical reactions taking place (Section 4.3). The simulated water composition was then compared (see Paper I) with the observed composition of the water emerging in the spring at the peat site. Section 4.1 describes the conceptual model.

4.1. Conceptual model

Carbonate rock containing metal sulphides undergoes chemical weathering. Dissolved oxygen in the infiltrating rainwater is the main weathering agent. The rainwater that infiltrates into the carbonate rock generates acidity by oxidative dissolution of pyrite and leaches heavy metals from other metal sulphides that are also oxidised. The acidity generated is neutralised by carbonate minerals. Calcite is the main carbonate mineral in the rock and it is the primary buffering agent. Released metals may also form secondary minerals in the rock, e.g. sulphides, carbonates, oxides, etc., depending on the pH and redox conditions. The amount of dissolved carbon dioxide in the infiltrating water can be greater than in the rainwater, due to respiration and decay processes in the soil and sediments. This could lead to a further dissolution of calcite and to the precipitation of metal carbonates.
The metal-containing water flows through the rock and feeds the peat from below, possibly leading to metal accumulation there, due to processes such as sorption and precipitation. This accumulation is assessed further in the present work. The conceptual model is illustrated in Figure 10.

Figure 10 Conceptual model. The metal-rich groundwater recharging at the Oostriku peat bog site from below and atmospheric oxygen diffusing into the peat from above, and at a distance where the water meets the oxygen, ferric oxyhydroxide (ochre) formation occurs. Retention of metals in the peat occurs through sorption onto the ferric oxyhydroxide and humic substances.

Sudov and Tibar (1974a;b) using a hydro-geochemical method searched for sulphide minerals in the area surrounding the Oostriku peat bog. However, no detailed information on the composition of the surrounding rock was given. Thus, neither mineral composition of the rock nor relative amounts of mineral phases is known. The modelling here is performed using an assumed content of the metal sulphides in the rock (for details see Paper II). The water flowpaths through the rock are also unknown.
4.2 Sequence of mineral-aqueous phase reactions in carbonate rock over time

Coupled geochemical and transport calculations using the code PhreeqC were used to simulate flow and chemical reactions as the water moves through a one-dimensional column. The composition of the metal-laden water was simulated as the water containing dissolved oxygen was infiltrated into the column containing specified mineral phases. The infiltration of the water caused an oxidation reaction and the release of metals into the water, and a flow of the reacted water along the column. The column was divided into a number of cells that were modelled as well-mixed reactors. Only advective transport was considered in the simulations. All reaction rates were assumed to be so fast that equilibrium was always maintained in each reactor. It was not therefore necessary to know the actual water flow velocity or the progress in real time. For details see Paper II.

The amounts of sulphides used in the simulation were much smaller than these in the real system. The scaling down was necessary in order to speed up the computations. Tests have shown that the scaling down had no effect on the chemical evolution of the system. The relative amounts of the metal sulphides (Table 4) in the rock were used in the simulations, as the mineral composition of the carbonate rock was unknown. Pyrite is the most abundant sulphide mineral in the rock, and its content was assumed to account for 80% of the total sulphide content. Other sulphides had abundances such as galena 4%, sphalerite 4%, chalcocite (Cu$_2$S) 0.5% and orpiment (As$_2$S$_3$) 0.5%.

Metal carbonates and oxides other than calcite (CaCO$_3$) and rhodochrosite (MnCO$_3$) were not present initially, but these solid phases were allowed to precipitate if the aqueous phases became supersaturated (SI>0) with respect to these solids. Rhodochrosite was used as the stable mineral phase for Mn. From previous simulations, it was found that manganese sulphide (MnS) is unstable in the carbonate rock. Calcite was the main mineral composing the carbonate rock. It was also the main buffering agent. The amount of calcite specified in the phase assemblage of each cell of the column was essentially an unlimited supply for the number of pore volumes used in the simulations.

When the oxygenated water infiltrates into the column containing different minerals, the most reactive mineral is oxidised first and depleted over a longer distance than less
oxidisable minerals. After several fronts have formed along the flowpath, as e.g. pyrite is oxidised before galena, sphalerite, and chalcocite, the infiltrated oxygenated water meets the less reactive mineral first (e.g. ZnS or Cu2S) and oxidises these sulphides. Modelled solid phase concentrations of metal sulphides along the flowpath are shown in Figure 11.

Orpiment is the sulphide mineral that is oxidised first (R5), followed by pyrite (R6). Following pyrite oxidation, releasing ferrous iron into the aqueous solution, siderite (FeCO3) is precipitated (R7).

\[
\text{As}_2\text{S}_3(s) + 6\text{O}_2(aq) + 6\text{H}_2\text{O} \rightleftharpoons 2\text{H}_3\text{AsO}_3(aq) + 3\text{SO}_4^{2-} + 6\text{H}^+ \quad \text{(R5)}
\]
\[
\text{FeS}_2(s) + 7/2\text{O}_2(aq) + \text{H}_2\text{O} \rightleftharpoons \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad \text{(R6)}
\]
\[
\text{Fe}^{2+} + \text{CaCO}_3(s) \rightleftharpoons \text{FeCO}_3(s) + \text{Ca}^{2+} \quad \text{(R7)}
\]

As seen in Figure 11a, the orpiment depletion front moves ahead of the other depletion fronts, including the oxygen front (not shown) in the column. The downstream dissolution of orpiment is caused by upstream pyrite oxidation, releasing ferrous iron and sulphate, which make orpiment unstable with respect to pyrite (R8), and it is limited by the solubility of siderite.

\[
4\text{Fe}^{2+} + \text{SO}_4^{2-} + 7/3\text{As}_2\text{S}_3 + 10\text{H}_2\text{O} \rightleftharpoons \\
4\text{FeS}_2\text{S}_3(s) + \text{H}_2\text{O} + 14/3\text{H}_3\text{AsO}_3 + 6\text{H}^+ \quad \text{(R8)}
\]

When pyrite has been depleted, oxidation of galena (R9) and sphalerite (R10) occurs. In Figure 11a-d, the oxidation fronts of galena and sphalerite coincide, within the one cell resolution of the model, with the oxidation front of pyrite. The oxidation of galena occurs first, followed by the oxidation of sphalerite and, whereas released zinc is free to be transported away with the water, lead is dominantly precipitated as cerrusite (PbCO3; R11), which has a very low solubility. Zinc is precipitated as ZnCO3:2H2O (R12), when galena is depleted, such that extensive oxidation of sphalerite occurs.

\[
\text{PbS}(s) + 2\text{O}_2(aq) \rightleftharpoons \text{Pb}^{2+} + \text{SO}_4^{2-} \quad \text{(R9)}
\]

40
Chalcocite has a very low solubility and, in the presence of other sulphides, releasing sulphide into the aqueous solution, the chalcocite dissolution reaction is further suppressed (e.g., Figure 11b). When metal sulphides, such as pyrite, galena, and sphalerite have been depleted, and the sulphide concentration in the aqueous solution is consequently low, chalcocite is no longer stable and is transformed into cuprite (Cu$_2$O).

With further infiltration of oxygenated water, siderite and rhodochrosite are oxidatively dissolved, and Fe, and Mn are precipitated (R13-14) as amorphous iron oxide (Fe(OH)$_3$) and nsutite (MnO$_2$). At the same time, cuprite is oxidised and malachite is precipitated (Cu(CO$_3$)$_2$:H$_2$O; R15).

Upon dissolution of Zn, Pb, and Cu phases upstream in the column, the released metals (e.g., Zn or Cu) are transported with the water downstream. This metal-containing water encounters the phase assemblage beyond the depletion fronts where there still is pyrite, and considerable accumulation of secondary sulphides occurs. The metals form secondary sulphide minerals (e.g., ZnS or Cu$_2$S) expelling Fe from the pyrite and causing sulphur disproportionation, at the same time releasing sulphate into solution, and the pyrite depletion front advances further downstream.
volumes 504, 2208, and 3960), sphalerite and chalcocite have concentrations at the dissolution front nearly 10 times higher than they have in the original rock.

Figure 11 Modelled sulphide mineral contents along a flow path through the carbonate rock, represented by a 100-cell column, after infiltration of different numbers of cell pore volumes of water to the column. a) 216 pore volumes; b) 504 pore volumes; c) 2208 pore volumes; d) 3960 pore volumes.

4.3 Effluent evolution along a flowpath in the carbonate rock

The water composition differs considerably when different mineral fronts appear and disappear along the water flowpath in the column and the mineral phases controlling the metal solubility in the aqueous solution change. The secondary phase content and the aqueous phase composition along the flowpath, when 2208 pore volumes have been infiltrated, are shown in Figures 12 and 13. The corresponding pH and pE profiles are shown on Figure 14.
Figure 12 Modelled secondary carbonate and oxide contents along a flow path through the carbonate rock, represented by a 100-cell column, after infiltration of 2208 cell pore volumes of water.

Figure 13 Modelled water composition along a flow path through the carbonate rock, represented by a 100-cell column, after infiltration of 2208 cell pore volumes of water.
Downstream of the redox front (cell 43 when 2208 pore volumes have been infiltrated; Figure 14), the solubility of Zn, Cu, and Pb is controlled by sulphide mineral phases (Figure 11c), whereas the solubility of Mn and Fe is controlled by carbonate phases (Figure 12). Upstream the redox front, the solubility of Zn, Cu, and Pb is controlled by carbonate mineral phases (Figure 12), yielding higher dissolved metal concentrations, and the solubility of Mn and Fe is controlled by oxide mineral phases (Figure 12), yielding lower dissolved metal concentrations than downstream (Figure 14). When the carbonate mineral phases (ZnCO$_3$·H$_2$O, Cu$_2$(OH)$_2$CO$_3$·H$_2$O, PbCO$_3$) are depleted out of the column, the dissolved concentrations of metals (Zn, Cu, and Pb) drop to zero, as no source of these elements remains.

The composition of the water discharging from the column remains constant over time (or infiltrated pore volumes) as long as there is no change in the sulphide mineral content in the column (Figures 15a-b). For a 100-cell column, the first 100 pore volumes discharged is the initial, equilibrated pore water solution that is being flushed out of the column. In the next stage (from 100 to 254 pore volumes), the discharging solution composition is determined by the flow of reacted water through the column, where
orpiment ($\text{As}_2\text{S}_3$) is still present in the column and none of the other sulphide minerals have been yet depleted (Figure 15a).

After orpiment has been depleted and As is flushed out the column (from 255 to 5040 pore volumes), the equilibrium is shifted and the metal concentrations increase by a factor of 2-4 (e.g., Fe, Zn, Pb), and this water composition remains constant as long as pyrite is still present in the column (Figures 15a-b). With further infiltration of water (from 5040 to 6000 pore volumes), when one or more minerals have been exhausted and different mineral fronts pass along the flowpath, the water composition changes drastically (Figure 15b).

![Graph showing water composition over pore volumes](image-url)
The decrease in sulphur concentration in Figure 15b is caused by depletion of sulphide minerals upstream of the oxygen depletion front in the flowpath. There is no oxygen in the water that reaches the sulphides, as it has been consumed in the formation of hydroxide/oxide phases (R13-14). The formation of secondary sulphides downstream (R16-17) is then the only source of dissolved sulphur. The subsequent increase in sulphate concentration occurs when reactions R16-17 are completed upstream and, with further infiltration, oxygen reaches and oxidises pyrite that remains at this position.

The simulated water composition is also compared with the independently observed (Paper I) water composition, emerging in the spring at the peat site (Figure 15). The observed concentrations of elements are shown as symbols in Figure 15. The simulated concentrations of major elements, such as Ca and S, are in good agreement with the observed concentrations throughout the simulation. The simulated pH 7.3 (Figure 14) furthermore approximately agrees with the observed pH 7.7 of the spring water at the peat site.
During the stage where the dissolved concentrations of Pb and Zn are controlled by the solubility of sulphides (up to \( \sim 5000 \) infiltrated pore volumes for a 100 cell column; Figure 15), the simulated water has concentrations of these elements one to two orders of magnitude lower than those in the observed water. The simulated concentration of Cu is even lower, due to the very low solubility of copper sulphide. However, when the secondary minerals control the solubility, the simulated concentrations of Zn, Cu, and Pb exceed the observed concentrations by one to two orders of magnitude. For Fe and Mn, which have lower solubility under oxidising than under reducing conditions, these trends are reversed. The simulated concentration of As, finally, is about three orders of magnitude higher than those observed at the peat site, as long as As is not depleted from the phase assemblage. However, such depletion occurs much earlier than depletion of other sulphide minerals.

These results imply that the mixing of a small amount of water from oxidised flow paths into water from flow paths where the sulphide minerals still remain could explain the observed overall composition of the spring water.

We have also performed simulations of metal sulphide oxidation in a column closed to CO\(_2\). Table 3 gives the results of the effluent composition from both simulations for comparison with the observed composition of the water emerging in the spring. There is a better match between metal concentrations in the spring-water and the effluent from the column open of CO\(_2\), except Mn and Fe concentrations. The pH for the closed system is much higher and the calcium concentration is much lower compared with those observed values in the spring water.
Table 3. Comparison of simulated effluent composition and analysed composition of the water emerging in the spring at the peat site.

<table>
<thead>
<tr>
<th>Elements</th>
<th>^1Open to CO₂</th>
<th>^1Closed to CO₂</th>
<th>Spring-water</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>pH 7.3</td>
<td>pH 9.4</td>
<td>pH 7.2-8.4</td>
</tr>
<tr>
<td>Ca</td>
<td>2.4 \times 10^{-3}</td>
<td>2.9 \times 10^{-4}</td>
<td>2.0 \times 10^{-3}</td>
</tr>
<tr>
<td>Mn</td>
<td>7.2 \times 10^{-6}</td>
<td>1.3 \times 10^{-6}</td>
<td>2.0 \times 10^{-6}</td>
</tr>
<tr>
<td>Fe</td>
<td>1.4 \times 10^{-5}</td>
<td>1.9 \times 10^{-6}</td>
<td>2.2 \times 10^{-6}</td>
</tr>
<tr>
<td>Zn</td>
<td>4.2 \times 10^{-8}</td>
<td>2.2 \times 10^{-9}</td>
<td>1.5 \times 10^{-6}</td>
</tr>
<tr>
<td>Pb</td>
<td>1.5 \times 10^{-8}</td>
<td>1.7 \times 10^{-10}</td>
<td>5.8 \times 10^{-8}</td>
</tr>
<tr>
<td>Cu</td>
<td>4.1 \times 10^{-17}</td>
<td>1.4 \times 10^{-18}</td>
<td>4.7 \times 10^{-8}</td>
</tr>
<tr>
<td>As</td>
<td>1.3 \times 10^{-5}</td>
<td>2.0 \times 10^{-5}</td>
<td>6.7 \times 10^{-8}</td>
</tr>
<tr>
<td>S</td>
<td>1.7 \times 10^{-4}</td>
<td>1.6 \times 10^{-4}</td>
<td>2.8 \times 10^{-4}</td>
</tr>
</tbody>
</table>

^1Metal aqueous concentrations are controlled by the solubility of sulphide mineral phases. Concentrations of elements are in mol/l.

The pH and Ca concentration in the simulated system open to atmosphere agree better with observed values than in the system that is closed (Table 3). These two entities we deem should agree better in order to have credible simulation results. We thus base much of our conclusions on the open system results.

### 4.4 Conclusions

Dynamic simulations of the oxidative dissolution of metal sulphides in the carbonate rock showed that a complex series of mineral-aqueous phase reactions occurs along the flowpath and controls the composition of the aqueous phase. The solubility of metals in the water was controlled mainly by carbonate phases when sulphides have reacted, and, in the presence of oxygen, by oxide phases (Fe(OH)$_3$ and MnO$_2$). A considerable accumulation of secondary sulphides (e.g. ZnS, Cu$_2$S) was observed as the sulphides were oxidised upstream and the released metals were transported downstream and equilibrated with pyrite. The simulated water composition remained constant over time as long as no sulphides had been depleted. When secondary minerals formed and
disappeared again to some extent along the flowpath, the composition of the water changed considerably.

The concentrations of major elements such as Ca and S throughout the simulations of pore volumes infiltrating into the column are in good agreement with the observed concentrations in the water emerging in the spring. This suggests that the water in the spring can originate from the carbonate rock. Differences between the simulated concentration of trace elements and the observed concentrations is not wholly unexpected, since the actual composition of the minor minerals along the flowpath is not known. It is possible that minor elements occur in mixed minerals or as traces in pyrite. Furthermore, it is possible that more than one flowpath carries water to the spring and that the spring water is a mixture of water from several flowpaths. Different flowpaths, with different pore volumes infiltrated, may, therefore, have different water compositions. Mixture of water with these different compositions could thus explain the water composition entering the peat from below.
5. Retention of metals in a peat bog

To model the metal retention in the peat, three types of simulations were made (for details see Paper IV). The first aimed at assessing ferric oxyhydroxide precipitation in the peat through dynamic simulations and the possible formation of other heavy metal solid phases (see Section 5.3). The second type was batch simulation assessing equilibrium sorption of heavy metals on peat (see Section 5.4). The third type of simulation assessed the dynamics of sorption along the peat profile over time (Section 5.5). In the second and third type of simulation, modelling of sorption was a key component, and Section 5.2 describes how this was done. The conceptual model is described in Section 5.1.

Metal sorption onto the peat was considered to be an important binding process preceding other, stronger binding mechanisms. Sorption was considered to occur on ferric hydroxide and on solid organic material in the peat, for which we adopted a mechanistic modelling approach involving surface complexation reactions at discrete surface sites on the sorbents (Paper IV). Predicted amounts of metals sorbed were then compared with the experimentally observed (Paper III) amounts of metals sorbed in the peat, which were obtained by means of the sequential extraction.

5.1 Conceptual model

In the peat bog, the water flow direction is from below and upwards. The water that flows through the peat contains alkalinity in equilibrium with calcite and heavy metals due to the oxidation of sulphide minerals in the upstream carbonate rock (Paper II). Seen in the direction of the water flow, the peat profile is characterised by a transition from anaerobic, permanent water-saturated conditions to largely oxygenated, aerobic, conditions at and above the water table. The main source of oxygen in the peat is considered to be diffusion from the atmosphere, where molecular oxygen easily diffuses through the highly porous, partially water-saturated peat.

The possible formation of ferric oxyhydroxide is assessed in the model, assuming that essentially all the ferrous iron transported with the water through the peat is oxidised by
atmospheric oxygen and precipitated as amorphous ferric oxyhydroxide at the water table, forming the ochre layer. This is subsequently shown to be the case in the simulations. Furthermore, the possible precipitation of other metals (e.g. Mn, Pb, and Cu) as secondary mineral phases along the peat profile is assessed through the calculation of saturation indices in the aqueous phase with respect to different solids.

The retention of heavy metals transported by water in the peat through sorption on organic matter and amorphous ferric oxyhydroxide is also assessed in the model. Metal sorption on organic matter is assessed by surface complexation with humic substances (fulvic acids). Buffering is considered through the surface acid-base and metal-complexation reactions, and reactions with the dissolved alkalinity. Peat sulphur geochemistry is not considered in the model. This means that possible sulphate reduction to sulphide is not taken into account. The organic degradation processes in the peat are considered to be balanced by the peat growth and are also not assessed in the model.

Metal sorption is modelled using an equilibrium approach reflecting the long time involved in metal accumulation by the peat and the relatively long water residence time in the peat.

5.2 Formation of ferric oxyhydroxide in the peat bog and other possible metal precipitation

The formation of ferric oxyhydroxide in the peat was simulated in a one-dimensional column (see Paper IV). Water with ferrous iron was infiltrated from the bottom of the column upwards and oxygen diffused from the top of the column downwards. All the infiltrated ferrous iron was oxidised by atmospheric oxygen (R18) and precipitated as ferric oxyhydroxide (R19). When more water infiltrated into the column, more ferric oxyhydroxide accumulated.

\[
\text{Fe}^{2+} + \frac{1}{4} \text{O}_2^{(aq)} + \text{H}^+ \leftrightarrow \text{Fe}^{3+} + \frac{1}{2} \text{H}_2\text{O} \quad \text{(R18)}
\]

\[
\text{Fe}^{3+} + 3 \text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_{3(s)} + 3 \text{H}^+ \quad \text{(R19)}
\]
The advective flux of water in the model was derived from a mass balance of the Fe (solid) observed in the ochre layer of the peat and the mass of the ferrous iron infiltrated with water (Table 4) into the peat. 26.5 kg/m² of ferric oxyhydroxide was found to be accumulated in the ochre layer where the maximum total Fe reached 40%-wt and the peat had an age of 3 500 years (see Paper I).

Table 4 Composition of the water emerging in the spring at the peat site.

<table>
<thead>
<tr>
<th>Element</th>
<th>C, (M)</th>
<th>Element</th>
<th>C, (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>2.3 \times 10^{-3}</td>
<td>HCO_3^-</td>
<td>5.0 \times 10^{-3}</td>
</tr>
<tr>
<td>Fe</td>
<td>2.3 \times 10^{-6}</td>
<td>SO_4^{2-}</td>
<td>3.2 \times 10^{-4}</td>
</tr>
<tr>
<td>Mn</td>
<td>2.2 \times 10^{-6}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>1.5 \times 10^{-6}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>5.8 \times 10^{-8}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>4.7 \times 10^{-8}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Predicted concentration of alkalinity in equilibrium with calcite in the upstream carbonate rock (Paper II).*

In order to test whether other metals (e.g. Mn, Pb, Cu) were likely to precipitate in the peat as discrete, pure secondary solid phases, the infiltrating water was examined for pH and saturation indices with respect to various relevant solid phases as it passed through the column.

Downstream of a redox front in the column, where oxidation of ferrous iron and precipitation of ferric oxyhydroxide occurred, the modelled solution pH was about 7.3 and upstream the redox front it was about 8.3. These pH values fall within the reported range of 4.0 to 8.5 in peats (Urban et al., 1986), but they are somewhat higher than the pH of about 6.0 that was observed in the pore-water in the Oostriku peat (Paper III).

Downstream of the redox front in the column, the aqueous solution was supersaturated with respect to manganese oxide (MnO_{2(s)}). The aqueous solution was not, however, supersaturated with respect to Pb or Cu (hydr)oxides, or to any metal carbonates or sulphate phases. This is consistent with previous X-ray diffraction results (1% detection limit; see Paper I) indicating the presence of no metal (hydr)oxide phases or solid phases other than ferric hydroxide. Sequential extraction results (Paper III) indicated, however,
that most of the Pb, Zn, and Mn was present in the oxide fraction, possibly coprecipitated with ferric oxyhydroxide in the peat.

Upstream of the redox front in the column, the aqueous solution was supersaturated with respect to metal sulphides, if sulphate reduction is considered. Previous X-ray diffraction results, however, showed the presence of no metal sulphides in the peat, except traces of pyrite at a depth of 1.00-1.05 m (Paper I). In the sequential extraction of metals from the peat, it was not possible to distinguish between the fraction of metals bound in sulphides (if sulphides were present in the peat) and the fraction of metals strongly bound in the organic matter (organic fraction), as the sulphide fraction of metals would be leached together with the organic fraction of metals in the oxidisable step of the sequential extraction (see Paper III).

The organic/sulphide fraction of metals, except for Cu, was in any case observed to be negligible in the peat (Figure 8; Paper III). A considerable amount of the Cu found in the organic/sulphide fraction is believed to be strongly bound with the organic matter, consistent with other observations showing that Cu is the most strongly metal bound with organic matter (Logan et al., 1997; Lo et al., 1998; Balasoiu et al., 2001). Thus, the occurrence of metal sulphides under reducing conditions in the peat cannot be excluded, although it is not here considered to be a dominating metal (e.g. Cu) -binding mechanism.

5.3 Approach to modelling metal sorption in peat

    Metal sorption on organic matter

    One of our aims in this study was to model the sorption of metals on peat organic matter (humic substances) by using independently obtained data available in the literature. Different approaches exist to model metal complexation with humic substances, including discrete non-electrostatic models (Woolard et al., 1999), continuous distribution models (Kinniburgh et al., 1996; Benedetti et al., 1996; Kinniburgh et al., 1999), and discrete electrostatic models (De Wit et al., 1990; Bartschat et al., 1992; Tipping et al., 1992; Tipping et al., 1998).
Crawford (1995) stressed that several workers considered the discrete site electrostatic modelling approach to be the most suitable method of simulating the processes of organic complexation. Kinniburgh et al. (1996) noted that the discrete-site electrostatic Model V of Tipping et al. (1992) is probably closest to being a comprehensive model that can describe ion binding by a range of humics. The Model V of Tipping et al. (1992) has been implemented (Crawford, 1995) into the established inorganic speciation code (PHREEQ) to yield the code PHREEQEV that accounts for complexation with organic molecules in aqueous solutions. The Tipping model was favoured because it has been validated by application to a wide range of published data for organic material (more soluble fulvic-type or less soluble humic-type material) on proton dissociation and metal binding (covering the metals of interest: Ca\(^{2+}\), Mn\(^{2+}\), Zn\(^{2+}\), Fe\(^{2+}\), Pb\(^{2+}\), and Cu\(^{2+}\)).

For our modelling purposes, we favour a sorption description as simple as possible in order to simplify coupling to physical transport and interpretation of the model results. The sorption behaviour of the organic matter in peat was considered to be similar to the complexation behaviour of fulvic acids. To describe this, we simplified the Tipping Model V (Tipping et al., 1992) in terms of the acid-base properties of surface sites. In our simplified version, we used only two proton-dissociating groups, one group for each type of site, carboxylic and phenolic, and the logarithmic median intrinsic proton-dissociation equilibrium constants (see Table 5). The total amounts of binding sites at the fulvic acids and the site distribution were taken to be the same as in Model V (Table 6).

Binding of metals was characterised by cation-surface complexation according to Model V. Conditional equilibrium constants for metal surface-complexation at the carboxylic type-sites (K\(_{\text{RCOOH-Me}}\)) were taken directly from Model V (Table 8 in Tipping et al., 1992) for the metals of interest (Ca\(^{2+}\), Mn\(^{2+}\), Zn\(^{2+}\), Fe\(^{2+}\), Cu\(^{2+}\), and Pb\(^{2+}\)) and solution conditions (e.g. pH and pM) close to the conditions observed in the Oostriku peat. The \(pK_{\text{RCOOH-Me}}\) values for the metals indicate that the binding strength increases in the order: Ca\(^{2+}\) < Mn\(^{2+}\) < Zn\(^{2+}\) < Pb\(^{2+}\) < Fe\(^{2+}\) ~ Cu\(^{2+}\) (see Table 5).

Conditional equilibrium constants for metal surface-complexation at the phenolic type-sites (pK\(_{\text{ROH-Me}}\)) and at the carboxylic type-sites (pK\(_{\text{RCOOH-Me}}\)) have been reported to be correlated through Eq.5, which was used to calculate pK\(_{\text{ROH-Me}}\) values for our simplified model.
log $K_{ROH-Me^{2+}} = 1.38 \log K_{RCOOH-Me^{2+}} + 2.57$ \hspace{1cm} (Eq.5)

Sorption of the metals on the fulvic acids was first simulated assuming monodentate complex formation only, but, this approach underestimated the sorption of metals, e.g. Cu and Pb that occur at very low concentrations ($10^{-8}$ M) in the water infiltrating into the peat. Therefore, both monodentate (R20 and R21) and bidentate complex formation (R22 and R23) at the fulvic acids had to be considered in the model. The following deprotonation reactions (R24-R27) were considered in our model. When bidentate metal sorption occurred, the monodentate site equilibrium constants were multiplied together following the approach of Tipping et al. (1992). Table 5 summarises the equilibrium constants used in the simplified model.

Monodentate complex formation:

$$\text{RCOOH} + \text{Me}^{2+} \Leftrightarrow \text{RCOOMe}^+ + \text{H}^+ \hspace{1cm} (R20)$$

$$\text{ROH} + \text{Me}^{2+} \Leftrightarrow \text{ROMe}^+ + \text{H}^+ \hspace{1cm} (R21)$$

Bidentate complex formation

$$\text{R(COOH)}_2 + \text{Me}^{2+} \Leftrightarrow \text{R(COO)}_2\text{Me} + 2 \text{H}^+ \hspace{1cm} (R22)$$

$$\text{RCO(OH)}_2 + \text{Me}^{2+} \Leftrightarrow \text{RCO(O)}_2\text{Me} + 2 \text{H}^+ \hspace{1cm} (R23)$$

Deprotonation of surface sites:

$$\text{RCOOH} \Leftrightarrow \text{RCOO}^- + \text{H}^+ \hspace{1cm} (R24)$$

$$\text{ROH} \Leftrightarrow \text{RO}^- + \text{H}^+ \hspace{1cm} (R25)$$

$$\text{R(COOH)}_2 \Leftrightarrow \text{R(COO)}_2^{2-} + 2 \text{H}^+ \hspace{1cm} (R26)$$

$$\text{RCO(OH)}_2 \Leftrightarrow \text{RCO(O)}_2^{2-} + 2 \text{H}^+ \hspace{1cm} (R27)$$

We further modified the Model V using the diffuse double layer approach (without considering the explicit composition of the double diffuse layer) to account also for surface charge effects on the surface-complexation reactions at the organic material in the peat.
## Table 5 Metal complexation reactions on fulvic acids and their stability constants.

<table>
<thead>
<tr>
<th>Surface reaction</th>
<th>Stability constant</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Monodentate complexation:</strong></td>
<td></td>
</tr>
<tr>
<td>RCOOH = RCOO⁻ + H⁺</td>
<td>$^{1}\log K_{RCOOH} = -3.3$</td>
</tr>
<tr>
<td>ROH = RO⁻ + H⁺</td>
<td>$^{1}\log K_{ROH} = -9.6$</td>
</tr>
<tr>
<td>RCOOH + Ca²⁺ = RCOOCa⁺ + H⁺</td>
<td>$^{2}\log K_{RCOOH-Ca^{2+}} = -1.86$</td>
</tr>
<tr>
<td>RCOOH + Mn²⁺ = RCOOMn⁺ + H⁺</td>
<td>$^{2}\log K_{RCOOH-Mn^{2+}} = -1.7$</td>
</tr>
<tr>
<td>RCOOH + Zn²⁺ = RCOOZn⁺ + H⁺</td>
<td>$^{2}\log K_{RCOOH-Zn^{2+}} = -1.5$</td>
</tr>
<tr>
<td>RCOOH + Fe²⁺ = RCOOFe⁺ + H⁺</td>
<td>$^{2}\log K_{RCOOH-Fe^{2+}} = -0.6$</td>
</tr>
<tr>
<td>RCOOH + Pb²⁺ = RCOOPb⁺ + H⁺</td>
<td>$^{2}\log K_{RCOOH-Pb^{2+}} = -0.9$</td>
</tr>
<tr>
<td>RCOOH + Cu²⁺ = RCOOCu⁺ + H⁺</td>
<td>$^{2}\log K_{RCOOH-Cu^{2+}} = -0.5$</td>
</tr>
<tr>
<td>ROH + Ca²⁺ = ROCa⁺ + H⁺</td>
<td>$^{3}\log K_{ROH-Ca^{2+}} = -5.14$</td>
</tr>
<tr>
<td>ROH + Mn²⁺ = ROMn⁺ + H⁺</td>
<td>$^{3}\log K_{ROH-Mn^{2+}} = -4.92$</td>
</tr>
<tr>
<td>ROH + Zn²⁺ = ROZn⁺ + H⁺</td>
<td>$^{3}\log K_{ROH-Zn^{2+}} = -4.64$</td>
</tr>
<tr>
<td>ROH + Fe²⁺ = ROFe⁺ + H⁺</td>
<td>$^{3}\log K_{ROH-Fe^{2+}} = -3.39$</td>
</tr>
<tr>
<td>ROH + Pb²⁺ = ROPb⁺ + H⁺</td>
<td>$^{3}\log K_{ROH-Pb^{2+}} = -3.81$</td>
</tr>
<tr>
<td>ROH + Cu²⁺ = ROCu⁺ + H⁺</td>
<td>$^{3}\log K_{ROH-Cu^{2+}} = -3.26$</td>
</tr>
<tr>
<td><strong>Bidentate complexation:</strong></td>
<td></td>
</tr>
<tr>
<td>R(COOH)₂ = RCOO⁻² + 2 H⁺</td>
<td>$^{4}\log K_{R(COOH)₂} = -6.6$</td>
</tr>
<tr>
<td>RCO(OH)₂ = RCO(O)⁻² + 2 H⁺</td>
<td>$^{4}\log K_{RCO(OH)₂} = -12.9$</td>
</tr>
<tr>
<td>R(COOH)₂ + Ca²⁺ = R(COO)₂Ca⁺ + 2 H⁺</td>
<td>$^{4}\log K_{R(COOH)₂-Ca^{2+}} = -3.72$</td>
</tr>
<tr>
<td>R(COOH)₂ + Mn²⁺ = R(COO)₂Mn⁺ + 2 H⁺</td>
<td>$^{4}\log K_{R(COOH)₂-Mn^{2+}} = -3.4$</td>
</tr>
<tr>
<td>R(COOH)₂ + Zn²⁺ = R(COO)₂Zn⁺ + 2 H⁺</td>
<td>$^{4}\log K_{R(COOH)₂-Zn^{2+}} = -3.0$</td>
</tr>
<tr>
<td>R(COOH)₂ + Fe²⁺ = R(COO)₂Fe⁺ + 2 H⁺</td>
<td>$^{4}\log K_{R(COOH)₂-Fe^{2+}} = -1.2$</td>
</tr>
<tr>
<td>R(COOH)₂ + Pb²⁺ = R(COO)₂Pb⁺ + 2 H⁺</td>
<td>$^{4}\log K_{R(COOH)₂-Pb^{2+}} = -1.8$</td>
</tr>
<tr>
<td>R(COOH)₂ + Cu²⁺ = R(COO)₂Cu⁺ + H⁺</td>
<td>$^{4}\log K_{R(COOH)₂-Cu^{2+}} = -1.0$</td>
</tr>
<tr>
<td>RCO(OH)₂ + Ca²⁺ = RCO(O)₂Ca⁺ + 2 H⁺</td>
<td>$^{4}\log K_{RCO(OH)₂-Ca^{2+}} = -7.0$</td>
</tr>
<tr>
<td>RCO(OH)₂ + Mn²⁺ = RCO(O)₂Mn⁺ + 2 H⁺</td>
<td>$^{4}\log K_{RCO(OH)₂-Mn^{2+}} = -6.62$</td>
</tr>
<tr>
<td>RCO(OH)₂ + Zn²⁺ = RCO(O)₂Zn⁺ + 2 H⁺</td>
<td>$^{4}\log K_{RCO(OH)₂-Zn^{2+}} = -6.14$</td>
</tr>
<tr>
<td>RCO(OH)₂ + Fe²⁺ = RCO(O)₂Fe⁺ + 2 H⁺</td>
<td>$^{4}\log K_{RCO(OH)₂-Fe^{2+}} = -3.99$</td>
</tr>
<tr>
<td>RCO(OH)₂ + Pb²⁺ = RCO(O)₂Pb⁺ + 2 H⁺</td>
<td>$^{4}\log K_{RCO(OH)₂-Pb^{2+}} = -4.71$</td>
</tr>
</tbody>
</table>
\[ \text{RCO(OH)}_2 + \text{Cu}^{2+} = \text{RCO(O)}_2\text{Cu} + 2 \text{H}^+ \quad 4\log K_{\text{RCO(OH)}_2\text{-Cu}^{2+}} = -3.76 \]

Data were taken from \(^1\)Table 4, \(^2\)Table 8 in Tipping et al., (1992), \(^3\)values were calculated using the relation (Eq.1), and \(^4\)values were calculated multiplying monodentate constants together following the approach of Tipping et al., (1992).

\textit{Table 6 Binding sites at the fulvic acids surface (from Tipping et al., 1992).}

<table>
<thead>
<tr>
<th>Sites at the surface</th>
<th>Formula(^1)</th>
<th>Amount(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total sites</td>
<td>((1-f_{pr})(n_a + n_a/2) + \frac{1}{2} f (n_a + n_a/2))</td>
<td>(7.5 \times 10^{-3})</td>
</tr>
<tr>
<td>Carboxylic sites, RCOOH</td>
<td>((1-f_{pr}) n_a)</td>
<td>(2.82 \times 10^{-5})</td>
</tr>
<tr>
<td>Phenolic sites, ROH</td>
<td>((1-f_{pr}) n_a/2)</td>
<td>(1.41 \times 10^{-5})</td>
</tr>
<tr>
<td>Bi-carboxylic sites, R(COOH)(_2)</td>
<td>(4/12 \left(\frac{1}{2} f_{pr} (n_a + n_a/2)\right))</td>
<td>(4.7 \times 10^{-4})</td>
</tr>
<tr>
<td>Salicylic acid-like sites, RCO(OH)(_2)</td>
<td>(8/12 \left(\frac{1}{2} f_{pr} (n_a + n_a/2)\right))</td>
<td>(9.4 \times 10^{-4})</td>
</tr>
</tbody>
</table>

\(^1f_{pr}\) is a proximity factor defined by Tipping et al., (1992) as a fraction of the monodentate sites that form bidentate sites for metal binding; \(n_a\) and \(n_a/2\) is the total amount of carboxylic sites \((4.7 \times 10^{-3} \text{ mol/g})\) and phenolic sites \((2.35 \times 10^{-3} \text{ mol/g})\) used on the basis of published data in case if only monodentate binding considered; \(^2\) amounts of binding sites is given in moles per gram of fulvic acids

We tested how well our simplified model could predict the experimental data used by Tipping et al. (1992) in their Model V, which is more complex. Metal-surface complexation on fulvic acids was simulated in PhreeqC for Ca \((1.0 \times 10^{-1} \text{ M})\), Cu \((2.5 \times 10^{-8} \text{ M}; 1.0 \times 10^{-9} \text{ M})\), and Pb \((1.0 \times 10^{-6} \text{ M})\) in the pH range 5.0-7.0 and the ionic strength \(1.0 \times 10^{-1} \text{ M}\). Published experimental data was selected as close as possible to the conditions observed in the Oostriku peat. As seen in Figure 16, the predicted sorbed concentrations agreed with the experimental data within half an order of magnitude, with the exception of Cu \((2.5 \times 10^{-8} \text{ M}, \text{pH 5})\), for which the model over-predicted the sorption by one order of magnitude. We accept these differences for the purpose of our study.
Metal sorption on ferric oxyhydroxide

The sorption of metals on ferric oxyhydroxide was modelled using the surface complexation model with electrostatic correction according to the double-layer model of Dzombak et al. (1990). Sorption sites on the ferric oxyhydroxide (the reactive hydroxyl groups) were divided into weak and strong sites. For both type-sites, the following reactions (R28-30) were considered in the model.

\[
\begin{align*}
\text{Fe} \equiv \text{OH}_2^+ & \leftrightarrow \text{Fe} \equiv \text{OH}^0 + \text{H}^+ \\
\text{Fe} \equiv \text{OH}^0 & \leftrightarrow \text{Fe} \equiv \text{O}^- + \text{H}^+ \\
\text{Fe} \equiv \text{OH}^0 + \text{Me}^{2+} & \leftrightarrow \text{Fe} \equiv \text{Me}^+ + \text{H}^+ 
\end{align*}
\]  

(R28)  
(R29)  
(R30)

The database Wateq4f (Ball et al., 1991) containing thermodynamic data for the ferric oxyhydroxide surface, such as acid-base and metal complexation reactions and their
intrinsic equilibrium constants, was used for the simulation. The code PhreeqC was used in the simulations.

**Some comments on the sequential extraction procedure**

The predicted amounts of metals sorbed onto amorphous ferric oxyhydroxide and onto solid organic matter have been compared with the observed sorbed amounts of metals in peat (Paper III). The amounts of metals sorbed in the peat have been determined by sequential extraction, but, due to incomplete selectivity of reagents or metal re-adsorption during the sequential extraction, some uncertainty may have been introduced into the extraction results (Qiang et al., 1994; Gomez Ariza et al., 1999; Gomez Ariza et al., 2000).

Using our model, we tested whether the metals sorbed in the peat were desorbed as expected in the sequential extraction in reaction with the 1M ammonium acetate adjusted to pH 5 that was used to leach the metals weakly associated with the peat (sorbed). The simulations were also performed for 25 vol-% acetic acid that was used to eliminate metal re-adsorption among undissolved solid material in the subsequent reducible step of the sequential extraction, when iron oxide was dissolved and metals strongly bound or coprecipitated were released. This step was considered here since any metals remaining sorbed after the 1M ammonium acetate treatment might be released in reaction with the acetic acid. In both simulations, the ratio of the amount of reagent to the mass of solid was kept at the value that was used in the sequential extraction. Metal-complexation reactions of acetate and their stability constants were taken from the database Minteq in PhreeqC.

Results indicated that most of the Pb, but only half of the amount of Ca, Mn, and Zn sorbed on the organic matter were desorbed in reaction with the 1M ammonium acetate solution (pH 5) as aimed for in this step of the sequential extraction, and that Cu and Fe, to a large degree, remained sorbed (Figure 17a). In the presence of 25 vol-% acetic acid (pH 2) used in the subsequent reducing step of the sequential extraction scheme, most of the Pb and one third of the amount of Ca, Mn, and Zn remaining sorbed on the organic matter were desorbed, while Cu and Fe still remained sorbed at the surface (Figure 17b). Manganese, Zn, Pb, and Cu sorbed on the amorphous ferric oxyhydroxide were desorbed
from the surface in reaction with 1M ammonium acetate, while Ca remained to a large degree sorbed (Figure 17c).

**Figure 17** Model prediction of the proportion of the metal desorbed from organic matter and ferric oxyhydroxide (a) metal desorption from organic matter in reaction with 1M-ammonium acetate solution adjusted to pH 5 (b) metal desorption from organic matter in reaction with 25vol-% acetic acid, pH 2 (c) metal desorption from ferric oxyhydroxide in reaction with 1M ammonium acetate solution adjusted to pH 5. Sorbed metal amounts are in moles per gram.
5.4 Model performance of metal sorption in peat and the relative importance of different sorbents

Metal sorption onto the peat was considered to be an important binding process preceding other, stronger binding mechanisms. In order to test the ability of the model to reproduce the sorption of metals onto the ferric oxyhydroxide and organic material in the peat, batch equilibrium sorption modelling was used (for details see Paper IV). To evaluate the performance of this sorption model, the predicted amounts of metals sorbed on organic matter and amorphous ferric oxyhydroxide were compared with the experimentally observed (see Paper III) amounts of metals sorbed on the peat in the Oostriku peat bog, which were obtained by means of sequential extraction.

In the sequential extraction, different chemical reagents were used to selectively leach metals bound by different mechanisms in the peat. The fraction of metals leached with a 1M-ammonium acetate solution (pH 5) and assigned as relatively weakly bound (Gomez-Ariza et al., 2000), most probably sorbed on amorphous ferric oxyhydroxide and solid organic matter in the peat, is of main interest for the evaluation of the model performance. As already mentioned (see previous section) there may, however, be some experimental uncertainty related to the incomplete selectivity of reagents or to the extent of post-extraction redistribution of leached metals in the sequential extraction. Taking this into consideration, the fractions of metals leached as the “reducible” and “oxidisable” (i.e. organic) were also included for the model performance evaluation.

In the modelling, sorption on ferric oxyhydroxide and sorption on organic matter were considered separately. The results presented in Figure 18 were obtained by taking into account for the relative amounts of ferric oxyhydroxide and organic matter in the peat, which varied with depth (see Paper III). As seen in Figure 18, the model results suggest that sorption of metals on organic matter is more important than the sorption on the ferric oxyhydroxide in the peat. However, the combined behaviour of both sorbents is used to evaluate the model performance, since it was not possible to experimentally distinguish the extents to which the metals were sorbed on ferric oxyhydroxide or on organic matter in the peat, respectively.
The model predicts the sorption of Mn and Zn well through sorption on the organic matter alone (Figure 18b,c). The predicted amounts of Ca and Fe sorbed on organic matter are higher by up to two orders of magnitude than the observed amounts (Figure 18a,d). This is consistent with the possible incomplete removal of the metals from the solid surfaces from the peat in the sequential extraction procedure. As indicated by the modelling, only a part of the sorbed amounts of Ca and Fe was desorbed in the extraction step with the ammonium acetate reagent (Figure 17a,b).

The sorption of Pb in the peat is quite well predicted by sorption on organic matter, except in the uppermost peat (Figure 18e). There, the predicted amount was one to two orders of magnitude lower than the observed amount. The sorbed amount of Cu on the fulvic acids predicted by the model is overestimated by one order of magnitude comparing with the observed amount of Cu sorbed in the peat (Figure 18f). This over-prediction is consistent with the trend of the model to over-predict Cu sorption at very low dissolved concentrations (see Figure 16).

With a few exceptions, the model thus quite well describes the sorption of metals in the peat by sorption on organic matter. It should be noted that the model quantification of the sorption has been done using data that are independent from the site observations. The success of the model thus suggests that the employed modelling approach might be generally applicable for predicting the sorption of metals in peat.
Figure 18 Modelled and experimentally observed (Paper III) sorption of metals versus depths in the peat, a) Ca; b) Mn; c) Zn; d) Fe; e) Pb; f) Cu; Solid and dotted lines are the predicted sorbed amounts at the organic matter and ferric oxyhydroxide respectively; Symbols are the results from the sequential extraction experiments where open triangles are the amounts of metal assigned to be sorbed on any solid surfaces in the peat; filled diamonds are the amounts of metals strongly bound or coprecipitated with the amorphous ferric oxyhydroxide in the peat, filled squares are the amounts of metals strongly bound to the organic matter in the peat.
5.5. Importance of metal-metal competition effect on Pb and Cu sorption in peat over time

In general, the simulated results described the metal sorption in the Oostriku peat quite well. However, in the case of Cu and Pb, the observed sorbed amounts of the metals in the uppermost peat layer were higher than in the lower peat layer (Syrovtenik et al., 2004; 2005a), a feature that was not reproduced in the batch modelling. In order to test whether the Pb and Cu accumulation in the uppermost peat layer could be caused by competition for sorption sites, the evolution of metal sorption fronts along a column of organic matter was assessed over time with a dynamic model (for details see Paper IV). In the simulation, the water composition, pH, and redox conditions changed with infiltrated pore volumes due to the chemistry within the column. We assumed equilibrium sorption reactions during transport. Physical transport through advection was assumed to dominate, and diffusion and dispersion were neglected.

In order to reduce the calculation time, the amount of organic matter used in the dynamic simulations was scaled down to one gram per litre of solution. To test the effects of the scaling down on reducing the sorption capacity of the organic matter, simulations were also performed with a larger amount of organic matter per litre of solution. Scaling down of the mass of organic matter made no noticeable difference and was acceptable for our modelling purposes.

The results are shown in Figures 19 (bottom of the column, cell 1) and 20 (top of the column, cell 15). Prior to infiltration of the metal-containing water, deprotonation of the carboxylic (R20) and bicarboxylic sites (R22) controls the pH in the aqueous solution. When the metal-containing solution is infiltrated into the column, the sorption of Ca releases protons from the surface into the aqueous solution lowering the pH further up in the column (Figure 19g). With more pore volumes being infiltrated, the pH is buffered by the incoming alkalinity (Figure 20g). The low pH front moves beyond the metal sorption fronts in the column, and thus has no effect on the heavy metal sorption.

Calcium is present at the highest concentration in the incoming aqueous solution and dominates the sorption at the organic matter (see Paper IV). At the bottom of the column, calcium is also the first metal being sorbed by the sorption sites on the organic matter.
The sorption of Mn (Figure 19b) and Zn (Figure 19c), characterised by similar binding strengths to the organic matter (see Table 5), but present at a concentration three orders of magnitude lower than that of Ca in the aqueous solution, succeed the sorption of Ca on the organic matter in the column.

Lead, Cu, and Fe strongly sorb to the organic matter (Table 5), preferably at the bidentate sites (see Paper IV). Lead and Cu are present at similar, very low concentration in the infiltrated solution. However, Cu is more strongly sorbed to the organic matter than Pb, and it thus takes a longer time (more pore volume is needed to be infiltrated) for Cu (Figure 19e) than for Pb (Figure 19d) to occupy the sorption sites.

Iron is present at a concentration that is two orders of magnitude higher than the concentration of Cu and Pb, but three orders of magnitude lower than the concentration of Ca in the infiltrated aqueous solution and, at the same time, Fe is sorbed strongly on organic matter. By sorbing on the organic solid surface, Fe (Figure 19f) is competing for the bidentate sorption sites, especially the salicylic acid-like sites, with Ca and the other metals (Mn, Zn, Pb and Cu), thus expelling these metals from the surface with time. This explains why the sorbed amounts of Ca, Mn, Zn, Pb, and Cu decrease with time (Figure 19-20) after the first peak. The evolution of metal concentration in the aqueous solution with time (or pore volume infiltrated) is shown in Figure 19h.
Figure 19 Metal sorption on organic matter with the pore volumes infiltrated into the column (cell 1) a) Ca ($2.3 \times 10^{-3}$ M); b) Mn ($2.2 \times 10^{-6}$ M); c) Zn ($1.49 \times 10^{-6}$ M); d) Pb ($5.8 \times 10^{-8}$ M); e) Cu ($4.7 \times 10^{-8}$ M); f) Fe ($2.3 \times 10^{-6}$ M); g) pH profile; h) total aqueous solution composition. Model results were obtained for the total dissolved metal concentrations given in parenthesis and observed in the water feeding the peat from below.

Figure 20 shows a similar evolution of sorption fronts at the top of the column (cell 15), but occurring later in time, as indicated by a larger number of infiltrated pore volumes. Interestingly, it is seen that at the bottom of the column (cell 1; Figure 19) the sorbed amounts of Pb and Cu are lower by a factor of two than at the top of the column (cell 15; Figure 20), for example, at 2500 pore volumes. This is because the fact that Fe that is already sorbed on the organic matter at the bottom of the column (Figure 19f) and has expelled the Pb and Cu into the solution, while Fe has not yet reached the top of the column (Figure 20h). Thus, the model predicts that, during some time, the Pb and Cu sorption will be higher at the top of the column (Figure 19d,e). This is what was observed in the peat.

To analyse whether the Pb and Cu could pass the ochre layer and show a similar behaviour in the uppermost peat above the ochre, the sorption front evolution across cell sixteen, containing the amorphous ferric oxyhydroxide, was also assessed in the model. In general, the sorption of metals on the ferric oxyhydroxide was less important than the sorption on the organic matter (see Figure 18) for the metal sorption in the peat. Results of the dynamic simulations showed that the evolution of metal sorption fronts at the top of the column (cells 17-20) is determined mainly by the sorption of metals on the organic matter below the cell containing ferric oxyhydroxide. Thus, the sorption on the ferric
oxyhydroxide has no major effect on the sorption front evolution in the dynamic simulations. As the column was open to the atmosphere at the top (cells 16 - 20), the ferrous iron in the aqueous solution was oxidised by atmospheric oxygen and precipitated as ferric oxyhydroxide. This has the important implication that there is no Fe present in the solution to compete with the metals; thus, Pb and Cu are sorbed to their highest degree and not displaced by Fe.
Figure 20 Metal sorption on organic matter with the pore volumes infiltrated into the column (cell 15) a) Ca \((2.3 \times 10^{-3} \text{ M})\); b) Mn \((2.2 \times 10^{-6} \text{ M})\); c) Zn \((1.49 \times 10^{-6} \text{ M})\); d) Pb \((5.8 \times 10^{-8} \text{ M})\); e) Cu \((4.7 \times 10^{-8} \text{ M})\); f) Fe \((2.3 \times 10^{-6} \text{ M})\); g) pH profile; h) aqueous composition. Model results were obtained for the total dissolved metal concentrations given in parentheses and observed in the water feeding the peat from below.

To summarise, the dynamic model predicted that Pb and Cu are sorbed at higher amounts on organic matter in the uppermost peat layer, above the ochre, than in the lower peat, and this agrees with the observations in the peat. The lower amounts of Pb and Cu sorbed in the lower peat layer are explained in the model by Fe competition during the sorption on organic matter. Sorption on the ferric oxyhydroxide was found to have no pronounced effect on the evolution of the metal sorption front along the peat profile over time.

5.6 Conclusions

The predicted sorption of metals on the organic matter modelled using a simplified quantitative model approach and independently obtained data explained the observed sorption of metals in the Oostriku peat quite well. This indicated that our model might be generally useful for predicting the sorption of metals in peat and similar environments e.g. MSW deposits. The model predicted no pronounced effect on metal sorption on ferric oxyhydroxide in the peat, even though ochre constituted up to 40 wt-% of the total matter.

The dynamic model predicted that Pb and Cu would be sorbed to the greatest extent on the organic matter in the uppermost peat layer, in agreement with the observations at the
Oostriku peat bog, where no Fe was present in pore water to compete with sorbed metals, as all the ferrous iron was oxidised and precipitated as ferric oxyhydroxide.

As shown by the model, all the ferrous iron was oxidised and precipitated as ferric oxyhydroxide in the peat when the upwelling water encountered atmospheric oxygen. Either Pb or Cu were likely to precipitate in the peat as discrete, pure secondary solid phases, however, Mn, Zn, and possibly Pb might be coprecipitated with ferric oxyhydroxide in the peat as suggested by the results of the sequential extraction.

The general good agreement between the model results and independent observations made at the Oostriku peat bog suggest that our relatively simple model approach might be generally useful for assessing other peat sites and similar applications.
6. Discussions and overall conclusions

This thesis work was aimed to describe the long-term retention processes of heavy metals in a peat bog through field studies and modelling where a simplified quantitative approach and independent data were used, and predicted results were compared with independent observations made at the Oostriku peat bog (central Estonia). The Oostriku peat bog has been exposed to a metal-rich groundwater discharge over a long period of time and was found to have accumulated high concentrations of Fe, other heavy metals (Cu, Pb, Zn, Mn, Ni, Cd, etc) and As.

The Oostriku peat bog was characterised in detail with respect to metal depth distribution and the main metal-binding mechanisms. The uppermost peat layer and the underlying ochre layer (accumulation of ferric oxyhydroxide) were found to be the main geochemical barriers accumulating heavy metals in the peat bog (Syrovtenik et al., 2004, 2005b). A sequential extraction procedure made it possible to differentiate between the metals weakly bound with the peat and the metals strongly bound within the peat. Iron was found to occur mostly as amorphous iron oxide in the peat. This iron oxide was also the dominating binding agent for the metals Pb, Zn, and Mn that can be coprecipitated or strongly adsorbed being incorporated within the mineral phase. Copper was the only metal that was strongly bound to organic matter at an appreciable amount, although a considerable amount of Cu was also strongly bound to ferric oxyhydroxide. The major fraction of Ca and minor fractions of Pb, Zn, and Mn were relatively weakly bound with the peat by sorption on ferric oxyhydroxide and on solid organic matter.

Metal accumulation in the Oostriku peat bog was found to be localised to an area surrounding a spring at the peat site known to contain heavy metals in considerable amounts in its water. The water emerging in the spring at the peat site and peat pore-water were analysed with regard to their compositions. It was hypothesized that the water feeding the peat from below has the same origin as the water emerging in the spring. The peat pore-water results showed reasonably good agreement with the results of the spring-water analysis, supporting the hypothesis.
The oxidation of metal sulphides in the surrounding carbonate bedrock was hypothesized to be the long-term source of heavy metals in the water emerging in the spring and the water entering the peat from below. The dissolution sequence of the sulphide minerals and evolution of the water composition along a flowpath in the carbonate rock over time was modelled, and the simulated water composition was compared with the observed water emerging at the peat site. The simulated water composition remained constant over time as long as no sulphides had been depleted. However, when one or more minerals were depleted and secondary minerals formed and disappeared again along the flowpath, the composition of the water changed considerably. The solubility of metals in the water was controlled mainly by carbonate phases when sulphides have reacted, and in the presence of oxygen by oxide phases (Fe(OH)$_3$ and MnO$_2$).

The concentrations of major elements such as Ca and S were found to be in good agreement throughout the simulation with the observed concentrations in the water emerging in the spring at the peat site. This suggests that the water in the spring can originate from the carbonate rock and may have done so for a very long time. The simulated concentrations of trace elements varied considerably and, by closest, differed by an order or more from the observed concentrations. The actual mineral composition of the minor minerals along the flowpath in the rock is unknown. Furthermore, it is possible that more than one flowpath carries water to the spring and the spring water is a mixture of waters from several flowpaths. Different flowpaths, with different pore volumes infiltrated, may, therefore, have different water compositions. In this case, mixture of waters with these different compositions thus could explain the water composition entering the peat from below.

Although, the concentrations of the heavy metals in the spring water were found to be only slightly above the environmental standards, the long-term infiltration of metal-containing water into the peat could lead to an extremely high accumulation of metals through precipitation of ferric oxyhydroxide and metal attenuation by sorption on solid organic matter and newly formed mineral phases e.g. ferric oxyhydroxide.

The retention of metals transported by water through the peat was assessed by modelling equilibrium sorption on solid organic matter (humic substances) and amorphous ferric oxyhydroxide using a simplified quantitative modelling approach and
independently obtained data. Metal sorption onto the peat was considered to be an important binding process, preceding other, stronger binding mechanisms. The predicted sorption of metals on the organic matter explained the observed sorption of metals in the Oostriku peat quite well. The modelled sorption on ferric oxyhydroxide had no pronounced effect on metal sorption in the peat. This indicated that our model might be generally useful for predicting the sorption of metals in peat and similar environments where organic matter has degraded to humic substances, e.g. municipal solid waste deposits.

The dynamic evolution of metal sorption fronts along a peat profile over time was assessed with the model to test metal-metal competition effects on Pb and Cu sorption. Consistent with the independent observations made at the Oostriku peat bog, the model results showed that Pb and Cu were sorbed to the greatest extent on the organic matter in the uppermost peat layer, above the ochre layer, since no Fe was present in the peat pore-water to compete with the sorbed metals for the sorption sites, because oxidation and subsequent ferric oxyhydroxide precipitation removed the Fe from the aqueous solution. Iron out-competing these metals with time explained the observed lower degree of sorption of the metals in the lower peat layer.

The possible formation of ferric oxyhydroxide was assessed with the model showing that all the ferrous iron transported with water is oxidised and precipitated as ferric oxyhydroxide in the peat when it encounters atmospheric oxygen. Either Pb or Cu were likely to precipitate in the peat as discrete, pure secondary solid phases, however, Mn, Zn, and possibly Pb might be coprecipitated with ferric oxyhydroxide in the peat as suggested by the results of the sequential extraction.

In conclusion, the general good agreement between models results and independently made observations at the Oostriku peat bog suggests that our relatively simple model approach has a capacity to describe major sorption properties and thus may be generally useful for assessing other peat sites and similar applications.
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