Wetlands as a Means to Reduce the Environmental Impact of Mine Drainage Waters

Åsa Sjöblom
Linköping Studies in Arts and Science

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Department of Water and Environmental Studies

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Cover: The wetland downstream from the sampling station Rökå (6313) in September 1999. The alchemists’ symbols for water, earth, copper and iron.

To whom it may concern.

*Count the stars in the sky.*
*Measure the waters of the oceans with a teaspoon.*
*Number the grains of sand on a seashore.*
*Impossible, you say.*

Samuel M. Johnson
This thesis is based on the following papers, which will be referred to in the text by their Roman numerals:


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1. INTRODUCTION

In many mining regions of the world, pollution of surface water and groundwater by drainage from mines and mining waste poses either a serious threat to the environment, or a severe environmental problem. During the last two and a half decades, treatment of mine drainage waters in constructed and natural wetlands has emerged as an alternative to more conventional methods to handle the problem. In this thesis, wetland treatment of mine drainage waters will be examined from a biogeochemical, and partly also from a socio-economical, perspective.

The purpose of this section is to provide a context and a background to the studies presented in the thesis. A special emphasis will be given to mine drainage waters. The causes (Section 1.2.4) and the consequences (Section 1.2.5) of such waters will be outlined, along with alternative methods to handle the problem (Section 1.3). A number of concepts related to metals and mining will be introduced and defined. The section begins with a quick look into the role that metals and the mining industry play in Sweden and the rest of the world.

1.1. Mining and Society

1.1.1. Use of Metals

**Metals** are elements that have metallic luster, are easily malleable, and have good conductance (Naturvårdsverket, 1993). This already gives some clues as to their versatility. In fact, metals have been integrated into our everyday life to such an extent, that it is almost difficult to imagine how we would manage without them. Metals may also be ‘hidden’ in, for instance, buildings or additives to paint and plastics. In the end, it is our own desire for these products that is the driving force behind the mining industry.

Arsenic (As), cadmium (Cd), calcium (Ca), copper (Cu), iron (Fe), lead (Pb), and zinc (Zn) are the metals in focus in this thesis. As is a metalloid, but for the sake of simplicity, it will be referred to as a metal. Since they occur in comparatively low concentrations in the crust of the earth, metals such as Cd, Cu, Pb, and Zn are often referred to as **trace metals**.

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1 This reflects an ambition of the author that researchers from other disciplines shall be able to read, and understand, what is written in the thesis.
2 For easy reference, bold italics will be used when defining an important word or concept.
3 Throughout the text, a term (related to metals, minerals, and mining) that is followed by a dagger will be given a Swedish translation in Appendix 1.
Cu, Pb, and Zn are the metals that have been and still are mined at the selected field site, the Kristineberg mine in the County of Västerbotten, northern Sweden (Boliden, 2003). Since these metals are less expensive than some of the others on the world market (462-1698 US$/ton March 3; The London Metal Exchange Limited, 2003), they are often referred to as *base metals*. The Kristineberg mine also produces silver (Ag) and gold (Au) (Boliden, 2003). Ag and Au are often referred to as *precious metals* (148 and 11 109 US$/kg\textsuperscript{1} March 3; Kitco Inc., 2003).

Lohm et al. (1997) have made an extensive survey of the use and accumulated amounts of a number of metals in Stockholm, the capital of Sweden. From it we learn that Cu is used in, for instance, electric equipment, cables, and plumbing (partly as brass\textsuperscript{2}, an alloy\textsuperscript{2} between Cu and Zn). Pb is used in cables, plumbing, batteries, et cetera. For instance, Zn is used in plumbing (as brass) and to prevent corrosion. Cd is often found as an impurity in Zn. It has been, and still is, used mainly in batteries, and as a stabilizer in plastics.

As and Fe are discussed in the thesis because they are present in the bedrock at the field site, both at the Kristineberg mine and in the surrounding catchment area. Ca is discussed in the thesis because slaked/hydrated lime\textsuperscript{3} (Ca(OH)\textsubscript{2}) is used to treat the drainage at the mine.

### 1.1.2. Mining in Sweden, a Part of a Globalized World

In Sweden, mining operations have been carried out for more than 1000 years (Malmsten, 1993; Naturvårdsverket, 1998; Gustafsson et al., 1999). During the Middle Ages, mining of Cu and Ag in the mines in the mining district in Bergslagen was an important prerequisite for the social and cultural development of the country (Nationalencyklopedin, 1992; Malmsten, 1993; Ek et al., 2001). For many centuries, Sweden was one of the main suppliers of steel, Cu, and Ag to Central Europe, and in the 16\textsuperscript{th} and 17\textsuperscript{th} centuries the mine in Falun was the largest Cu mine in the world (Malmsten, 1993; Gustafsson et al., 1999; Ek et al., 2001).

Today Sweden is still one of the major mining countries within the European Union (EU). In 2001, 93\% of the Fe, 60\% of the Ag, 42\% of the Cu, 41\% of the Pb, 26\% of the Au, and 23\% of the Zn that was produced within the EU was produced in Sweden (Svenska Gruvföreningen, 2003). Other important metal mining countries within the EU include Finland, Ireland, Portugal, and Spain (ibid.). Australia, Brazil, Canada, Chile, India, Russia, and South Africa are other major metal mining countries in the world (Naturvårdsverket, 1998).

\textsuperscript{1} Recalculated from the London prices, originally stated in cents (Ag) or dollars (Au) per troy oz (31.1 g).
The mining industry in Sweden constitutes only 1% of the market value of the total industrial production (ibid.). Still, there are regions, especially in the northern part of the country, where mining constitutes the backbone of the local industry.

Between 1993 and 1996, the privately financed prospecting activities in Sweden doubled (Naturvårdsverket, 1998). Annually, 250 million Swedish crowns (SEK\(^1\)) are invested in prospecting in Sweden (Weihed, 1999). It is likely that parts of these activities will result in the opening of new mines. However, a conflict may arise between goals related to development, and goals related to the environment. For instance, the Swedish environmental quality objectives (miljömålen) include good-quality groundwater, flourishing lakes and streams, thriving wetlands, natural acidification only, a magnificent mountain landscape, and a non-toxic environment (Statistiska Centralbyrån and Naturvårdsverket, 2000). As will be discussed in some more detail (Sections 1.2.3-1.2.5), all of these goals are potentially threatened by mining activities, unless preventive measures are taken. If the costs associated with these measures become too large, it may be difficult for the Swedish mining industry to compete on the global market (cf. Aubertin et al., 1997). Thus, cheaper treatment methods are, or will become, a competitive advantage.

The above also raises the question if the mining industry in Sweden has a future, and whether this is a problem or not. If mining activities were to stop altogether, it is most likely that the number of people employed in the mining and metal industries would decrease. In Sweden, this is a question of approximately 140,000 persons (Naturvårdsverket, 1998). Furthermore, the potential environmental impact from mining and mining waste does not necessarily end with the mining activities (ibid.). One must also ask if Sweden will manage its demand for metals solely by increased recycling, or if the country will have to import more metals from other countries. If that is the case, will this be to the benefit of the environment?

The effects of mining are often comparatively localized in comparison to, for instance, the effects from the burning of fossil fuels. Thus, one may create a better environment within the borders of a nation by importing the metals needed. However, when the global environment is considered, the best option is probably a trade-off between mining the highest grade ores\(^1\), the ores that are situated as close as possible to the place where the metals are to be used, and the ores where the waste products generated will be the most harmless and/or taken care of properly.

\(^1\) For the reader’s convenience, a list of some of the abbreviations and acronyms used will be given in Appendix 2.
A sustainable development “meets the needs of the present without compromising the ability of future generations to meet their own needs” (The World Commission on Environment and Development, 1987). The important role that metals play in the industrialized world has already been mentioned, and it can be assumed that they will play a more prominent role also in developing countries in the future. Unless we are planning to redistribute parts of the world stock of refined metals, these needs will probably have to be satisfied by more mining activities. There are also examples of how the mining industry has played an important part in the development of a country, Sweden (previous Section) is but one example. For instance, income, infrastructure, and education associated with mining activities may be beneficial for future development in an area (McCommon et al., 2001; see also Struthers, 2001).

Having touched upon some of the developmental aspects, we may ask if mining can contribute to a sustainable development, and indeed if mining as such can be considered to be sustainable. The first of these issues has been investigated in considerable detail in the ‘Mining, Minerals and Sustainable Development project’, the final report from which has recently been published (International Institute for Environment and Development and World Business Council for Sustainable Development, 2002). Mining at a particular site generally undermines the possibility for future generations to mine there for the same commodities, but this does not necessarily mean that future generations will not have any access to the resource itself. For some resources, such as metals, this is mainly a question of a sound resource management. Being elements, metals are not destroyed upon usage, but they may be spread out into the environment, or incorporated into less useful products. Thus, in a sense, the metal related industries could pose claims that parts of their activities are sustainable.

However, since mining activities are sometimes of relatively short duration, it is important to ensure that they do not compromise the future use of other resources in the same area, especially from the perspective of a sustainable development. Some of the resources in the area, apart from the ore, will always be lost following mining. These include large-scale modifications of the landscape as a result of surface mining\(^1\) and/or the disposal of waste products (Section 1.2.3; cf. Marcoux, 2001). Other resources in the area may, at least partly, be protected by the use of proper prevention and/or treatment techniques (Section 1.3). Thus, improved methods to handle mining waste, and drainage originating from mines and mining waste, may also be beneficial in the global transition to sustainable development.
1.2. Waste and Environment

1.2.1. Occurrence of Metals

There are a few elements that may occur in their elemental form in nature. Among the metal(loid)s, these native elements include Ag, As, Au, Bi (bismuth), Cu, Hg (mercury), Pt (platinum), and Sb (antimony) (Pellant, 1995). All other metals are only found in association with other elements.

The average crustal abundance tells us how common a certain element is. Al, Fe, and Ca are the most common metals in the crust of the earth (Benjamin and Honeyman, 1992). A mineralization is a site where the concentration of one or several metals is significantly higher than the average crustal abundance. Where the location and composition of the mineralization make mining economically feasible, with respect to the world market prices of the metals, we have an ore (Naturvårdsverket, 1998; Weihed, 1999).

1.2.2. Means of Extraction

Ore is mined in surface (Figure 1.1) or below ground operations. Often the ore first has to be uncovered by removing the surrounding waste rock†. In Sweden, the mining companies mine mainly for iron ore and sulfidic ore (Nationalencyklopedin, 1992; Malmsten, 1993; Naturvårdsverket, 1998). For reasons that will be discussed in Section 1.2.4, the mines in focus of this thesis are those that extract coal, uranium (U), and sulfidic ore. Above all, the sulfidic ore is mined for its contents of base and precious metals.

The sulfidic ore is processed in a concentrator†. The process may include crushing, grinding, gravimetric separation of Au, and flotation. Flotation is the use of specifically designed chemicals, which will cause the metals to flow on top of the suspension of ground ore (Malmsten, 1993).

Sometimes the treatment process include a step in which sodium cyanide (NaCN) is added, in order to increase the recovery of Au (Eisler et al., 1999). Microorganisms may also be employed in order to increase the recovery of the metals, to treat ores whose composition makes them difficult to treat in the ordinary process, or even as an alternative mining method (Poulin and Lawrence, 1996).

The product from the concentrator, the metal concentrates, is transported to smelters† for further treatment. Thus, the mining industry does not produce metals, but metal concentrates. A typical metal mine uses more water by weight...
in production of the metal concentrate than the weight of the ore grade material itself (Allan, 1997).

Figure 1.1. Parts of the former pit at the Kristineberg mine.

1.2.3. Mining Waste

The two kinds of ore that are mined in Sweden today give rise to two kinds of waste products with very different characteristics. Swedish iron ore basically consists of hematite† (Fe₂O₃) and magnetite (Fe₃O₄) (Lundegårdh, 1991). Thus, the waste products generated from the extraction of Fe are relatively inert when deposited above ground. Consequently, the most pressing environmental issues related to this kind of waste seem to be the enormous quantities generated, and how to restore the landscape once it has been deposited (Figure 1.2). It is estimated that approximately 380 million tons of the Swedish mining waste come from the extraction of iron ore, and that another 14 million tons are added
annually (the figures refer to the situation in 1996; Naturvårdsverket, 1998). As a comparison, approximately 3.2 million tons of domestic waste are generated each year (ibid.).

Figure 1.2. The waste piles at LKAB’s mine in Kiruna, Sweden – giving the Swedish metaphor ‘avfallsberget’ (the mountain of waste) its proper dimensions. Note that these piles contain waste from the extraction of iron ore and thus pose far less risk to the environment than waste from the extraction of sulfidic ores.

Waste from the extraction of iron and sulfidic ores can be divided into waste rock and tailings†, which is the waste product from the concentrators. It has been estimated that 18 billion m³ of mine tailings are generated worldwide, every year (Förstner, 1999). This is of the same order of magnitude as the discharge of sediments to the oceans (ibid.). In Sweden, there are approximately 250 million tons of waste rock and 400 million tons of tailings from the mining of sulfidic ores (Naturvårdsverket, 1998). An additional 13 million tons (waste rock) and 22 million tons (tailings) are added each year (ibid.). Apart from problems related to deposition, sulfidic mine waste may also give rise to acid mine drainage (next Section).

Waste rock is either deposited or used for construction purposes. It ranges in size from dust to boulders (Malmsten, 1993; Naturvårdsverket, 1998). Waste rock surrounding sulfidic ore also tends to have a lower content of pyrite‡ (next Section) than the tailings. Tailings are either used as backfill in the mine or they are deposited. They consist of mineral particles with a size ranging from 1 µm –
1 mm (Paktunc, 1999). Older means of extracting metals from the ore gave rise to a coarser waste product, ranging in size from 100-200 mm (Naturvårdsverket, 1998). It is interesting to note that, in Sweden, some of these older deposits have been classified as ancient monuments (ibid.). The grain size and the composition of the mining waste are important factors to consider when trying to predict the characteristics of future drainage waters (Paktunc, 1999).

1.2.4. Acid Mine Drainage

Mining exposes minerals in host rock and ore to ambient air and moisture, both in the mine itself and upon disposal of waste rock and tailings. A number of minerals associated with ores formed under anoxic conditions, such as those containing coal, uranium, and sulfides, are thermodynamically unstable in this new environment. The typical example of such a mineral is pyrite (FeS_2). In FeS_2, both the Fe and S atoms may get oxidized;

\[
2 \text{FeS}_2(s) + 7 \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{2+} + 4 \text{SO}_4^{2-} + 4 \text{H}^+ \quad \text{(Eq. 1.1)}
\]

\[
4 \text{Fe}^{2+} + \text{O}_2(\text{aq}) + 10 \text{H}_2\text{O} \rightarrow 4 \text{Fe(OH)}_3(s) + 8 \text{H}^+ \quad \text{(Eq. 1.2)}
\]

(Jacks, 1976; Banks et al., 1997). The resultant drainage water will contain sulfuric acid (H_2SO_4), and a mixture of ferrous Fe\(^{2+}\) (Fe\(^{2+}\)) and ferric Fe\(^{3+}\) (Fe\(^{3+}\)) species. The speciation (Section 1.2.6) of the Fe will be determined mainly by the redox potential and pH of the system. Fe\(^{3+}\) may act as an oxidizing agent instead of oxygen (O_2) in Eq. 1.1 (Singer and Stumm, 1970). Thus, oxidation of FeS_2 may occur even in the absence of O_2 if such oxidizing agents are already present in, or transported to, the system. Metal sulfides other than FeS_2 are commonly associated with above-mentioned mines, in particular with base and precious metal mines. These sulfides will undergo oxidation similar to that described in Eq. 1.1, with release of the constituent metal/s. Furthermore, the solubility of many other minerals is greatly increased in the acidic environment that will result from these oxidations.

The drainage water that is formed by combining the reactions outlined above is commonly referred to as acid mine drainage (AMD). Sometimes the term acid rock drainage (ARD) is used instead. Apart from preferential use of one term or the other by interested parties, or in different countries, this reflects a growing awareness that natural weathering processes may also give rise to drainage waters that are more or less indistinguishable from those that have anthropogenic origins. This is especially the case in mining regions, where the bedrock tends to be more highly mineralized (Alpers and Nordstrom, 2000). This in turn has important implications both for what waters that can be considered to be
polluted, and what restoration goals that are realistic to achieve (Runnells et al., 1992; Alpers and Nordstrom, 2000).

In this thesis, the term AMD will be used, since the primary topic is how to treat polluted drainage originating from mines and mining waste. It should be noted that, before it reaches the surrounding environment, the acidity and metal content of the AMD are sometimes reduced upon contact with weathering products originating from nearby buffering minerals (Hedin et al., 1993; Banks et al., 1997). Such drainage waters, as well as treated AMD, will also be considered.

1.2.5. Environmental Impact

Untreated AMD that escapes to nearby surface waters and groundwater may act as a significant point source for acidification and metals, often with negative impact on affected biota (e.g. Besch and Roberts-Pichette, 1970; Cherry et al., 2001). Too high concentrations of metals give rise to toxic effects, but the Fe in AMD may also cause physical damage and habitat destruction by precipitating and forming dense, rust colored layers on the bottom of the water courses (Hedin et al., 1993; Hellier et al., 1994; Cherry et al., 2001). These precipitates are sometimes referred to as *ochre* or ‘yellow boy’.

The impact that the AMD has on the environment may vary over the year due to, for instance, a seasonal variation in the proportions between the AMD and recipient waters mixed (cf. Paper III). AMD may also have a devastating impact on reproduction and younger life stages of certain organisms, which tend to be more sensitive than the adult ones (cf. Naturvårdsverket, 1999). Such younger life stages are often present during spring.

Even though the effects of AMD are often comparatively localized, the AMD problem is global (Allan, 1997). It has been described from all continents except Antarctica, where no mining has taken place. Furthermore, although its effects are often localized, AMD may still pose an important national or regional environmental problem. For instance, it is estimated that 64% of the Zn, 44% of the Cu, and 42% of the Cd released to Swedish waters each year come from mines and mining waste (Statistiska Centralbyrån and Naturvårdsverket, 2000), and that 10 370 km of streams in the Mid-Atlantic and Southeastern United States (US) are acidic due to, or strongly impacted by, AMD (Herlihy et al., 1990).

In recent years, attention has been called to the fact that, in present day Sweden, the annual amount of a number of metals released to the environment from consumer products (consumption emissions) are greater than those released
when these products are produced (production emissions) (Bergbäck, 1992). Parts of the explanation to this phenomenon is to be found in an improved control of the production emissions (cf. Statistiska Centralbyrån and Naturvårdsverket, 2000). Unfortunately, the amount of metals released from the Swedish mine waste deposits has been estimated to increase tenfold until the year 2100 if no further action is taken (Malmsten, 1993; Naturvårdsverket, 1993; Naturvårdsverket, 1998; Gustafsson et al., 1999).

1.2.6. Metal Ecotoxicology and Speciation

In an environmental context, metals are most often thought of as potentially toxic pollutants. For instance, an essential metal ion may be replaced by a non-essential element with similar chemical properties (Brooks, 1983; Sigg, 1987). A metal may also block essential biological functional groups of biomolecules (e.g. active sites of enzymes), or modify the active configuration of biomolecules (ibid.). However, some metals, such as Cu, are also essential for most living organisms (Naturvårdsverket, 1993). This means that both too low and too high concentrations of certain metals may be harmful.

Apart from situations where for instance aluminum (Al) precipitates on the gills of fish (Bertills and Hanneberg, 1995), metals generally have to be taken up by the living organisms in order to inflict harm. This puts the concept of bioavailability in focus. It is the bioavailable fraction of the metals, rather than the total amount of metals present, that determines the concentration of metals in the organisms (cf. Hall and Pulliam, 1995; Jackson and Bistricki, 1995; Jackson, 1998).

The bioavailability of metals is tightly coupled to metal speciation. In the aquatic environment, the metals may be found either in dissolved or particulate forms. Filters are often used to separate the two fractions. However, a closer inspection of the filtrate by other analytical methods may reveal that smaller particles are still present. Thus, in the case of filtration, it is often more accurate to talk in terms of the pore size, or cut-off, of the filters employed, than to state that a substance is ‘dissolved’. Truly dissolved metal species include free (hydrated) metal ions (e.g. Cu$^{2+}$), inorganic complexes (e.g. CuCO$_3$), and organic complexes (e.g. Cu bound to dissolved humic substances) (Stumm and Morgan, 1996). Free metal ions are generally considered to be the most bioavailable (Sigg, 1987).

Metal speciation influences not only the bioavailability of the metals, but also how they are transported. In an aquatic environment, it is often of great interest to be able to distinguish between particles that are large enough to settle (gravitoids), and those that are not (colloids) (Gustafsson and Gschwend, 1997;
cf. Kimball et al., 1995). Again, filters are not perfect, since in order to settle, the particles have to be not only large, but also dense enough.

Metals recovered in particulate forms (Sigg, 1987) may be incorporated in mineral lattices in the particles themselves. Such particles are generally the result of erosion processes, or that the solubility products of certain minerals have been exceeded, which has caused previously dissolved metals to precipitate. Particulate metals may also be associated to the surfaces of particles by means of adsorption (Section 4.4.2). Metals that have been taken up by bacteria and plankton constitute yet another kind of particulate metals.

Here it should be emphasized that even though free metal ions are considered to be the most bioavailable, particles may in fact increase the amount of metals that certain multicellular organisms are exposed to. A typical example of this would be a filter feeder such as a mussel, but even grazing animals, such as snails, can be affected (Goulet et al., 2001). In order for this to happen, the metals will first have to be transferred to dissolved forms upon passing through the animal’s gut (cf. Lawrence et al., 1999). This illustrates another important point, namely that living organisms may have a large impact on the bioavailability of metals in their surrounding environment.

1.3. Prevention and Treatment

1.3.1. Prevention...

The problems with AMD may be handled either by preventing its formation in the first place, or by treating the drainage waters (Sections 1.3.4-1.3.5). Prevention is generally considered to be the best approach. There are also some advocates of maximizing the weathering of the waste rock and tailings during the time of operation of the mine, when the generated AMD can be treated under controlled circumstances, leaving a more stable solid waste. This approach may be the best option in a highly sensitive environment where the integrity of the prevention or treatment system cannot be satisfactorily guaranteed, or where the locally available resources favor treatment instead of prevention, but otherwise prevention seems to be the far better option from a resource perspective.

Different means to prevent the formation of AMD include reduced mining activities, location of the mine sites, water management, and waste disposal. The number of alternatives available depends on whether past, present, or future mining activities are considered. For instance, ceasing all mining activities today will have little impact on the formation of AMD from old mines and mining waste. In fact, since the environmental impact from active mines often is lower than that from abandoned or inactive mines (Naturvårdsverket, 1998), this may
even have a negative impact on the environment. A viable mining industry may also be the best guarantee that there is enough money to reclaim† old sites.

Another example is that sometimes after the closing of a mine, it is realized that remediation of the site would have been cheaper and easier if it had been planned already at the onset of the mining activities (Kalin, 1989 and 1997). There is a great potential to avoid such problems in the future by applying state-of-the-art knowledge in environmental impact assessments (EIA) and management plans. Baseline investigations are often undertaken as a part of an EIA (e.g. Rönnblom Pärson and Ljungberg, 2001). The purpose of such investigations is to determine the levels of metals in the vicinity of a planned mine, so that any future changes can be detected.

The personal consumption of metals may be reduced by increased public awareness, leading to changes in attitudes, and by finding suitable substitutes to metals. Taken together with improved recycling and improved means of metal extraction, this could reduce future needs for mining. However, it is important to take the environmental impact of the alternatives into account too, so that the problems are not just moved to another sector.

1.3.2. ...by Mineralogical and Hydrological Considerations

Sometimes a mining company has the opportunity to choose between a number of alternative sites for their new mine. At some of these sites, the ores and surrounding rocks may contain enough buffering materials to neutralize the AMD, thereby also reducing its metal content, before it reaches the recipient (cf. Banks et al., 1997). An additional advantage of this is that the buffering material is mined along with the ore, and that it does not have to be mined elsewhere and transported to the particular site, saving landscape features and energy for transport. A review of issues relevant to characterize mine wastes for the prediction of AMD is given in Paktunc (1999).

Water management may include concentrating mining activities to certain catchment areas, avoiding placing tailings impoundments on water divides, and redirecting water flows through the mining area, minimizing the volume of water transformed to AMD, and the volume that will require treatment (Kalin, 1989 and 1997; Skousen and Foreman, 2000). Site hydrology may also govern if the AMD formed will affect primarily the surficial vegetation or the groundwater (Carlson and Carlson, 1994).
If it is likely that the mining waste will generate AMD that is not neutralized before it reaches the surroundings, buffering materials may be added to the waste (Malmsten, 1993; Naturvårdsverket, 1998). Since ferric Fe will form sparingly soluble precipitates with phosphate (PO$_4^{3-}$), addition of PO$_4^{3-}$-containing materials may also act to reduce the metal load to the surroundings (Renton et al., 1988). Alternatively, waste with a higher acid generating potential may be taken care of separately, reducing the requirement for buffering materials and/or covers (see below) for the bulk of the material (Malmsten, 1993; Naturvårdsverket, 1998). Finally, the weathering rate may be reduced by application of bactericides (Watzlaf, 1988) or covers.

Figure 1.3. A model of the soil cover applied at the former uranium mine in Ranstad, Sweden.
Generally speaking, mining waste covers can be divided into soil and water covers. Soil covers† aim at reducing the infiltration of precipitation, and the transport of oxygen, through the waste (cf. Eq. 1.1). A soil cover often consists of at least one tight sealing layer† (e.g. clay) and a protective layer† (e.g. till†) aimed at maintaining the integrity of the sealing layer (Figure 1.3). For a more thorough description of the construction of soil covers, refer to, for instance, Malmsten (1993), Naturvårdsverket (1998), and Gustafsson et al. (1999). One of the major problems with soil covers is to protect their integrity, so that they will function as planned for hundreds or thousands of years.

Since the diffusion of oxygen in water is 10 000 times slower than in air (Malmsten, 1993; Davé et al., 1997), a water cover† will also reduce the amount of oxygen that the waste is exposed to. As the name implies, a water cover involves submergence of the waste (Figure 1.4). The major problems with water covers (if man made reservoirs are employed) are to ensure dam stability and water saturation (cf. Aubertin et al., 1997; Ljungberg, 1999; Martin et al., 2001). Some concerns regarding weathering via galvanic interactions (Kwong, 2001), and elements that may be more mobile under reducing conditions, such as barium (Ba) and radium (Ra) (Banks et al., 1997) have also been posed.

![Figure 1.4](image_url)  
*Figure 1.4. Impoundment 4 at the Kristineberg mine, April 2000. Here the water cover also serves as a settling pond for precipitates formed when treating runoff and drainage water from the mine area. The impoundment is covered with ice and snow.*
Old weathering products (i.e. Fe$^{3+}$; cf. Section 1.2.4) may counteract parts of the positive effects of reclamation activities undertaken once a mine is closed down, such as covering of former tailings ponds, or filling abandoned mines with water (Malmsten, 1993; Naturvårdsverket, 1998). Therefore it is often emphasized nowadays that measures should be taken to reduce weathering already upon disposal. This may be achieved through sub-aqueous disposal in an artificial pond, nearby lake, or in the ocean (cf. water cover above). According to the 1996 protocol for the 1972 London Dumping Convention, ‘inert, inorganic geological material’ may be considered for dumping in the ocean (Ellis and Robertson, 1999). Since tailings after placement in the ocean may be considered to be such ‘inert, inorganic geological material’, this would open up for disposal in the ocean (ibid.). The advantage of disposal in natural systems is that their integrity is not threatened by a possible failure of a dike† (cf. Aubertin et al., 1997), but great care has to be taken so that the natural flora and fauna are not irreversibly harmed by the increased load of sediments (cf. Ellis and Robertson, 1999). Creeks and rivers are less suitable for disposal of tailings since they may carry the tailings further downstream (cf. Johns, 1995). Furthermore, the tailings may get oxidized in aerated waters.

### 1.3.4. Active Treatment

The most common method to treat drainage waters originating from mines and mining waste is to raise the pH of the water by adding, for instance, caustic soda (NaOH), soda ash (Na$_2$CO$_3$), lime (CaO), Ca(OH)$_2$, limestone (CaCO$_3$), or ammonia (NH$_3$) (Wieder, 1989; Stark, 1990; Hedin et al., 1993; Stark et al., 1994a). The raise in pH will cause precipitation of metal hydroxides and increased adsorption of metals cations (Section 4.4.2). Different metals require different pH in order to precipitate, which will affect the choice of chemical reagents.

Active chemical treatment as described above is generally efficient, but it is costly and requires regular maintenance. Another problem with this kind of treatment is the huge amounts of metal contaminated sludge generated. In extreme situations, the cumulative volume of sludge produced in the long-term can exceed the volume of stored tailings (Orava et al., 1995). In Sweden, the sludge is also classified as a mining waste (Naturvårdsverket, 1998). Active chemical treatment may occur either in open ponds or in treatment plants. In the case of treatment plants, it is sometimes possible to reduce the volume of sludge produced, for instance by applying the high-density sludge method (Orava et al., 1995). An additional problem with active chemical treatment is that the chemicals used may pose a hazard to the workers. Furthermore, liming may lead to artificially high pH levels in the receiving waters. This may result in alkaline deposits on streambeds that may inhibit aquatic life (Stark, 1990).
In an attempt to save chemicals, energy, and/or increase the possibility to recover metals from the waste products generated, many different treatment systems based on various biological processes and materials have recently been proposed (Brierley, 1990). These range from batch and fluidized bed-type reactors (Nakamura, 1988; Dvorak et al., 1991; Kalin, 1991) and re-usable adsorbents (e.g. BIO-FIX beads; Bennett et al., 1991) to harvesting of plant material and associated metals. Like any engineered system, such treatment systems will have to be maintained on a regular basis. For instance, unless present in the drainage water (cf. Kalin and Smith, 1997), nutrients must be supplied to microorganisms and plants. Furthermore, filters have to be regenerated, and plants must be harvested.

1.3.5. Passive Treatment and Walk-away-solutions

Weathering processes may go on for centuries after a mine has been closed, which makes the active treatment methods outlined above costly, long-term commitments. The situation gets especially problematic in remote areas that tend to be entirely abandoned after the closing of a mine. This has led to an increased interest in passive treatment methods.

“Passive technologies take advantage of natural chemical and biological processes that ameliorate contaminated water conditions. Ideally, passive treatment systems require no input of chemicals and little or no operation and maintenance requirements.” (Hedin et al., 1993).

Reactive barriers, anoxic limestone drains (ALDs), successive alkalinity producing systems (SAPS), and wetlands are among the treatment methods that are often considered to be passive. Reactive barriers (Blowes et al., 2001; Morales, 2001) are used to treat polluted groundwater. The barrier contains materials that will raise the pH and favor sulfate reduction (Section 4.4.6). Mechanisms of metal removal include precipitation (both as oxides and sulfides) and adsorption to the bulk material. The groundwater is directed through the barrier by creating preferential flow paths. ALDs, SAPS, and wetlands will be described in more detail in Section 4.

The ultimate aim is to find passive treatment systems that will work as long as needed without requiring any maintenance. Such systems are usually referred to as walk-away-solutions. Certain kinds of covers may also be considered to be walk-away-solutions. However, according to Aubertin et al. (1997) it does not appear to be realistic to walk away completely from water covers without ensuring proper care of any man-made reservoirs.
1.3.6. Legislation, Certification, and Prizing

In many countries, an increasing awareness of environmental problems caused by anthropogenic activities led to the establishment of environmental protection agencies, and the passing of environmental protection laws, in the late 1960’s. In Sweden, the Environmental Protection Act (miljöskyddslagen) was passed in 1969. In 1998, it was incorporated into the new Environmental Code (miljöbalken).

Darpô has interpreted the Swedish Environmental Code from the perspective of mining and mining waste, as well as how it relates to the Minerals Act (minerallagen) (Naturvårdsverket, 1998). It is interesting to note that storage of waste products is considered to be an ongoing activity that may be harmful to the environment. This means that the mining companies are considered to be the ones that are primarily responsible for reclaiming a site, even if no additional waste has been deposited after July 1, 1969. However, factors such as the need for environmental protection, the costs associated with reclamation, the time that has passed since the waste was deposited, and the demands for reclamation posed at the time of deposition, are also taken into account. Thus, parts of the costs for the reclamation of old sites will probably still be paid by the state. It is estimated that reclaiming the 27 most problematic mine waste deposits in Sweden would cost 790-1400 million SEK (ibid.).

Today mining companies in for instance Australia, Quebec (Canada), Sweden, and the US are obliged to set aside funds to cover at least a minimum of future reclamation activities (Wieder, 1989; Aubertin et al., 1997; Förstner, 1999; Gustafsson et al., 1999; Hellier, 1999; Marcoux, 2001). This approach poses a financial burden on the mining companies, but it also ensures that reclamation will take place even if the mining company would go bankrupt. If there is no money, no reclamation will take place, even if it is stated in the law.

Legislative measures are not the only way to combat possible environmental and societal problems related to mining. Certification that the metals in consumer products have been obtained with greatest possible care taken to the environment, the people living nearby, as well as the workers, is another approach. Furthermore, activities such as ‘the Global Mining Initiative’ (http://www.globalmining.com) show that there is an ambition within the mining industry itself to improve its somewhat tarnished reputation among environmentalists (Rönnbäck, 2001) and the general public.

It is puzzling to find that the prizes of many metals fall (Lomborg, 2001), while the most easily available, higher grade ores probably have been mined, at the same time as the cost for high-tech equipment, environmental protection, and
salaries probably have risen. Thus, it is possible that the world market prizes of metals do not cover their ‘true’ cost. If this cost is not paid by the consumers of the metals, it will be paid by the public in the mining regions (cf. Baker et al., 1991).
2. SCOPE AND AIM OF THE THESIS

This thesis is based on work that has been performed within the Swedish research program Mitigation of the Environmental Impact from Mining Waste (MiMi) (http://www.mimi.kiruna.se). Different methods to prevent the formation of AMD, as well as to treat it once it has been formed, are studied within this program. The aim is that this research will ultimately result in cheaper and more sustainable methods than the ones that are presently in use.

The overall objective of this thesis was to investigate the potential for using metal immobilization in wetlands as a complementary and/or sustainable method to treat AMD. The general case has been investigated by means of a literature survey, the results from which are presented in Paper VII, as well as in Section 4. The aim of the literature survey was to collect and synthesize previous experiences regarding the behavior of metals in wetlands. A special emphasis was put on wetland treatment of mine drainage waters.

A specific case, metal immobilization in wetlands situated along the river Vormbäcken, northern Sweden, has been examined by studying old monitoring data (Paper I), and by collecting surface water samples (Papers II-IV). Vormbäcken is the recipient of the treated drainage from the Kristineberg mine area. The aim of the introductory study presented in Paper I was to investigate whether the wetlands situated along Vormbäcken had any impact on river water chemistry, in particular if any metals appeared to be immobilized.

The aim of the field sampling campaigns was to quantify metal immobilization in the wetlands (Papers II and III), and to study any seasonal effects (Paper III). In order to be able to draw any conclusions regarding the mechanisms behind any immobilization, the metal speciation in the surface water samples collected was investigated by means of filtration and an ion exchange technique (Paper IV).

Since Fe appeared to have a large impact on metal speciation in the system (Paper IV), it was decided to study the role of Fe in more detail. More specifically, it was investigated whether Fe could be used in a complementary treatment system based on natural attenuation processes. A laboratory study, using authentic river waters, was carried out to test the hypothesis that the metal speciation patterns found along the river could be reproduced by adding small amounts of ferrous Fe, simulating groundwater inputs (Paper V). If this is the case, such a metal scavenging mechanism, followed by sedimentation in a downstream wetland, could well be incorporated as a final polishing step in a mine drainage treatment system based on natural attenuation processes. Seasonal
effects, as well as the role of particles and bacteria initially present, were also taken into account.

From a treatment perspective, it is interesting to know if addition of Fe from groundwater or surface water is the preferred design option. It was hypothesized that Fe precipitates in the river water, originating from discharging groundwater, are more efficient scavengers of trace metals than Fe precipitates supplied by the tributaries. The hypothesis was tested in a laboratory study based on synthetic river waters (Paper VI). The role of humic acid and particles initially present in the river water was also investigated. This is another important design consideration, since these factors determine in what waters the treatment method can be applied successfully.

The specific aim of this thesis was twofold. The first aim was to describe processes that act to immobilize metals in wetlands and to discuss factors that influence the efficiency and longevity of these processes, based on previous experiences from wetlands exposed to mine drainage waters. The second aim was to investigate whether processes occurring in natural wetlands situated along a mining region recipient could be used as a complementary treatment system for mine drainage waters.
3. MATERIALS AND METHODS

The work behind this thesis can be divided into two parts. The first part consists of a literature survey (Section 4 and Paper VII). The second part consists of a case study, which can be further divided into a study of old monitoring data (Paper I), sampling of surface water in the field (Papers II-V), and two laboratory experiments (Papers V and VI).

In this section, the materials and methods employed during the work will be outlined. This includes an overview of the studied field site (Section 3.2.2) and archival material (Section 3.3).

3.1. Literature Survey

The databases Environmental Sciences and Pollution Management (Cambridge Scientific Abstracts) and Science Citation Index (ISI Web of Knowledge) provided useful starting points in searching primarily the scientific literature. Other relevant literature was identified mainly through reference lists in the texts themselves. Bibliographies on wetland treatment of mine drainage waters can also be found in The Society for Mining, Metallurgy, and Exploration, Inc. (1998) and on the Internet, for instance at http://www.nal.usda.gov/wqic/Constructed_Wetlands_all/cwamd.html.

3.2. Field Site – Vormbäcken

3.2.1. Selection of Field Site

The work presented in this thesis has been performed as a part of a national research program. It was decided to focus the research effort to a single field site. The choice fell on the Kristineberg mine in the county of Västerbotten, northern Sweden (Lindvall et al., 1997; Figure 3.1).

When trying to estimate the longevity of certain man-made systems, it may be informative to look at similar natural systems, or so called natural analogues. For instance, natural analogues are often investigated when searching for safe methods to dispose of radioactive waste (Smellie et al., 1997). Natural wetlands that are or have been exposed to mine drainage waters may serve as natural analogues to constructed wetlands. While the oldest wetlands constructed for the treatment of mine drainage waters are less than 20 years old (Section 4), a natural wetland situated close to a mine may have been exposed to mine drainage waters for several hundred years. Metal immobilizing processes acting in natural wetlands merit additional interest when trying to establish wetland treatment systems that will require little or no maintenance.
Since the focus of the present investigations was to study wetlands as a complement to other treatment methods, it was desired to avoid water with too low pH and too high metal concentrations. Thus, it was finally decided to investigate metal immobilization in the natural wetlands surrounding the small river Vormbäcken, the recipient of the treated drainage water from the Kristineberg mine area. An advantage of this particular site is that Vormbäcken has been part of different environmental monitoring programs since the 1940’s (Section 3.3). The Swedish Geological Survey (SGU) has collected samples of peat† from the area for prospecting purposes. A number of more detailed investigations have also been carried out in the area.

3.2.2. Description of the Field Site

A detailed description of the field site is given in Paper III as well as in Brânin et al. (1976; see also Råberg, 2000). Here only some of the most important characteristics will be summarized. Photos from the area can be found on the front cover, as well as between the seven papers included in the thesis.

Vormbäcken is situated in the county of Västerbotten, northern Sweden (65°N). It is a secondary tributary to the river Umeälven, which flows into the Bothnian Sea at Umeå. The river (Figure 3.2) drains the lake system Sörsjön-Holmträsket-
Norrsjön (8 km²) and then flows for approximately 40 km before joining the river Vindelälven at Vormsele. The difference in elevation between Sörsjön-Holmträsket-Norrsjön and Vormsele is approximately 130 m. On its way through the catchment area, Vormbäcken flows through the lake Vormträsket (8 km²). The major tributaries to Vormbäcken are drainage from the lake Holmtjärn, and the rivers Kimbäcken, Svältamyrbäcken, Svartbäcken, and Rökån. The river system also contains a bifurcation, allowing parts of Vormbäcken to join Rökån.

Figure 3.2. Vormbäcken, its tributaries, and associated lakes. ‘Utskov’=spillway. From Paper II.

The catchment area of the river upstream from its confluence with Vindelälven is approximately 370 km². It is dominated by coniferous forests and mires. The soil is morain, and the bedrock is mainly composed of granite (Brånin et al.,
The mean annual precipitation in the area is 577 mm, and the mean annual temperature is 0°C (Eriksson and Dahlström, 1975; Brånin et al., 1976). The area is a part of the Skellefte mining district, which is one of the major mineralizations (complex sulfidic ores) in Sweden. Mining in the area around the Kristineberg mine started in the 1940’s. Today the mines at Rävliden, Hornträsket, and Kimheden have all been reclaimed. At the Kristineberg mine, the reclamation activities are run in parallel to the continued operation of the mine.

The AMD at the Kristineberg mine is treated with Ca(OH)$_2$. Earlier, when there was a concentrator at Kristineberg, the neutralization was generally performed with process water from alkaline flotation, which started in the early 1960’s (Brånin et al., 1976; Boliden, 1978). Apart from reducing the metal concentrations of the drainage water significantly, liming also gives rise to a recipient situation which is rather different from that usually studied in mine drainage water contexts (e.g. Chapman et al., 1983; Johnson, 1986; Ranville et al., 1991; Kimball et al., 1994; Kimball et al., 1995; Paulson and Balistrieri, 1999).

There are two major reasons why Vormbäcken still constitutes a relevant object for the studies presented in this thesis. The concentrations of a number of metals are elevated already at ‘the background station’, situated upstream from ‘the point source’, represented by the Kristineberg mine area (Papers II and III). This means that any immobilization of metals in the wetlands situated along the river would improve the quality of the water transported to areas downstream. Furthermore, release of water with elevated concentrations of Ca to recipients with elevated metal concentrations is likely to be common in many mining areas. So far, this phenomenon appears to have attracted comparatively little attention. To some extent, mixing of the river water with the treated drainage water resembles the situation encountered in estuaries. Immediately downstream from the Kristineberg mine area, the water actually contains similar amounts of Ca as seawater (Paper III; cf. Stumm and Morgan, 1996). However, since Ca$^{2+}$ is the major cation (positively charged ion) found in Vormbäcken, the salinity is still comparatively low.

Three major wetland areas were identified along the river. Between the sampling stations Aspliden and Timmervägen (330 and 300 m above sea level, respectively), the river flows in a channel lined by macrophytes such as reed (Phragmites australis$^1$) and sedges (Carex spp.). Between the sampling stations Rökå and Mickeldammet (both 280 m above sea level), the river meanders through a vast wetland dominated by sedges, reed, horsetail (Equisetum

$^1$ Swedish translations of genera and species are given in Appendix 3.
fluviatile), and cotton grasses (Eriophorum spp.). Between the sampling stations Brännfors and Vormsele, the river flows through Vormträsket. The shallow parts of the lake constitute the third wetland area.

3.3. Monitoring Data

The Kristineberg mine is run by Boliden Mineral AB. The company archives contain a wealth of data, as well as correspondence and newspaper cuttings. The latter reflect the work with pollution permits and the development of monitoring programs over the years, as well as public concerns for the environment close to the mine.

The majority of the data has its origin in regular monitoring programs carried out at the mine, along the recipient, and in the surrounding area. On some occasions, additional investigations related to specific topics, such as the occurrence of chemicals used in flotation, have also been performed. The oldest data found date back to 1943. The data related to Vombäcken are dominated by analyses of water chemistry. The most extensively studied sampling station is the effluent water from the mine area (the spillway='Utskov'/6306). The Vombäcken data set also includes analyses of the metal concentrations of sediments and various components of the biota, as well as the results from investigations of species composition (e.g. Brånin et al., 1976; Råberg, 2000).

Water chemistry data from 1971-1981 were selected for the study. During this period, all the stations of interest (Table 3.1) were sampled monthly.

Table 3.1. In Paper I, the investigated stations are named according to their numbers in the environmental monitoring program. The location of these sites coincides with the following stations sampled by the author and co-workers during the work with this thesis.

<table>
<thead>
<tr>
<th>Station number in environmental monitoring program</th>
<th>Station name in field sampling campaigns conducted during 1999 and 2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>6300</td>
<td>Storkalven</td>
</tr>
<tr>
<td>6306</td>
<td>Utskov</td>
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<tr>
<td>6312</td>
<td>Aspliden</td>
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<td>-</td>
<td>Timmervägen</td>
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<tr>
<td>6313</td>
<td>Rökå</td>
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<td>-</td>
<td>Mickeldammet</td>
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<tr>
<td>6315</td>
<td>Brännfors</td>
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<tr>
<td>6316</td>
<td>Vormsele</td>
</tr>
</tbody>
</table>
3.4. Field Sampling

3.4.1. Sampling

Surface water samples were collected from seven sampling stations situated along Vormbäckcn on six occasions during 1999 and 2000. On all of these occasions, samples were collected also from the effluent water from the mine area. Except for the background station, the location of the sampling stations along Vormbäckcn (Figure 3.2) was based on their positions in relation to different kinds of wetlands, as well as ease of access. The exact location of the sampling sites is given in Sjöblom et al. (2000). During 2000, additional surface water samples were collected both from the river and its major tributaries (Figure 3.2). The exact location of the additional sampling sites is given in Sjöblom et al. (2000) and Sjöblom and Håkansson (2000).

In order to be able to assess any seasonal variations in metal immobilization, samples were collected during snowmelt (middle of May 1999), summer (late July 1999 and late June 2000), low autumn flow before snowfall (early October 1999 and middle of October 2000), and before ice-out (middle of April, 2000). A major precipitation event occurred during the sampling campaign conducted in October 2000.

On all sampling occasions, two parallel water samples were collected from every sampling station. One of the samples was intended for metal analyses, and the other one was intended for all other analyses performed (Section 3.6). The samples were collected from the shore, except in April 2000 when the samples were collected from the ice. Great care was taken not to disturb the soft riverbanks or the underlying bottom sediments. In order to avoid collecting any surface film, as well as contamination from airborne particles, the bottles were generally opened and closed under water. Single use, powder free vinyl gloves (Evercare from SelefaTrade) were used when sampling and during treatment of the samples.

3.4.2. Sample Treatment

The initial treatment of the samples was generally performed in the field immediately after sampling and always within 5 h of sampling. For the determination of total concentrations, samples from all collection bottles were poured into smaller storage bottles. All samples from the ordinary sampling campaigns, and some of the additional samples from 2000, were also subjected to filtration. In 1999 and April 2000, filters with two different pore sizes (0.2 and 0.4 µm) were used. On the remaining sampling occasions, only 0.2-µm filters were employed. For a more detailed description of the filtration
procedures, refer to Paper IV. All samples intended for metal analyses were acidified by adding suprapur nitric acid (HNO₃, Merck).

The fraction of the total concentration of different metals that was associated with dissolved organic matter was investigated by treating filtered (<0.2 µm) samples with diethylaminoethyl-cellulose (DEAE), a weak anion exchanger (Whatman). For a more detailed description of the ion-exchange procedures, refer to Paper IV.

The samples were kept in iceboxes during transport and stored in a refrigerator until analysis.

3.4.3. Equipment and Washing Procedures

All bottles (brand new) used to collect and store the surface water samples taken in 1999 and 2000 were made of high-density polyethylene. 500-ml bottles with wide necks were used for the collection and storage of the samples, and 30-ml bottles were used for the storage of various subsamples. The bottles used for samples intended for metal analyses were acid washed according to the procedure described in Papers II and III. The bottles used for samples intended for other analyses were washed according to the procedure described in Papers II and III.

The samples were filtered through isopore polycarbonate (PC) filters (0.2 and 0.4 µm) from Millipore using 47-mm polypropylene filter holders from Micro Filtration Systems, and single use 20-ml plastic syringes from Codan. The filter holders were acid washed in warm 0.03 M HNO₃ (suprapur diluted with MilliQ-water) and rinsed with MilliQ-water. Separate baths were used for the filter holders and the rubber gaskets.

3.5. Laboratory Experiments – The Role of Iron

3.5.1. Ferrous Iron in Authentic River Waters

Authentic river waters were collected from the sampling station Storkalven in March and June 2002. The Fe concentration of the waters was increased by 0-1.5 mg/l by adding a freshly prepared FeSO₄ solution. In order to investigate the influence of particles and bacteria initially present, filtered (<1 kDalton and <0.2 µm) river waters were also included in the experimental set-up. The experiment was performed at 0 and 22°C, respectively. Any changes in metal speciation were studied by means of filtration (0.2 µm) for a maximum of seven days. To be able to compare the results with the actual conditions on site, new surface
water samples were also collected from Vormbäcken. A more detailed description of the experiment is given in Paper V.

3.5.2. Ferrous and Ferric Iron in Simulated River Waters

Four artificial river waters, three artificial surface waters, and one artificial groundwater were prepared from MilliQ-water and analytical grade chemicals (Table 3.2). The composition of the waters was largely based on the results from the field sampling campaigns conducted during 1999 and 2000 (Paper III).

Table 3.2. The experimental set-up illustrating the original waters mixed and the resulting 16 treatments. H, M, and S all contained humic acid (HA) corresponding to 12 mg TOC/l (black). Grey=treatments where the initial concentration of HA was halved following mixing. White=original waters and treatments without HA. P and M contained alumina ($\alpha$-Al$_2$O$_3$, 0.063-0.125 mm) corresponding to 500 µg Al/l. Before mixing, O and S were bubbled with air. The waters were mixed in a 1:1 ratio. Modified from Paper VI.

<table>
<thead>
<tr>
<th>All waters</th>
<th>‘Surface waters’</th>
<th>‘Groundwater’</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaHCO$_3$ 0.5 mmol/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaSO$_4$ 0.1 mmol/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>‘River waters’</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn 500 µg/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu 100 µg/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As 4 µg/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb 2 µg/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>‘Particles’ H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>‘Humic acid’ M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>‘Mixture’</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D=dilution</td>
<td>DC</td>
<td>SC</td>
</tr>
<tr>
<td>O=oxidized</td>
<td>OC</td>
<td>G=groundwater</td>
</tr>
<tr>
<td>S=surface water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P=particles</td>
<td>DP</td>
<td>SP</td>
</tr>
<tr>
<td>H=humic acid</td>
<td>DH</td>
<td>SH</td>
</tr>
<tr>
<td>M=mixture</td>
<td>DM</td>
<td>SM</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GM</td>
</tr>
</tbody>
</table>

In order to assess the initial metal speciation and procedural variability, before the start of the experiments, triplicate samples were collected from the river waters and the surface waters to which Fe had been added.

The different river waters were mixed with equal volumes of the different surface waters and the groundwater, giving a total of 16 treatments (Table 3.2). The metal speciation was followed by means of filtration (0.2 and 1.2 µm) for 48 h. This was considered to be an appropriate time frame from a treatment perspective. A more detailed description of the experiment is given in Paper VI.
3.6. Measurements and Analyses

3.6.1. Water Flow

In June and October 2000, the flow of water at some of the investigated sampling stations was measured with different methods, which differed in accuracy. For a more detailed description of the methods used, see Paper III.

3.6.2. pH

In general, the field pH (Papers II-V) was measured on site at the ambient temperature, using a portable pH meter (Radiometer Copenhagen PHM 201). On some occasions, the pH was measured somewhat later, but always at the field temperature.

Upon return to the lab, the pH of the samples was also measured at room temperature, using a Radiometer Copenhagen PHM 84 Research pH meter. In July and October 2000, the pH at 25°C was measured according to standard procedures (Standardiseringskommissionen i Sverige, 1979).

3.6.3. Conductivity

The electric conductance of the water, the conductivity, reflects the total concentration of ions in the water. In natural fresh waters with low ionic strength, conductivity can provide a comparatively easy means to trace sources of certain kinds of pollution. The conductivity of the samples at 25°C was measured using a Radiometer Copenhagen CDM 83 Conductivity meter. In July and October 2000, the conductivity at 25°C was measured according to standard procedures (Standardiseringskommissionen i Sverige, 1994).

3.6.4. Organic Carbon

The concentration of organic carbon in filtered (DOC <0.2 μm, <0.4 μm, and <1.2 μm) and unfiltered (TOC) samples from the field (Papers II-V) and the laboratory experiments (Papers V and VI) was measured using a Shimadzu TOC-5000 Total Organic Carbon analyzer.

3.6.5. Sulfate and Other Anions

The concentration of chloride (Cl⁻), fluoride (F⁻), nitrate (NO₃⁻), and sulfate (SO₄²⁻) in the field samples (Papers II and III) was measured using a Waters Quanta 4000 Capillary Electrophoresis System from Millipore. The analyses
were performed on newly filtered (0.2-µm isopore PC filters from Millipore) samples from the 500-ml bottles that had been machine-washed.

3.6.6. Metals

The metal analyses were generally performed using a Perkin Elmer SCIEX Elan 6000 ICP-MS or a Perkin Elmer SCIEX Elan 6100 DRC ICP-MS. Certified reference material (SRLS-3, riverine water, from National Research Council Canada) were analyzed along with the samples to check the analytical precision. The Ca and Fe concentrations of some of the field samples (Papers II-IV), as well as the Fe concentrations of all samples from the two laboratory experiments (Papers V and VI), were analyzed using a Perkin Elmer 1100 Atomic Absorption Spectrophotometer (AAS).
4. METALS AND WETLANDS – A LITERATURE SURVEY

In this section, the results from the literature survey will be summarized. The interactions between metals and wetlands have been studied in a number of different contexts. An overview of the research field is given in Section 4.1. The purpose of the following four sections is to outline wetland structure (Sections 4.2-4.3) and function (Sections 4.4-4.5), as well as to introduce a number of related definitions and concepts. The focus of the literature survey is wetland treatment of mine drainage waters. Some of the experiences from this particular research field will be highlighted in Sections 4.6-4.9.

4.1. An Overview

Apart from a purely scientific interest in elucidating the complex behavior of natural ecosystems, there are several reasons to study the interactions between wetlands and metals. For instance, wetlands may serve as archives of past and present levels of (airborne) pollutants, which can be very helpful in establishing natural background levels, and estimating the impact of man on the global biogeochemical cycles of certain elements. This subject has been treated in some detail by, for instance, Schell et al. (1989), Markert and Thornton (1990), and Callaway et al. (1998). The tendency of some wetland materials to reflect the metal content of their surrounding environment has also been used by economic geologists to locate metal ores (Brooks, 1972 and 1983). In fact, sometimes even the wetlands themselves may act as an economic source for certain metals (Brooks, 1983; Owen and Otton, 1995; Sobolewski, 1997 and 1999b). Deposits of limonite† (FeO(OH).nH₂O) are probably the most conspicuous examples of this. Limonite was the most important source of Fe till well into the Middle Ages (Nationalencyklopedin, 1992).

Anthropogenic activities may lead to a more concentrated release of pollutants into wetland environments, which in turn may affect the functioning of the entire ecosystem (e.g. Besch and Roberts-Pichette, 1970; Wheeler et al., 1991; Carlson and Carlson, 1994). An increasing awareness of the problem, in combination with modern treatment technologies and legislation, have reduced such emissions in the industrialized countries. However, the problem still remains in certain developing countries (Denny et al., 1995), as well as in the case of accidents (Pain et al., 1998; Hernández et al., 1999). If releases of pollutants into a wetland environment do occur, it is important to be able to predict what will happen to the pollutants and what risks they constitute (cf. Pascoe et al., 1996), so that a suitable remediation and/or monitoring strategy can be chosen. During the last centuries, humans have also changed the wetland environments, primarily by draining, for instance to get more arable land, or for the recovery of peat. Such changes may lead to an increased mobility of metals.
that have been stored in the wetlands for millennia, which calls for concern for the quality of for instance drinking water (Owen and Otton, 1995).

Recently wetland treatment of polluted water has received considerable attention. Different kinds of natural and constructed wetlands are used to treat water that is polluted by metals to varying degrees. There has been a dramatic increase in the use of wetlands to treat municipal wastewater (Cole, 1998), water that may also contain elevated levels of metals from, for instance, water pipes (Sörme and Lagerkvist, 2002). Removal of metals in such wetlands can be seen more as a bonus, or as a potential threat to the functioning of the wetland, if toxic levels of certain metals should accumulate. Run-off water from roads and roofs may also contain elevated levels of metals (ibid.). Since some of these metals are transported in particulate forms, detention ponds may provide an efficient means to prevent the metals from being further transported to nearby watercourses (Hammer, 1989; Pettersson, 1999). More traditional wetlands have also been employed to treat such waters (Hammer, 1989; Meiorin, 1989; Zhang et al., 1990; Ellis et al., 1994; Reinelt and Horner, 1995; Fortin et al., 2000; Goulet et al., 2001). Furthermore, wetlands may be used to treat industrial wastewater (Gillespie et al., 2000), as well as drainage water from municipal landfills (Peverly et al., 1995; DeBusk et al., 1996) and from mines and mining waste (Sections 4.6-4.9).

The establishment of wetlands on mining waste may be beneficial to reduce the formation of drainage water in the first place (Eger et al., 2000; Stoltz, 2001). Thus, wetlands are sometimes established on tailings impoundments as part of a water cover. The basic idea is that the plants will supply organic material, the breakdown of which will consume oxygen, keeping the tailings anoxic, thereby preventing weathering according to Eq. 1.1. Presence of plants may also reduce the risk that the tailings are re-suspended into the water column due to wave action. The problem is that plants may increase the weathering rates by releasing oxygen at their roots (Armstrong et al., 1990), and that they may also serve as vectors for transporting metals from the tailings to the water phase. The role of plants as a part of a water cover is studied within another part of the MiMi-program (Stoltz, 2001).

Even though every wetland environment is unique, it should be possible to learn a lot about general metal biogeochemistry in wetlands by combining results from the various research fields outlined above. Furthermore, several of the biogeochemical processes occurring in wetlands (Section 4.4) have also been investigated in considerable detail in other contexts, which makes a complete state-of-the-art on metal biogeochemistry in wetlands a task well beyond the scope of this thesis. To quote Sobolewski (1999a);
“Few people appreciate the number of studies that have described wetlands that remove metals and metalloids from contaminated waters. This information is broadly disseminated in the scientific and technical literature and requires some effort to assemble.”

In this literature survey, it was decided to focus on wetland treatment of mine drainage waters. In the following four sections, which are more general in character, some experiences from other research fields have also been included.

4.2. Wetland Definitions

The term ‘wetland’ will lead different people to think of entirely different environments. Thus, when talking about wetlands, it is often important to be more specific, so that other people will be able to picture the wetland in question accurately.

According to Cowardin et al. (1979), which is the classification scheme used by the American Fish and Wildlife Service;

“…wetlands are lands where saturation with water is the dominant factor determining the nature of soil development and the types of plant and animal communities living in the soil and on its surface. …wetlands must have one or more of the following three attributes: (1) at least periodically, the land supports predominantly hydrophytes… (2) the substrate is predominantly undrained hydric soil… and (3) the substrate is nonsoil and is saturated with water or covered by shallow water at some time during the growing season of each year.”

For inland areas, the boundary between wetlands and deepwater habitats lies at a depth of 2 m (ibid.). Thus, what is traditionally called bogs, fens, marshes, swamps, and ponds all may be classified as wetlands. These different environments all have different hydrology and chemistry, which in turn will affect the character of the metal immobilizing processes in action (Section 4.3.1). The influence that wetland hydrology and location in the landscape have on its assimilative capacity are emphasized by Brinson (1988).

4.2.1. Treatment Wetlands

Wetlands intentionally or unintentionally used for the treatment of polluted water may be either natural, voluntary, or constructed. Volunteer wetlands may develop close to a mine where changes have occurred in the local hydrology (Noller et al., 1994; Sobolewski, 1997). Thus, to some degree both voluntary and constructed wetlands may be considered to be man-made. However, the constructed wetlands have been built on purpose. Some of the differences between natural and constructed wetlands will be discussed in more detail in Sections 4.5.1-4.5.2 and 6.1.4.
Since they are based on similar biogeochemical principles, it is sometimes difficult to distinguish certain wetland treatment systems from, for instance, reactive barriers and certain kinds of filter systems. Reactive barriers will not be considered here, since they are studied within another part of the MiMi-program (Morales, 2001). In a true filter system, the major (bio)geochemical processes operating would be retention of larger particles and adsorption to the filter material. The distinction is obscured by the fact that sometimes microbiological processes are incorporated into water saturated filter systems, and that certain wetland treatment systems do not rely on the presence of any biota other than bacteria.

4.3. The Components of a Wetland

Independent of morphology, all wetlands contain water and a solid substrate, even though the proportions between these components may vary significantly (Figure 4.1). The ecosystem wetland is also distinguished from mere settling basins or filters by containing biota such as microorganisms, plants, and animals (cf. discussion in Giblin, 1985; Hemond and Benoit, 1988).

![Diagram](image)

*Figure 4.1. A simplified wetland, illustrating the major components of a wetland ecosystem.*
4.3.1. The Water – Hydrology and Chemistry

A knowledge of water movement is essential for understanding the biogeochemistry of any wetland system (Hemond, 1980). This would apply both to overall treatment efficiency (Sections 4.5.1-4.5.2), and to what metal immobilizing processes that may act in them.

The major pathway by which the metals end up in the solid substrate, thereby remaining in the wetland, is likely to differ with the height of the overlying water column. Direct uptake of metals by the solid substrate (e.g. by adsorption processes) may occur from water that flows through or immediately across it, or by sediment particles that have been re-suspended in the water column. If the volume of water that flows across the surface of the solid substrate is comparatively large, settling of metal bearing particles may turn out to be more important for overall metal retention. Furthermore, the rate of various processes that act to immobilize the metals in a wetland (Section 4.4) must always be considered in relation to the velocity by which the water moves through the system (cf. Kimball et al., 1994). The velocity of the water will also affect the oxygen conditions in the wetland. More rapidly flowing water tends to increase the amount of oxygen available (Sparling, 1966).

Water chemistry parameters, such as pH, redox, salinity, and presence of inorganic and/or organic ligands, play a central role in determining what mechanisms of metal immobilization that can be expected to work in a given wetland system (Section 4.4; and reviews by e.g. Giblin, 1985; Hedin, 1989; Dunbabin and Bowmer, 1992; Hedin et al., 1993; Gambrell, 1994; and Sobolewski, 1999a).

4.3.2. The Substratum – Sediments, Peat, and Spent Mushroom Compost

The solid substrates most commonly associated with natural wetlands are soil/sediments and peat. Soil and sediments commonly consist of mineral particles and organic detritus. In general, wetland soils/sediments are reduced, rich in organic matter, and have a near-neutral pH, factors which tend to favor their capacity for metal immobilization (Giblin, 1985; Faulkner and Richardson, 1989; Gambrell, 1994).

Peat is a mixture of partially decomposed plant material in a matrix of aggregate particles and dissolved substances from the decomposition process (Bohlin, 1993). Many natural peat systems can be divided into two layers; the acrotelm and the catotelm (Ingram, 1978). The lower layer, the catotelm, possesses a negligibly small hydraulic conductivity and is not subject to air entry (ibid.).
However, Hill and Siegel (1991) have shown that groundwater flow may occur also in humified peat.

Due to its large capacity to accumulate metals, peat was used as a solid substrate in some of the earliest wetlands built to treat mine drainage. Nowadays spent mushroom compost (SMC), a by-product from the growing of white button mushroom (*Agaricus bisporus*), seems to be one of the most popular solid substrates used. SMC contains horse manure bedded with wheat straw, dried chicken manure, dried brewers grain, gypsum (CaSO₄), rye grain spawn, *Sphagnum* peat moss, and ground limestone. A detailed description of the production of mushroom compost is given in Stark et al. (1991).

A trade-off between hydraulic conductivity (favored by larger particles) and total adsorptive/reactive surface area (favored by smaller particles) is often necessary in treatment wetlands where the water is supposed to be transported through the solid substrate. Sometimes the problem is solved by mixing an adsorbent such as clay or peat with, for instance, gravel or sand (Lapakko and Eger, 1988; Faulkner and Richardson, 1989). Too high a porosity of the substrate may also have a negative influence on its ability to filter out fine-grained precipitates (Gammons et al., 2000).

### 4.3.3. The Biota – Microorganisms, Plants, and Animals

In wetlands used for the treatment of mine drainage waters, the most frequently studied groups of microorganisms are the iron-oxidizing bacteria, the iron-reducing bacteria, and the sulfate-reducing bacteria (Sections 4.4.4-4.4.6; see also reviews by Brierley, 1990; Johnson, 1995; and Ledin and Pedersen, 1996). Cyanobacteria or blue green algae will be treated among the plants.

Plants encountered in a wetland include planktonic and macroscopic algae, mosses (mainly *Sphagnum*), and angiosperms (flowering plants, which form seeds inside protective chambers). Macroscopic forms of aquatic vegetation are often referred to as aquatic macrophytes (Wetzel, 1983). All plants may reduce the metal content of the surrounding water by direct uptake (Section 4.4.3). Metals may also adsorb to, or precipitate against, the surfaces of plant tissues. Macrophytes such as *Sphagnum* and sedges may later on transform into peat (Bohlin, 1993), thereby forming part of the solid substrate.

In addition, plants may perform several other ecological services to a treatment wetland. These include slowing down the velocity of the water (Section 4.4.1), stabilizing the solid substrate, providing organic material to the microorganisms (especially important for the sulfate-reducers; Section 4.4.6), and reduction of Cr(VI) into less toxic Cr(III) (Lytle et al., 1998). Depending on the type of
wetland system, release of oxygen by plant roots may be either beneficial (Peverly et al., 1995; Doyle and Otte, 1997) or detrimental to the functioning of the system. However, in the study by Sencindiver and Bhumbla (1988), presence of cattails (*Typha latifolia*) was found to render the wetland sediments more reducing. Furthermore, plants may enhance the aesthetic appearance of the treatment wetland.

Treatment wetlands may provide habitats for a wide range of animals. Insects can have a devastating effect on wetland function and public acceptance. For instance, Brodie et al. (1988a and 1989b) and Snoddy et al. (1989) report about an infestation of armyworms (larvae of the moth *Smyra henrici*) in a cattail wetland used for the treatment of acid drainage from an ash pond. Mosquitoes can become a nuisance to people living nearby. Sometimes mosquitofish (*Gambusia affinis*) and fathead minnows (*Pimephales promelas*) are used to control mosquito populations in treatment wetlands (Brodie et al., 1987; Brodie, 1990 and 1993). For the same purpose, bathouses and birdhouses have also been installed at a number of wetlands (Brodie, 1990 and 1993).

As reported by Brodie et al. (1988a and 1989a), Brodie (1990), and Stark et al. (1988 and 1994c), damming and burrowing mammals such as beavers (*Castor*) and muskrats (*Ondatra zibethicus*) may also have a detrimental impact on treatment wetlands, a problem that may be avoided by fencing and/or trapping. In natural systems, beavers may act as ecosystem engineers by creating dams, turning upland soils into wetlands. Even though this may have a negative impact on downstream concentrations of, for instance, methylmercury (cf. Porvari and Verta, 1995), presence of dams and wetland geochemical conditions may be beneficial from a mine drainage treatment perspective.

To some extent, the establishment of constructed wetlands may replace wetland habitats that have been lost due to draining activities. Amphibians and birds are among the species that could be favored by an increased number or area of wetlands (Brooks, 1989; cf. Lacki et al., 1992; Witthar, 1993). Even though minor changes to the original design may give added value to a treatment wetland by providing habitat for rare species, some researchers prefer to view wetlands as outdoor treatment plants, and would like to exclude animals if possible. Given that too high metal concentrations may pose a health hazard to the animals, the latter approach may be a sensible one for mine drainage treatment wetlands. However, in one of the few studies found, no signs of elevated metal concentrations were found in the frogs investigated (Lacki et al., 1992). Furthermore, both species abundance (frogs) and species richness (snakes) appeared to be favored by the wetland establishment.
4.4. Mechanisms of Metal Immobilization in Wetlands

The fact that metals are elements poses a number of constraints on wetland treatment of metal polluted water. For instance, unlike NO$_3^-$ and certain organic pollutants, metals cannot be transformed or decomposed to less harmful substances, such as nitrogen gas (N$_2$) and carbon dioxide (CO$_2$). However, metals may be transformed into forms that are less harmful from a bioavailability or toxicity perspective (cf. Gillespie et al., 2000). Furthermore, metals may be removed from the water phase, but by necessity they will end up in another wetland compartment, usually the solid substrate or the biota. This means that, unless they are removed by humans, the metals permanently removed from the water phase will gradually accumulate in the wetland treatment system. Metals such as Hg and Se (selenium) may also leave the water phase by the formation of volatile compounds (Brierley, 1990). Although beneficial from a localized water treatment perspective, treatment systems incorporating uncontrolled volatilization of the pollutants would only tend to move the problem to other areas. Therefore this section will focus on processes that act to immobilize metals in the treatment wetlands.

4.4.1. Sedimentation

One of the ecological functions provided by a wetland containing macrophytes is to reduce the velocity of the water flow (Boto and Patrick, 1978; Brooks, 1989; Hellier, 1999). The increased residence time makes it possible for larger particles, and metals associated with them, to settle before leaving the wetland. When treatment wetlands are talked about in terms of filters, it is generally this phenomenon that it is being referred to.

A prerequisite for sedimentation processes to have any impact on metal retention is that a significant part of the metals is found in association with particles that are large enough to settle. The settling rate of particles is proportional to the square of their diameter (Wetzel, 1983). Precipitation of Fe oxyhydroxides (Section 4.4.4) and adsorption to particles (Section 4.4.2) are two important mechanisms by which metals in AMD are transferred to particulate species. As pointed out by Hedin et al. (1993), an increased residence time also means that some of the processes, that otherwise would have taken place in the recipient, will occur in the treatment system instead. These processes include those that transfer metals from dissolved to particulate species.

From the perspective of sustainability, one of the major problems of metal immobilization coupled to sedimentation processes is that the particles gradually will accumulate in the system. This means that, unless these newly formed
sediments are removed on a regular basis, the total volume of the wetland basin will decrease over time, resulting in shorter residence times.

Trapping of colloidal particles is similar to sedimentation. Boult et al. (1997) have showed that extracellular polymeric substances, constituting the matrix of a biofilm encountered in a stream contaminated by AMD, are able to attract and trap colloidal Fe hydroxides. Such a process could potentially be important in certain kinds of treatment wetlands.

4.4.2. Adsorption and Ion Exchange

In a wetland environment, adsorption processes are most often associated with the solid substrate(s), even though adsorption to particles that are large enough to settle may also be of importance for metal immobilization (previous Section). In both cases, the chemistry behind the adsorption phenomena is similar.

Depending on the pH of the surrounding solution, a surface may be either neutral (when the pH is equal to the zero point of charge (ZPC), which is different for different minerals), positively charged (when pH<ZPC), or negatively charged (when pH>ZPC). Therefore metals that are found in their cationic forms (e.g. Cu$^{2+}$) are usually adsorbed more strongly at a higher pH, whereas adsorption of elements that are found in their anionic forms (e.g. AsO$_4^{3-}$) is often augmented at a lower pH.

The pH interval where the most rapid transition from dissolved to adsorbed metal species occurs is referred to as an adsorption edge. Different metals often have different adsorption edges for the same mineral, that is, at a certain pH 100% of the Pb$^{2+}$, 50% of the Cu$^{2+}$, and 0% of the Zn$^{2+}$ may be adsorbed to the solid phase. The position and width of an adsorption edge is influenced by the identity of the adsorbing species, the composition of the solid phase, and the water chemistry.

The situation above can be viewed as competition for binding sites between cations and hydrogen ions (H$^+$), or between anions and hydroxide ions (OH$^-$). Similarly, in more saline waters, other cations and anions that are more abundant (e.g. Ca$^{2+}$ and SO$_4^{2-}$) may out-compete trace metals for binding sites. In addition, other components of the aqueous phase (e.g. dissolved organic matter, DOM) can have a negative influence on adsorption by forming soluble complexes with the dissolved metals. However, at lower pH, natural complexing substances can increase trace metal adsorption by forming bridges between the solid phases and the metals (Xu, 1991; Düker et al., 1995; Tessier et al., 1996). For a more comprehensive description of adsorption processes in general, refer to, for instance, Bourg (1988), Benjamin and Honeyman (1992), or Drever (1997).
In ion exchange processes, ions weakly associated with a solid substrate such as a clay, an oxohydroxide, or a natural organic compound are replaced by ions from the surrounding solution (Drever, 1997). The cation exchange capacity of a material is determined by factors such as pH, and what metal ions that were associated with the solid substrate in the first place (ibid.). Both adsorption and ion exchange may be referred to as sorption.

All observed solid phases are not thermodynamically stable. For instance, sulfides are generally unstable under oxic conditions (cf. Section 1.2.4) and oxyhydroxides of Fe and manganese (Mn) are unstable under anoxic conditions (cf. Section 4.4.5). Thus, sorption is limited by a number of geochemical constraints. Furthermore, the number of sorption sites is finite, which means that, unless new substrate is added or formed, eventually the solid substrates will become saturated with sorbed metals. In a study by Eger et al. (1994) it was calculated that, in order to balance the formation of new removal sites, the input flow would have to be reduced by one order of magnitude.

When designing laboratory experiments to investigate sorption phenomena in wetland environments, it is important to consider also the aspects of hydrology. Batch experiments, where wetland sediments or peat are suspended in the water column, will tend to overestimate the rate and efficiency of the metal scavenging processes in comparison to those under field conditions, due to the increased contact between the particles and the water. However, they may still be useful to study the impact of different water chemistry variables, maximum sorption capacities, and competition between different metals (cf. Wieder, 1990; Machemer and Wildeman, 1992). If the sediments or peat are kept only at the bottom of the experimental bottle, the water will have to be replaced on a regular basis in order to simulate a field situation with running waters. Fox and Doner (2001) used permeable bags containing soil or mineral samples to study metal retention in situ at a constructed wetland.

In a column study, the flow of water through the solid substrate can be optimized. Using data from such an experiment to determine the total metal accumulating capacity of a natural peatland may lead to gross overestimations. In a natural peatland, it is unlikely that the flow of water will be homogenous throughout the entire volume of peat, unless the water to be treated is forced to move through the substrate vertically (cf. Lapakko and Eger, 1988; Eger, 1994; Eger et al., 1994). For instance, Eger and Lapakko (1988) found the contact zone between the studied drainage water and peatland to be confined to the upper layer (approximately 20 cm) of the peat.
4.4.3. Biological Uptake

In mine drainage treatment wetlands, macrophytes are generally the only organisms that have been considered when the influence of biological uptake of metals on total metal retention has been investigated. Results from general studies indicate that microorganisms may play an important role in trace metal accumulation in soil (Ledin et al., 1999). Samples of the algae *Microspora* collected from a constructed wetland have been found to contain 85 mg Mn/g (Hedin, 1989). Stevens et al. (1989) also report encrustations containing Fe and Mn on the cell walls of algae living in AMD environments. However, the total biomass of algae is often too low for this to have any effect on overall metal retention in a mine drainage treatment wetland (Hedin, 1989; Kleinmann, 1989; Kleinmann et al., 1991). For animals, the major concerns are that biological uptake shall not result in metal concentrations that are harmful to the organisms (cf. Section 4.3.3).

Aquatic macrophytes occur in different growth forms (Figure 4.2). While freely floating macrophytes accumulate all of their metals and nutrients from the water phase, rooted macrophytes can also accumulate metals and nutrients from the sediments. In fact, in rooted plants, uptake of trace metals is considered to be dominated by uptake from the roots (Jackson, 1998). Thus, unless the water to be treated is made to move through the root zone, rooted plants may prove to be inefficient at treating large volumes of water. On the other hand, since the concentration of nutrients generally is higher in the porewaters of the sediments than in the overlying water column, freely floating plants tend to require higher nutrient concentrations in the water (cf. Wetzel, 1983). The growth form also affects if the plants are suitable candidates for incorporation into a treatment system where management is planned. In rooted macrophytes, a substantial amount of the metals accumulated is often stored in the roots (Lundholm and Andersson, 1985; Blake et al., 1987; Sencindiver and Bhumla, 1988; Fennessy and Mitsch, 1989; Lan et al., 1990; Ellis et al., 1994; DeBusk et al., 1996). Thus, removal of these metals from the wetlands will require digging into the sediments. In comparison, it is relatively easy to remove the freely floating macrophytes (cf. DeBusk et al., 1996).

There are a number of potential problems associated with treatment systems incorporating plants. One of the most important is that the plants have to tolerate the metal concentrations in the water to be treated (cf. Besch and Roberts-Pichette, 1970; Kleinmann and Girts, 1987), as well as those that gradually accumulate in the system. In addition, a steady supply of nutrients must be ensured. Flocculent precipitates may also pose a threat to wetland plants (P. Lane and Associates Limited, 1990).
Figure 4.2. Different growth forms of aquatic macrophytes. Many of the plants encountered in mine drainage treatment wetlands, such as cattails, are emergent plants.

Plants of *Sphagnum fallax* and *Sphagnum henryense* can grow in solutions with Fe concentrations up to 10 mg/l, but at concentrations of 100 mg/l or more, they turn brown and stop growing (Spratt and Wieder, 1988). Emerick et al. (1988) report that *Carex aquatilis* growing in a natural wetland exposed to drainage waters from a metal mine appeared to have a high tolerance for metals and low pH.

Wenerick et al. (1989) have investigated the tolerance of *Typha latifolia*, *Sphagnum recurvum*, and *Pohlia nutans* to AMD in a greenhouse experiment. *Typha* was found to be the most tolerant of the three species. Still, it was negatively affected by undiluted AMD (411 mg/l dissolved Fe, 71 mg/l dissolved Mn, pH 3.4-3.5) already after five weeks exposure. In the mesocosm wetlands investigated by Wieder et al. (1990), aboveground parts of *Typha latifolia* were almost completely dead by the sixth week of exposure to synthetic AMD (pH 3.5, containing e.g. 78.8 mg/l Fe$^{2+}$, 10.0 mg/l Al$^{3+}$, and 5.2 mg/l Mn$^{2+}$).

The influence of a number of water quality parameters on the distribution of *Typha latifolia* in natural wetlands affected by AMD has been investigated by Samuel et al. (1988). *Typha* was found to be present at seven sites where the pH of the water was below 2.5, but only at three sites where the total concentration of Fe was above 100 mg/l. The total Fe concentrations in the water were also found to be lower at sites where *Typha* was present than in nearby sites where it was absent. Furthermore, it was suggested that lower pH and higher Al
concentrations of the soil may present problems for the survival and germination of *Typha*.

In some cases, a gradual loss of nutrient base cations (Ca\(^{2+}\), K\(^{+}\), Mg\(^{2+}\), and Na\(^{+}\)) from the substrate of wetlands exposed to AMD has been noticed (Wieder et al., 1990; Wieder, 1993). It was suggested that this phenomenon might lead to a depletion of nutrients, and that application of fertilizers then would be required to maintain viable plant populations. High concentrations of ferrous Fe have also been suggested to induce a nutrient deficiency in *Sphagnum*, due to competition with nutrient base cations (Spratt and Wieder, 1988).

In order for plant *uptake* to have any influence on total metal transport, the metals must also occur in a form that is bioavailable. In some instances however, the metals are merely adsorbed to, or precipitated against, the surfaces of living organisms. For instance, Mays and Edwards (2001) found that metals contained in root coatings accounted for 32-93% of the total metal concentration in the roots. Knowledge of the exact mechanism behind metal accumulation is important when trying to predict, or improve, metal retention in a system (cf. Kepler, 1988). It may also govern the future fate of the accumulated metals.

The total amount of metals that plants can remove from the water phase (by direct uptake) is limited by how much metal each plant can accumulate on a weight basis, and how much biomass each plant produces. Since plants have different capacities to accumulate metals (Brooks, 1983), the amount of metals removed may be increased either by a careful selection of what species that are incorporated into the constructed wetland, or by increasing the biomass production (Sencindiver and Bhumbla, 1988). Both of these approaches will probably require some maintenance. For instance, foreign species may be out-competed by native species better adapted to the conditions on site, and a higher biomass production may require regular additions of nutrients.

However, the overall contribution of plant uptake to total metal retention in mine drainage treatment wetlands is often found to be insignificant (Eger and Lapakko, 1988; Hiel and Kerins, 1988; Sencindiver and Bhumbla, 1988; Spratt and Wieder, 1988; Fennessy and Mitsch, 1989; Eger et al., 1994; Mitsch and Wise, 1998; Mays and Edwards, 2001).

From the perspective of sustainability, it is also interesting to consider the fate of the metals amassed in plants upon senescence and death of these organisms. Studies have shown that metals can be leached from decaying plant material to the surrounding water (Rice and Windom, 1982). Ultimately, only the metals that are associated with permanently buried plant material will remain immobilized in the wetland. Lower pH and higher metal concentrations may
also have an impact on the rates of plant decomposition, and thereby affect the recycling of nutrients (Kittle et al., 1995).

4.4.4. Oxidation and/or Hydrolysis

In freshly produced AMD, Fe is often found in its ferrous form. Upon contact with oxygen, the ferrous Fe will get oxidized to ferric Fe;

\[ 4 \text{Fe}^{2+} + \text{O}_2(aq) + 4 \text{H}^+ \rightarrow 4 \text{Fe}^{3+} + 2 \text{H}_2\text{O} \]  
(Eq. 4.1)

The rate of the reaction is dependent on a number of factors such as pH, temperature, and presence of microorganisms. At pH above 4.5, Singer and Stumm (1970) found the rate of the chemical oxidation to increase with increasing pH. At pH below 3.5, the rate was found to be independent of pH (ibid.). The influence of temperature on the rate of the chemical oxidation appears to be related to the temperature dependence of the ionization constant of water (Sung and Morgan, 1980).

The oxidation reaction may also be catalyzed by iron-oxidizing bacteria, such as \textit{Thiobacillus ferrooxidans} and \textit{Ferrobacillus ferrooxidans} (Singer and Stumm, 1970). In a series of treatment ponds studied, Kirby et al. (1999) found ferrous Fe oxidation to be negatively correlated with pH and catalyzed by \textit{Thiobacillus ferrooxidans} between pH 2.8 and 5. Between pH 5 and 6.4, the oxidation was abiotic and positively correlated with pH. Above pH 6.4, the oxidation rate was independent of pH.

At pH >3.5 (Cravotta and Trahan, 1999; Sobolewski, 1999a), the ferric Fe formed will generally undergo hydrolysis and precipitate;

\[ \text{Fe}^{3+} + 3 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3(s) + 3 \text{H}^+ \]  
(Eq. 4.2)

Note that H\(^+\) is liberated in this reaction. This means that, unless the water is sufficiently buffered, the pH of the solution will fall. A lower pH can have a negative influence on the rate of ferrous Fe oxidation and hydrolysis, as well as trace metal adsorption (Section 4.4.2).

The exact product of the oxidation of ferrous Fe in surface waters depends on a number of factors. For instance, in AMD environments, ferrihydrite (Fe(OH)\(_3\)), goethite (\(\alpha\)-FeOOH), iron(III)oxyhydroxysulfates, jarosite ((H,K,Na)Fe\(_3\)(SO\(_4\))\(_2\)OH\(_6\)), and schwertmannite (Fe\(_8\)O\(_8\)(OH)\(_6\)SO\(_4\)) are all among the minerals that may form (cf. Webster et al., 1998; Cravotta and Trahan, 1999). Sung and Morgan (1980) found that lepidocrocite (\(\gamma\)-FeOOH) was the product of the oxidation of ferrous Fe in aqueous solutions of various compositions. This
observation is supported by studies performed with natural and model lakewaters (Tipping et al., 1989). However, in the presence of Si(OH)₄, the product of the oxidation of ferrous Fe was found to be Fe(OH)₃ (ibid.). In the sediments investigated by Tessier et al. (1996), a mixture of Fe(OH)₃ and γ-FeOOH was found. In the following text, the term **Fe oxyhydroxides** will be used when referring to (unspecified) Fe-containing precipitates. At pH >7, the Fe oxyhydroxides formed have been found to catalyze the removal of ferrous Fe from solution (Sung and Morgan, 1980).

The behavior of Mn is similar to that of Fe in that it is sensitive to changes in pH and redox, but it typically reacts less willingly (Faulkner and Richardson, 1989; Kleinmann et al., 1991; Stark et al., 1995 and 1996; Sobolewski, 1999a). Al can also undergo hydrolysis and precipitate as gibbsite (Al(OH)₃). Precipitation as hydroxides is not common for other metals encountered in mine drainage treatment wetlands. However, Fe and Mn oxyhydroxides formed may scavenge trace metals present by adsorption and/or co-precipitation (Chapman et al., 1983; Johnson, 1986; Kimball et al., 1995; Webster et al., 1998).

Apart from the effect on pH outlined above, there are two major problems with removal of Al, Fe, and Mn as oxyhydroxides. The precipitates formed will gradually accumulate in the wetland or settling basin, leading to shorter residence times (cf. Section 4.4.1). Demko and Pesavento (1988) and Stark et al. (1994c) have recorded sediment accumulation rates of 3.8 cm/year. Since wetland sediments tend to be reducing, the post-depositional fate of the Fe and Mn oxyhydroxides also has to be considered (next Section, Sections 4.8.5 and 6.3.3).

4.4.5. Iron Reduction

In an anoxic environment, microbial decomposition of organic matter may be accomplished by using alternative electron acceptors. After the oxygen has been depleted, NO₃⁻, Mn(IV), Fe(III), SO₄²⁻, and CO₂ are used, more or less in turn (Faulkner and Richardson, 1989; Westermann, 1993). The order between these alternative electron acceptors is largely based on energy yield (ibid.). However, SO₄²⁻ reduction may occur before, or at the same time as, Fe(III) reduction, depending on the stability of the Fe oxide (Postma and Jakobsen, 1996).

In principle, Fe(III) reduction would remobilize Fe that has been precipitated as oxyhydroxides. Thus it may interfere with immobilization coupled to Fe oxidation and hydrolysis (previous Section). It may also interfere with sulfate reduction (following Section; cf. Lovley and Phillips, 1987). The major reason to study Fe reduction in treatment wetlands is that it may raise the pH and
generate alkalinity, buffering the pH of the surrounding water (Vile and Wieder, 1993). Both of these effects are likely to be beneficial for metal immobilization.

4.4.6. Sulfate Reduction

One of the first observations that sulfate reduction could potentially be used to treat AMD is ascribed to Tuttle et al. (1969 a and b), who noticed significant improvements in drainage quality after it had passed through a pile of sawdust. Herlihy et al. (1987) have shown that sulfate reduction can act as a buffering mechanism even at the ecosystem level.

Sulfate reduction is accomplished by sulfate-reducing bacteria (SRB) such as Desulfomonas, Desulfotomaculum, and Desulfovibrio (Perry, 1995). In the absence of oxygen, they use $\text{SO}_4^{2-}$ as a terminal electron acceptor to mineralize low molecular weight organic compounds, here represented as CH$_2$O (Hedin et al., 1989 and 1993);

$$\text{SO}_4^{2-} + 2 \text{CH}_2\text{O} \rightarrow \text{H}_2\text{S} + 2 \text{HCO}_3^- \quad \text{(Eq. 4.3)}$$

From a treatment perspective, there are three major possible effects of sulfate reduction; to generate bicarbonate alkalinity (Eq. 4.3), to raise the pH by removing $\text{H}^+$ from solution;

$$\text{H}_2\text{S(aq)} \rightarrow \text{H}_2\text{S(g)} \quad \text{(Eq. 4.4)}$$

and to precipitate metals (Me) as sulfides;

$$\text{HS}^- + \text{Me}^{2+} \rightarrow \text{MeS(s)} + \text{H}^+ \quad \text{(Eq. 4.5)}$$

Reduction of the $\text{SO}_4^{2-}$ concentrations of the drainage water is an additional benefit in countries such as the Netherlands, where the emissions of $\text{SO}_4^{2-}$ are regulated by law (Poulin and Lawrence, 1996), and in areas with high evaporation rates, where one may also be interested in reducing the total salt loadings (Tyrrell et al., 1997). Another advantage is that Fe sulfides are more compact than Fe oxides (Hedin et al., 1988; Stark et al., 1994b).

Sulfate reduction will raise the pH of the surrounding water when more sulfide is generated than what is needed to precipitate the ferrous Fe present (Dietz and Unz, 1988). Metals such as Cd, Cu, Hg, Pb, and Zn form highly insoluble precipitates with sulfides (Hedin et al., 1993; Sobolewski, 1999a). An important exception to this basic rule is Mn (Hedin et al., 1993). Apart from precipitating as metal sulfides, many metals may also co-precipitate with, or adsorb to, other sulfides formed (Morse, 1994; Coles et al. 2000).
SRB are found in the greatest numbers in anoxic sediments (Perry, 1995). They can grow at pH ranging from 5 to 9.5, even though their activity is inhibited at pH <6 (ibid.). SRB can grow at temperatures ranging from −5 to 75°C (ibid.), and results from Fortin et al. (2000) even suggest that cold temperatures (approximately 1°C) do not affect their activity. SRB are tolerant to nickel (Ni), Pb, and Zn concentrations as high as 200 mg/l (Kleinmann, 1989). They can also tolerate Cd concentrations of 35 mg/l (ibid.), and grow vigorously at Cu concentrations above 100 mg/l (Wildeman et al., 1994). However, additions of the plant nutrient NO₃⁻ can have a negative effect on sulfate reduction (Groudev et al., 1999; cf. previous Section).

In near-neutral anoxic environments, sulfate reduction is generally limited by the availability of SO₄²⁻ or suitable organic matter (Hedin et al., 1989 and 1993). In freshwater systems, sulfate reduction is often limited by the availability of sulfate (ibid.). Since sulfate is a major component of the AMD, one of the major obstacles to sulfate reduction in mine drainage treatment wetlands is the availability of suitable organic matter.

Once immobilized, it is important that the sulfides formed are kept in a reducing environment (cf. Hedin et al., 1989, Martin et al., 2001). Otherwise the weathering processes (Eq. 1.1) will start again. Ferric Fe that is added to the system (e.g. bound to dissolved organic matter) may also be problematic in this respect (cf. Vile and Wieder, 1993). Some of the metal sulfides initially formed, the so-called acid volatile sulfides (AVS), may also become remobilized if exposed to acidic waters (Hedin et al., 1989).

### 4.5. How to Assess Wetland Performance

When assessing metal **immobilization** in wetlands, it is essential to be able to locate and quantify all sources of water and metals. As illustrated below, this may be achieved by direct measurements, tracer studies, and various modeling exercises. An advantage of constructed wetland treatment systems, in comparison to natural wetlands (cf. P. Lane and Associates Limited, 1990; Wildeman and Pavlik, 2000), is that some of the uncertainties associated with the latter may be avoided by a proper design.

#### 4.5.1. Hydrology

Since the total volume of water may change upon passing a wetland, decreasing metal concentrations are no guarantees that any metal immobilization has occurred (Figure 4.3). Similarly, constant, or even increasing, metal concentrations do not necessarily indicate low metal immobilization (Figure 4.3). In
order to ascertain if any metal immobilization has occurred, the first step would be to measure the volume of water flowing into and out of the wetland in question. Apart from a first indication on if there are any significant gains or losses of water in the system, this procedure allows for the calculation of **metal loadings** (L);

\[
L = [\text{Me}] \times Q \quad \text{(Eq. 4.6)}
\]

where \([\text{Me}]\) is the total metal concentration and \(Q\) is the flow of water. If the metal loadings decrease upon passing a wetland, this is a better indication of metal immobilization than decreasing metal concentrations (cf. Section 4.5.3).

Unfortunately, since water gains and losses may cancel, a constant volume of water passing through the system does not automatically imply that there are no additional sources of water, which may also have a bearing on the amount of metals in the system (next Section). In order to ensure that the basic assumptions
regarding the overall metal budgets are valid, it is still often informative to consider the whole hydrological situation of the wetland at the onset of a study.

Water may enter a wetland as drainage water to be treated, precipitation, surface runoff, tributaries, and groundwater (Figure 4.4). Water may leave a wetland as treated drainage water, evaporation, and transpiration, or it may infiltrate to the groundwater (Figure 4.4). It is comparatively easy to measure the amount of drainage water and precipitation. Measurements of drainage water are made easier if the inflow to and outflow from the wetland are well defined. This can be accomplished by building weirs in natural wetlands or incorporating these kinds of structures into constructed wetlands.

![Figure 4.4. The hydrology of a wetland.](image)

*Figure 4.4. The hydrology of a wetland. The importance of the various processes varies between different kinds of wetlands. Dark arrows mark pathways that can be restricted in constructed wetlands, without affecting the true treatment efficiency.*

Evapotranspiration and surface runoff can be modeled (e.g. Dombeck et al., 1998). It is worth stressing that evapotranspiration can be substantial, even in temperate climates (Hemond, 1980; Demko and Pesavento, 1988; Brooks et al., 1990; Stark et al., 1994c; Eger et al., 2000). Contributions by, and losses to, the groundwater are harder to quantify. In constructed wetlands, this problem can be avoided by incorporating liners aimed at minimizing the exchange of water between the wetland and the groundwater (Hellier, 1999). In natural wetlands, contributions and losses to the groundwater can be calculated if all the other components of the water budget are known, and the storage of water in the wetland can be assumed to be constant. An example of a hydrologic budget for a mine drainage treatment wetland is given by Mitsch and Wise (1998). This
budget has a residual of 13%, which according to the authors is not extraordinary in water budget calculations.

Tracers may also be used to estimate the water balance of a wetland. A good tracer is **conservative**, that is, it does not react when passing through the investigated system (Bencala et al., 1987). It is neither immobilized nor decomposed. Any changes in the concentration of a tracer that occur upon passing through the wetland can be explained by that water has been added to, or lost from, the system. For such an explanation to be valid also for substances that have a natural occurrence, the concentration of the tracer must be much higher in the water to be treated than in the tributaries and groundwater (ibid.).

Commonly used tracers include lithium and sodium bromide (LiBr and NaBr), as well as fluorescein and Rhodamine dyes (e.g. Chapman et al., 1988; Eger and Lapakko, 1988; Brooks et al., 1990; Eger et al., 1993 and 1994; Eger, 1994; Demchak et al., 2001). Bencala et al. (1987) have investigated the potential for using various components of a water similar to AMD as tracers in a natural river system. They suggested that $\text{SO}_4^{2-}$ and Mn might be used as tracers. $\text{SO}_4^{2-}$ and/or Mn have been used as tracers also by Hedin and Watzlaf (1994) and Noller et al. (1994), as well as in Paper III. Unfortunately, $\text{SO}_4^{2-}$ is likely to be a poor tracer in a wetland where sulfate reduction can be expected. $\text{SO}_4^{2-}$ can also be lost from a system through the formation of, for instance, gypsum, Fe(III) oxyhydroxysulfates, jarosites, or schwertmannite (cf. Section 4.4.4). Hedin and Nairn (1993) have suggested that, in some cases, magnesium (Mg) may be used as a tracer in wetlands used to treat coal mine drainage. For instance, Mg has been used as a tracer by Hedin et al. (1993), Hedin and Watzlaf (1994), as well as by Kepler and McCleary (1994).

Addition of tracers may also be useful in determining residence times in different compartments of a pond, a wetland, or a watercourse (e.g. Jones et al., 1995). A problem with tracers is that a substantial sampling campaign may be necessary. If a tracer experiment is conducted in a fairly large watercourse, the amount and cost of tracer needed may also be prohibitive. Furthermore, a tracer experiment does not mean that there is no need to sample tributaries and groundwater, but it may give good indications as to where such sampling efforts should be focused.

### 4.5.2. Metals

Generally speaking, metals may enter a wetland by the same routes as water (previous Section). Metals may also enter a wetland by dry deposition. In a constructed wetland, the solid substrate used constitutes another potential source of metals (Wieder et al., 1990; Wieder, 1993). For the majority of the metals,
exit from a wetland is restricted to the treated drainage water, infiltration to the groundwater, or removal of biomass and/or sediments.

What potential sources of metals that has to be considered in calculating overall metal budgets is largely determined by the characteristics of the drainage water to be treated. As the concentration of metals in the drainage decreases, other sources of metals than the drainage water itself become comparatively more important. For instance, if the wetland is used to treat water with low metal concentrations, and the wetland is situated close to an uncovered tailings pile or smelter, metal contributions made by dust may have to be taken into account (cf. Kalin, 1989; Sobolewski et al., 1995; Sobolewski, 1996). Significant contributions of metals to natural wetlands may also be made by tributaries and groundwater, in particular in mineralized areas (cf. Emerick et al., 1988; Runnells et al., 1992; Alpers and Nordstrom, 2000; Wildeman and Pavlik, 2000; Paper III).

4.5.3. Performance Indices

The performance of treatment wetlands can be compared using a number of different indices. Two of the most common indices are treatment efficiency (the percentage of contaminant removed by the wetland based on inlet and outlet concentrations; measured as %) and area adjusted mass removal (taking the concentration, flow, and wetland area into account; measured as g contaminant m\(^{-2}\) day\(^{-1}\)).

Hedin et al. (1993) and Stark and Williams (1995) discuss the merits of these two indices in detail. According to Stark and Williams (1995), area adjusted mass removal gives some valuable information regarding the sizing of wetlands. It may also be useful when comparing the cost of different treatment options. However, a problem with this index is that it makes small wetlands that receive high flows of drainage appear to be highly effective, even if they only have a limited influence on the metal concentrations of the water. One of the advantages of treatment efficiency is that this index is tightly coupled to outlet pollutant concentrations, which is the legal basis for compliance with discharge requirements.

Tarutis et al. (1999) extends the discussion about performance indices to include also first-order removal, where the rate of pollutant removal is concentration dependent. The authors found significant correlations between several of the performance indices, but concluded that this may reflect that they are mathematically related to one another. There are indications that pollutant removal in a treatment wetland is concentration dependent, which means that recommendations for the sizing of wetlands may have to be revised. The authors
do not recommended the use of treatment efficiency for comparisons between wetlands, since this index does not account for differences in influent concentrations. Neither is the use of area adjusted mass removal recommended, since this index fails to separate the influence of pollutant concentrations from that of flow.

4.6. Treatment of Mine Drainage Waters in Wetlands

The modern history of treatment of mine drainage waters in wetlands began in the late 1970’s and early 1980’s when Huntsman et al. and Wieder and Lang reported that natural peatlands improved the chemistry of AMD that passed through them. However, descriptions of wetlands that improve the quality of mine waters were made already in 1965 (Sobolewski, 1997, 1999 a and b).

In the following three sections, some of the experiences regarding the treatment of mine drainage waters are summarized. In this section, a brief overview of this particular research field is given.

4.6.1. Characteristics of Different Kinds of Mine Drainage Waters

The majority of the studies on wetland treatment of mine drainage waters are concerned with drainage water from coal mines. Coal mine drainage is characterized by low pH and high concentrations of primarily Al$^{3+}$, Fe$^{2+}$, and Mn$^{2+}$. When these metals are oxidized and/or hydrolyzed, H$^+$ is liberated (Section 4.4.4). Thus, the water is actually more acidic than can be deduced from its content of H$^+$ alone. Acidity is a measure of the base neutralization capacity of a water, which also considers, among other, the influence of dissolved metals (Hedin et al., 1993; Hellier, 1999). Consequently, the majority of the studies concerned with coal mine drainage are focused on pH, acidity, Al, Fe, and Mn.

Most of the field experiences with wetland treatment of AMD from coal mines come from the coal mining regions in the Appalachia of the US. Wetlands have been constructed in Alabama, Indiana, Kentucky, Maryland, Ohio, Pennsylvania, South Carolina, Tennessee, Virginia, and West Virginia. Case studies from Great Britain are discussed in Brown et al. (2002). Therefore only a few British cases will be discussed in this text. Constructed wetlands to treat coal mine drainage have also been reported from Queensland, Australia. In Sweden, mining of coal ceased in the 1960’s (Nationalencyklopedin, 1992). However, since drainage from base and precious metal mines may also have a low pH and contain high concentrations of Al, Fe, and Mn, experiences from the treatment of coal mine drainage are still valuable from a Swedish perspective.
Trace metals found in drainage water from base and precious metal mines pose additional problems (Wildeman and Laudon, 1989). Field experiences from wetland treatment of such waters have been reported from Australia (Northern Territories), Canada (British Columbia, Ontario, Saskatchewan, and Yukon Territory), China, and the US (California, Colorado, Minnesota, Montana, and New York).

4.6.2. Different Kinds of Wetland Studies

Various approaches have been used to investigate wetland function and performance. These include laboratory studies (usually batch or column studies, in some cases also studies of miniature wetlands), mesocosm studies (studies of wetlands of intermediate size, either in a greenhouse, a laboratory, or in the field), case studies (field scale applications), and studies of natural wetlands that have been exposed to mine drainage waters.

With results from these and other studies as a base, efforts have been made to model system performance (Baker et al., 1991; Klusman, 1991; Flanagan et al., 1994; Mitsch and Wise, 1998; Kirby et al., 1999). The model presented by Klusman (1991) considers the fate of trace metals. A number of reviews has also been compiled. The report by Hedin et al. (1993) and the article by Sobolewski (1999a) are two of the most comprehensive and recent ones. An overview of the wetland studies reviewed in this thesis is given in Appendix 4.

From a management point of view, there is an interest in how large a wetland must be in order to treat a certain kind of drainage, as well as in how much it will cost. Numerous sizing guidelines have been published. The guidelines are usually stated in terms of the area required to remove a specified amount of Fe, Mn, and/or acidity (Brodie et al., 1988a; Kleinmann et al., 1991; Hedin et al., 1993; Dietz et al., 1994; Hellier et al., 1994; Manyin et al., 1997). Hellier (1989) has suggested sizing guidelines that considers only the area required to treat a certain flow of water. Older guidelines are typically based on empirical results rather than the rates of the processes behind metal immobilization (Sobolewski, 1999a). According to Wieder (1993), the recommended size of treatment wetlands has had a tendency to increase over time. Aerobic wetlands (Section 4.7.3) generally require smaller areas than compost-based wetlands (Kleinmann et al., 1991). In some cases, the area available for wetland establishment has been found to be insufficient in comparison to the area needed to achieve a satisfactory treatment (e.g. Cambridge, 1997).

Examples of costs associated with the construction, operation, and maintenance of treatment wetlands are given by Kleinmann and Girts (1987), Hiel and Kerins (1988), Brodie et al. (1989b), Hedin (1989), and Kolbash and Romanoski
(1989). Brodie et al. (1987, 1988a, and 1989a), Brodie (1993), Faulkner and Skousen (1994), McCleary and Kepler (1994), Gusek (1995), and Sanders et al. (1999) also compare the cost of wetland treatment of mine drainage waters with the costs of other treatments. The costs for wetland construction are usually larger than the costs associated with maintenance. Wetlands are often a cheaper alternative than conventional treatment methods. According to the model presented by Baker et al. (1991) factors such as the loadings of pollutants (Fe) and the desired degree of treatment will determine if it is more economical to treat mine drainage waters in wetlands than in conventional treatment systems. Hellier et al. (1994) found wetlands to be the best available technology for treatment of postmining groundwater seeps, particularly for mildly acidic and alkaline seeps.

4.7. Water Chemistry

It is evident from Appendix 4 that most studies of wetlands in connection with mine drainage waters are concerned with water chemistry. However, with the exception of the studies presented by Karathanasis and Thompson (1991 and 1993), few studies address changes in metal speciation that occur as the AMD passes through the wetland. In many cases, the quality of the drainage waters improves, at least initially, even though there are exceptions (e.g. Hiel and Kerins, 1988; P. Lane and Associates Limited, 1990). In some of the cases that do not include metal and/or water budgets, it cannot be excluded that improvements in water quality are due to dilution, rather than immobilization of metals within the wetland.

An improvement in water quality does not always represent a satisfactory treatment. Of the more than 400 constructed wetlands reviewed by Kleinmann (1989) and Kleinmann et al. (1991) only about 20% of the systems discharged water that met the US effluent limits. However, since the funding available for treatment of mine drainage waters often is limited, McCleary and Kepler (1994) argue that wetlands, being a comparatively cheap treatment method, may still be an appropriate means to improve overall ecosystem health.

At the sites where the regulatory limits were not entirely achieved, cost savings may be realized as a reduction in chemicals needed (Brodie et al., 1988a; Kleinmann, 1989; Kleinmann et al., 1991; Brodie, 1993). In some cases, the costs for wetland construction were repaid within 1 year (Brodie et al., 1988a; Hedin, 1989; Kleinmann, 1989; Kleinmann et al., 1991).
4.7.1. Wetland Design

The performance of a treatment wetland is governed by the quality of the water (next Section) and the design. Wetland design considerations include choice of solid substrate, addition of sources of organic carbon, incorporation of plants, as well as hydrology (Section 4.7.3) and size (Section 4.6.2).

All solid substrates provide potential adsorption sites. Howard et al. (1989) have compared the capacity of charcoal and various kinds of forest litter and humus to remove trace metals from solution. Certain minerals (e.g. CaCO₃) and organic materials (e.g. peat) can provide an initial buffering capacity. In some cases, wetlands where limestone was present or absent in the substrates have been found to behave similarly. This was probably due to encrustations on the limestone (Faulkner and Skousen, 1994; cf. Section 4.9.1).

Substrates rich in organic matter are often used in order to create reducing conditions in the wetland sediments. The organic material may also serve as a source of carbon and nutrients for microorganisms and plants. Gross et al. (1993), Eger and Wagner (1995), and Groudev et al. (1999) have compared the ability of a number of waste materials to support sulfate reduction. Materials investigated include (composted) chicken litter, cow manure, horse manure, municipal compost, rice hulls, sawdust, sheep manure, SMC, wheat straw, and yard waste (ibid.).

There are also a number of studies that have compared the overall wetland performance obtained with various substrates (Brodie et al., 1988b; Wildeman and Laudon, 1989; Karathanasis and Thompson, 1993; Wieder, 1993; Stark et al., 1996). Materials investigated include clay, ground hay, limestone, aged manure, mine spoil, pea-gravel, peat, ground pine needles, sawdust, SMC, various soils, *Sphagnum*, straw/manure, natural wetland soil, and decomposed wood products (ibid.). SMC is among the substrates that have proven to be successful (Wildeman and Laudon, 1989; Wieder, 1993).

Attempts have been made to increase the microbiological activity, and associated metal removal, by the addition of organic amendments such as alfalfa, barley, bran, cooked meat, flax, floating cattail rafts, glucose, hay, hydroseedling mulch, and potato waste (Wheeler et al., 1991; Fyson et al., 1994; Kalin, 1997 and 2001; Kalin and Smith, 1997), straw (Eger et al., 1993), and whey (Stark et al., 1991; Stark et al., 1995). The addition of organic amendments may reduce the area required for treatment. It may also improve treatment longevity. With regular additions of whey, Stark et al. (1991) found the retention of Fe to improve over time.
Several studies suggest that even though plant uptake may only have a limited influence on the total amount of metals retained by a wetland (cf. Section 4.4.3), the presence of plants, as well as plant density and diversity, may still have a positive influence on the overall wetland performance (Brodie et al., 1988b; Mitsch et al., 1988; Samuel et al., 1988; Stark, 1990; Stark et al., 1994c; Stark and Williams, 1995). For instance, transpiration may decrease the flow rates through the wetland (Stark et al., 1994c; cf. Section 4.7.3). There are also studies in which the presence of plants did not appear to affect metal retention in the wetlands investigated (e.g. Mitsch and Wise, 1998). In the studies by Hedin and Nairn (1993) and Hedin et al. (1993), absence or presence of emergent plants did not have a significant effect on the rates of either Fe or Mn removal at alkaline mine water sites.

In constructed wetlands, various approaches have been used in order to increase the residence time of the water, and to avoid short-circuiting. The total wetland area can be divided into a number of cells (Stark et al., 1988). This also allows for aeration of the water between the different cells, which is beneficial in cases when the oxidation of ferrous Fe may be limited by a lack of oxygen (Hedin et al., 1993; Witthar, 1993). An emphasis may be put on elongated shapes of the wetlands (Stillings et al., 1988; Witthar, 1993). Alternatively, hay bales, peat berms, or baffles, which promote a serpentine flow, can be incorporated (Hedin et al., 1988; Stark et al., 1988; Eger et al., 1993; Witthar, 1993; Faulkner and Skousen, 1994). Such hay bales can also act as organic amendments (Hedin et al., 1988; Stark et al., 1988). Incorporation of plants may also be beneficial to promote uniformity of flow across the surface of the wetland (Hedin et al., 1993; Stark et al., 1994c; Hellier, 1999).

When wetlands are used to treat alkaline mine drainage, or drainage which has been pre-treated in an ALD or a SAPS (Section 4.9), a settling pond is usually incorporated upstream from the wetland in order to collect the precipitates formed, a practice which will improve the treatment life of the wetland (Brodie et al., 1993).

4.7.2. Influent Drainage Quality

The influence of drainage quality on wetland treatment performance has been investigated in controlled laboratory experiments (Wieder and Lang, 1986; Lapakko and Eger, 1988; Stark et al., 1995; Manyin et al., 1997). It has also been investigated by exposing an individual wetland to drainage of different compositions, either due to natural variations (Stark et al., 1994c) or experimental releases (Brodie et al., 1987; Samuel et al., 1988; Eger et al., 1993 and 1994; Sobolewski et al., 1995; Sobolewski, 1996). Furthermore, larger data sets from natural (Stark, 1990; Stark and Williams, 1995; Sobolewski, 1997) and
With the exception of the study by Wieder (1989), most studies indicate that the performance of a treatment wetland improves as the quality of the drainage improves. A possible exception to this general rule would be if the processes that act to immobilize a certain metal were concentration dependent. Fe is the metal that most often is mentioned in this context (cf. Wieder, 1993; Kirby et al., 1999; Tarutis et al., 1999).

Brodie et al. (1987), Hellier (1989), Brooks et al. (1990), Stark (1990), Hedin and Nairn (1993), and Hedin et al. (1993) report that higher pH has a positive influence on wetland treatment of AMD. However, in the SMC mesocosm wetlands studied by Stark et al. (1995), there was no difference between the outlet concentrations of Mn from wetlands receiving drainage of pH 4.0 and pH 7.0. Adsorption of ferrous Fe to peat appears to be unaffected by pH in an interval between 3 and 6 (Wieder and Lang, 1986), whereas the mass of trace metals removed has been found to increase with increasing pH (Lapakko and Eger, 1988). Higher alkalinity has also been found to be beneficial for treatment (Hellier, 1989; Hedin and Nairn, 1993; Hedin et al., 1993; Hellier et al., 1994).

A positive influence of lower concentrations of Fe has been reported by Stark (1990), Hedin et al. (1993), Stark et al. (1994c), Stark and Williams (1995), and Manyin et al. (1997). In the study by Eger et al. (1993 and 1994), removal of Ni decreased as the experimental wetland was exposed to drainage with higher concentrations of trace metals (Co, Cu, Ni, and Zn). Sobolewski et al. (1995) and Sobolewski (1996) report a loss of Cu treatment efficiency as the Cu concentration of the drainage was increased by a factor >35 and the pH was lowered from 6-8 to 3. However, unless controlled experiments are performed, it may be difficult to separate the influence of higher pollutant concentrations from the influence of higher pollutant loadings.

In the study by Kleinmann and Girts (1987) no wetland treated drainage with more than 85 mg Fe/l well enough to meet discharge criteria of 3 mg/l. Constructed wetlands where the effluent waters meet discharge requirements have been found to be associated with moderate inflow water quality (<69 mg Fe/l, <17 mg Mn/l), relatively high total Mn to total Fe ratios in the influent (an average of 0.44), and significant inflow alkalinity (>35 mg/l) (Brodie, 1990 and 1993). In northern Appalachia, there is no known compost wetland that consistently transforms highly acidic water (>300 mg/l) into alkaline water (Hedin et al., 1993). Similarly, Sobolewski (1997) found no natural wetland treating acidic water that produced environmentally acceptable discharges.
4.7.3. Surface Water Depth and Flow Rate

The water depth has a large influence on the oxygen conditions in a wetland, both in the water column and in the sediments. Shallow water depths enhance oxygenation (Brodie et al., 1988a). Thus, in aerobic, free water surface, or surface flow wetlands, the water depth is usually restricted to 50 cm (Hedin et al., 1993). These kinds of wetlands are usually employed to treat neutral or net alkaline mine drainage waters. Mechanisms behind metal removal in aerobic systems include oxidation and hydrolysis (Section 4.4.4), as well as adsorption and ion exchange (Section 4.4.2) (e.g. Hedin et al., 1993; Eger, 1994; Gusek, 1995). According to Gusek (1995), aerobic systems are appropriate for removing Al, As, Fe, Hg, and Mn.

In anaerobic, sub-surface flow, or compost-based wetlands, there is an emphasis on the contact between the water to be treated and the anoxic wetland sediments. In wetlands in warmer climates, an added benefit of sub-surface flow is that it may reduce the loss of water due to evaporation (Tyrrell et al., 1997). Anaerobic wetlands are usually employed to treat acidic mine drainage waters. Mechanisms behind metal removal in these systems include sulfate reduction (Section 4.4.6) and the formation of metal carbonates (e.g. Hedin et al., 1993; Eger, 1994; Gusek, 1995). According to Gusek (1995), anaerobic systems are ideal for removing Al, Cd, Cu, Fe, Hg, Pb, U, and Zn.

Deep pockets or ponds may serve as recharge zones in draught events (Brodie et al., 1988a; Brodie, 1990). Larger basins may also be used to store and attenuate spring discharges (Sanders et al., 1999). Furthermore, ponds may serve as refugia for aquatic fauna when shallower parts of the wetlands either dry out or freeze (Brodie et al., 1988a; Brodie, 1993; Witthar, 1993). In large ponds, thermal stratification and wind action can have a negative influence on the residence time of the drainage (Jones et al., 1995).

Controlled experiments have shown that larger surface water depths (~15 cm) can have a negative influence on metal removal, due to less contact between the drainage and the substrate (Eger et al., 1993; Eger, 1994). Similarly, free surface water of a depth of ~2.5 cm had a negative impact on Mn retention in mesocosm wetlands containing limestone (Stark et al., 1996). However, as suggested by the study by Tyrrell et al. (1997), a water table at or below the surface of the substrate may also be detrimental to the functioning of a treatment wetland, since enhanced oxygen exchange at the surface may inhibit sulfate reduction and promote re-oxidation of sulfides.
A number of case studies indicate that an increased contact between the drainage and the substrate is favorable, in particular for the treatment of acidic drainage (Hedin et al., 1988; McIntire and Edenborn, 1989; Karathanasis and Thompson, 1993; Flanagan et al., 1994; cf. Hiel and Kerins, 1988; P. Lane and Associates Limited, 1990; Dietz et al., 1994). Parts of this effect may be coupled to an increased residence time when the drainage is forced to move through the substrate (Eger et al., 1993; Karathanasis and Thompson, 1993; Eger, 1994).

A problem when trying to achieve flow through a substrate is that this may necessitate a more sophisticated hydrologic design. The studies by Emerick et al. (1988) and Hiel and Kerins (1988) indicate that it may be difficult to achieve flow through saturated peat. Eger (1994) and Eger et al. (1994) also point to the fact that there is often little or no hydraulic gradient down into the peat, and that the hydraulic conductivity decreases as the depth and degree of decomposition increase. Thus, transport into the anaerobic zone will be controlled by diffusion and very slow (ibid.). Eger (1994) suggests that larger volumes of water may be transported through organic substrates if vertical, rather than horizontal, flows are employed. If pipes are incorporated into the system in order to direct the water flow through the substrate, problems may occur due to clogging (McIntire and Edenborn, 1989).

Many constructed wetlands receive fairly low water flows (e.g. Wieder, 1989). Decreased treatment efficiencies during periods of high flow have been noticed by Stillings et al. (1988), Karathanasis and Thompson (1991), and Stark et al. (1994c). Controlled experiments also indicate increased retention of metals at lower flow rates (Stark et al., 1996; Manyin et al., 1997). A loss of treatment efficiency during high flow may be due to insufficient residence times, or that the metal immobilizing processes in the wetland are unable to cope with the increasing metal and/or acidity loadings. A positive influence of increased residence times has been noted by Noller et al. (1994), Sobolewski et al. (1995), and Sobolewski, 1996 (cf. Hiel and Kerins, 1988). Low flow rates have also been found to stimulate sulfate reduction (Kwong and Van Stempvoort, 1994; Stark et al., 1994b and 1995; cf. Gammons et al., 2000). This may be due to that it is easier to achieve anaerobic conditions at low flow rates (Stark et al., 1994b and 1995).

### 4.7.4. Temporal Variability

A temporal variability in wetland treatment efficiency is important to take into account both in the evaluation of existing wetlands (Wieder, 1994), and in the prediction of future wetland performance.
Pronounced diurnal patterns of metal removal in wetland systems have been reported by a number of authors. In cases when an improved treatment efficiency has been noticed during the daytime, photosynthesis by algae and cyanobacteria has been suggested to create a water chemistry more favorable for metal removal, or less favorable for metal remobilization, such as higher pH and oxygen concentrations (Wieder, 1994; Jones et al., 1995). In cases when the treatment efficiency has decreased during the day, photoreduction of ferric Fe has been suggested to have a negative influence on metal retention (Henrot et al., 1989). However, in the studies by Henrot and Wieder (1990) and Wieder (1994) the influence of photoreduction was found to be negligible.

Rainfall events may influence the pH and metal concentrations of drainage that flows through a wetland by increasing the flow rate (previous Section), by remobilizing deposited precipitates, or simply by diluting the drainage water. Brooks et al. (1990) have investigated the performance of two constructed wetlands under a variety of hydrologic conditions, including heavy rains and drought. The authors found no evidence of disruption of the wetland sediments, and it was concluded that increased flow rates did not cause any appreciable increases in metal concentrations or releases. This was probably due to the fact that the surface water depth (several cm) was sufficient enough so that raindrops or increased flow rates did not disturb the sediment surface. The results from one of the wetlands (Hartzfeld) are also discussed in Stark et al. (1994a) (see below).

At two constructed wetlands, the pH and the total concentrations of Fe and suspended solids in the effluent waters increased above baseline values during storm events (Taylor et al., 1993). Total Mn concentrations increased at one of the wetlands, and decreased at the other one. The important storm characteristics appeared to be the rainfall intensity and the first flush mechanism. Dry-season storms also appeared to be more significant than wet-season storms. These results are contradictory to those presented by Brooks et al. (1990).

Stark et al. (1994a) have investigated how storm events affect the water quality and flow rates at two constructed wetlands of different sizes. At the large wetland, rainfall was positively correlated with outflow rates, but not with outflow pH, during the year of the study. Outflow rates, but not rainfall, were also positively correlated to outlet Fe concentrations. During single storm events, outlet pH was slightly elevated, relative to inlet pH, at the large wetland and reduced at the small wetland. The outlet concentration of Fe was increased during a storm event at the small wetland (>20 times more Fe was exported per time unit), but not at the large wetland.
Several cases of decreased wetland treatment efficiency during autumn and/or winter have been reported (Hellier, 1989; McIntire and Edenborn, 1989; Wieder, 1993; Dietz et al., 1994; Faulkner and Skousen, 1994; Stark et al., 1994c; Wildeman et al., 1994; Heal and Salt, 1999; Gammons et al., 2000). Low temperatures may have a negative effect on both biological and chemical mechanisms of metal removal. The negative influence of low temperatures on the abiotic processes appears to be less pronounced (Kepler and McCleary, 1994). In fact, Gammons et al. (2000) even found dissolution of CaCO$_3$ to be more pronounced during winter. Henrot and Wieder (1990) investigated the retention of Fe in *Sphagnum* peat at 3, 15, 25, and 37°C, and found a slight optimum at 25°C.

In cold climates, problems with freezing may occur during winter. Strategies to combat this problem include covering with hay (Machemer and Wildeman, 1992), application of thermal blankets such as artificial snow (Gammons et al., 2000), and continuous flow through pipes (Sanders et al., 1999). Other difficulties occur in areas with hot climate and low rainfall, where there is a risk that the wetlands will dry out each year (cf. Noller et al., 1994; Tyrrell et al., 1997; Martin et al., 2001).

From a long-term perspective, changes in wetland performance over time are of great interest. This is the subject of the following section.

4.7.5. Sustainability

There are two major reasons to be interested in for how long metal retention in treatment wetlands can be sustained. First, treatment life is an important variable when comparing the costs associated with different treatment options (cf. Section 4.6.2). Second, sustained treatment efficiency is a key issue if wetlands are to be used as sustainable walk-away-solutions.

An obvious problem when trying to estimate for how long treatment of mine drainage in constructed wetlands can be sustained is that the first of these systems were constructed only some 20 years ago (Appendix 4). In this study, the longest time series found covers eight years of measurements of wetland performance (Stark et al., 1994c).

Several investigators have tried to estimate the time required to reach saturation of various wetland treatment systems (e.g. Wieder et al., 1990; Beining and Otte, 1997). Treatment life is typically dependent on the concentrations of pollutants in the drainage, the size of the wetland, and the capacity of various substrates to accumulate metals. For instance, by summarizing the maximum retention of Fe by a number of different mechanisms, such as formation of Fe
oxides and sorption to organic matter, Wieder (1988) calculated the maximum Fe retention in a Sphagnum wetland to be 5.8 kg/m².

Sometimes a decrease in treatment efficiency has been noticed as wetland substrates or treatment wetlands are exposed to increasing loadings of metals (Howard et al., 1989; Karathanasis and Thompson, 1991; Wieder, 1993; Sobolewski et al., 1995; Sobolewski, 1996). This may be due to saturation of ion-exchange sites (Howard et al., 1989), metal overloading (Karathanasis and Thompson, 1991), a gradual acidification of the substrate (Wieder, 1993; Tarutis and Unz, 1994; Sobolewski et al., 1995; Sobolewski, 1996), or that insufficient decomposable organic carbon is available for the sulfate reducing bacteria (cf. Tarutis and Unz, 1994).

The behavior of an individual metal reflects its affinity for the solid substrate and/or its ability to partake in different kinds of metal immobilization processes. For instance, in one of the systems studied by Wildeman and Laudon (1989), there was a dramatic increase in the Mn and Zn concentrations of the effluent water after 30 days of treatment, while the concentrations of Cu and Fe did not increase until day 100. This was probably due to that Cu and Fe were better competitors for adsorption sites. As sulfide was generated, Cu and Zn were completely removed. Wieder (1993) describes changes in wetland treatment efficiency for Al, Ca, Fe, K, Mg, Mn, and Na that occurred over a period of 111 weeks. All of the five wetlands investigated were net sources of Ca²⁺, K⁺, Mg²⁺, and Na⁺. The author suggests that this reflects replacement from cation exchange sites by H⁺, Al³⁺, Fe³⁺, and Fe²⁺.

Eger and Wagner (1995) have compared the ability of four different organic materials to sustain sulfate reduction and treat AMD. A decrease in treatment efficiency was noted already after two field seasons, as the organic material became more refractory. This is in sharp contrast to estimates presented by Gusek (1995), who suggests that the lifetime of an anaerobic treatment system may approach 100 years, provided that a substrate is selected that releases nutrients slowly.

Even with regular additions of a carbon source (whey) Stark et al. (1995) did not achieve sustained retention of Mn (a consistent pattern of removal for >60 days, with no signs of an elevation in concentration) under reducing conditions in mesocosm wetlands containing SMC. Sustained retention of Mn was achieved in limestone mesocosm wetlands where surface water was absent and when the inlet water had a pH of 7 and no appreciable Fe (Stark et al., 1996). Stark et al. (1994b) have also shown that it may be possible to increase the metal accumulating capacity of SMC if it is exposed to AMD under lower flow rates and less oxidizing regimes.
Sustainable treatment of mine drainage must also consider the fate of the accumulated metals (cf. Section 4.8.5). For instance, in the study by Stark et al. (1994b) Fe was first exported from SMC as reducing conditions were established, and then retained on a stable basis.

4.8. Solid Substrate Chemistry

A number of wetland studies have been devoted to more or less detailed investigations of the solid substrate. In this section, some of the results from these studies are highlighted.

Analyses of the solid substrate in a wetland serve a number of functions. Estimations of the total metal content of the solid substrate can be used to verify the total amount of metals removed, calculated from water chemistry data (Eger and Lapakko, 1988; Wieder, 1988; Eger et al., 1994). Spatial patterns of total concentrations in the solid substrate may reveal a gradual saturation along the water flowpath, which in some instances can be used to estimate system longevity (Section 4.8.5). They can also be used to indicate if metal removal occurs primarily in the aerobic or anaerobic parts of the wetland (Section 4.8.3), and how much of the solid substrate that is actually active in metal removal (Eger and Lapakko, 1988; Eger et al., 1994). The latter is important when trying to estimate the total capacity of a wetland to accumulate metals.

Analyses of metal speciation in the solid substrate are often done by a chemical extraction procedure. Depending on the method employed, the total metal content can be divided into a number of different operationally defined fractions. Chemical and mineralogical characterization of precipitates formed have also been made using energy dispersive spectrometry (EDS), energy dispersive X-ray analysis (EDX), energy dispersive X-ray fluorescence (XRF), evolved gas analysis (EGA), qualitative wavelength dispersive spectrometry (WDS), scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) (Hedin et al., 1988; Faulkner and Richardson, 1990; Kwong and Van Stempvoort, 1994; Sobolewski, 1996; Barton and Karathanasis, 1999). Solid phase metal speciation can be used to elucidate the mechanisms behind metal removal and to quantify their relative importance. It can also be used to separate precipitates formed in situ from dust originating from mine sites nearby (Sobolewski et al., 1995; Sobolewski, 1996). Changes in metal speciation over time can be used to estimate system longevity (Section 4.8.5). Furthermore, metal speciation in the solid phase can be used to estimate the bioavailability of the accumulated metals, as well as the risk that the metals will eventually become remobilized.
The dominant form of metal removal may differ both between different kinds of wetlands and between different metals. For instance, metals such as Fe, Mn, and Zn are often precipitated as oxyhydroxides, sulfides, sulfates, or carbonates, while metals such as Al, Cu, Ni, and U tend to be associated with the organic material (Karathanasis and Thompson, 1991; Eger et al., 1994; Sobolewski, 1999a). Fe oxyhydroxides formed have been identified as α-FeOOH (Faulkner and Richardson, 1990), Fe$_2$O$_3$, Fe(OH)$_3$ (Barton and Karathanasis, 1999), and ferric hydroxide (Kwong and Van Stempvoort, 1994).

4.8.1. Wetland Design

The choice of solid substrate can influence the total amount and chemical stability of metals accumulated in the wetland. The accumulation of water-soluble and sulfide Fe in wetlands exposed to AMD is heavily influenced by the composition of the solid substrate (Taddeo and Wieder, 1991). The accumulation of water-soluble Fe decreased in the order sawdust > SMC > straw/manure > Sphagnum peat with lime and fertilizer. The accumulation of sulfide Fe decreased in the order SMC > straw/manure > sawdust > Sphagnum peat with lime and fertilizer > Sphagnum peat. Fe sulfides exhibited the greatest contribution to total Fe accumulation in the SMC and straw/manure wetlands.

Karathanasis and Thompson (1993) have compared the patterns of metal (Al, Cu, Fe, Mn, and Zn) retention in mesocosm wetlands containing mixtures of different kinds of organic material (hay, peat, pine needles, and Sphagnum) and soil (surface soil, subsoil, and mine spoil). Cu was retained mainly in organic forms. For the other metals investigated, ‘residual 2’ (oxyhydroxides) and ‘residual 1’ (carbonates, sulfates, and sulfides) dominated.

Stark et al. (1996) investigated Mn speciation in CaCO$_3$ and SMC in wetland mesocosms exposed to synthetic, near-neutral (pH 6.9) mine drainage containing dissolved Mn (44 mg/l). For both substrates, removal was dominated by the formation of Mn oxides at the surface. In CaCO$_3$, 72% of the retained Mn was present as oxides and 16% was present as carbonates. In SMC, 38% of the retained Mn was present as oxides. Exchangeable (22%), carbonate (16%), organic/sulfide (13%), and water-soluble (12%) phases were also important. The partitioning of Mn in SMC differed slightly from that obtained by Stark et al. (1995). In the latter study, most of the Mn (37%) was retained in exchangeable phases.

In a study by Wieder et al. (1990) the presence of plants (Typha latifolia and Sphagnum or Sphagnum only) had no significant influence on ferrous Fe retention in wetland peat mesocosms, neither regarding the total amount of Fe
accumulated, nor regarding the chemical state. Similar results were obtained for Ca. The authors suggest that the effect of plants on the retention of Fe would have been more pronounced if the pH of the synthetic AMD employed had been higher than 3.5, a suggestion which is not supported by the findings presented by Hedin and Nairn (1993) and Hedin et al. (1993). However, the total concentrations of Al, Mg, and Mn were greater in mesocosms containing *Typha*.

The latter observation is supported by results presented by Mitsch and Wise (1998), who found the substrate concentrations of Al, Fe, and Mn to be higher at vegetated sites than at unvegetated sites. Samuel et al. (1988) also found higher concentrations of Fe in soil samples collected from mesocosm wetlands where *Typha latifolia* was present.

### 4.8.2. Influent Drainage Quality

Henrot et al. (1989) found no remarkable difference in Fe speciation in peat between mesocosm wetlands exposed to 50 or 100 mg Fe/l. In peat exposed to AMD containing different concentrations (0-400 mg/l) of Fe, the highest concentration of Fe oxides was found in peat exposed to 100 mg Fe/l (Henrot and Wieder, 1990).

The distribution of Fe and Mn in sediments collected from two constructed surface flow wetlands has been investigated by Tarutis and Unz (1990). One of the wetlands received drainage of pH 6 and low metal loading rates, while the other received drainage of pH 3 and high metal loading rates. At both sites, metal precipitation in the oxidized zone was the dominant process behind metal removal.

Results presented by Sobolewski et al. (1995) and Sobolewski (1996) suggest that precipitation of sulfides may be the main mechanism behind removal of Cu from low strength mine drainage (0.3-1 mg/l, pH 6-8). Cu removed from high strength mine drainage (40-50 mg/l, pH 3) was largely organically bound.

### 4.8.3. Surface Water Depth and Flow Rate

In surface flow wetlands, the highest metal concentrations are usually found in the uppermost layers of the solid substrate (Eger and Lapakko, 1988; Faulkner and Richardson, 1990; Tarutis and Unz, 1990; Eger et al., 1994).

Sulfate reduction may occur also in surface sediments. In the study by Taddeo and Wieder (1991), Fe sulfide accumulation was greater in the deep substrate only for one of the substrates investigated (sawdust). This observation is somewhat contradictory to that of Calabrese et al. (1991). The latter authors
found the highest concentrations of Fe sulfides in the bottom sediments at the effluent end of the studied wetland mesocosms. The sulfides accumulated primarily as AVS, but pyritic disulfides were also noted in all of the samples (ibid.). Hedin et al. (1988) found FeS₂ in samples collected from a constructed wetland at a depth of 15-20 cm.

Metals may be stored in different forms in different parts of a wetland. For instance, Kwong and Van Stempvoort (1994) found ferric hydroxide and native Cu in the sediments close to the inlet of the investigated pond. Near the outlet, the sediments were reducing and contained framoidal FeS₂ in association with Fe monosulfides.

Mitsch and Wise (1998) report total metal and sulfate concentrations in different kinds of substrates collected from a series of wetland basins. The lowest concentrations of Fe were found in substrate (fermway; i.e. animal waste mixed with grain, fed to livestock and collected again) collected from a subsurface flow, anaerobic wetland basin. On the other hand, this substrate contained the highest concentrations of Cu and Zn. It also contained more Al than substrate collected from some of the aerobic basins upstream.

In a natural wetland exposed to AMD, the vertical distribution of metals in the sediments may also be influenced by groundwater containing dissolved O₂ and additional metals. For instance, Wildeman and Pavlik (2000) found Fe to be enriched close to the wetland surface, as well as in oxidized sediments below a layer of anaerobic peat. The highest Zn concentrations were found in the deepest sediments. Presumably Zn originating from the groundwater precipitated as a sulfide when the water reached the reduced zone of the peat.

The formation of different Cu species in constructed wetlands appears to be sensitive to the hydraulic retention time (Sobolewski et al., 1995; Sobolewski, 1996). At a hydraulic retention time of approximately 23 days, 13.3% of the Cu were retained as sulfides. At a hydraulic retention time of approximately 12 days, only 7.2% of the Cu were retained as sulfides. However, the partitioning of Mn in substrate from SMC wetland mesocosms does not appear to be affected by the flow regime (Stark et al., 1995).

4.8.4. Temporal Variability

The majority of the studies concerned with temporal variation of metal concentrations and speciation in the solid substrate deal with long-term changes, which will be discussed in the following section. However, the relative importance of the various mechanisms that act to immobilize metals in a wetland may also vary with the season.
For instance, Henrot and Wieder (1990) investigated the retention of Fe in *Sphagnum* peat at 3, 15, 25, and 37°C. The precipitation of Fe oxides was found to increase by a factor of three between 3 and 15°C, while the organically bound fraction decreased with temperature, possibly as a result of increased decomposition. When the effect of the two processes was added, the optimum temperature for Fe retention was 25°C.

4.8.5. Sustainability

Changes in the mechanisms behind Fe removal in *Sphagnum* peat over time have been investigated by Wieder and co-workers in a series of studies (Henrot et al., 1989; Henrot and Wieder, 1990; Wieder et al., 1990). In all cases, the retention of Fe was dominated by organically bound forms and Fe oxides. While the concentration of organically bound Fe reached a saturation level of approximately 10 mg/g dry peat, the concentration of Fe oxides often increased during the whole experiments. However, the total capacity of the peat to accumulate Fe appeared to be exhausted at about 235 mg Fe/g (Wieder et al., 1990). The authors suggested that precipitation of Fe as oxides may be limited by a gradual coating of organic sites suitable for Fe precipitation, or that the coatings limit the access to organic carbon for certain kinds of Fe-oxidizing bacteria.

Some metals, such as Al, Ca, Mg, and Mn that are accumulated by, or initially present in, the wetland sediments may be lost from the system if exposure to AMD continues (Wieder et al., 1990). Most probably, the Ca, Mg, and Mn are displaced from exchange sites by ferrous Fe and H⁺.

Taddeo and Wieder (1991) have followed how the retention of sparingly soluble and sulfide Fe in different kinds of wetland substrate changes over time. In *Sphagnum* peat, there were minimal further increases in the concentration of sulfide Fe following an initial sharp increase. In contrast, there were gradual, continual increases in the concentration of Fe sulfides in substrates composed of SMC, straw/manure, and sawdust.

The mobility of the metals accumulated in the solid substrate has attracted comparatively little attention. Henrot and Wieder (1990) found little remobilization of Fe accumulated in peat when the peat was exposed to acidic (pH 3.9) waters. The influence of acidic (pH 4) waters on the remobilization of trace metals from peat appears to be more pronounced (Lapakko and Eger, 1988). Lapakko and Eger (1988) also found remobilization of trace metals accumulated in peat when it was exposed to salt solutions or bog water. There is some evidence that Zn that initially is loosely bound to bog material with aging
will become unavailable to most extractants (Boyle (1965) quoted in Sobolewski, 1997 and 1999a).

The results from experiments where the fate of Fe oxyhydroxides under reducing conditions has been investigated are somewhat contradictory. Henrot and Wieder (1990) found little or no remobilization, while Tarutis and Unz (1995) found that substantial remobilization could occur, at least from amorphous precipitates (cf. Postma and Jakobsen, 1996). To some extent, increasing concentrations of dissolved Fe following dissolution of the Fe oxyhydroxides can be counteracted by the formation of Fe sulfides (Tarutis and Unz, 1995). At least at some field sites, there is a potential for the conversion of $\alpha$-FeOOH to FeS$_2$ or siderite (FeCO$_3$) (Tarutis and Unz, 1990).

4.9. Pre-treatment Systems that Improve the Performance of Treatment Wetlands

As outlined in the preceding sections, the performance of wetlands constructed to treat AMD may be improved by adapting wetland design to conditions on site. An alternative way to improve wetland performance is to add alkalinity to the water to be treated before it enters the wetland. This may be done by allowing the water to pass through an ALD or a SAPS.

An example of a case where incorporation of ALDs and SAPS has greatly improved the overall efficiency of an existing wetland treatment system is given by Barton and Karathanasis (1999). The authors stress the usefulness of combining the three different treatment technologies, and that this approach may also reduce the area required for treatment.

4.9.1. Anoxic Limestone Drains (ALDs)

Dissolution of limestone (calcite, CaCO$_3$) raises the pH and increases the concentration of Ca and HCO$_3^-$ alkalinity;

$$\text{CaCO}_3(s) + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \quad \text{(Eq. 4.7)}$$

Consequently, CaCO$_3$ can be used to neutralize AMD, and to counteract the acidification caused by the hydrolysis of metals (Section 4.4.4). CaCO$_3$ is inexpensive (Hedin et al., 1994), but in oxidizing environments, the Fe hydroxides formed will coat or ‘armor’ the CaCO$_3$, inhibiting further dissolution (Brodie et al., 1993).

The benefits of anoxic limestone drains (ALDs) were discovered when improvements in water quality were noted downstream from a road bank.
constructed of high-calcium limestone (Brodie, 1990 and 1993; Brodie et al., 1993). The first description of an ALD is usually ascribed to Turner and McCoy.

An ALD is sealed from the atmosphere (Brodie et al., 1993; Hedin et al., 1993), which means that the oxidation of Fe$^{2+}$, and the following hydrolysis of Fe$^{3+}$, will be restricted until the water leaves the system. O$_2$ already present in the AMD can compromise the function of an ALD (Brodie et al., 1993; Kepler and McCleary, 1994; Skousen, 2001). High concentrations of Al$^{3+}$ and Fe$^{3+}$ can also be problematic, since (oxy)hydroxides of these metals will form once the pH of the drainage has been raised (Brodie et al., 1993; Hedin and Watzlaf, 1994; Kepler and McCleary, 1994). However, Fe$^{2+}$ does not precipitate as Fe(OH)$_2$ at pH $<$ 6 (Skousen, 2001). Brodie et al. (1993), Hedin et al. (1993), and Hellier (1999) discuss when an ALD will be beneficial for the overall efficiency of a passive AMD treatment system.

Presence of carbonic acid (H$_2$CO$_3$) may also cause dissolution of CaCO$_3$;

$$\text{CaCO}_3(s) + \text{H}_2\text{CO}_3 \rightarrow \text{Ca}^{2+} + 2 \text{HCO}_3^- \quad \text{(Eq. 4.8)}$$

In the ALDs investigated by Hedin et al. (1994), this was found to be the principal HCO$_3^-$ producing process.

Investigated ALDs have sometimes been found to be (super)saturated with respect to siderite (FeCO$_3$) and rhodocrocite (MnCO$_3$) (Hedin and Watzlaf, 1994; Hedin et al., 1994). However, the kinetics of the formation of these minerals is slow, which means that FeCO$_3$ is unlikely to form in an ALD unless the water is retained in the system for $>$ 650 h (Hedin and Watzlaf, 1994). In the study by Hedin and Watzlaf (1994), no ALD was supersaturated with respect to CaSO$_4$ as long as the SO$_4^{2-}$ concentrations were below 2000 mg/l.

The size of an ALD should be dimensioned so that the minimum residence time of the water in the ALD is between 14 and 23 h (Faulkner and Skousen, 1994; Hedin and Watzlaf, 1994). The recommended sizes of the CaCO$_3$ in an ALD range from 1.9-3.8 cm (Brodie et al., 1993) to 8-25 cm (Faulkner and Skousen, 1994). Larger particles increase the hydraulic conductivity and may reduce the potential for plugging, but they also provide less surface area. Any pipes incorporated into the system must be large in diameter and have large perforations in order to reduce the risk for plugging (ibid.). Hay, used as an oxygen sink and a source of CO$_2$, should not be buried in proximity to the limestone in an ALD, since it encourages the growth of microorganisms, reducing pore space and dissolution of limestone (ibid.). The establishment of trees should also be discouraged, since their roots could penetrate the ALD and render it ineffective (Brodie et al., 1993).
Theoretical lifetimes of ALDs range from >20 years to approximately 80 years, but it is unknown for how long anoxic, porous conditions within an ALD can be maintained (Brodie et al., 1993; Hedin et al., 1993 and 1994). The simplest way to estimate the expected lifetime of an ALD is to calculate how long it will take for all of the CaCO$_3$ to dissolve (Hedin and Watzlaf, 1994; Hedin et al., 1994). A more accurate estimation involves calculations of how long a satisfactory residence time of the AMD within the ALD can be maintained (ibid.).

According to experiments performed by Cravotta and Trahan (1999), satisfactory treatment of acidic (pH <4), dilute AMD (1-4 mg/l Al$^{3+}$, Fe$^{3+}$, and Mn$^{2+}$) may occur also in an oxic limestone drain (OLD). In an OLD, access of oxygen is limited to oxygen originally dissolved in the water to be treated. Due to the low pH, dissolution of limestone continued despite the formation of oxyhydroxide coatings. Some of the oxyhydroxides formed were also transported to areas with higher pH downflow, where they acted as scavengers of other metals present (cf. Paulson and Balistrieri, 1999). The authors suggested that an OLD followed by a settling pond may require less land area than an ALD followed by an oxidation-settling pond or wetland.

4.9.2. Successive Alkalinity Producing Systems (SAPS)

**Successive alkalinity producing systems (SAPS)** were first described by Kepler and McCleary (1994). A SAPS is basically a SMC based wetland overlying a limestone drain. The water moves vertically downward through the system. Thus, SAPS are sometimes referred to as vertical flow wetlands (Demchak et al., 2001). The function of the compost is to remove dissolved oxygen and to reduce ferric Fe to ferrous Fe before the water reaches the limestone drain.

Removal of metals may occur also in the wetland part of a SAPS. In order to investigate in what solid phases the metals were retained, and if any changes occurred upon aging, Thomas et al. (2000) sequentially extracted compost exposed to ARD from a coal storage pile. In the systems studied, Al, Cu, Fe, Ni, and Zn accumulated over time. Mn was accumulated initially, but it was not retained in the end. With time and continued loading, Fe shifted towards the amorphous and crystalline oxide phases. Al shifted towards the acid soluble phase, and Ni and Zn shifted towards the acid soluble and amorphous iron oxides phases. Cu was always recovered in the sulfide and residual phases. It was concluded that metal accumulation in the organic substrate over time will compromise its ability to promote anoxic conditions. The rate of this degradation is dependent on the loading rate of the ARD and the neutralization potential of the organic substrate.
Removal of Fe also occurred in a SAPS in Pelenna, South Wales (Rees et al., 2001). Since little removal of $\text{SO}_4^{2-}$ occurred, and ochre precipitates were found by visual observation of the SAPS, this removal was most probably due to the oxidation and hydrolysis of Fe. Supplementary experiments revealed that the precipitates formed may have had a catalytic effect on these processes (cf. Sung and Morgan, 1980). Furthermore, the authors investigated how the precipitates influenced the vertical permeability of the SAPS. It was estimated that problems with vertical permeability would occur approximately 5 years after construction. It was concluded that successful treatment of net acidic minewater requires separation of the alkalinity supplementation and Fe removal stages (cf. Cravotta and Trahan quoted above).

Demchak et al. (2001) report on a SAPS where the treatment efficiency did not decrease over a six-year treatment life. At another site, the compost layer was compacted and subsequently hindered downward water flow. Construction recommendations presented include periodic replacement or addition of fresh compost material and increasing the number of drainage pipes underlying the limestone. The authors also compare the costs for AMD treatment in a SAPS with conventional treatment methods. SAPS are more expensive than aerobic wetlands and anaerobic wetlands without plants, which means that they have to work for approximately seven years in order to break even with the costs for NaOH chemical treatment.
5. RESULTS AND DISCUSSION

In this section, the results from the case study and the laboratory experiments are presented. In order to lay the foundation for a more comprehensive discussion (Section 6), some initial interpretations of the results are also given.

5.1. Vormbäcken Case Study

5.1.1. Monitoring Data

The introductory study of old monitoring data showed that the water chemistry changed along the river (Paper I). With the exception of color, average values of all investigated parameters (SO$_4^{2-}$, conductivity, pH, turbidity, Cu, Fe, and Zn) decreased downstream from Aspliden (6312). Aspliden is the sampling station where the effluent water from the mine area can be assumed to be completely mixed with the background river water (Figure 3.2), and it can therefore be considered to be a suitable reference station for some of the comparisons made in this thesis. Average color increased down to the sampling station Brännfors (6315), and then decreased slightly upon passing Vormträsket. Since color is a measure of the organic carbon content of the water, this would indicate that the first two wetland areas acted as sources of organic carbon (in agreement with findings presented in Papers II-IV; as well as by Hemond, 1990). The lowest average turbidity values were found at the sampling stations situated downstream from lakes, as expected if the lakes act as settling basins.

Without simultaneous measurements of water flow, and not knowing if any of the investigated parameters can be used as a conservative tracer, it is very difficult to determine if any immobilization of metals occurred in the wetlands investigated (cf. Section 4.5.1). In an attempt to quantify effects caused by dilution, the averages of all investigated parameters were plotted against upstream catchment area (Paper I). Downstream from Aspliden (at 50 km$^2$), total Fe concentrations decreased in a linear fashion (Figure 5.1). Cu and Zn exhibited a pattern in which the initial decrease in total concentrations was more rapid (exemplified by Zn in Figure 5.1). This pattern was similar to that obtained for SO$_4^{2-}$, conductivity, and pH.

During measurements conducted in 2000, the water flow in the river was proportional to upstream catchment area, at least upstream from Brännfors (Paper III). Upstream from Brännfors (at 187 km$^2$), the concentrations of Cu and Zn also decreased in a highly approximately linear fashion, but the decrease was much more pronounced than that for Fe (Figure 5.1). Furthermore, the measurements conducted in 2000 revealed that SO$_4^{2-}$ appeared to behave in a fairly conservatory manner (Paper III). Thus, the most likely interpretation of
the results presented above is that the decreasing concentrations of Cu and Zn along the river were caused by dilution with other surface water and groundwater from the rest of the catchment area, and that no significant immobilization occurred in the wetlands studied. For Fe, the rapid dilution was probably counteracted by additions from the catchment area (Section 5.3.1).

![Figure 5.1. Surface water samples collected from Vormbäcken 1971-1981. Average total iron and zinc concentrations as a function of upstream catchment area. Error bars represent standard error of the mean. Modified from Paper I.](image)

5.1.2. Total Metal Concentrations

The field sampling campaigns conducted in 1999 and April 2000 had the same limitations as the previous monitoring program. No measurements of water flow were performed. An additional problem, when trying to assess metal immobilization in the investigated wetlands, is that the location of the original sampling stations made it impossible to distinguish between effects caused by the wetlands and dilution by water from the major tributaries (Section 3.2.2). Furthermore, in a mineralized area, significant contributions of the investigated metals may be made from the catchment area (Runnells et al., 1992; Alpers and Nordstrom, 2000), canceling the effect of any immobilization that may be occurring. In order to handle some of these problems, two extended sampling campaigns were conducted in 2000 (Papers II and III).

By including more sampling stations along the river, the sites of major changes in metal concentrations can be narrowed down. It was observed that the major reduction in the concentration of total Ca, Cd, Cu, and Zn between the sampling stations Aspliden (A) and Timmervägen (T) occurred downstream from the confluence with drainage water from Holmtjärn, and not in the most pronounced wetland area, which is situated between A and sampling station 5 (Paper II; exemplified by Zn in Figure 5.2).
Figure 5.2. The total concentration of zinc in surface water samples collected from Vormbäcken in June and October 2000. The sampling stations are given in downstream order. For location of the stations, refer to Figure 3.2. Vertical lines mark entry of important tributaries. The figure is based on results presented in Paper II. The October results will be discussed in more detail in Section 5.3.4.

The hypothesis that any reduction in metal concentrations that occur upon passing the first wetland area (between A and T) is caused primarily by dilution of the river water gains further support from calculated metal loadings. Given the uncertainties associated with some of the water flow measurements performed in June (Paper III), the loadings of Ca, Cd, Cu, and Zn appeared to be relatively constant all the way between A and the sampling station Brännfors (B) (exemplified by Zn in Figure 5.3). This area also includes the second wetland area, which is situated between the sampling stations Rökå (R) and Mickeldammet (M).

A third way to elucidate if any metal immobilization occurs in the studied wetlands is to compare the behavior of a given metal with that of a conservative tracer (cf. Section 4.5.1). Results presented in Paper III indicate that SO₄²⁻ may be used as a tracer in the investigated system. This allows an assessment of the metal immobilizing capacity of Vormträsket, as well as of any metal immobilization that may have occurred on the other sampling occasions, when no measurements of water flow were performed. With the exception of May 1999, when the pH at the uppermost stations along the river was unusually high, and April 2000 (Section 5.3.4), the total concentrations of Cd, Cu, Pb, and Zn were never reduced more than 5% more than the concentration of SO₄²⁻ (Paper III; exemplified by the data from October 1999 in Figure 5.4).
Figure 5.3. The loadings of zinc at five ordinary sampling stations situated along Vormbäcken in June and October 2000. The sampling stations are given in downstream order. The sampling stations Timmervägen (between A and R) and Vormsele (downstream from B) have been omitted, since the flow of water was not measured at these stations. The height of the bars equals loadings measured. Difference=the difference (either positive or negative) between the loadings measured and the sum of the loadings at the upstream station and those contributed by the tributaries. The figure is based on results presented in Paper II.

Figure 5.4. The ratio between the sulfate and metal concentrations measured at an ordinary sampling station along Vormbäcken to those measured at the reference station Aspliden in October 1999. The stations are given in downstream order. The results for arsenic and iron will be commented on in Section 5.3.1. Modified from Paper III.

With the exception of a small ditch by the dike of the tailings pond at the Kristineberg mine, the concentration of Cd, Cu, and Zn in all of the tributaries investigated in 2000 was much lower than those encountered in Vormbäcken (Paper II). Budget calculations presented in Paper III suggest that it is unlikely that any significant immobilization of these metals was masked by contributions from the catchment area.
5.1.3. Metal Speciation

Metal speciation changed along the river. From a wetland perspective, the most pronounced changes occurred between the sampling stations Brännfors and Vormsele. Upon passing Vormträsket, which is situated between these stations, the fraction of metals recovered in the particulate (>0.2 µm) phase decreased (Figure 5.5a), while the fraction of As, Cu, Fe, and Pb associated with DOM increased (Paper IV). This suggests that Vormträsket acts as a settling basin for particles (in agreement with the low turbidity values presented in Paper I).

Addition of the treated effluent water from the Kristineberg mine area also had a pronounced influence on metal speciation in the river water. In particular, a larger fraction of most of the investigated metals was recovered in the particulate (>0.2 µm) phase downstream from the spillway† (Figure 5.5b; cf. Egeberg and Håkedal, 1998). At the sampling station Aspliden, the fraction of the metals that was found in association with particles appeared to be governed by pH and/or the concentration of particulate Fe (Paper IV). Larger fractions of particulate Cd and Zn were only found at pH ≥7.7. Above this pH, the fraction of particulate As, Cu, and Pb was lower than expected when the concentration of particulate Fe at the time of sampling was comparatively low (ibid.).

In Vormbäcken, the concentration of particulate (>0.2 µm) Fe was the best predictor of the fraction of particulate metals (Paper IV; Figure 5.6). The fraction of particulate As, Cu, and Pb clearly increased with increasing
concentrations of particulate Fe. For Cd and Zn, the increase was less pronounced, and large fractions (>20%) of particulate Cd and Zn were found only at pH ≥ 7.7.

Figure 5.6. The fraction of the total metal concentration that was recovered in particles >0.2 µm as a function of the concentration of particulate (>0.2 µm) iron in 36 surface water samples from the ordinary sampling campaigns conducted along Vormbäcken in 1999 and 2000. The samples with the four highest pH-values have been excluded. a) Zinc, copper, and iron. b) Cadmium, arsenic, and lead. From Paper IV.

5.2. The Role of Iron

The hypothesis that the metal speciation in Vormbäcken is governed by additions of ferrous Fe from the groundwater could not be verified by adding ferrous Fe to water from the sampling station Storkalven (Paper V). A clear difference was noted between the rate of formation of the Fe oxyhydroxides in the March and June experiments (Figure 5.7). Most likely, the faster precipitation rate in June was caused by the higher temperature during that experiment (22°C instead of 0°C as in the March experiment; cf. Sung and Morgan, 1980). The experimental setup does not allow for a separation of the influence of particles and bacteria initially present in the water. However, it is unlikely that the filtered (<0.2 µm) waters in the June experiment were devoid of slightly smaller particles (cf. Forsberg, 2002). Thus, the fact that the Fe oxyhydroxides in the June experiment were formed more rapidly in the treatments that contained unfiltered river water (Figure 5.7) suggests that the process was catalyzed by bacteria, which are usually considered to be >0.2 µm. All of the Fe added did not appear to precipitate. It is likely that complexation by DOM prevented this from happening (in agreement with findings presented in Paper VI, see below).
In the laboratory experiment with artificial waters, the presence of Fe oxyhydroxides increased the fraction of As, Cu, and Pb recovered in particles (>0.2 µm) in the treatments without DOM (OC, GC, OP, and GP in Figure 5.8; refer to Table 3.2 for experimental set-up). The speciation of Zn was largely unaffected by the presence of Fe oxyhydroxides (Figure 5.8). The major difference between particles formed in the absence and presence of trace metals (simulating Fe contributions made by surface water and groundwater, respectively) was that trace metal scavenging was more rapid if the particles were formed in the presence of the trace metals (Paper VI). Co-precipitation also rendered a more efficient scavenging of Cu (GC and GP in Figure 5.8). This suggests that the sites available for sorption to the Fe oxyhydroxides added were saturated with respect to Cu.

Presence of DOM rendered the scavenging of As and Pb by the Fe oxyhydroxides added or formed less efficient (OH, GH, OM, and GM in Figure 5.8; refer to Table 3.2 for experimental set-up). It also prevented any scavenging of Cu to occur (Figure 5.8). The concentration of DOM had a large influence on the amount and size of the Fe oxyhydroxides formed (cf. Vaughan and Ord, 1994). In the absence of DOM, >80% of the Fe added was recovered in particles >1.2 µm (Paper VI; cf. Tipping et al., 1989). In the presence of DOM (<0.2 µm) corresponding to 5 mg DOC/l, <80% of the Fe was recovered in particles >0.2 µm and <40% in particles >1.2 µm (Paper VI). In the presence of DOM corresponding to 9 mg DOC/l, all of the Fe added appeared to bind to DOM or particulate organic matter (POM; ibid.). No conclusions regarding the influence of (mineral) particles initially present on the processes studied could be drawn.
Figure 5.8. The fraction of arsenic, copper, lead, and zinc recovered in particles >0.2 µm. For the original river waters (C, P, H, and M) averages and standard deviations for triplicate samples are given. For the different treatments (DC-GM) averages and standard deviations for samples collected on four different sampling occasions are given. White bars=no DOM. Gray bars=DOM corresponding to 4.9 mg DOC/l. Black bars=DOM corresponding to 8.4 mg DOC/l. Dotted bars=treatments to which iron had been added. A more detailed
A description of the composition of the waters is given in Table 3.2. Modified from Paper VI. The results for the treatments DH and DM will be discussed in Section 5.3.6.

5.3. Additional Observations

In this section, some additional observations made during the practical work are outlined and discussed. These observations are not directly related to wetland performance, or the research questions initially asked, but they may still be of interest to the reader who is planning to perform similar investigations, or who has a special interest in the studied field site.

5.3.1. Sources of Metals

In order to be able to quantify metal immobilization accurately, it is important to locate and quantify the sources (cf. Section 4.5.2). Seasonal variations in the source terms are of interest from a management perspective, since they determine when a higher efficiency of the treatment system may be needed. This subject is treated in some detail in Papers III and VII. In this section, the focus will be on the major sources to different metals in Vormbäcken.

Perhaps the most conspicuous finding is that the major source of Cd, Cu, Pb, and Zn was situated upstream from the spillway from the Kristineberg mine area (Paper III). The elevated metal concentrations already at the background station Storkalven (Paper II) may be the result of weathering processes occurring in a highly mineralized area, that is, they may reflect the natural background situation (cf. Runnells et al., 1992; Alpers and Nordstrom, 2000). Alternatively, the source of the metals may be one of the reclaimed mines surrounding Sörsjön-Holmträsket-Norrsjön (Figure 3.2). A water sample collected from a small watercourse that drains the area around the Kimheden mine towards the west (Figure 3.2) in June 2000 excluded any major contributions of these metals from that site. The comparatively high concentrations of a number of trace metals in Sörsjön-Holmträsket-Norrsjön are presently under investigation (Pia Lindström, Boliden Mineral AB, personal communication).

During normal operation of the treatment facilities at the Kristineberg mine, the trace metal contributions made by this point source were of similar order of magnitude as those made by the natural tributary Svältamyrbäcken (Papers II and III; but cf. Section 5.3.4). In October 2000, a small ditch by the dike of impoundment 4 at the Kristineberg mine also made a significant contribution of many metals (Papers II and III; cf. Figures 5.2 and 5.3). The catchment area was the major source of As and Fe (Paper III). A major source of As appears to be situated in the area between the sampling stations Timmervägen and Rökå (Figure 5.4), or more specifically, between the sampling stations 9 and Rökå.
(Paper II). Parts of this particular area have been hydrothermally altered (Bergström and Sträng, 1999). Naturally elevated concentrations of As have been found elsewhere in the Skellefte mining district (Rönnblom Pärson and Ljungberg, 2001).

It is interesting to compare the situation during the 1970’s (Paper I) with the measurements conducted in 1999 and 2000 (Papers II and III). Even though the latter results are based on fewer observations, it is apparent that the average concentration of total Zn at the background station Storkalven (6300) was higher in 1999 and 2000. However, the average concentration of total Cu remained the same. Regarding metals released from the Kristineberg mine, the average concentrations of total Cu, Fe, and Zn in the effluent water (6306) was lower in 1999 and 2000 than in the 1970’s. This may reflect the fact that the effluent water sampled in 1999 and 2000 had a higher average pH.

5.3.2. The Role of Calcium

The Ca present in the treated drainage water from the Kristineberg mine area may influence the metal speciation in the water in Vormbäcken in a number of different ways. First of all, Ca may compete with other metals that are present in lower concentrations for binding sites on particles and DOM (Cowan et al., 1991; Tipping, 1993; Moniruzzaman et al., 2001; cf. Bendell-Young, 1999). Presumably, this would lead to an increasing fraction of the other metals being recovered in more bioavailable forms, such as free metal ions and inorganic complexes. It is also likely that the other metals would be transported further downstream if they were not associated to particles. In the Vormbäcken data set from 1999 and 2000 however, no signs of such competition could be found (Paper IV). Ca may also compete with other metals for uptake routes into biota, which would reduce the toxicity of the water (cf. Hall and Pulliam, 1995).

Furthermore, Ca may cause flocculation of DOM and associated metals (Sholkovitz and Copland, 1981; Świderska-Bróź, 1991; Romkens and Dolfing, 1998), as well as coagulation of smaller particles and associated metals (Tipping and Higgins, 1982; Przepiora et al., 1998). Such processes, leading to a larger fraction of metals being associated with (larger) particles, could further reduce the metal transport to areas downstream. In the Vormbäcken data set from 1999 and 2000, there were some signs of DOM flocculation downstream from the spillway at the Kristineberg mine, but this alone could not explain the increasing fraction of particulate metals (Paper IV). More interestingly, the discrepancy between the field and experimental data in Paper V suggested that Ca may have caused smaller Fe particles and associated metals to coagulate, an observation supported by experiments performed by Lyth et al. (2003). If this is the case,
active liming at the Kristineberg mine would tend to improve the efficiency of natural attenuation processes occurring along the receiving waters.

5.3.3. *Wetland Hydrology*

An interesting observation regarding the wetland situated downstream from the sampling station Rökå is that the bottom was actually frozen in spring (May, 1999). A possible explanation to this phenomenon is given in Figure 5.9. This would lead to reduced wetland treatment efficiency during a critical time period (Paper III), assuming that the exchange between the river water and the bottom substrates was hindered. Alternatively, the frozen character of the bottom substrate may also prevent sediment particles from being re-suspended during spring flow.

5.3.4. *Sampling Difficulties*

A difficulty when trying to assess metal immobilization based on single measurements at two different sampling stations is that the metal concentrations and/or loadings at the upstream station may vary over time. If the residence time of the water between the sampling stations is comparatively large, there are two possible explanations to any changes in metal concentrations and/or loadings that occur between the two sampling stations. Either a real change has occurred, or a comparison has been made between water packages of different original composition.

In the case of Vormbäcken, the problem became especially apparent during the sampling campaign in April 2000 (Paper III). A couple of weeks earlier, the treatment facilities at the Kristineberg mine had been temporarily out of order, leading to higher concentrations of a number of metals in the water that entered Vormbäcken (Anders Widerlund, Luleå University of Technology, personal communication). By the time of sampling, this pulse had reached the area situated between the sampling stations Rökå (R) and Brännfors (B) (Figure 5.10). This is the reason for the observed abnormal behavior of Ca (cf. Figure 5.4).
Figure 5.9. An illustration of a hypothesis regarding the hydrology of the wetland downstream from the sampling station Rökå. During autumn, the wetland vegetation die back, and the wetlands dry up. This allows the ground/sediments to freeze (X). In winter, the central channel through the wetland is covered with ice. The movements of the ice cut off the surficial parts of the wetland vegetation. The whole system is covered with snow. When spring comes, the frozen ground/sediments is inundated by water from the snowmelt.
The results from the field sampling campaigns may also be influenced by the weather at the time of sampling. This is shown by data from the sampling campaign conducted in October 2000 (exemplified by Cu, Fe, and Zn in Figure 5.11). The samples from sampling stations 3 and 5 were collected following a day of heavy rainfall. The concentrations of Zn, which occurs almost exclusively in the dissolved (<0.2 µm) fraction is reduced in comparison to the upstream sampling stations, whereas the concentrations of Cu, which has a pronounced particulate fraction, remain more or less constant (Figure 5.11). Most likely, the explanation behind this phenomenon is that the Zn concentrations have been diluted by the rainwater, while particulate Cu has been remobilized from the river bottom or banks due to the increased water flow (cf. Cravotta, 2000). There was also a corresponding increase in the concentrations of (particulate) Fe (Figure 5.11). Between the sampling stations 2 and 3, this increase, which cannot be explained by contributions from the effluent water from the mine, occurred within only a couple of hundred meters. At sampling station 5, the river water was visually turbid with particulate Fe.

5.3.5. Field and Laboratory pH

Dealing with waters affected by mine drainage, one would normally expect the pH of the samples to decrease during storage, due to the formation of Fe precipitates (cf. Eqs. 1.2 and 4.2). However, this was not the case for the water samples collected from Vormbäcken. Instead the pH measured upon return to the lab was usually higher than that measured in the field (Figure 5.12). Apart from a systematical difference related to the different pH meters employed, this may also be an analytical artifact caused by the temperature of the water at the
time of sampling. In Figure 5.12, it is apparent that the largest differences in pH were recorded for the samples collected at the lowest temperatures, that is, when the difference in temperature between the field and laboratory measurements was the greatest. Here it should be stressed that the pH meters had been calibrated with buffer solutions of ambient field and room temperature, respectively. When trying to understand what is happening in Vormbäcken, the pH values measured in the field have been used.

Figure 5.11. The total concentration of copper, iron, and zinc in surface water samples collected from Vormbäcken in October 2000. The iron concentrations have been divided by 5. The sampling stations are given in downstream order. For location of the stations, refer to Figure 3.2.

Figure 5.12. The difference between the pH values measured upon return to the lab and those measured in the field as a function of the water temperature at the time of sampling. Surface water samples collected from Vormbäcken during the ordinary sampling campaigns conducted in 1999 and 2000.
One of the problems encountered when filtering a water sample is that the particles present gradually will accumulate on the filter surface, thereby reducing the efficient pore size, a phenomenon known as *clogging* (Karlsson et al., 1994). When filtering the samples collected from Vormbäcken in 1999, 2000, and 2002 (Papers IV and V), it was often found that the resistance posed by the filters increased as the filtration progressed. Thus, most probably, the final pore size was less than the nominal one. Since the same volume (45 ml) of water was always filtered, this fact does not necessarily affect the comparisons made between the different field samples (Paper IV).

However, the true size of the particles is important when considering transport (Paper IV). Differences between the field and laboratory samples in Paper V (cf. Section 5.3.2) may be explained by the fact that only 30 ml of water were filtered in the laboratory experiment, instead of 45 ml for the field samples. If efficient clogging of the filters occurred at larger volumes, this would also lead to apparently larger amounts of particles in the samples collected from the field. The results from the experiment performed in June (Paper V) are one of the strongest arguments against such a clogging. In this experiment, some of the treatments were based on river water that had been filtered through a sequence of filters. If a significant clogging had occurred when this large amount of water was prepared, it is unlikely that the total metal concentrations of these treatments would have matched the dissolved metal concentrations of the treatments containing untreated surface water so closely (cf. Paper V).

Signs of clogging were noticed in the laboratory experiment using artificial river waters (Paper VI). In this experiment, the fraction of particulate organic carbon (POC) and particulate Fe appeared to decrease in the treatments where the original concentration of humic acid was halved. These results may reflect either that the waters with 13 mg TOC/l were over-saturated with respect to HA, or more likely that presence of approximately 5 mg POC (>0.2 µm)/l clogged the filters already before 30 ml of samples had been filtered. Here it should be stressed that the concentration of POC in the field samples collected in 1999 and 2000 never exceeded 2 mg/l, and that presence of as much as 2 mg particulate Fe/l did not appear to clog the filters in the laboratory experiment (ibid.).

Another problem that also has to be considered when employing filtration techniques is how the cleaning procedures influence the results obtained. Results presented in Paper VI suggest that, if the total volume of filtrate is small, it may become diluted by traces of wash solution present in the filter holders. Traces of acid remaining could shift the carbonate equilibria. The problem can be circumvented by discarding the first fraction of the filtrate, which was done for
the samples collected in the field (Paper IV). However, in order to collect the volume of sample needed, a larger volume of water then has to be filtered, which may have a negative influence on clogging.

5.3.7. The Fraction of Organically Complexed Metals

Dissolved organic material may act as a carrier of metals (Mierle and Ingram, 1991; Kalbitz and Wennrich, 1998; Romkens and Dolfing, 1998). It may also have a decisive influence on metal bioavailability (McKnight, 1981; Rouleau et al., 1998). During the field sampling campaigns, the amount of metals associated with DOM was estimated using the weak anion exchanger DEAE (Paper IV). This method is fairly convenient, but it clearly needs to be more thoroughly investigated (ibid.). During the work with this thesis, three attempts have been made to investigate the performance of the method.

Herbert (2001) measured the amount of Cu associated with DOM in water samples collected from Vormbäcken in June 2000 using adsorptive cathodic stripping voltammetry (CSV). Since these samples were collected at the same time as the samples exposed to the DEAE-treatment, it was possible to make a comparison between the results obtained with the two methods (Table 5.1).

Table 5.1. A comparison between the data regarding the speciation of Cu obtained by the methods employed in Paper IV (untreated samples, filtrates, and DEAE supernatants analyzed with ICP-MS) and those employed by Herbert (2001) (CSV). Four surface water samples collected from Vormbäcken in June 2000 were investigated.

<table>
<thead>
<tr>
<th>Location</th>
<th>pH</th>
<th>DOC (mg/l)</th>
<th>Filtration and DEAE2</th>
<th>CSV3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>PCu (µg/l)</td>
<td>DOCu (µg/l)</td>
</tr>
<tr>
<td>Storkalven</td>
<td>5.3</td>
<td>6.0</td>
<td>19.1</td>
<td>b.d.</td>
</tr>
<tr>
<td>Aspliden</td>
<td>5.8</td>
<td>4.9</td>
<td>22.3</td>
<td>16.3</td>
</tr>
<tr>
<td>Rökå</td>
<td>5.8</td>
<td>7.6</td>
<td>9.3</td>
<td>7.4</td>
</tr>
<tr>
<td>Brännfors</td>
<td>6.1</td>
<td>9.1</td>
<td>4.0</td>
<td>4.2</td>
</tr>
</tbody>
</table>

1. Field pH.
2. PCu=Cu associated with particles >0.2 µm. DOCu=Cu associated with dissolved (<0.2 µm) organic matter (µg/l or % of total Cu <0.2 µm). DICu=Cu <0.2 µm that was not associated with DOM, that is, Cu²⁺ or inorganic Cu complexes.
3. TCu=Cu <0.2 µm. LCu=Cu labile to catechol under the voltammetric conditions employed during the experiment, probably Cu²⁺, CuCO₃⁺, CuSO₄⁰, and undefined (labile) Cu-organic complexes. DOCu=Calculated for this table by subtracting labile Cu from TCu (µg/l or % of TCu).
4. B.d.=below detection limit.

The fraction of the Cu that appeared to be associated with DOM differed between the two methods. In three out of four cases, DEAE yielded lower
estimations of the fraction of Cu that appeared to be associated with DOM than voltammetry (Table 5.1). However, it should be emphasized that voltammetry yielded much lower concentrations of dissolved (<0.2 µm) Cu than ICP-MS (ibid.). Our Cu concentrations have been confirmed by independent studies (eg. Forsberg, 2002; cf. Paper V). The reasons behind the discrepancies mentioned above merit further study.

Due to the formation of Fe oxyhydroxides, it can be hypothesized that storing the filtered (<0.2 µm), unacidified water together with the DEAE may have an influence on the amount of metals that appears to be associated with the DOM (Paper IV). This was investigated on one occasion in 2002 by preparing two parallel DEAE samples. One of these samples was re-filtered through a 0.2-µm filter already after a short exposure time. The filtrate was acidified and then stored along with the ordinary DEAE sample.

The differences between the concentrations of Cu and Pb in the two samples were less than 5%. As expected, the concentration of Fe of the re-filtered sample was higher (18%) than in the untreated sample. For As, Ca, Cd, and Zn, the concentrations of the re-filtered sample was lower (13-22%) than in the untreated sample. However, when calculating the amount of metal associated with DOM according to the method outlined in Paper IV, for this particular water sample, both methods yielded similar results. Only Fe appeared to be associated with DOM. According to the untreated sample, 8.8% of the Fe was associated with DOM. According to the re-filtered sample, the fraction was somewhat smaller (5.4%). Further study is needed in order to determine if the difference in the fraction of metals that appears to be associated with DOM, due to sample treatment, is always this small.

Finally, the amount of As, Ca, Cu, Fe, Pb, and Zn associated with DOM, as estimated by the DEAE-method, was investigated under controlled conditions, using waters from the 16 different treatments described in Paper VI. 30 ml of water was filtered through the 0.2-µm filters employed, and the filtrates were exposed to approximately 0.8 g (wet weight) of preconditioned DEAE (Whatman). After approximately 1 hour and 45 minutes, the suspensions were re-filtered through 1.2-µm filters, and 20 ml of filtrates were collected. These filtrates were then acidified. The results from this experiment are presented in Table 5.2.

In the absence of HA, the fraction of Cu, Fe, Pb, and Zn that appeared to be associated with DOM was negligible. A significant amount of As was adsorbed on the DEAE, but this was probably due to the fact that it was present as an anion (AsO₄³⁻). In the presence of Fe oxyhydroxides, As was recovered mainly in the particulate form (Paper VI).
Table 5.2. The fraction of the total metal concentration that was associated with DOM\(^1\), estimated using the weak anion exchanger DEAE, for the various treatments of the experiment presented in Paper VI. The samples were collected on the last sampling occasion. The corresponding pH and concentration of DOC are also given. For a description of the experimental set-up, see Table 3.2. White, gray, and black indicate increasing concentrations of HA.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>DOC (mg/l)</th>
<th>pH</th>
<th>As (%)</th>
<th>Ca (%)</th>
<th>Cu (%)</th>
<th>Fe (%)</th>
<th>Pb (%)</th>
<th>Zn (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC</td>
<td>2</td>
<td>7.15</td>
<td>75</td>
<td>20</td>
<td>b.d.(^3)</td>
<td>-</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>DP</td>
<td>-</td>
<td>7.26</td>
<td>80</td>
<td>20</td>
<td>b.d.</td>
<td>-</td>
<td>b.d.</td>
<td>1</td>
</tr>
<tr>
<td>OC</td>
<td>-</td>
<td>7.05</td>
<td>b.d.</td>
<td>17</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>OP</td>
<td>-</td>
<td>7.15</td>
<td>b.d.</td>
<td>21</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>GC</td>
<td>-</td>
<td>7.18</td>
<td>b.d.</td>
<td>27</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>1</td>
</tr>
<tr>
<td>GP</td>
<td>-</td>
<td>7.28</td>
<td>b.d.</td>
<td>27</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>DH</td>
<td>4.5</td>
<td>n.a.(^4)</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>DM</td>
<td>4.9</td>
<td>7.33</td>
<td>69</td>
<td>14</td>
<td>34</td>
<td>21</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>OH</td>
<td>4.7</td>
<td>7.21</td>
<td>54</td>
<td>11</td>
<td>29</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>OM</td>
<td>5.0</td>
<td>7.23</td>
<td>58</td>
<td>18</td>
<td>28</td>
<td>b.d.</td>
<td>10</td>
<td>b.d.</td>
</tr>
<tr>
<td>GH</td>
<td>4.6</td>
<td>7.31</td>
<td>30</td>
<td>5</td>
<td>38</td>
<td>8</td>
<td>22</td>
<td>b.d.</td>
</tr>
<tr>
<td>GM</td>
<td>4.9</td>
<td>7.30</td>
<td>30</td>
<td>21</td>
<td>36</td>
<td>b.d.</td>
<td>10</td>
<td>b.d.</td>
</tr>
<tr>
<td>SC</td>
<td>5.0</td>
<td>7.29</td>
<td>42</td>
<td>20</td>
<td>25</td>
<td>13</td>
<td>14</td>
<td>b.d.</td>
</tr>
<tr>
<td>SP</td>
<td>5.2</td>
<td>7.37</td>
<td>46</td>
<td>21</td>
<td>29</td>
<td>17</td>
<td>21</td>
<td>b.d.</td>
</tr>
<tr>
<td>SH</td>
<td>8.8</td>
<td>7.41</td>
<td>65</td>
<td>22</td>
<td>55</td>
<td>48</td>
<td>52</td>
<td>b.d.</td>
</tr>
<tr>
<td>SM</td>
<td>9.1</td>
<td>7.35</td>
<td>57</td>
<td>24</td>
<td>40</td>
<td>23</td>
<td>29</td>
<td>b.d.</td>
</tr>
</tbody>
</table>

1. Calculated as the difference between the metal concentration of the 0.2-µm filtrate and the metal concentration of the DEAE-treatment, divided by the total metal concentration.
2. No HA or Fe had been added to treatments marked with (-).
3. B.d.=below detection limit, here arbitrarily given as ≤0.
4. N.a.=not analyzed due to lack of experimental solution.

When the concentration of HA was increased to approximately 5 mg DOC/l, the fraction of Cu, Fe, and Pb that appeared to be associated with the DOM generally increased, while the corresponding fraction of Zn remained low. This pattern was repeated when the concentration of HA was increased to approximately 9 mg DOC/l. Thus, the behavior of these metals is along the lines with previous observations (cf. Pandey et al., 2000).

The fraction of As adsorbed on the DEAE was lower in the presence of HA than in its absence. There were also large differences between the different treatments containing 5 mg DOC/l, ranging from 30% for the treatments GH and GM to 69% for treatment DM. These differences may reflect the scavenging of As by particulate Fe oxyhydroxides that were present.

That some Ca appeared to be associated with the DOM in all of the samples is surprising. First, Ca should be present as a cation. Second, Ca associated with
DOM was only indicated for a few of the samples collected in the field (Paper IV). Third, any contamination by Ca from the DEAE would have led to that the concentrations of Ca in the DEAE-treatments would have been higher, and not lower, than in the 0.2-µm filtrates. A possible explanation then is that the matrix of the DEAE-treatments, which may include organic matter originating from the cellulose (Paper IV), has affected the results from the metal analyses.
6. SYNTHESIS

6.1. Wetlands as a Sustainable Means to Treat Mine Drainage Waters

There are several different approaches to reduce the environmental impact of mine drainage waters. Wetland treatment represents one of these approaches, which range from conventional chemical treatment to increasing the public awareness of the causes to, and the consequences of, AMD (Section 1.3). In the ideal case, different methods to treat AMD first come into play when the methods employed to prevent its formation have been found to be insufficient, or when a shortage of locally available materials has prevented the construction of covers.

When comparing wetland treatment with other strategies to reduce the environmental impact of mine drainage, it is most appropriate to compare with other treatment methods. Some of the potential problems associated with wetlands, such as the generation of precipitates, are common for most treatment methods.

Since the first wetlands for the treatment of AMD were constructed, a deeper understanding of how these systems work has been achieved (Section 4). This makes it possible to improve the performance of future treatment wetlands by better adapting them to site specific conditions. Incorporation of structures such as ALDs and SAPS into wetland treatment systems represents such adaptations, which allow treatment of a broader spectrum of mine drainage waters. They may also reduce the size required for a treatment wetland (Brodie et al., 1993; Hellier et al., 1994; Kepler and McCleary, 1994; Barton and Karathanasis, 1999).

6.1.1. A Question of Sustainability

When evaluating wetland systems for mine drainage treatment from the perspective of sustainability, it is necessary to define the concept ‘sustainable’. Sustainable may refer to the outcome of the treatment, for instance, good water quality and viable populations of fish along the recipient. Sustainable may refer to a treatment process that is based on renewable resources. Sustainable may also indicate treatment processes that are maintenance-free.

Good water quality is generally considered to be a prerequisite for human sustenance in an area. Thus, a method that consistently produces insufficiently treated drainage water can hardly be considered to be ecologically sustainable. A possible exception to this would be if the pollution problem is only temporary and local, and the desired natural resources are available elsewhere. Then the
income generated from the mining and associated activities may suffice to compensate for the local resources lost (cf. Wiggering and Rennings, 1997).

Wetland treatment systems are usually powered by potential and solar energy. They are often built using waste products from other industries, rather than chemicals manufactured or mined for this particular purpose. This makes wetlands comparatively more sustainable than many other treatment systems. However, if regular maintenance, such as harvesting of plants and/or dredging, is planned, a different kind of waste problem has been generated.

If maintenance-free wetlands can be achieved, no additional land areas will be claimed for disposal of the waste products generated, since the disposal occurs within the wetland itself. Thus, maintenance-free wetlands can be considered to be more sustainable than wetlands where regular maintenance is required.

The following discussion will focus on maintenance-free wetlands that produce water of acceptable quality for as long as needed. Other wetlands, acting as outdoor treatment plants, may still be a good alternative or complement to other treatment systems, but maintenance-free wetlands are the only ones that can be considered to be true walk-away-solutions.

6.1.2. The State of the Sustainability Issue

The major mechanisms of metal immobilization may change as the wetland is exposed to increasing loadings of AMD (Sections 4.8.5 and 4.9.2). Metals that were retained initially may also become remobilized (ibid.). Signs of ‘aging’ usually occur earlier if the wetland is exposed to AMD having lower pH and higher concentrations of metals (e.g. Baker et al., 1991).

When the sites available for metal sorption to the wetland substrate have been saturated, the long-term removal of trace metals will be dependent on sulfate reduction, and the precipitation of metal sulfides (e.g. Machemer and Wildeman, 1992; Sobolewski et al., 1995; Sobolewski, 1996). In net acidic systems, enough buffering capacity to counteract acidification must either be present in the wetlands initially, be added from tributaries and/or groundwater, or be generated by sulfate reduction during the course of the treatment. This will ensure that conditions favorable for the SRB, as well as for the precipitation of metal sulfides, will be maintained (cf. Sobolewski et al., 1995; Sobolewski, 1996). In order to sustain sulfate reduction, the availability of suitable, low molecular weight, organic compounds must be ensured (Eger and Wagner, 1995). In net alkaline systems, Fe can be removed as oxyhydroxides. Again, buffering capacity present in the wetlands, added from tributaries and/or groundwater, or generated by sulfate reduction, is crucial for the treatment of net acidic waters.
In the literature reviewed in this thesis, the oldest constructed treatment wetlands found were built in the early 1980’s (Appendix 4). The longest documented period during which a mine drainage treatment wetland has worked satisfactorily without addition of chemicals is 3 years and 10 months (Stark et al., 1994c). During this time, the wetland was still periodically maintained. Maintenance activities included reinforcement of straw dikes, used to improve the flow of water through the wetland cells, and trapping of beavers and muskrats. Calculated treatment longevity range from conservative estimates to hundreds of years (Beining and Otte, 1997). There are examples of natural wetland systems which have been accumulating metals for thousands of years (Owen and Otton, 1995; Sobolewski, 1999 a and b), but long-term accumulation in the solid phase does not necessarily correspond to satisfactory long-term reduction of metal concentrations in the water phase.

6.1.3. A Systems Approach

When the longevity of wetland treatment systems is discussed, the focus is often on the system itself, and means to improve its efficiency. Alternatively, the wetland may be viewed as a part of a larger system, including also the source of metals (the mine, the waste rock, and/or the tailings) and the receiving waters (Paper VII). From this point of view, reducing the source term appears as an alternative approach to increase the longevity of wetland treatment. That is, the longevity of wetland treatment systems may be increased if they are used primarily as a complement to other treatment methods.

A number of arguments support this statement. Decreasing the concentrations of acidity and metals in the water entering a wetland reduces the risk that the organisms that accomplish the metal immobilization processes will be poisoned. If decreasing pollutant concentrations are accompanied by decreasing flow rates, that is, decreasing pollutant loadings, it will take longer before the total metal accumulating capacity of the wetland has been claimed. It may even be possible to balance the rate of metal input with the rate of formation of new removal sites (cf. Eger et al., 1994). Furthermore, Sobolewski et al. (1995) and Sobolewski (1996) have shown that Cu may be retained in more stable forms (sulfides) if the treatment wetland is exposed to lower flows of mine drainage having higher pH and lower metal concentrations. It should also be mentioned that the constructed wetland with the longest documented record of successful treatment was accompanied by other reclamation activities, which improved the quality of the water entering the wetland (Stark et al., 1994c).

Sustainable treatment of mine drainage waters in wetlands can be divided into a treatment and a post treatment phase. During the treatment phase, the rate of the
processes that act to immobilize metals in the wetland will have to balance the rate by which the drainage water is produced (cf. Kalin, 2001), minus the fraction of metals that can be allowed to pass through to the receiving waters. As pollutants accumulate in the system, the efficiency of the processes that act to immobilize metals may decrease. Such a decrease may be due to saturation of the sites available for sorption, heavy metal poisoning of biological organisms, or depletion of buffering capacity, suitable low molecular weight organic compounds, and/or plant nutrients.

However, decreasing treatment efficiency over time does not necessarily lead to unsatisfactory treatment. Either the system has been dimensioned to allow for a decreasing treatment efficiency, or the methods used to reduce the weathering processes upstream have been successful (cf. Kalin, 2001). Following remediation activities such as flooding of old mine workings and application of soil covers, the quality of the drainage water may improve significantly in the nearest decades, after old weathering products have been washed out (Younger, 1997; Corrège, 2001).

In order to ensure sustainable treatment, it is also important that the total metal accumulating capacity of the wetland is not exceeded by the cumulative load of metals. Again, measures that serve to reduce the total amount of minerals exposed to weathering, and consequently also the amount of metals that the wetland is exposed to, will prove to be beneficial.

Post treatment, the wetland must not act as a secondary source of metals. This requires that the wetland substrate and associated metals is contained within the wetland. The material must not be re-suspended and/or washed out from the wetland. In order to prevent remobilization of metals, it is also important that conditions favorable for metal retention are maintained. Metals that have been immobilized as sulfides may become remobilized if the wetland would dry out. The importance of a constant water supply to a wetland that has been receiving mine drainage is stressed by Sobolewski (1997 and 1999a).

6.1.4. The Use of Natural versus Constructed Wetlands

Most of the studies reviewed in this thesis are concerned either with treatment of mine drainage waters in constructed wetlands or investigations of natural wetlands that unintentionally have been exposed to such waters. One of the explanations to this is likely that natural wetlands are protected by law in many countries (e.g. Hedin, 1989; Skousen, 2001), since they constitute valuable biotopes. Another explanation to this is that it may be possible to achieve a higher treatment efficiency in a constructed system (cf. Herbert and Ekström, 2003). Many researchers are also reluctant to use natural wetlands for the
treatment of metal polluted water before the effects on the ecosystem have been more thoroughly investigated (e.g. Hammer, 1989; Meiorin, 1989; Dunbabin and Bowmer, 1992).

It is obvious that it is easier to control the fluxes of metals in a constructed wetland. For instance, there is potential to protect groundwater quality by incorporating liners which will restrict the downward flow of the drainage (Hellier, 1999). Furthermore, one may be interested in avoiding future harvesting of plant material and dredging in a natural wetland.

However, there may be instances when treatment of mine drainage has less impact on a wetland ecosystem than treatment of, for instance, municipal wastewater having high nutrient concentrations and biological oxygen demand. Such a situation could occur if the metals in the drainage do not reach harmful concentrations and the accumulated metals are stored in a biologically unavailable form (DeBusk et al., 1996; cf. Lacki et al., 1992; Pascoe et al., 1996; Wood and Shelley, 1999). It should also be pointed out that in many cases, constructed wetlands claim fairly large land areas, and that material for the construction of a treatment wetland (e.g. plants and peat) is sometimes harvested from natural wetlands.

To conclude, it cannot be excluded that there may be situations where treatment of mine drainage waters in natural wetlands may prove to be the best option when the environmental impact of no treatment, treatment in constructed wetlands, as well as other treatment methods, are taken into account.

6.1.5. Literature Used and Accessibility of Scientific Information

To be well acquainted with previous research on an investigated topic is a scientific ideal that is closely related to another scientific ideal, namely that research shall generate new knowledge. In this respect, the large accumulated body of knowledge of a research field such as metal biogeochemistry poses a distinct problem to the young researcher; how to make sure that all the relevant literature has been covered?

It is soon discovered that one has to focus on a more specific topic, without loosing important input from closely related topics. For more general aspects one sometimes has to rely on reports, textbooks, and review articles, rather than the original articles. However, it is still difficult to cover a whole topic completely. This thesis contains a thorough review on wetlands for the treatment of mine drainage, but it cannot claim to constitute a complete state-of-the-art.
Modern databases are a great asset in the search for literature. A problem with databases is that they often do not include ‘older’ literature, which still may be relevant. They also have a tendency to be biased towards international scientific papers published in English, which may result in overlooking, for instance, Russian research on the interactions between metals and peat. The literature cited in the review part of the thesis (Section 4) is heavily biased towards experiences from the US and Canada. This may either reflect the real situation, or it may be an artifact of the methods employed when collecting the literature.

A problem when working with applied science is that part of this research is performed by civil servants, consultants, or company employees, who may only have a limited interest in publishing scientific papers. Therefore many interesting, high-quality results can be found only in reports from various agencies or companies and in conference proceedings. This kind of literature is sometimes also included in the databases, but it may still be difficult to get access to it. While conferences are excellent media for interchanging information, conference proceedings can seldom be found in public or university libraries. In most cases, reports and conference proceedings can still be obtained, but this tends to be comparatively expensive. If access to research results is coupled to large costs, this may prevent the results from being disseminated to researchers and practitioners in developing countries.

6.2. Metal Immobilization in the Wetlands along Vormbäcken

6.2.1. Why is There so Little Immobilization of Metals in the Wetlands Investigated?

Some metal immobilization may take place in the wetlands situated along Vormbäcken. However, with the possible exception of As and Fe, the immobilization was low (Paper III). Any immobilization of As and Fe could not be quantified, since an unknown amount of these elements was contributed from the catchment area (ibid.). In this particular case, this makes As and Fe less interesting from a treatment perspective.

It is possible that the wetlands have acted as traps for metals before, but that they now have been saturated with accumulated metals. If this is the case, the wetlands were probably saturated with metals already in the 1970’s (Paper I). That is, following the onset of mining activities, the wetlands only had a positive influence on the metal concentrations in the river water for about 30 years, at most.

The results from the study of metal immobilization in the wetlands situated along Vormbäcken are in agreement with results from previous studies, which
suggest that all wetlands do not work as efficient traps for metals (e.g. Hiel and Kerins, 1988; P. Lane and Associates Limited, 1990). The pH values recorded along Vormbäcken were close to neutral (Papers II-V), a fact which ought to be favorable for metal immobilization processes. No negative influences of Ca, the major cation in the system, were recorded (Paper IV). The presence of DOM may have influenced the behavior of certain metals, but then larger differences between a metal such as Cu (which is known for its high affinity for organic material) and a metal such as Zn (which is not) should have been visible. Thus, in the case of Vormbäcken, the explanation is most likely to be found in wetland hydrology.

Given the depth of the water column, at any point in time, only a comparatively limited fraction of the water is actually in contact with the bottom substrates. The channelized character of the river also makes the water move fairly rapidly through the wetland areas, limiting the time available for chemical and biological reactions, as well as for sedimentation processes (cf. Brinson, 1988; P. Lane and Associates Limited, 1990; Kimball et al., 1994).

The period of time when the liming facilities at the Kristineberg mine were out of order (Anders Widerlund, Luleå University of Technology, personal communication), in combination with measurements of water chemistry along the river, allowed the velocity with which the water moved through the first two wetland areas in April 2000 to be estimated to approximately 0.01 m/s. The measurements of water flow in June and October 2000 (Papers II and III) suggest that this velocity is low in comparison to the velocity during periods of higher flow.

The influence of wetland plants on processes such as sedimentation is likely to be limited by the comparatively short growing season (approximately June to September) at these latitudes (65°N).

6.2.2. The Chosen Field Site and Approach

The study of natural analogues to man-made systems has many advantages, in particular when trying to estimate the longevity of new technologies. Examination of the present day functioning of these ‘experiments’ of nature may reveal real time processes that are hard to discover in short-term studies. However, as illustrated by the Vormbäcken example, the interpretation of natural wetland systems poses a number of different problems.

Natural wetlands are complicated ecosystems. A substantial sampling campaign may be required in order to produce a reliable quantification of the flows of water and metals (cf. Giblin, 1985). In the case of Vormbäcken, complicating
features include groundwater contributions and a bifurcation point (Paper III). Stark (1990) and Stark and Williams (1995) solved this problem already at the onset of their study by only including wetlands where local surface runoff entering the wetland was minimal, and where peripheral or internal seepage into the wetland was insignificant. A total of 290 natural wetlands were inspected for inclusion in the study, but only 35 wetlands met these and a number of other criteria posed by the authors.

Another problem is that wetlands are highly dynamic systems. The performance of a wetland may change dramatically during the day, during a storm event, or over the seasons (Section 4.7.4). This means that in order to evaluate wetland performance accurately, regular monitoring is needed (cf. Pettersson, 1999). Alternatively, the research effort can be focused on probable worst case scenarios. These include winter (with low temperatures, slowing down the rate of biological reactions), spring flow (large volumes of water to be treated), and autumn rains (saturating parts of the wetland which may have been subjected to drying-out during summer).

Evaluating wetland performance over longer time is even more difficult. Here it is worth remembering that both the pollution situation and the character of the wetland may have changed over the years. For instance, the wetlands along Vormbäcken have been affected by metals originating from the mining activities at the Kristineberg mine for only about 60 years, which naturally limit their value for predictions of system performance over even longer time periods. Many wetlands are also transient systems (Wetzel, 1983). The transition from aquatic to terrestrial systems via wetlands is often slow, but it is worth stressing that, due to activities such as draining, what is a wetland today may in reality have been a shallow lake not more than a couple of decades ago.

In the study of Vormbäcken, a top down approach was followed. That is, an investigation of overall system performance was made before more detailed studies were initiated. No doubt it would have been possible to determine the amount of metals immobilized in the wetlands investigated more accurately if a more comprehensive sampling program had been launched. Given that the low efficiency of the investigated system was discovered early during the project, it was possible to redirect the research effort to other studies. By starting with the field studies, it was also possible to test site-specific hypotheses in the following laboratory experiments.
6.3. Natural Attenuation of Contaminants by Iron

6.3.1. General Aspects

Scavenging of trace metals by Fe oxyhydroxides formed upon neutralization of AMD by other surface water or groundwater has been investigated in a number of studies (e.g. Chapman et al., 1983; Johnson, 1986; Kimball et al., 1995; Webster et al., 1998; Paulson and Balistrieri, 1999). Given enough oxygen and/or time, Fe oxyhydroxides will also precipitate in alkaline drainage (Kleinmann et al., 1991; Hedin et al., 1993). In both of these cases, the Fe originates from the AMD itself. AMD may contain rather high concentrations of Fe. For instance, in July 1998, the drainage water at the Kristineberg mine area contained 52 mg Fe/l before liming. Precipitation of large amounts of Fe oxyhydroxides may have a negative influence on pH (Eqs. 1.2 and 4.2), which in turn may have a negative influence on the adsorption of cationic metals (cf. Section 4.4.2). For an efficient adsorption of trace metals to occur, it is important that the Fe oxyhydroxides are still present in the water when the pH is high enough to favor adsorption processes (Cravotta and Trahan, 1999; Paulson and Balistrieri, 1999).

6.3.2. The Case of Vormbäcken

There are numerous studies that address how different water chemistry parameters affect adsorption processes (e.g. Benjamin and Leckie, 1981; Cowan et al., 1991; Xu, 1991; Düker et al., 1995; Hamilton-Taylor et al., 1997). Somewhat surprisingly, the concentration of adsorbents used appears to have attracted comparatively little attention. That the concentration of an adsorbent may have an influence on the outcome of adsorption studies has been shown by, for instance, DiToro et al. (1985). In a study by Webster et al. (1998), the adsorption edges for Cu, Pb, and Zn were shifted towards higher pH when the ratio between the concentration of trace metals and adsorbents was increased by a factor of ten. In the case of Vormbäcken, the results from the field studies even suggested that the association of a number of metals to particles was limited by a shortage of efficient adsorbents (Paper IV). This hypothesis was tested in a laboratory experiment (Paper V).

Today the catchment area is the major source of Fe to Vormbäcken (Paper III). Since the concentrations of Fe from the Kristineberg mine area have decreased since the 1970’s, the relative importance of Fe originating from the catchment area has increased (cf. Papers I and III). In a way, ferrous Fe from the groundwater, and particulate Fe from the tributaries, can be regarded as nature’s own precipitation forming and/or metal scavenging agents. Using such naturally supplied Fe to achieve a reduction in the transport of trace metals to areas
downstream, would be an excellent example of a passive, complementary treatment system based on natural attenuation processes.

An additional advantage is that, provided that the amount of ferrous Fe contributed by the groundwater is comparatively small, precipitation of the Fe oxyhydroxides may not have a devastating impact on the pH of the system (cf. Paper V). The geography of the river, with a number of minor rapids (favorable for the oxidation of the ferrous Fe) and wetland areas (favorable for sedimentation processes), could also prove to be beneficial for overall system efficiency.

The observations made in the field, regarding the important role played by Fe in the metal speciation, could not be verified in the laboratory experiment (Paper V). However, it is too early to state that Fe does not have any impact on metal speciation in Vormbäcken. In particular, the role played by Ca in the coagulation of smaller Fe particles merits further studies (cf. Section 5.3.2). In the data set, there are also indications that Fe, and possibly also other metals associated to particles (Paper IV), are immobilized in Vormträsket, as well as in wetlands situated along Rökån (Paper III). Analyses of Fe precipitates collected from the wetland situated downstream from the sampling station Rökå contain elevated concentrations of As (3910 mg/kg), Hg (1.59 mg/kg), and Zn (1200 mg/kg) (Lars Lövgren, Umeå University, personal communication).

6.3.3. Aspects on Efficiency and Sustainability

The results from the field sampling campaigns (Paper IV) and the laboratory experiments (Papers V and VI) suggest that not all metals will be affected to similar extent by an increase of the amount of particulate Fe. For instance, Zn was affected to a much less degree than Pb. A likely explanation to this phenomenon is that the adsorption edge of Zn typically is found at a higher pH than that of Pb (e.g. Hamilton-Taylor et al., 1997; Webster et al., 1998; cf. Paulson and Balistrieri, 1999). Thus, unless the pH of the water is raised artificially, adsorption to Fe oxyhydroxides may prove to be an inefficient means to reduce the amount of Zn that is transported to areas further downstream.

At the near-neutral pH investigated, presence of DOM had a negative influence on the efficiency of the trace metal scavenging processes (Paper VI; cf. Papers IV and V). Presence of DOM also had a negative influence on the formation of the Fe precipitates (Paper VI). Based on the studies presented in this thesis, it is not possible to state what concentration of DOM that is critical. The results from the laboratory experiments suggest that precipitation of Fe oxyhydroxides occurred at lower concentrations of DOM (approximately 7 mg TOC/l), even if
not all Fe added precipitated (Papers V and VI). If one is interested in using trace metal scavenging by Fe oxyhydroxides to reduce metal transport to areas further downstream, the presence of DOM must be taken into account.

Trace metal adsorption to the Fe oxyhydroxides added or formed was rapid, ranging from <1 h to <24 h (Paper VI). In the laboratory experiment based on synthetic river waters, precipitation of the Fe occurred within 1 h at 21°C and pH slightly above 7 (ibid.). In the laboratory experiment based on authentic river waters, precipitation of the Fe occurred within 50 h at 22°C and pH slightly above 6 (Paper V). This suggests that immobilization of trace metals associated to Fe oxyhydroxides along Vormbäcken may be limited by the settling rate of these particles, at least during periods of low flow (cf. Section 6.2.1).

Low temperatures clearly had a negative influence on the rate of formation of the Fe precipitates (Paper V). This means that using trace metal scavenging by Fe oxyhydroxides to reduce metal transport to areas further downstream may be of limited value during winter in cold climates. A limited capacity during the winter months may not be crucial for the overall performance, since the water flow in northern Sweden generally is low during winter (Sveriges meteoro-logiska och hydrologiska institut, 1979). However, during snowmelt a pronounced peak in the water flow (ibid.) coincides with low water temperatures. At high flows, old weathering products and small particles may also become mobilized from the source (e.g. Stillings et al., 1988; Ljungberg, 1999; Widerlund et al., 2001). This means that the overall performance of a treatment system will be heavily influenced by its capacity to handle snowmelt events, both with respect to the total amount of metals immobilized, and the risk of re-suspension of previously sedimanted material.

Assuming that the Fe particles are dense enough to settle, the fate of the metals once they have reached the wetland/lake sediments also has to be considered. For instance, trace metals that have been co-precipitated along with the Fe oxyhydroxides may be released back into the water column as the precipitates age (Martínez and McBride, 1998). Presence of organic matter may counteract this process by having an inhibitory effect on the crystallization of the Fe oxyhydroxides (Schwertmann, 1966). Furthermore, in a reducing environment, the Fe will be reduced and possibly also released back into the water column (cf. Vile and Wieder, 1993; Tarutis and Unz, 1995; Olivie-Lauquet et al., 2001). The fate of the trace metals is then dependent on whether other good adsorbents, such as POM, are still present in the sediments, or if enough sulfide is present for the precipitation of metal sulfides to occur (cf. Shaw et al., 1990; Jackson and Bistricki, 1995; Hamilton-Taylor et al., 1996).
6.4. To Reclaim or Not to Reclaim, That is the Question

Following the closing of a mine, attempts are generally made to reduce the risks that the former mine, and the waste products generated, may pose to human and environmental safety and health. Mine shafts are sealed to prevent access and accidental falls (e.g. Marcoux, 2001). Waste rock and tailings may receive additional treatment in order to reduce the formation of AMD, and sometimes new treatment facilities are installed to take care of drainage water that is produced (cf. Section 1.3). The purpose of this section is not to question these and similar activities, but to point to some aspects of these activities, which tend to be overlooked.

Several of the reclamation activities mentioned above are concerned with isolation. The mineshafts are isolated from the public, the waste is isolated from oxygen, and the pollutants are isolated from the environment. An added benefit of isolating metal pollutants from the surrounding environment is that they are concentrated geographically. Thus, a tailings impoundment or treatment system may become an interesting site for future mining activities (cf. Gusek, 1995).

Another set of reclamation activities is concerned with integration. In order to integrate the former mining area into the surrounding landscape, it is often desired to make it ‘look like nature’. For instance, the establishment of vegetation on a tailings pile may be facilitated by improving the growth conditions on site. At the Kristineberg mine, there are plans to divert Vormbäcken into impoundments 3 and 4 in order to turn them into a lake (Boliden, 1997). In the ideal case, creating natural environments also has a positive influence on the biogeochemistry of the reclamation activities (ibid.). In the worst case scenario, the integrity of covers and dikes is destroyed by plant roots or burrowing animals, or the newly established environment attracts humans and animals which are harmed by the elevated metal concentrations in the first sections of a treatment system.

Another integration oriented activity is trying to foresee future changes and incorporate these into the design of the reclamation activities. For instance, at the Kristineberg mine, an embankment separates impoundment 4 from Vormbäcken. By diverting the river into impoundments 3 and 4 under controlled conditions, one will also avoid gradual erosion of the embankment, which could lead to a catastrophic failure of the embankment, as well as release of tailings stored in the impoundments.

Protecting humans and the environment from negative effects caused by mining activities requires that use is made of other natural resources. These include energy used for powering treatment plants and/or transport of various kinds of
materials, *minerals* used for covers and/or various kinds of treatment purposes, and *land areas* used for wetlands and/or disposal of the sludge generated. When these resources are used, there is an implicit assumption that these resources are less valuable than those that shall be protected. Still, one has to compare the value of, for instance, viable fish populations in a river receiving AMD with the value of a pristine landscape, where no till has been extracted in order to construct soil covers. One also has to consider the geographic and time scales involved. If the pollution problem is only temporary and local, fish populations may recover quicker than new morain is generated.

There are legal and moral obligations to reclaim former mine sites. Still, it must be asked if reclaiming *all* sites can be advocated. Consider, for example, a hypothetical case where a limited part of a remote area will be exposed to AMD for a limited time period. Can the costs, energy, and material associated with reclaiming such a site be defended, when alternative uses of these resources elsewhere in the society are taken into account?

From a reclamation perspective, the remoteness of a site is often quoted as problematic. It is interesting to note that this was rarely considered to be a problem when the ore was transported away. It is possible that there is a hidden potential to prepare for future reclamation activities by using the working infrastructure of the active mine.
7. SUMMARY AND CONCLUSIONS

This thesis gives a systematic description of wetland structure and some of the processes that can be used to treat metal polluted water in wetlands. Factors that can influence the efficiency and longevity of these processes are discussed based on previous research results, primarily from wetlands exposed to drainage originating from mines and mining waste. Wetland treatment of mine drainage is also put in a context, outlining the formation of the drainage, its environmental impact, and alternative methods to handle the problem.

It is concluded that correctly constructed wetlands can treat certain kinds of drainage to compliance with discharge requirements, and that they in some cases can be attractive alternatives to other methods to treat mine drainage, both with respect to treatment costs and overall resource utilization. From a management perspective, it may be instructive to distinguish between situations where the biogeochemical processes operating in wetlands are employed in more or less regular ‘outdoor treatment plants’ and situations where the wetlands are intended to be used as walk-away-solutions.

In both cases, the rate of the processes that act to immobilize the metals in the wetland has to balance the rate with which the drainage water is produced, minus the fraction of metals that can be allowed to pass through to the receiving waters. The rate of the processes that act to immobilize metals in a wetland may decrease over time. In a treatment plant wetland, this phenomenon can be counteracted by regular maintenance. In a walk-away wetland on the other hand, decreasing rates of metal immobilization will have to be balanced by decreasing rates of drainage water production. Alternatively, such a wetland must have been dimensioned to allow for a gradual loss of treatment efficiency.

Furthermore, while metals may be removed from a treatment plant wetland, there is a risk that metals accumulated in a walk-away wetland will eventually exceed its total metal accumulating capacity. The likelihood that walk-away wetlands will work as planned for as long as needed is increased if they are used in combination with other treatment and preventive methods, which serve to reduce the total metal loadings to the wetland. Post treatment it is important to ensure that the conditions favorable for metal immobilization in a wetland are maintained, so that it will not act as a secondary source of metal pollutants.

This thesis also presents the results from a case study aimed at investigating metal immobilization in natural wetlands as a complement to other treatment methods. The studied wetlands are situated along the river Vormbäcken, which flows through parts of the Skellefte mining district, northern Sweden. The river receives treated (liming) drainage from the area surrounding an active mine.
However, the major source of trace metals such as Cd, Cu, Pb, and Zn is situated upstream from this area.

The investigated wetlands had a limited influence on the transport of Cd, Cu, Pb, and Zn to areas downstream. The low immobilization of trace metals is probably due to limited contact between the river water and the bottom substrates, the channelized character of the river, and/or low settling rates of metal bearing particles. Any immobilization of As and Fe in the wetlands could not be quantified, since an unknown amount of these metals was added to the river as it flowed through the catchment area.

The fraction of the total concentration of As, Cd, Cu, Pb, and Zn that was associated with particles >0.2 µm increased when the river water was mixed with the treated drainage from the active mine. This was probably due to an increase in pH and/or increasing amounts of particulate Fe, originating from the catchment area. When the river passed through a lake, the fraction of the total concentration of As, Cu, Fe, and Pb that was associated with particles >0.2 µm decreased, while the fraction that was associated with dissolved (<0.2 µm) organic matter increased. This was probable due to settling of particulate matter in the lake. For As and Fe, contributions from the catchment area may also have been of some importance.

The fraction of the total concentration of As, Cu, and Pb that was associated with particles >0.2 µm increased with increasing concentrations of particulate (>0.2 µm) Fe. It was hypothesized that this phenomenon could be explained by trace metals scavenging by Fe particles formed when groundwater containing ferrous Fe discharged into the river, or by Fe particles added from the tributaries. If these particles then could be made to settle, for instance in a wetland, such a mechanism could be used to reduce trace metal transport to areas further downstream. This would be an excellent example of a complementary, passive treatment system based on natural attenuation processes.

A laboratory experiment based on authentic river waters showed that the patterns of trace metal speciation encountered along the river could not be reproduced simply by adding ferrous Fe (simulating groundwater inputs) and allowing it to precipitate. The difference between the field and laboratory data may be explained by that the concentrations of Ca were higher in the river water downstream from the active mine, which could lead to coagulation of smaller Fe particles and associated trace metals.

It was also shown that the rate of formation of the Fe precipitates was low at 0°C, which means that the treatment system outlined above may be of limited
value during winter. At 22°C, bacteria and/or particles originally present in the river water catalyzed the precipitation process. Not all of the added Fe precipitated, presumably due to the formation of complexes with dissolved organic matter.

A laboratory experiment based on synthetic river waters showed that even small amounts (~1 mg/l) of particulate (>0.2 µm) Fe can increase the fraction of the total concentration of As, Cu, and Pb that is associated with particles. Trace metal scavenging by Fe particles formed in the river water (simulating groundwater inputs) was more rapid than trace metal scavenging by Fe particles added (simulating contributions from tributaries). Fe particles formed in the river water were also more efficient scavengers of Cu, and of As and Pb in the presence of humic acid. The amount of trace metals associated with particles decreased in the presence of humic acid (~6.5 and 13 mg TOC/l). Presence of humic acid also reduced the total amount and the size of the precipitates formed following the addition of ferrous Fe. No conclusions regarding the influence of particles originally present in the river water could be drawn.
8. FUTURE RESEARCH

The literature cited in this thesis shows that during the last two decades, wetlands used for the treatment of mine drainage waters have left the ‘black-box’ stage. Today we actually know a lot about how these systems work. Consequently, the best contribution to this particular research field is probably not another general case study, but a deepened integration and synthesis of the results already obtained. It is important to document not only the present state-of-the-art, but also how this was achieved. This will help future researchers and practitioners to avoid re-investigating or using approaches that have proved to be unsuccessful in the past. It will also make it easier to identify areas where there is a lack of data, or where the results from previous studies point in different directions. By focusing the future research effort to these areas, it will be possible to optimize its output, and to bring this research field forward.

Some of the major questions that still need to be answered are related to the sustainability of maintenance-free treatment wetlands, which is inherently difficult to study. It would be of value to be able to define more clearly what combinations of drainage waters and wetland types that can be expected to work satisfactorily over longer time periods, and what combinations that clearly cannot. Furthermore, comparatively little attention appears to have been given to what happens to the metals accumulated in a mine drainage treatment wetland if it gets damaged by, for instance, accidental draining. By now, there should be plenty of material available on which controlled experiments could be performed.

There are also numerous examples of low retention of Mn in otherwise successful mine drainage treatment wetlands (cf. Stark et al., 1995 and 1996). Manganese is difficult to remove as oxyhydroxides in aerobic systems since their formation requires a comparatively high pH (ibid.). The successful removal of Mn in anaerobic systems is limited by the comparatively high solubility of MnS (ibid.). Innovative methods to solve this problem would probably be most welcomed.

It is not uncommon that tailings are disposed of in natural depressions in the landscape. Thus, some tailings piles, such as impoundment 1 at the Kristineberg mine (Corrège, 2001), are underlain by peat. It would be interesting to investigate if this peat has prevented pollutants in the drainage water formed from migrating to the groundwater.
8.1. Different Aspects of Sulfate Reduction

There are a number of issues related to sulfate reduction that may deserve further studies. For instance, what will happen to the trace metals that have been adsorbed to and/or co-precipitated with Fe oxyhydroxides, when these particles reach the often anoxic wetland sediments (cf. Section 6.3.3)? Will the rate of sulfate reduction be high enough to compensate for the loss of substrate, so that the wetlands will remain a sink for the trace metals?

Other interesting aspects of sulfate reduction include the rate of the water flow in relation to oxygenation, and possible inhibition of this anaerobic process (cf. Sparling, 1966; Stark et al., 1994b and 1995). Is there a limit on how much surface water that can be treated in an anaerobic wetland per unit of time? By diverting surface water into an anaerobic treatment wetland, ferric Fe may become introduced to the system. Is there a risk then that the activity of the sulfate-reducing bacteria will be reduced, due to competition for suitable substrates by iron-reducing bacteria (cf. Lovley and Phillips, 1987)? Is there also a risk that previously deposited sulfides will get oxidized by the ferric Fe (cf. Vile and Wieder, 1993)?

Natural wetlands are known to be sources of methylmercury to ecosystems downstream (e.g. St. Louis et al., 1996). Since methylmercury is more easily accumulated by biological organisms than inorganic Hg is, and Hg may be found in mine drainage waters (Statistiska centralbyråns Naturvårdsverket, 2000), it would be highly unfortunate if the construction of treatment wetlands would lead to an increasing production of methylmercury. Still, methylation of Hg in mine drainage treatment wetlands appears to have attracted comparatively little interest. This is perhaps even more surprising given that sulfate-reducing bacteria are believed to be the principal methylators in anoxic sediments (Compeau and Bartha, 1985). In ordinary freshwater environments, sulfate reduction is sometimes considered to be limited by a lack of sulfate (Hedin et al., 1989 and 1993). However, this is unlikely to be the case in a mine drainage treatment wetland. In fact, it is even possible that the sulfate present in mine drainage will lead to an increasing methylation of Hg present in wetlands situated downstream from mines and mine waste deposits (cf. Herlihy and Mills, 1985).

The influence of sulfate reduction on the metal binding capacities of dissolved and/or particulate organic matter also merits further studies. For instance, Brown (1986) found that sulfate reduction could lead to incorporation of sulfur into organic matter. It is believed that sulfur-containing groups are involved in the very strong binding or complexation of, for instance, Hg to organic matter (Schuster, 1991; Hintelmann et al., 1995; Xia et al., 1999).
8.2. Particulate Iron as a Scavenger of Trace Metals

In a study of trace metal associations to plankton in lakes polluted with mine and smelter waste, Jackson and Bistricki (1995) found that Zn was selectively bound by MnOOH, whereas As and Cu were bound by FeOOH. It would be interesting to investigate if this phenomenon could be explained simply by slowly raising the pH of the AMD. In such a situation, it seems reasonable to assume that the Fe oxyhydroxides would form before the Mn oxyhydroxides (cf. above). Adsorption of Cu also tends to occur at a lower pH than adsorption of Zn (e.g. Hamilton-Taylor et al., 1997; Webster et al., 1998). Thus, if there is an excess of Fe oxyhydroxides, it is possible that the As and Cu available for adsorption and/or co-precipitation will be depleted before the Mn oxyhydroxides start to form, and the pH is high enough to allow for adsorption of Zn?

Presence of organic matter is well known to influence trace metal adsorption to Fe oxyhydroxides, for instance along pH gradients (cf. Section 4.4.2). However, results presented in this thesis and elsewhere suggest that, in order to understand the mechanisms behind trace metal scavenging by particulate matter, it is also important to consider the relationship between the concentrations of ferrous Fe and organic matter/carbon (Fe/C). If Fe/C is low, the formation of the Fe precipitates will be inhibited, and there will be fewer particles available for trace metal sorption (cf. Section 6.3.3). If Fe/C is high, dissolved organic matter will flocculate, and the precipitates will contain a mixture of POM and FeOOH (Rebhun et al., 1998). Provided that they are not displaced during the flocculation, metals initially bound to the organic matter may then end up in the organic fraction of the sediments (cf. Sholkovitz and Copland, 1981; Romkens and Dolfing, 1998). At intermediate Fe/C, the organic matter will either adsorb to, or co-precipitate with, the Fe oxyhydroxides (McKnight et al., 1992 a and b; Hamilton-Taylor et al., 1996). Ranville et al. (1991) have shown that in a water receiving mine drainage, the surface charge of the particles, which is of great importance from a trace metal perspective, is sometimes governed by a delicate balance between the amount of Fe oxyhydroxides formed and the amount of organic matter available. Trace metal association to particles along a gradient of Fe/C needs to be further investigated.
9. SAMMANFATTNING (Summary in Swedish)

Under de senaste 25 åren har det bedrivits forskning för att undersöka om biogeokemiska processer i våtmarker skulle kunna utnyttjas för att rena lakvatten från gruvor och gruvavfall.

I denna avhandling ges en systematisk beskrivning av våtmarkers struktur och några av de processer som kan utnyttjas för rening av metallförörenat vatten (adsorption, bioupptag, jonbyte, järnreduktion, oxidation och/eller hydrolyssedimentation, samt sulfatreduktion). Olika faktorer som kan påverka effektiviteten och uthålligheten hos dessa processer diskuteras, med utgångspunkt från erfarenheter av tidigare forskning rörande rening av lakvatten från gruvor och gruvavfall i våtmarker. Vidare sätts rening av denna typ av lakvatten in i ett större sammanhang. Sålunda beskrivs även lakvattnets bildning och miljöpåverkan, liksom de bakomliggande orsakerna och alternativa metoder att hantera problemet.

Tillfredsställande rening av vissa typer av lakvatten från gruvor och gruvavfall kan uppnås med hjälp av korrekt anlagda våtmarker. Anlagda våtmarker kan också vara ett konkurrenckraftigt alternativ till mer konventionella metoder att rena lakvatten, både med avseende på ekonomi och miljöhänsyn. Frågan om det finns underhållsfria våtmarker där tillfredsställande rening av lakvatten från gruvor och gruvavfall skulle kunna upprätthållas under en längre tid väntar emellertid ännu på sitt svar. Sannolikheten att en sådan situation skulle kunna uppstå bör öka om våtmarken i första hand används som ett komplement till andra förebyggande och/eller behandlande åtgärdsmetoder, vilka minskar den totala belastningen på systemet.

I avhandlingen redovisas även resultaten från en fallstudie av metallfastläggning i naturliga våtmarker belägna längs en bäck som rinner igenom ett mineraliserat område med pågående och avslutat gruvverksamhet. De undersökta våtmarkerna påverkade inte tungmetalltransporten (Cd, Cu, Pb och Zn) i området i någon större utsträckning. Däremot noterades att fördelningen av flera metaller mellan olika faser (partikulärt (>0,2 µm), löst (<0,2 µm) och bundet till löst (<0,2 µm) organiskt material) förändrades under det att bäckvattnet transporterades genom avrinningsområdet. Andelen As, Cd, Cu, Pb och Zn som återfanns i den partikulära fasen ökade då bäckvattnet blandades med det behandlade vatten som släpptes ut från området runt den aktiva gruvan. Förmodligen orsakades denna omfördelning av att bäckvattnets pH i allmänhet ökade efter blandningen. En del av omfördelningen kan sannolikt även tillskrivas de ökande halterna av partikulärt Fe, vilka var ett resultat av tillförsel av Fe från det övriga avrinningsområdet. Andelen partikulärt As, Cu, Fe och Pb minskade vid passage genom en sjö, medan andelen av dessa metaller bundna
till löst organiskt material ökade. Sedimentation av partikulärt material är en möjlig förklaring till denna omfördelning. För As och Fe kan även tillförsel från avrinningsområdet ha varit av betydelse.

Halten av partikulärt Fe föreföll spela en betydande roll för andelen As, Cu och Pb som återfanns i den partikulära fasen. Om så är fallet, skulle tillförsel av Fe från avrinningsområdet kunna utnyttjas för att uppnå en ökad metallfastläggning i systemet, under förutsättning att dessa partiklar också kan fås att sedimentera, till exempel i en närbelägen våtmark. Järnets betydelse för spårmetallernas fördelning undersöktes därför närmare i två labförsök. I frånvaro av löst organiskt material påverkades andelen As, Cu och Pb som återfanns i partikulär form även av små mängder partikulärt Fe (~1 mg/l). Partiklar bildade i närvaro av spårmetallerna var i vissa avseenden effektivare på att ta upp dessa. Närvapo av humussyra (~6.5 och 13 mg TOC/l) minskade mängden spårmetall bunden till partikulärt Fe, samt den totala mängden och storleken på de bildade Fe-partiklarna. Vintertid kan man även få problem med att det tar längre tid för Fe(II) att oxidera och falla ut om vattentemperaturen är låg (0°C). Andelen partikulärt As, Cu och Pb i bäckvattnet kunde emellertid inte endast förklaras med halten av partikulärt Fe. Det är möjligt att de höga halterna av Ca längs bäcken hade medfört en koagulering av mindre Fe-partiklar och därtill associerade spårmetaller.
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Through his involvement in the MiMi-program, Karsten Håkansson, Swedish Geotechnical Institute (SGI), got a PhD-student to take care of, and he has been acting as my co-supervisor since the spring of 1998. Since Bert left Linköping, Karsten has probably found himself involved in discussions on different theoretical and practical issues much more often than the average co-supervisor, but I cannot remember that I have ever heard him complains about this. I owe Karsten a thank you from the bottom of my heart – without him this thesis would probably never have been finished. Apart from years of experience in mining related issues, field sampling, sequential leaching, and analytical techniques, Karsten has done a great job in trying to lower my ambitions to a more realistic level.

During my first year in the MiMi-program, Maria Ledin also served as an unofficial co-supervisor. She played an important part in laying a solid foundation to build my thesis on. I admire Maria a lot for her genuine curiosity and thoroughness, in everything from literature surveys to published papers of her own, and for her courage to leave the academic world. Since Maria left us, I have had the privilege to keep Maria as a friend, and I have enjoyed the company of her and her family a lot.

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Here I should start by mentioning Lena Lundman and Anders Düker, who have performed the majority of my metal analyses. Lena, where would I be without you?! Mattias Bäckström helped me out with the sequential leaching of
my peat/sediment samples, the results from which are not included in the thesis. Britt Aurell and Cecilia Toomväli (SGI) also helped with the sequential leaching, as well as some analyses of the field samples collected in 2000.

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Regarding wetlands, I have really enjoyed discussions with Mats Öqvist, Elisabeth Johansson, H-B Wittgren, Karin Tonderski, and Sofia Kallner-Bastviken. Bo Svensson is acknowledged for help in finding a suitable peat sampler.

I am very much indebted to Roger Herbert, who acted as the opponent at my final seminar. I hope I have been able to do justice to at least some of his comments on an earlier version of the thesis, as well as the manuscripts included herein. Karin von Arnold, David Bastviken, Anna Bratt, Gunnar Börjesson, Anette Jönsson, Sofia Kallner-Bastviken, Maria Ledin, and Pascal Suër also contributed with valuable suggestions on improvements.

Patricia Ödman kindly squeezed in Paper VII among the rest of her work, and even spent part of the Whitsun Eve correcting the English of it. Thanks for
your good job and lovely e-mail messages! If I had contacted you earlier, the English of the rest of the thesis would definitely have been better. On short notice, Göran Karlsson (SGI) translated my Word files into pdf documents. Dennis Netzell (UniTryck) then skillfully turned it all into a book with a pleasant cover.

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Ian Dickson deserves a special mentioning for invaluable help with various computer-related issues, including bringing files and e-mails I feared I had lost forever back from cyberspace, as well as for his jokes. Dan Lindmark is always willing to help in the lab. Susanne Eriksson, Marie Arvidsson, and Kerstin Sonesson have done a good job in booking my field and conference trips, taking care of my travel statements, and sorting out the project economy (I know that especially the last one was not always easy). The university librarians have also been very helpful in helping me to collect interesting literature.

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During my first two years in Linköping, Linköpings Akademiska Orkester occupied a substantial part of my spare time. I had a great time there, and I would like to thank all the other members of the orchestra at that time for all the fun we had. More recently, Linköpings filmklubb Cinemax has helped me to widen my perspectives. Thanks also to some of my neighbors in Linköpingshus 34, in particular Ann-Charlotte Torstensson with family.
Apart from learning to appreciate the true value of spare time, during my time in Linköping, I have also become very aware of how important my friends are to me. Living in Linköping, I fear that I have been neglecting my oldest friends – Elisabet Hagman, Linda Smedin, Sara Mellgren, and Ylva Nilsson – as well as my friends from Stockholm University – Anna Palmé, Karin Reuterswärd, Helena Högländer, and Eva Stensland. I hope I soon will be able to make it up to you! I would also like to grab the opportunity to thank my friends in writing – Paulo Barrocas, Marie Hjärne, and Gunilla Åsberg-Floria – for interesting discussions about the world we live in, and life in general.

Travelling being one of my new passions, I would like to thank my patient travelling companions; my father, my mother, Anna Bratt (a trip which accidentally resulted in me getting a clearer vision), Pascal Suèr, Mattias Bäckström, and Thomas Lifvergren. Furthermore, there are a number of persons who have played an important part in creating a number of days out of the ordinary, days that constitute quite a disproportionate portion of my memories from these almost six years. These include Mauro Rebello, Susanna Nuutinen, Petri Porvari, Paulo Barrocas, Elisabet Hilding, Vendula Wanstad, Marie Hjärne, Gunilla Åsberg-Floria, and Karin Reuterswärd.

Last, but definitely not least, I would like to thank my parents, Bror and Birgitta Sjöblom, FOR EVERYTHING.
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<table>
<thead>
<tr>
<th>English</th>
<th>Swedish</th>
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</thead>
<tbody>
<tr>
<td>alloy</td>
<td>legering</td>
</tr>
<tr>
<td>brass</td>
<td>mässing</td>
</tr>
<tr>
<td>chalcopyrite</td>
<td>kopparkis</td>
</tr>
<tr>
<td>concentrator</td>
<td>anrikningsverk</td>
</tr>
<tr>
<td>dike</td>
<td>dammvall</td>
</tr>
<tr>
<td>ferric iron</td>
<td>trevärt Fe (Fe$^{3+}$)</td>
</tr>
<tr>
<td>ferrous iron</td>
<td>tvåvärt Fe (Fe$^{2+}$)</td>
</tr>
<tr>
<td>hematite</td>
<td>järnglans</td>
</tr>
<tr>
<td>limonite</td>
<td>sjömalm/myrmalm</td>
</tr>
<tr>
<td>metalloid</td>
<td>halvmetall</td>
</tr>
<tr>
<td>ore</td>
<td>malm</td>
</tr>
<tr>
<td>peat</td>
<td>torv</td>
</tr>
<tr>
<td>protective layer</td>
<td>täckskikt</td>
</tr>
<tr>
<td>pyrite</td>
<td>svavelkis</td>
</tr>
<tr>
<td>reclaim</td>
<td>efterbehandla</td>
</tr>
<tr>
<td>sealing layer</td>
<td>tätskikt</td>
</tr>
<tr>
<td>slaked/hydrated lime</td>
<td>släckt kalk</td>
</tr>
<tr>
<td>smelter</td>
<td>smältverk</td>
</tr>
<tr>
<td>soil cover</td>
<td>torrtäckning</td>
</tr>
<tr>
<td>spillway</td>
<td>utskov</td>
</tr>
<tr>
<td>surface mining</td>
<td>dagbrott</td>
</tr>
<tr>
<td>tailings</td>
<td>anrikningssand</td>
</tr>
<tr>
<td>till</td>
<td>morän</td>
</tr>
<tr>
<td>waste rock</td>
<td>gråberg</td>
</tr>
<tr>
<td>water cover</td>
<td>våttäckning</td>
</tr>
</tbody>
</table>
APPENDIX 2 – Abbreviations and Acronyms

AAS  atomic absorption spectrophotometry
AB  aktiebolag (limited company)
ALD  anoxic limestone drain
AMD  acid mine drainage
ARD  acid rock drainage
AVS  acid volatile sulfides
CSV  cathodic stripping voltammetry
CTW  constructed treatment wetland
DEAE  diethylaminoethyl-cellulose
DOC  dissolved organic carbon
DOM  dissolved organic matter
DRC  dynamic reaction cell
EIA  environmental impact assessment
HA  humic acid
ICP-MS  inductively coupled plasma mass spectrometry
LKAB  Luossavaara-Kiirunavaara AB
MiMi  Mitigation of the Environmental Impact from Mining Waste
MISTRA  Stiftelsen för miljöstrategisk forskning (the Foundation for Strategic Environmental Research)
OLD  oxic limestone drain
PC  polycarbonate
POC  particulate organic carbon
POM  particulate organic matter
RSA  South Africa
SAPS  successive alkalinity producing systems
SEK  svenska kronor (Swedish crowns)
SGI  Statens geotekniska institut (Swedish Geotechnical Institute)
SGU  Sveriges geologiska undersökning (Swedish Geological Survey)
SMC  spent mushroom compost
SRB  sulfate-reducing bacteria
Tema V  Tema vatten i natur och samhälle (Department of Water and Environmental Studies)
TOC  total organic carbon
TVA  the Tennessee Valley Authority
ZPC  zero point of charge
## APPENDIX 3 – English-Latin-Swedish Glossary (Living Organisms)

<table>
<thead>
<tr>
<th>English</th>
<th>Latin</th>
<th>Swedish</th>
</tr>
</thead>
<tbody>
<tr>
<td>beaver</td>
<td><em>Castor</em></td>
<td>bäver</td>
</tr>
<tr>
<td>birch</td>
<td><em>Betula</em></td>
<td>björk</td>
</tr>
<tr>
<td>bog moss</td>
<td><em>Sphagnum</em></td>
<td>vitmossa</td>
</tr>
<tr>
<td>cattail</td>
<td><em>Typha latifolia</em></td>
<td>kaveldun</td>
</tr>
<tr>
<td>‘cattail caterpillar’</td>
<td><em>Simyra henrici</em></td>
<td>ett nattfly</td>
</tr>
<tr>
<td>‘copper moss’</td>
<td><em>Pohlia nutans</em></td>
<td>vanlig nickmossa</td>
</tr>
<tr>
<td>cotton grass</td>
<td><em>Eriophorum</em></td>
<td>ull</td>
</tr>
<tr>
<td>a SRB</td>
<td><em>Desulfomonas</em></td>
<td>en SRB</td>
</tr>
<tr>
<td>a SRB</td>
<td><em>Desulfotomaculum</em></td>
<td>en SRB</td>
</tr>
<tr>
<td>a SRB</td>
<td><em>Desulfovibrio</em></td>
<td>en SRB</td>
</tr>
<tr>
<td>fathead minnow</td>
<td><em>Pimephales promelas</em></td>
<td>‘amerikansk’ elritsa</td>
</tr>
<tr>
<td>an Fe-ox. bacterium</td>
<td><em>Ferrobacillus ferrooxidans</em></td>
<td>en Fe-ox. bakterie</td>
</tr>
<tr>
<td>horsetail</td>
<td><em>Equisetum fluviatile</em></td>
<td>sjöfräken</td>
</tr>
<tr>
<td>a green alga</td>
<td><em>Microspora</em></td>
<td>en grönalg</td>
</tr>
<tr>
<td>mosquitofish</td>
<td><em>Gambusia affinis</em></td>
<td>moskitfisk</td>
</tr>
<tr>
<td>muskrat</td>
<td><em>Ondatra zibethicus</em></td>
<td>bisonråta</td>
</tr>
<tr>
<td>reed</td>
<td><em>Phragmites australis</em></td>
<td>vass</td>
</tr>
<tr>
<td>sedge</td>
<td><em>Carex</em></td>
<td>starr</td>
</tr>
<tr>
<td>an Fe-ox. bacterium</td>
<td><em>Thiobacillus ferrooxidans</em></td>
<td>en Fe-ox. bakterie</td>
</tr>
<tr>
<td>white button mushroom</td>
<td><em>Agaricus bisporus</em></td>
<td>trädgårdschampinjon</td>
</tr>
</tbody>
</table>
APPENDIX 4 – Studies on Wetland Treatment of AMD

The following table is an overview of studies, specifically aimed at investigating the capacity of wetlands, and similar/associated passive systems, to ameliorate AMD, that were reviewed during the work with this thesis. The purpose of the table is to point at the number and diversity of studies on this particular subject that have already been made, and to show that a lot of valuable information is already available in the literature. Even though the table does not constitute a complete bibliography on the subject, it is hoped that it may prove to be useful to the researcher or practitioner new in the field. The studies are listed in chronological order.

<table>
<thead>
<tr>
<th>Origin/Type of Drainage Water</th>
<th>Type of Study or Wetland</th>
<th>Samples Collected</th>
<th>Duration of Study</th>
<th>Study Contains Information on e.g.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper mine</td>
<td>Natural (fen, Bersbo, Sweden)</td>
<td>Water, Biota</td>
<td>6 months</td>
<td>Fenny area as trap for Me in surface water</td>
<td>Lundholm &amp; Andersson (1985)</td>
</tr>
<tr>
<td>Coal surface mine (pH 2.2, Fe 1323 µmol/l)</td>
<td>Natural (fen, WV), Laboratory</td>
<td>Water, Substrate</td>
<td>2.5 hours</td>
<td>Solid phase speciation, Fe²⁺ adsorption</td>
<td>Wieder &amp; Lang (1986)</td>
</tr>
<tr>
<td>Coal refuse (pH 6, Fe 80, Mn &gt;10 mg/l)</td>
<td>Case (TVA Slurry lake 2, built in 1985)</td>
<td>Water, Diversity</td>
<td>1 year</td>
<td>Wetland exposed to acid shock</td>
<td>Brodie et al. (1987)</td>
</tr>
<tr>
<td>AMD (pH 4.9, Fe 33 mg/l, Mn 26 mg/l)</td>
<td>Case (#20, built before 1986)</td>
<td>Water</td>
<td></td>
<td>Sphagnum and Typha wetlands, costs</td>
<td>Kleinmann &amp; Girts (1987)</td>
</tr>
<tr>
<td>Coal facilities, Coal-fired power plants</td>
<td>Case (#11 TVA, built in 1985-1987)</td>
<td>Water</td>
<td></td>
<td>Planning, implementation, costs, sizing</td>
<td>Brodie et al. (1988a)</td>
</tr>
<tr>
<td>Coal mine (pH 5.9, Fe 37 mg/l, Mn 16 mg/l)</td>
<td>Mesocosm (#20 cells, Alabama)</td>
<td>Water</td>
<td>9 months</td>
<td>Comparison between 5 different substrates</td>
<td>Brodie et al. (1988b)</td>
</tr>
<tr>
<td>AMD (pH 2.5-3.2, Fe 100-400 mg/l)</td>
<td>Case (Elk County, Pennsylvania)</td>
<td>Water</td>
<td>1 year</td>
<td>CTW exposed to adverse AMD</td>
<td>Demko &amp; Pesavento (1988)</td>
</tr>
<tr>
<td>Synthetic (pH 3.5, Fe 30 mg/l)</td>
<td>Mesocosm (#3 peat and Sphagnum)</td>
<td>Water, Porewater, Microbiology</td>
<td>14 weeks</td>
<td>The behavior of ferrous and ferric Fe</td>
<td>Dietz &amp; Unz (1988)</td>
</tr>
<tr>
<td>Taconite (pH 7.2, Ni 18, Cu 0.62 mg/l)</td>
<td>Natural (white cedar peatland, Minnesota)</td>
<td>Water, Groundwater, Substrate, Biota</td>
<td>13 months</td>
<td>The movement of water in a peatland</td>
<td>Eger &amp; Lapakko (1988)</td>
</tr>
<tr>
<td>Mine Type</td>
<td>Location/Details</td>
<td>Water, Substrate</td>
<td>Duration</td>
<td>Outcome</td>
<td>Reference</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------------------------------------------------------</td>
<td>------------------</td>
<td>----------</td>
<td>------------------------------------------------------------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Au/Ag mine (pH 3.6, Fe 50, Zn 25 mg/l)</td>
<td>Natural (Carex and Betula fen, Colorado)</td>
<td>Water, Groundwater, Substrate, Biota</td>
<td>1 year</td>
<td>Experimental release of AMD into a fen</td>
<td>Emerick et al. (1988)</td>
</tr>
<tr>
<td>Coal mine (pH 2.9, Fe 181 mg/l, Mn 36 mg/l)</td>
<td>Case (Latrobe, PA, built in 1987)</td>
<td>Water, Substrate</td>
<td>1 day</td>
<td>Advantages of sulfate reduction</td>
<td>Hedin et al. (1988)</td>
</tr>
<tr>
<td>Coal mine (pH 2.7/3.1, Fe 284/148 mg/l)</td>
<td>Case (#2 Tracy, MT, built in 1986)</td>
<td>Water, Substrate, Biota</td>
<td>15 months</td>
<td>Retention time, AMD-peat contact, costs</td>
<td>Hiel &amp; Kerins (1988)</td>
</tr>
<tr>
<td>Base metal mine (pH 4)</td>
<td>Mesocosm, Natural (lake)</td>
<td>Biota</td>
<td>6 months</td>
<td>Metal accumulation by a moss and an alga</td>
<td>Kalin (1988)</td>
</tr>
<tr>
<td>Coal mine (pH 5, Fe 130 mg/l, Mn 71 mg/l)</td>
<td>Review, Case (algal ponds, built in 1987)</td>
<td>Water</td>
<td>4 months</td>
<td>The potential role of algae</td>
<td>Kepler (1988)</td>
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<tr>
<td>Taconite (pH 3.2-7.9, Me 1.2-580 mg/l)</td>
<td>Laboratory (peat)</td>
<td>Water</td>
<td>168 hours</td>
<td>Me removal by peat, efficiency, kinetics</td>
<td>Lapakko &amp; Eger (1988)</td>
</tr>
<tr>
<td>AMD</td>
<td>Case (Ohio)</td>
<td>Water</td>
<td></td>
<td>Distribution and influence of Typha</td>
<td>Mitsch et al. (1988)</td>
</tr>
<tr>
<td>AMD (pH 2.9, Fe 25 mg/l, Mn 16 mg/l)</td>
<td>Natural (#56 sites in WV), Mesocosm (#2)</td>
<td>Water, Substrate</td>
<td>1 year</td>
<td>Survival and influence of Typha</td>
<td>Samuel et al. (1988)</td>
</tr>
<tr>
<td>Synthetic ('bog water' + Fe 0-10 000 mg/l)</td>
<td>Laboratory (Sphagnum)</td>
<td>Biota</td>
<td>33 days</td>
<td>Sphagnum tolerance, uptake, removal/area</td>
<td>Spratt &amp; Wieder (1988)</td>
</tr>
<tr>
<td>Coal mine (pH 6, Fe 80-241 mg/l)</td>
<td>Case (Simco #4, built in 1985)</td>
<td>Water, Biota, Diversity, Microbiology</td>
<td>2 years</td>
<td>Simco #4 wetland history</td>
<td>Stark et al. (1988)</td>
</tr>
<tr>
<td>Coal mine (pH 5.5, Fe 13 mg/l, Mn 30 mg/l)</td>
<td>Case (Ohio, built in 1986)</td>
<td>Water, Interstitial water</td>
<td>10 months</td>
<td>Hydrology, flow, wetland length</td>
<td>Stillings et al. (1988)</td>
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<tr>
<td>Synthetic (pH 2.8-5.5, Fe 37-45 mg/l)</td>
<td>Mesocosm (5 mosses, one alga, sawdust)</td>
<td>Water, Microbiology</td>
<td>14 hours</td>
<td>Fe reduction by plants and sawdust</td>
<td>Webster et al. (1988)</td>
</tr>
<tr>
<td>Coal mines</td>
<td>Review (Sphagnum wetlands, monitoring)</td>
<td>Literature, Data</td>
<td></td>
<td>Max. retention of Fe in Sphagnum wetlands</td>
<td>Wieder (1988)</td>
</tr>
<tr>
<td>Metal mine</td>
<td>Case (Big Five Tunnel, Colorado)</td>
<td>Microbiology</td>
<td>2 months</td>
<td>Fe and Mn oxidizers, SO4(^{2-}) reducers</td>
<td>Batal et al. (1989)</td>
</tr>
<tr>
<td>Coal mine (pH 6.1, Fe 14 mg/l, Mn 5 mg/l)</td>
<td>Case (TVA 950 IMP 3, built in 1986)</td>
<td>Water, Diversity</td>
<td>20 months</td>
<td>Planning, construction costs</td>
<td>Brodie et al. (1989a)</td>
</tr>
<tr>
<td>Origin/Type of Drainage Water</td>
<td>Type of Study or Wetland</td>
<td>Samples Collected</td>
<td>Duration of Study</td>
<td>Study Contains Information on e.g.</td>
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<td>3 years</td>
<td>Sulfate reduction and ice during winter</td>
<td>Gammons et al. (2000)</td>
</tr>
<tr>
<td>Coal storage</td>
<td>Laboratory, Mesocosm (SAPS)</td>
<td>Substrate</td>
<td>10 months</td>
<td>Solid phase speciation</td>
<td>Thomas et al. (2000)</td>
</tr>
<tr>
<td>Origin/Type of Drainage Water</td>
<td>Type of Study or Wetland</td>
<td>Samples Collected</td>
<td>Duration of Study</td>
<td>Study Contains Information on e.g.</td>
<td>Reference</td>
</tr>
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</tr>
<tr>
<td>Metal mine (pH 5, Fe 18 mg/l, Zn 0.6 mg/l)</td>
<td>Natural (Forest Queen, Colorado)</td>
<td>Water, Groundwater, Substrate</td>
<td>4 months</td>
<td>Wetland hydrogeology and geochemistry</td>
<td>Wildeman &amp; Pavlik (2000)</td>
</tr>
<tr>
<td>Coal mines</td>
<td>Case (#4 SAPS, PA, built in 1991-96)</td>
<td>Water</td>
<td>1 year</td>
<td>Redox, costs, design considerations</td>
<td>Demchak et al. (2001)</td>
</tr>
<tr>
<td>Hard rock mines</td>
<td>Review (planning and implementation)</td>
<td>Literature, Data</td>
<td></td>
<td>Sulfate removal and sulfate reduction rates</td>
<td>Kalin (2001)</td>
</tr>
<tr>
<td>AMD (Fe 70 mg/l)</td>
<td>Case (SAPS, Pelenna, South Wales, UK)</td>
<td>Water, Substrate</td>
<td>3 years</td>
<td>Permeability of substrate</td>
<td>Rees et al. (2001)</td>
</tr>
<tr>
<td>Pyrite (pH 2.3, Fe 2.6 mg/l, Zn 10.7 mg/l)</td>
<td>Natural (Sphagnum bogs, fens, Finland)</td>
<td>Water</td>
<td>5 months</td>
<td>Wetland as settling basin</td>
<td>Räisänen et al. (2001)</td>
</tr>
<tr>
<td>AMD</td>
<td>Review (passive treatment systems)</td>
<td>Literature, Data</td>
<td></td>
<td>Web site</td>
<td>Skousen (2001)</td>
</tr>
<tr>
<td>Nickel mine (pH ~4, Cu ~3, Zn ~3 mg/l)</td>
<td>Natural (minerotrophic fen, Sweden)</td>
<td>Porewater, Substrate</td>
<td></td>
<td>Sulfur speciation, sulfide accumulation</td>
<td>Herbert &amp; Ekström (2003)</td>
</tr>
<tr>
<td>Coal mine (metal load 800 mg/l)</td>
<td>Case (#5 aerobic basins and SAPS, KY)</td>
<td>Porewater</td>
<td></td>
<td>Depth gradients in SAPS</td>
<td>Karathanasis &amp; Robinson (2003)</td>
</tr>
</tbody>
</table>

1. Water chemistry given are examples of (average/median) characteristics. Base and precious metal mines are sometimes referred to as hard rock mines, as opposed to coal mines. Pyrite is mined as raw material for the production of H₂SO₄. Ash pond and coal storage seepage are sometimes similar to AMD in character. Sometimes problems with AMD occur also at iron mines (ironstone, taconite). However, in the studies by Eger and co-workers, the source of the AMD is not the taconite but waste rock from the Duluth Complex, which contains metal sulfides. RSA=South Africa.

2. Modeling may refer either to process modeling or geochemical modeling (i.e. what minerals could be expected to form). CTW=constructed treatment wetland. J.B.=Jones Branch. TVA=the Tennessee Valley Authority.

3. Biota=samples collected for metal analysis. Diversity=inventory of species composition. Microbiology=quantification, characterization, and/or determination of the activity of the microbiological community.

4. Here, ‘duration of study’ may reflect either that samples were collected at regular intervals during this period of time, the time that passed between the first and last samples were collected, or the contact time between the water and the solid substrate.
5. Only 30% of these references have been published in scientific magazines. More than half of the scientific papers was obtained from four magazines (Ecological Engineering; Journal of Environmental Quality; Water, Air, and Soil Pollution; and Water, Science, and Technology). The rest of the references were collected from books, conference proceedings, and reports.