Reclamation of Copper Mine Tailings Using Sewage Sludge

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Doctoral Thesis
Swedish University of Agricultural Sciences
Uppsala 2008

Acta Universitatis Agriculturae Sueciae
2008:88

Cover: The Aitik mine tailings deposit seen from the Dundret Mountain, Gällivare. (Photo: Stig Ledin)

ISSN 1652-6880
ISBN 978-91-86195-21-2

Tryck: SLU Service/Repro, Uppsala 2008

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Abstract
Tailings are the fine-grained fraction of waste produced during mining operations. This work was carried out on tailings from the Aitik copper mine in northern Sweden. Establishment of vegetation on the Aitik mine tailings deposit is planned to take place at closure of the mine, using sewage sludge as fertiliser. However, the tailings contain traces of metal sulphides, *e.g.* pyrite, FeS_2, and chalcopyrite, $CuFeS_2$. When the sulphides are oxidised, they start to weather and release metals and strong acid, affecting the plant establishment. This thesis investigated physical and chemical growing conditions for plants in tailings with and without sewage sludge, and how these conditions changed when the tailings were oxidised. Studies on tailings properties were related to growth and metal uptake by barley (*Hordeum vulgare*) and red fescue (*Festuca rubra*) cultivated on the tailings. Fine sand particles (diameter 0.06-0.2 mm) and moderately large pores (diameter 30-300 μm) dominated the tailings. Oxidation processes resulted in a slightly higher percentage of fine pores (diameter ≤5μm) due to the formation of aggregating iron(III)hydroxide and in a pH decrease due to the acid produced as sulphides oxidised. As oxidation proceeded and pH decreased from neutral to 4.5, Al, Cd, Cu, Pb and Zn concentrations in tailings solution increased by 2-3 orders of magnitude. Compared with mineral fertiliser, sewage sludge consistently increased plant biomass production, due to the contribution of nutrients and organic matter, and increased the percentage of large pores (30-300 μm) and fine pores (≤5 μm). The effect of the sludge on pH was generally limited. In the field trial, higher levels of Al, As, Cr, Cu, Pb and Zn were found in red fescue grown in sludge-treated tailings compared with tailings treated with mineral fertiliser. In the climate chamber experiment, sludge effects on Cu in tailings and plants depended on the degree of oxidation of the material. In unoxidised tailings, sewage sludge slightly increased Cu levels in solutions and fescue shoots, but in oxidised tailings the opposite occurred. In general, the sewage sludge did not counteract the toxic conditions caused by sulphide oxidation, but had beneficial effects on plant growth irrespective of oxidation degree of the tailings material.

Keywords: mine tailings, sewage sludge, sulphide oxidation, porosity, metals, DOC, plant uptake

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To my parents Birgit and Robert.
To my children Ludvig and Klara.

If you can see, look.
If you can look, observe.
The Book of Exhortations

Contents

List of Publications

This thesis is based on the work contained in the following papers, which are referred to in the text by their Roman numerals:

I Stjernman Forsberg, L. & Ledin, S. 2003. Effects of iron precipitation and organic amendments on porosity and penetrability in sulphide mine tailings. *Water, Air and Soil Pollution*, 142, 395-408.

II Stjernman Forsberg, L. & Ledin, S. 2006. Effects of sewage sludge on pH and plant availability of metals in oxidising sulphide mine tailings. *Science of the Total Environment*, 358, 21-35.

III Stjernman Forsberg, L., Gustafsson, J-P., Berggren Kleja, D. & Ledin, S. 2008. Leaching of metals from oxidising sulphide mine tailings with and without sewage sludge application. *Water, Air and Soil Pollution*, 194, 331-341.

IV Stjernman Forsberg, L., Berggren Kleja, D., Greger, M. & Ledin, S. Effects of sewage sludge on solution chemistry and plant uptake of Cu in sulphide mine tailings at different weathering stages. Accepted by *Applied Geochemistry* with minor revision.

Papers I-III are reproduced with the kind permission of the publishers.

The contribution of Lovisa Stjernman Forsberg to the papers was as follows:

I Planned the experiment together with Ledin. Performed field sampling and laboratory work. Performed data analysis and writing with assistance from Ledin.

II Planned the experiment together with Ledin. Participated in practical field work and performed field sampling. Performed data analysis and writing with assistance from Ledin.

III Planned the experiment with assistance from the co-authors. Performed the practical work with the column leaching test, solution sampling and pH measurements. Performed data analysis and writing with assistance from the co-authors.

IV Planned the experiment with assistance from the co-authors. Performed the practical work with the climate chamber experiment, solution sampling and measurements of pH and free copper concentration. Performed data analysis and writing with assistance from the co-authors.

Abbreviations

DM	Dry Matter
DOC	Dissolved Organic Carbon
SS	Sewage Sludge

1 Introduction

It has been estimated that 70% of the material excavated in mining operations worldwide ends up as waste (Hartman, 1987). Sweden is one of the main producers of copper, iron, lead, silver and zinc in the European Union and produces about 58 million metric tons of mine waste each year. To get a picture of the quantities produced, imagine a one metre high and one metre wide wall encircling the whole globe – this is the amount of mine waste produced in Sweden over two years. Of this waste, 76% is produced by sulphide mines (Fröberg & Höglund, 2004).

The fine-grained fraction of the waste is called tailings and constitutes about 50% of the total amount. The tailings are pumped out as sandy slurries on deposits, resulting in large areas of bare sand. Without any protective cover, the surface of the deposit will dry out and the sand will be exposed to wind and water erosion. The wind can carry the tailings particles to adjacent environments where they may silt up receiving streams. Dust storms from the deposits may also disturb surrounding villages and threaten human health (Draškovi, 1973; Bergholm & Steen, 1989; Sidle *et al.*, 1991). In addition, tailings from sulphide mines contain traces of metal sulphides, *e.g.* pyrite (FeS_2) and chalcopyrite ($CuFeS_2$), which start to weather when the tailings are exposed to the air and oxygen diffuses through the material. This can result in the liberation of metals and strong acid from the tailings, which may pollute adjacent areas (Kleinmann *et al.*, 1981; Allan, 1997).

One way to diminish those impacts on the surrounding landscape is to stabilise the tailings by vegetation. Mining companies and researchers have been working on vegetation establishment on mine tailings for over half a century (*e.g.* Peters, 1970; Archer *et al.*, 1988; Plass, 2000). During the past 30 years a considerable amount of research has been conducted on the feasibility of using municipal sludge (sewage sludge) to stimulate the revegetation of mine land by improving the physical and chemical conditions necessary for plant growth in the tailings (Sopper, 1993). Sewage sludge is the solid waste that has been separated through sedimentation from municipal sewage water. Fresh sewage sludge contains about 50% organic matter on a dry-matter basis and high amounts of nitrogen and phosphorus, and has a pH near 7.0. It has in many cases been reported to increase the survival and primary production of vegetation established on tailings deposits (Bergholm & Steen, 1989; Borgegård & Rydin, 1989; Pietz *et al.*, 1989; Sopper, 1993; Pichtel *et al.*, 1994; Lan *et al.*, 1998; Voeller *et al.*, 1998; Theodoratos *et al.*, 2000; Wang *et al.*, 2008).

The willingness to use sewage sludge on mine tailings has increased because the sludge nowadays constitutes a huge disposal problem and is available at a low cost, while the area of abandoned mine tailings deposits is expanding. A dream scenario for both the mining industry and municipal authorities would be for a mixture of the two wastes to form a growth substrate in which a sustainable ecosystem could develop. However, both materials are potentially hazardous (Sopper, 1993; Plass, 2000), and such a mixture needs to be thoroughly investigated. Of principal significance is how sewage sludge, due to its high content of organic matter, affects the potential for metals to enter the soil solution phase, where their mobility and bioavailability will increase the environmental risks.

As sulphidic mine tailings are highly reactive when exposed to air and water, the deposit environment is a complex system of coupled physical and biochemical processes (Younger *et al.,* 2002; Gleisner, 2005). This should be taken into account when adding a new material to the tailings. Mine tailings are usually saturated with water when deposited on the tailings pond, but are drained and oxidised when exposed to air at the time of plant establishment and sewage sludge application. The chemical reactions caused by the sulphide oxidation can then occur rapidly (Kleinmann *et al.*, 1981; Allan, 1997), drastically changing the growing environment. In addition, the decomposition rate of the sewage sludge is expected to be high during the first months after application (Ledin, 2006; Wennman & Kätterer, 2004). This requires improved knowledge about how growing conditions may change in the tailings during the initial stage of plant establishment, and how they are affected by sewage sludge application during this crucial period.

2 Objectives

The overall aim of this thesis was to investigate physical and chemical growing conditions in sulphide mine tailings with and without sewage sludge application, and to determine whether these growing conditions would change during the initial oxidation of the tailings. The term 'oxidised tailings' is used in the text to refer to tailings that have been drained and exposed to air during a limited time period. The studies were performed as field, column and climate chamber experiments.

The specific objectives were to:

1. Characterise physical and chemical conditions for plant growth in unoxidised and oxidised tailings with respect to:
    a. Texture, porosity and penetrability
    b. pH and contents of nutrient elements and trace elements

2. Study the effects of sewage sludge application on:
    a. Porosity and penetrability
    b. pH
    c. Chemical extractability and plant uptake of metals
    d. Leaching behaviour of metals
    e. The chemistry of copper in solution (total dissolved Cu and free Cu) in relation to the copper uptake in plants grown in tailings with different degrees of weathering

Figure 1 gives an overview of the studies performed to achieve the specific objectives. The trace elements studied included aluminium (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni) and zinc (Zn). Although As is not a metal in the strict sense, it is referred to as a 'metal' in the text. Metal speciation in tailings solution was carried out solely on Cu, as this element was expected to occur in high levels in both mine tailings and sewage sludge.

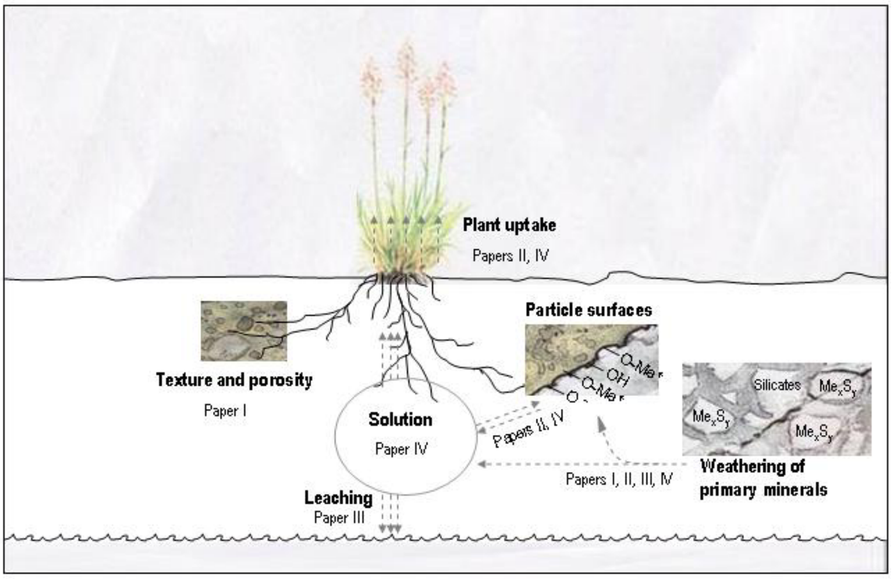

Figure 1. Overview of the studies performed (Papers I, II, III and IV) on the Aitik mine tailings and their relations to factors affecting growth and metal uptake by plants. Arrows represent the flow of metals (Me) between the different pools in the system. Illustrations of aboveground parts of the plant and the tailings particles by Martin Holmer.

The work reported in this thesis formed part of a remediation programme for the Aitik copper mine area in the county of Norrbotten in northern Sweden. In the following, the study object and the methodology used are briefly described in Chapter 3. The results of the studies related to objectives 1 and 2 are then presented in Chapters 4 and 5, respectively.

3 Studies Performed

3.1 The Aitik Copper Mine as a Study Object

Aitik is an open copper mine situated about 100 km north of the Arctic Circle and 15 km south-east of the town of Gällivare in the county of Norrbotten, northern Sweden. The mine was opened in the year 1968 and is planned to be used at least until the year 2025.

The Aitik deposit is hosted by strongly altered and deformed volcano-sedimentary rocks. The main ore zone is sheared in a north-south direction. It consists of biotite, quartz and muscovite. Sulphide minerals occur disseminated and consist mainly of chalcopyrite ($CuFeS_2$), pyrite (FeS_2) and sphalerite (ZnS). The chalcopyrite is the value mineral and the mean copper concentration in the ore is about 4000 g per ton (0.4%). In addition to copper, gold and silver are extracted from the ore and occur at concentrations of 0.2 g and 3.5 g per ton, respectively. The ore is finely crushed and milled to fine sand particles and mixed with water to separate the sulphide particles from the gangue minerals through flotation processes. Each year about 18-19 million tons of ore are produced, from which 68 000 tons of copper, 55 tons of silver and 1.5 tons of gold metal are produced. The rest of the ore remains as tailings, which mainly consist of silicate minerals (feldspar, plagioclase, biotite and muscovite), but also some of the sulphide minerals since a 100% metal recovery is not possible to achieve (Lindvall & Eriksson, 2003; Wanhainen *et al.*, 2003).

The tailings are pumped out as slurry into a lagoon (Figures 2 and 3). The area of the deposit, about 11 km^2, will have increased to about 13-14 km^2 at closure of the mine. In addition to the natural topography, the lagoon is delineated by dam walls. The thickness of the deposit in the lagoon is increasing by about 1 metre per year, and currently ranges from a few to about 40 metres. The deposit is gently sloping from the east side where the slurry is emitted from pipes to the far west side with a difference in height of about 30 metres over 5 000 metres, but the final design of the deposit at the time of closure has yet to be decided. The water from the tailings slurry is collected in a reservoir downstream from the tailings deposit. In the water reservoir, ultrafine particles are settled and the water is returned to the mill through a channel system. Each year, about 20% of the water from the tailings pond system is discharged into an adjacent river (Lindvall, 2005). The discharge occurs in late spring after the snow and ice melt in the tailings pond, and in summer after heavy rain falls.

Figure 2. The open pit of the Aitik copper mine (left) and one of the pipelines pumping out the mine tailings onto the deposit (right). (Photos: Stig Ledin and Åsa Sjöblom)

The climate of the region is sub-arctic, with cool summers (mean temperature 13 °C) and cold winters (mean temperature -14 °C). The average annual precipitation is around 680 mm (Eriksson, 1992). The surrounding landscape consists of glacial tills and bogs. The glacial tills are forested mainly by Scots pine (*Pinus silvestris*) and Norway spruce (*Picea abies*). The ground vegetation is dominated by dwarf shrubs, such as cowberry (*Vaccinium vitis idaea*), whortleberry (*Vaccinium myrtillus*) and crowberry (*Empetrum nigrum*), and different species of grass, mosses and lichens (Ledin, 2006). Due to the Midnight Sun, the vegetation is more luxuriant than expected in this climate. So far, no signs have been found of any impact of the mining activity on fish or bottom fauna in the surrounding surface waters, but increases in the metal content in moss species have been observed in the proximity of the mine (Lindvall, 2005).

A remediation programme for the Aitik copper mine area was started in 1989. Within this programme, investigations related to waste management strategies were carried out during about 15 years. The results from those investigations are presented in a licentiate thesis by Lindvall (2005).

A collaboration between the mining company Boliden Mineral AB and the Swedish University of Agricultural Sciences was initiated in 1995 and aimed at developing methods for establishing sustainable vegetation on the deposit at closure of the mine. The species selection trials, that were carried out close to the tailings deposit, did not fall within of the scope of the present thesis. They are presented in a report by Ledin (2006). The results of those trials showed that plant establishment on the mine tailings was only sustainable if sewage sludge had been added to the tailings. The results further suggested that grass species should be used as an initial vegetation, as grasses are less sensitive to wind erosion and cover the surface rapidly compared to trees and bushes. The native grass should be protected against the wind by a rapidly growing cereal, *e.g.* barley, during the first season (Ledin, 2006).

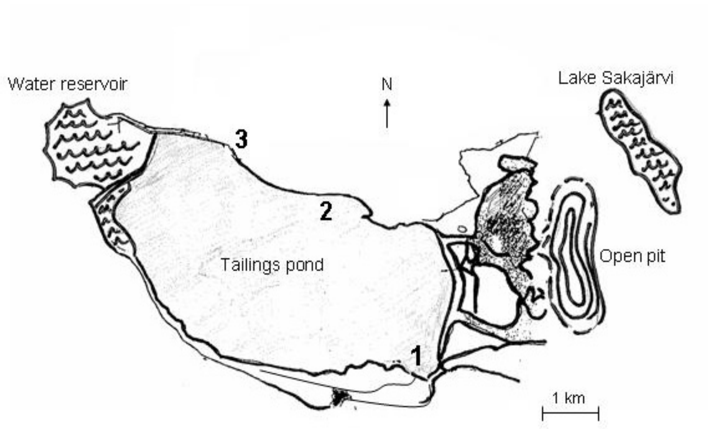

Figure 3. Overview of the Aitik mine site. Points 1, 2 and 3 show where sampling of the tailings took place.

3.2 Field Studies

Field trials were performed close to the north-western part of the main tailings deposit (point 3 in Figure 3). The experimental plots were prepared at a higher altitude than the main deposit and had therefore been effectively drained and oxidised.

3.2.1 Physical studies (Paper I)

The first field trial studied the physical conditions for plant growth in tailings with and without sewage sludge application and described how the conditions changed with the degree of oxidation of the tailings. The soil variables studied included texture, penetration resistance, pore size distribution, total porosity and plant-available water content. The plant available water was determined as the difference between water content at field capacity and the wilting point.

The site was originally one part of the species selection trials (Ledin, 2006) and had been prepared two years earlier. At that time, the site was divided into plots with the following treatments: (1) untreated, (2) mineral fertiliser addition corresponding to 0.007, 0.003 and 0.006 kg m^{-2} of nitrogen (N), phosphorus (P) and potassium (K), respectively, and (3) treatment with sewage sludge from the Gällivare treatment plant (30% by volume incorporated to a soil depth of 20 cm). The plots were originally vegetated, and desiccated plants occurred occasionally at the time of sampling. However, due to a low survival of the plants, the tailings samples used in the present studies did not contain roots or other plant material.

To compare oxidised with unoxidised tailings, studies were performed both on the experimental site (oxidised tailings) and on the main tailings deposit (unoxidised tailings) (Points 1 and 3 in Figure 3). Texture analyses were made on loose tailings from both sites, according to Carter (1993). Penetrability studies were made *in situ* with a penetrometer in which a loadcell measured the force required to push the penetrometer probe through the tailings. Soil cores (height 10 cm, diameter 7.2 cm) were sampled *in situ* down to 30 cm depth. In addition, loose unoxidised tailings from the deposit were transported to the laboratory, where they were mixed with fresh sewage sludge (0, 16 and 33% by volume), placed in steel cylinders (height 5 cm, diameter 7.2 cm) and subjected to packing by a compaction press. For the porosity measurements, the relationship between soil water potential and moisture content in the cores was determined using hanging-columns and pressure plates.

3.2.2 Chemical studies (Paper II)

The second field trial compared sludge effects on the chemical conditions for growth between unoxidised and oxidised tailings, with the focus on pH and the chemical distribution and plant availability of Al, As, Cd, Cr, Cu, Mn, Ni, Pb and Zn. The site was divided into 32 plots, containing eight treatments, but only two of the treatments were selected for the study: plots treated with mineral fertiliser (NPK-treated) and plots treated with sewage sludge from the Henriksdal treatment plant in Stockholm (20% by volume incorporated to 20 cm) (Figure 4). Mineral fertiliser was applied at a considerably higher rate than in the first field trial (0.02 kg N, 0.73 kg P and 1.4 kg K per m^2), with the intention of increasing the survival rate of the plants and decreasing the difference in nutrient supply between sludge-treated and NPK-treated plots. To study metal uptake in plants, plots were sown with red fescue (*Festuca rubra*) and barley (*Hordeum vulgare*). These species were chosen based on the results from previous species selection trials (Ledin, 2006).

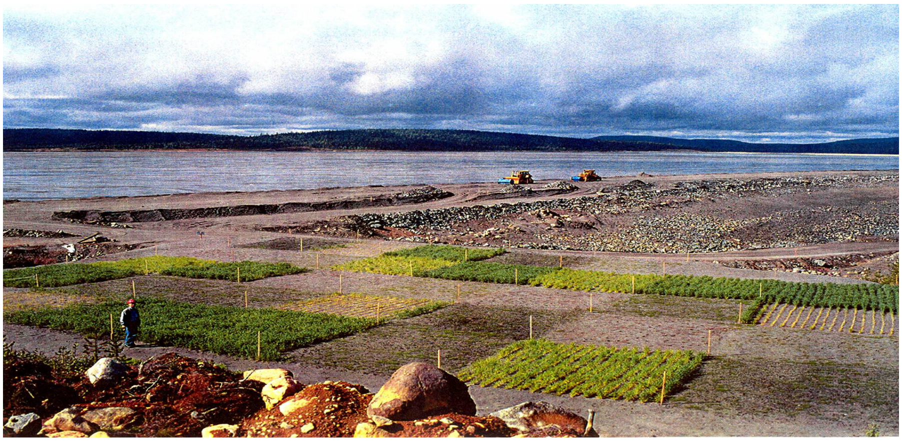

Figure 4. The second field trial performed close to the tailings deposit. Plots used for the study were NPK-treated or treated with sewage sludge and sown with barley and red fescue. (Photo: Stig Ledin)

Unoxidised tailings were sampled on the experimental site at the beginning of the experiment (in June, at the time of sowing), and in oxidised tailings three months later (in September, at the time of harvesting). Aboveground plant biomass was collected by clipping at the tailings surface. All plant material was dried (50°C) weighed, milled, boiled in 7 M HNO_3 and analysed with respect to concentrations of Al, As, Cd, Cr, Cu, Mn, Ni, Pb and Zn. The grain and straw of the barley were milled and analysed separately.

In addition to estimates of the metal uptake in plants, 'plant availability' was related to the following metal fractions in the tailings: (1) exchangeable non-specifically adsorbed elements extracted with 1 M NH_4NO_3; and (2) exchangeable specifically adsorbed elements extracted with 0.5 M NH_4Ac + 0.02 M EDTA. The remaining element fractions that could only be extracted with 7 M HNO_3, were assumed to be bound to primary and secondary minerals and not immediately available to plants. Thus, all tailings samples were subjected to pH measurement (1:5 tailings to water ratio) and then sequentially extracted by NH_4NO_3, NH_4Ac-EDTA and HNO_3 (1:10

tailings to liquid ratios). The levels of Al, As, Cd, Cr, Cu, Mn, Ni, Pb and Zn were analysed in the extracts.

3.3 Column Leaching (Paper III)

A column experiment running during 20 months examined the effects of sewage sludge on the leaching of Al, Cd, Cu, Mn, Ni, Pb and Zn from the Aitik mine tailings during the course of sulphide oxidation. The study examined how the effects of sludge on leaching behaviour of metals changed with the initial oxidation processes.

The experiment was performed in six plexiglass columns (inner diameter 3.2 cm, length 14 cm) filled with untreated tailings, collected at the tailings deposit (point 2 in Figure 3) and tailings treated with sewage sludge, from the Henriksdal treatment plant in Stockholm (3 replicates for each treatment). Deionised water was transported through silicon tubes into the columns by a peristaltic pump. The leachate from the columns was collected in plastic bottles placed in a vacuum chamber. To obtain unsaturated flow conditions, constant vacuum was maintained in the vacuum chamber using a pump controlled by a pressure sensor. To promote oxidation of the tailings, the leaching was temporarily interrupted after approximately 75 mL of leachate had been collected from each column and the columns were dried at room temperature (20°C) for 45 days. These leaching and drying cycles were performed 13 times in total. The leachate samples collected after each cycle were analysed with respect to pH, metals, dissolved organic carbon (DOC) and sulphate (SO_4^{2-}).

3.4 Solution Chemistry and Plant Uptake of Cu (Paper IV)

The final study examined whether effects of sewage sludge on Cu in tailings and plants differed between tailings with different degrees of sulphide weathering. The study focused on DOC, free Cu and total dissolved Cu in the tailings solution, and on growth and Cu content of roots and shoots of red fescue.

In this study, three different types of tailings were used, all derived from the Aitik copper mine: fresh unoxidised tailings (taken directly from the flotation process), moderately oxidised tailings (collected in a semi-dry area of the eastern part of the tailings deposit) and highly oxidised tailings (oxidised during three months in a climate chamber prior to the experiment). Pots were filled with the different tailings types (1 kg substrate/pot, four replicates) and treated with either nutrient solution (corresponding to 600 mg N, 250 mg P, 300 mg K kg^{-1} substrate) or sewage sludge (20% by volume), and placed in a climate chamber for 6 weeks. Seeds of red fescue were sown densely in the pots. The plants were irrigated with deionised water twice a week, in amounts corresponding to the water consumption, which was determined by weighing the pots. Tailings solution was sampled with Rhizon tension lysimeters (Rhizon SMS, Rhizosphere Research Products, Wageningen, the Netherlands) in the beginning of the experiment and then every second week, in total four times. These small lysimeters (length 100 mm, diameter 2.5 mm) are made from a hydrophilic porous polymer with a mean pore size of 0.1 µm, through which the soil solution is transferred. All solutions were analysed to determine their pH, free Cu activity, tot-Cu, tot-SO_4^{2-}, and DOC. The shoots of the fescue were harvested after 6 weeks by cutting the plants at the soil surface. The roots were then removed from the pots and rinsed. Both shoots and roots were dried, weighed, milled and analysed with respect to Cu concentrations.

3.5 Equipment Used for Chemical Analyses

Metal concentrations in tailings, plant materials and tailings solutions were determined by ICP-MS (Elan 6100) (Papers II, III and IV). Sulphate was determined on an anion chromatograph (Dionex, MODULE/SP) and DOC (dissolved organic carbon) was determined using a TOC-analyser (Shimatzu 5000A) (Papers II and III). The free copper ion concentration (Cu^{2+}) was measured potentiometrically using a copper ion selective electrode (Cu-ISE Orion 96-29, Thermo Electron Corporation, Beverly, MA) (Paper IV).

4 Conditions for Plant Growth in Sulphidic Mine Tailings

Mine tailings are low in the nutrients necessary for plant growth. In addition, as the tailings lack organic matter and usually have a coarse texture, the water- and nutrient-holding capacities are very low (Bradshaw & Chadwick, 1980; Clemensson-Lindell *et al.*, 1992). However, the most important process when it comes to the conditions for plant growth in sulphidic mine tailings is the dissolution of the sulphide minerals and the subsequent buffering processes. Weathering of sulphide tailings causes dissolution and leaching of metals because sulphuric acid is generated during the sulphide oxidation (Singer & Stumm, 1970; Kleinmann *et al.*, 1981). When percolating through the mine tailings, the leachate may react with buffering minerals, such as carbonates, aluminium hydroxide and alumino-silicates, and thus be partially or totally neutralised, depending on the sulphide oxidation rate and the abundance and neutralising capacity of the buffering minerals (Bruggenwert *et al.,* 1991: Blowes & Ptacek, 1994; Strömberg & Eriksson, 1996; Bellaloui *et al.*, 1999). Some silicates, *e.g.* muscovite and garnet, are more resistant to weathering than *e.g.* biotite and Ca-rich plagioclase (Ollier, 1969). The processes of sulphide oxidation and the subsequent reactions are described in more detail in the Special Appendix. They are strongly dependent on the mineralogy of the tailings and other soil properties, including particle size and hydrological regime (Gleisner, 2005).

Against this background, an important question was whether the metal sulphides in the Aitik mine tailings were able to produce acidity during the first growing season, despite the high content of buffering silicate minerals.

4.1 Physical Aspects

The physical properties of the tailings are of critical importance to both weathering processes and plant establishment, as they determine the hydrological regime (Passioura, 2002; Gleisner, 2005).

According to the results from the first field study (Paper I), particles of fine sand (diameter 0.06-0.2 mm) dominate the Aitik mine tailings (Table II in Paper I). The high percentage of sand particles implies a low specific surface area of the tailings, and thus a low aggregation and capacity for binding nutrients and retaining water (Brady & Weil, 1996). It also implies a lower amount of sulphide exposed to reaction compared with finer grained tailings (Gleisner, 2005). On the other hand, due to the coarse texture there is a risk of a low capacity of the buffering minerals to neutralise acid conditions.

Due to the sandy texture, moderately large pores (diameter 30-300 μm) constituted about 50-70% of the pore system in the material not treated with sludge in both unoxidised and oxidised tailings (Paper I). Those pores are rapidly drained and filled with air at field capacity, allowing high oxygen advection and hence a great degree of acid production (Ferguson & Eriksson, 1988; Gleisner, 2005). Plants only manage to capture a very small part of the 'free' water occurring in these pores. The percentage of fine pores (diameter <5 μm) was higher in oxidised tailings than in unoxidised ones. The iron(III)hydroxides eventually formed during sulphide oxidation probably caused increased aggregation and settling of particles (Blowes & Ptacek, 1994; Lin, 1997). However, although a higher aggregation of the particles would increase the capacity of the tailings to hold water and nutrients, it also gives rise to increased hardness of the tailings. The mechanical resistance was considerably higher in oxidised tailings on the experimental site than in the unoxidised tailings (Paper I). Root growth slows markedly once the resistance exceeds about 1 MPa and falls to almost zero at a resistance of about 5 MPa (Bengough & Mullins, 1990). Hence, according to the penetrometer studies on the Aitik mine tailings, roots were able to penetrate down to 40 cm in unoxidised, but only to 10-15 cm in oxidised tailings (taking only the mechanical aspects into consideration).

4.2 Chemical Aspects

Minimum and maximum values of chemical variables found in untreated tailings used in the different studies are summarised and compared with corresponding values in Swedish agricultural soils and guideline values for contaminated soils in Table 1. As the tailings were collected at different sites, some chemical properties differed between the tailings types used in the different studies, especially pH and total content of sulphur and copper.

Compared with agricultural soils, the nutrient status of untreated tailings was very low, especially regarding the nitrogen content (Paper II). Accordingly, plants were not able to survive in untreated tailings. This was observed at an early stage in tailings plots without any addition of nutrients.

Table 1. *Variations in selected chemical properties between different types of mine tailings collected at the Aitik copper mine and used in the different experiments (minimum and maximum values), compared with corresponding values in Swedish agricultural soils (mean ± standard deviation, n=25) (Eriksson, 2000, 2001) and to the guideline values for total metal content in contaminated soils (Swedish Environmental Protection Agency, 1998).*

Parameter	Aitik mine tailings	Agricultural soils	Limits
pH	3.5 - 7.5	6.3	-----
Tot-S (%)	0.1- 2.4	0.05	-----
Tot-N (%)	0.01-0.02	0.3	-----
P-AL (mg 100 g^{-1})	0.3-4.5	10.6	-----
K-AL (mg 100 g^{-1})	1.2-6.7	13.7 ± 8.5	-----
Al (mg kg^{-1})	8600 - 10400	-----	-----
As (mg kg^{-1})	3.9 - 7.1	4.0 ± 4.1	-----
Cd (mg kg^{-1})	0.09 - 0.14	0.23 ± 0.17	2
Cr (mg kg^{-1})	12 - 14	20.5 ± 13.2	100
Cu (mg kg^{-1})	180 - 570	14.6 ± 10.5	600
Fe (mg kg^{-1})	24000 - 37000	-----	-----
Mn (mg kg^{-1})	530 - 740	422 ± 356	-----
Ni (mg kg^{-1})	9 - 11	13 ± 7	50
Pb (mg kg^{-1})	3.5 - 11	17.1 ± 10.2	100
Zn (mg kg^{-1})	57 - 76	59 ± 29	800

Tot: total content. AL: ammonium lactate/acetic acid-extracted (Egnér *et al.*, 1960).
The metals were extracted by 7 M HNO_3.

The tailings only contained elevated levels of total Cu (Table 1). However, the total content of a metal is a poor prediction of its bioavailability. Metals and other elements occur in many different chemical forms in the environment and only a few of these forms, are bioavailable, *i.e.* they can be taken up by plants, animals or microorganisms (Viets, 1962; Landner & Reuther, 2004; Datta & Young, 2005). The metal fractions considered most plant-available are those occurring in aqueous solution. There are several chemical processes controlling these metals, of which the adsorption processes are considered the most important ones (Alloway, 1990). They include cation exchange at charged surfaces, such as silicate clays and organic matter, and specific adsorption at surfaces of minerals, such as iron and manganese oxides, hydroxides and amorphous aluminosilicates, as well as surfaces on organic matter (Ross, 1994).

Due to the sandy texture and the almost complete lack of organic matter, the cation exchange capacity is probably low in the Aitik mine tailings, decreasing the preference for cation exchange on the mineral surfaces. Specific adsorption is probably of greater importance due to the abundance of alumino-silicates, oxides and hydroxides of Fe, Al and Mn in the tailings (Bourg, 1988). The specific adsorption is highly pH-dependent and involves direct ionic and covalent bonding between the surface group and the adsorbed metal ion. At low pH the occupation of H^+ on the surface group leads to a decrease in the bonding of the metal to the particle and thus an increase in the metal concentration in solution (Ross, 1994). As long as the tailings remain reduced, *i.e.* are water saturated, the availability of the metals is rather low, as formation of metal sulphides, metal hydroxides and metal carbonates of low solubility are the main chemical processes. When the tailings oxidise, however, the minerals can dissolve and metals are released, as mentioned in the introduction to this chapter. In addition, the pH decrease associated with the sulphide oxidation leads to desorption of the metals from the mineral surfaces (Bourg, 1988) (Figure 1).

In all trials performed with the Aitik mine tailings, the oxidising sulphides gave rise to acidity. Thus, the weathering rate of the silicates did not exceed the rate of sulphide oxidation and acid production. At a rapid rate of acid production by the sulphide minerals, calcite is the dominant buffering mineral because of its faster dissolution kinetics compared to silicates. The low amounts of calcite in the tailings (Lindvall & Eriksson, 2003) were rapidly consumed, allowing the sulphides to produce an acid leachate.

The second field study (Paper II) showed that pH in the NPK-treated Aitik mine tailings decreased during the three months of oxidation, from 6.6 to 4.3, and the colour of the tailings turned from grayish to yellowish (Figure 5), due to the formation of iron (III) hydroxides during the oxidation process (Paper II). This rapid pH decrease was also observed during preparation of the tailings used in the climate chamber experiment (Paper IV). The column experiment (Paper III) also showed decreasing leachate pH during the course of oxidation of the material. In all these experiments, decreasing pH in the tailings resulted in increased solubility of all metals studied, which for several metals ended up in solution concentrations potentially toxic to plants (Bowen, 1979; Kabata-Pendias, 2001). Concentrations of Al, Cd, Cu, Pb and Zn in the leachate increased by 2-3 orders of magnitude as sulphide oxidation progressed (Paper III) (Figure 6).

Figure 5. Unoxidised tailings (left) and oxidised tailings (right) from the Aitik copper mine (scale 5:1). The light particles in the unoxidised tailings are mineral grains of quartz, muscovite and plagioclase. The dark grains are mainly biotite. In the oxidised tailings the particles are coated with yellowish iron (III) hydroxides formed during the weathering process. (Photo: Stig Ledin)

Figure 6 shows the strong relationship between pH and total dissolved Cu and free Cu found in solutions from untreated tailings in the column study (Paper III) and from NPK-treated pots in the climate chamber experiment (Paper IV). The concentration of total dissolved Cu in solution increased by 2-3 orders of magnitude as pH decreased from neutral to around 4.5-5 in both the column and climate chamber experiments, with similar regression equations for the two sets of results (Figures 6a and 6b). The concentration of free Cu increased by 6 orders of magnitude within the same pH interval (Figure 6c). The steep increase in free Cu with decreasing pH was probably due to the release of copper ions from both oxidising sulphides and labile Cu complexes in solution. This is relevant to consider as the free ion is postulated to be a better predictor of toxicity to plants than the total dissolved metal concentration (Morel, 1983; Minnich *et al.*, 1987; Sauvé *et al.*, 1996; Lofts *et al.*, 2004).

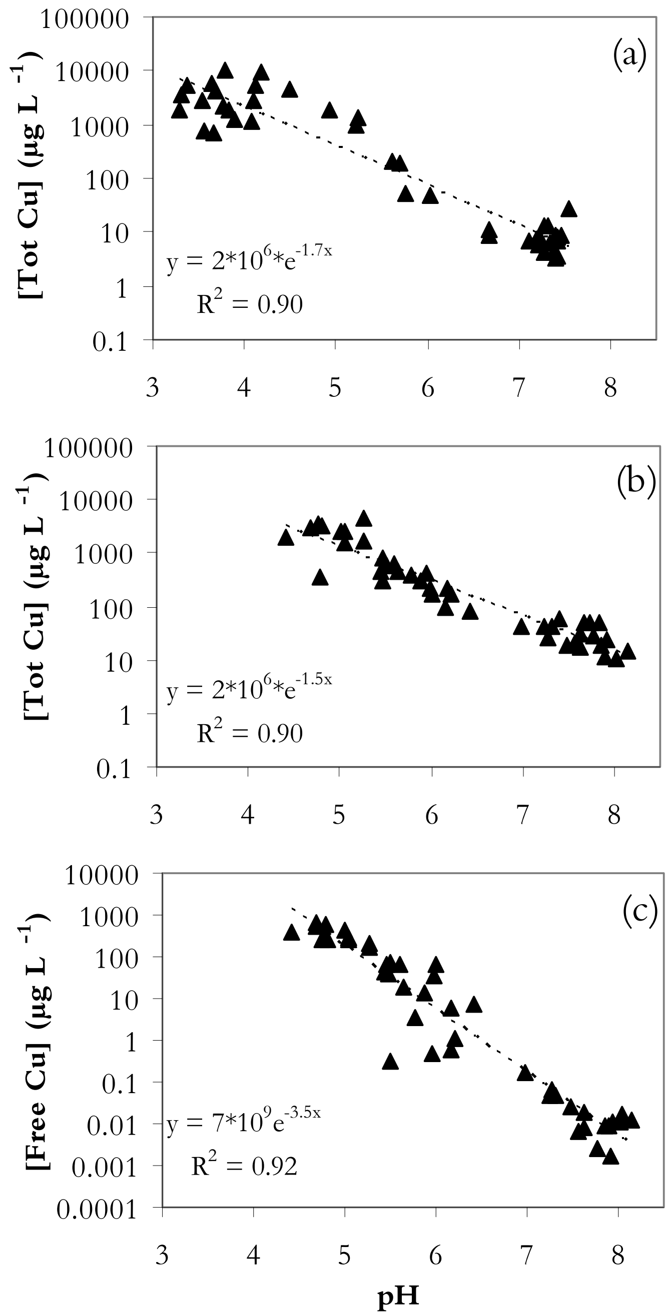

Figure 6. Total dissolved Cu (µg L^{-1}) as a function of pH in leachate from (a) columns and (b) pots in the climate chamber, and (c) free Cu (µg L^{-1}) in solution from pots in the climate chamber. Equations and correlation coefficients of exponential regressions are included.

The results from the column study showed that the total amounts of Al, Cu, Mn, Ni and Pb leached from each column correlated both to mean pH and total amounts of leached SO_4^{2-} (Paper III). In those columns that had the highest degree of sulphide oxidation, the percentage of metal leached in relation to the total element content was highest for Cd, Cu, Ni and Zn, which indicates a high mobility of those metals when the sulphides begin to oxidise. Similar results have been reported by other researchers investigating metals released due to the weathering of sulphidic material (Sohlenius & Öborn, 2004; Da Pelo *et al.*, 2008). In the field, the percentages of specifically adsorbed fractions were generally lower and the percentages of the most soluble fraction generally higher in oxidised tailings than in unoxidised ones, reflecting the lower pH in the former. The difference was greatest for Cd, Ni, Pb and Zn (Tables 2 and 3 in Paper II), which agrees with the data from the column experiment showing a high solubility of those elements (Paper III).

5 Use of Sewage Sludge on Sulphidic Mine Tailings

About 240 000 metric tons (dry weight) of sewage sludge are produced annually in Swedish municipal waste water treatment plants. The municipal waste is stabilised to sludge in sewage-treatment plants through putrefaction, aeration or liming, and is dewatered to a dry matter content of 20-30% (Swedish Environmental Protection Agency, 1996) (Figure 7).

Sewage sludge contains about 30-50% organic matter, and approximately 40 g nitrogen, 24 g phosphorus and 3 g potassium per kg dry matter (DM) (Swedish Environmental Protection Agency, 1996; Theodoratos *et al.*, 2000). The high carbon and nutrient content and the fast decomposition rate make the sludge suitable for use as a soil amendment on unfertile mine tailings, and it has been proven to improve the survival and biomass production of plants (Pietz *et al.,* 1989; Clemensson-Lindell *et al.*, 1992; Pichtel *et al.*, 1994; Ledin, 2006). Furthermore, recycling of the sludge would minimise the problem of sludge disposal, which is currently a serious issue due to the recent EU ban on landfilling of organic material. However, the beneficial aspects of using sewage sludge should be assessed together with the potentially detrimental ones. There are restrictions on using sewage sludge as a soil amendment on agricultural land due to its content of heavy metals and toxic organic pollutants and to the risk of spreading pathogens. Trace metals and organic pollutants in the sludge mainly derive from wastewater produced by industrial activities. In addition, Al and Fe are used during processing of the sewage sludge in the treatment plant in order to precipitate phosphorus, usually resulting in high levels of those elements in the sludge (Swedish Environmental Agency, 1996). Other problems associated with the sewage sludge are the leaching of nitrogen and phosphorus (Clemensson-Lindell *et al.*, 1992).

With regard to metals, the use of sewage sludge on mine tailings can be considered from a different perspective than sludge application on agricultural land. Accumulation of potentially toxic metals in agricultural soils due to the use of sewage sludge is the result of repeated applications of metal-contaminated sewage sludge (Alloway & Jackson, 1991), while the reclamation of abandoned mine deposits usually only involves a single treatment (Pichtel *et al.*, 1994). The total amount of metals applied to the tailings through the sewage sludge is therefore very small in relation to the high content of metals found in the tailings themselves. Nevertheless, although the sewage sludge does not contribute to any significant amounts of metals to the tailings, it can still have significant effects on the metals in terms of chemical distribution and plant availability.

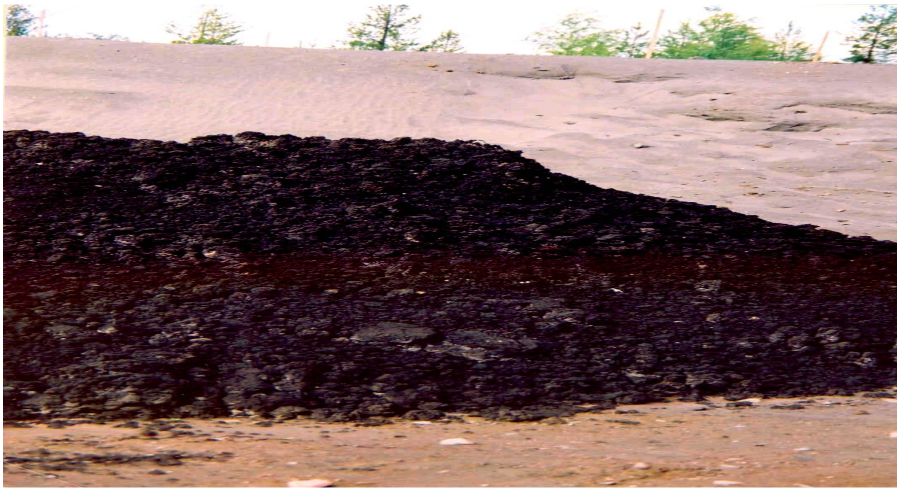

Figure 7. The sewage sludge used on the trials with the Aitik mine tailings. (Photo: Stig Ledin)

5.1 Sludge Effects on Physical Conditions

From a physical point of view, addition of sewage sludge to sandy soils is generally considered beneficial to plants, as the organic matter in the sludge decreases bulk density and mechanical resistance, and increases the total porosity and the content of plant-available water (Tester, 1990; Weber *et al.*, 2007; Asadu *et al.*, 2008).

This was confirmed by the results from the first field study (Paper I). In general, the addition of sewage sludge increased the total porosity in the Aitik mine tailings. A decrease in the percentage of large pores (diameter >30 μm) and an increase in moderately fine pores (5-30 μm) by the sewage sludge would have been the most beneficial effect for plants, as this should involve an increase in the content of plant-available water. Roots are able to extract water from pores with a diameter down to 6 μm (Brady & Weil, 1996). However, the sewage sludge increased the percentage of fine pores (diameter ≤5 μm), holding water partly not available to plants, and the largest pores (diameter 30-300 μm), which are filled with air most of the time (Paper I). Therefore, the addition of sewage sludge caused a smaller increase in the content of plant-available water than in total porosity. The increase in stored plant-available water by the sewage sludge was about 3% by volume in the fresh unoxidised material prepared in laboratory. This implies that the sewage sludge increased the volume of plant-available water in the tailings by about 60 000 litres per hectare in the uppermost 20 cm layer, corresponding to 6 mm of rain. Evapotranspiration from a grass field during a sunny summer day is around 3 mm (Johansson & Linnér, 1977). Thus, the sewage sludge can supply the vegetation with water for about two extra summer days.

The sludge effects on porosity observed in fresh material appeared to be long-lasting, as sludge-treated tailings that had been subjected to weathering for two years also contained a higher percentage of fine pores (diameter <5 μm) and large pores (diameter 30-300 μm) than oxidised tailings without any treatment (Paper I). However, the difference in mechanical resistance between unoxidised and oxidised tailings was significantly greater when the tailings had been treated with sewage sludge or mineral fertiliser (Figure 1 in Paper I). Yellowish hard pans, *i.e.* cemented layers of tailings, were observed in NPK-treated and sludge-treated plots at the experimental site, but not in the untreated plots. Adsorption of the added phosphates and/or organic matter on the iron oxides formed during sulphide oxidation may have caused increased aggregation and settling of particles, which resulted in increased cementation of the tailings (Blowes & Ptacek, 1994; Lin, 1997; Rietra *et al.*, 1997). This might have been a long-term effect, as hard pans were not observed in any of the treatments in the second field experiment (Paper II), where the tailings had been oxidised during a shorter period (three months).

5.2 Sludge Effects on Chemical Conditions

5.2.1 pH

In all experiments acidic conditions were found in oxidised tailings, irrespective of treatment. In the second field trial, however, slightly higher pH values were found in sludge treated tailings (pH 4.8) than in NPK-treated tailings (pH 4.3) at the end of the experiment (Paper II). In the column study the sewage sludge treatment resulted in a higher pH value in leachate on the first leaching occasion (Figure 2 in Paper III). The pH then decreased gradually in all columns, and no further influence of the sewage sludge on pH could be confirmed statistically (Paper III). In the climate chamber experiment, similar pH values were found between treatments throughout the experiment (Figure 1 in Paper IV).

The limited effect of the sewage sludge on pH suggests that the sludge did not have any impact on the sulphide oxidation process in the tailings. Other studies have shown either promoting effects (Wakao *et al.,* 1983; Evangelou, 1995; Cravotta, 1998; Meyer *et al.,* 1999) or inhibiting effects (Loomis & Hood, 1984; Younger *et al*., 1997; Cheong *et al*., 1998; Kim *et al*., 1999) of sewage sludge on sulphide oxidation. The column study (Paper III) showed a high sensitivity of the ongoing oxidation processes and indicated that indirect effects of the sewage sludge, such as effects on bulk density and water-holding capacity, might be important for the effect of sludge on pyrite oxidation. Such indirect effects – and problems in handling them practically – could be one explanation for the different results obtained by the different researchers cited above.

5.2.2 Metals

Humic acids are regarded as the metal-immobilising fraction of the organic matter in the sewage sludge, due to their low solubility and high ability to interact with soil particles. The mechanisms involved include ion exchange between H^+ and metal ions on acidic functional groups, especially R-COOH and R-OH groups, and specific adsorption processes (Kerndorff & Schnitzer, 1980; Schnitzer, 1986; McBride, 1989; Pinheiro *et al.,* 2000; Tipping, 2002; Milne *et al*., 2003). In addition to the solid-state organic matter acting as a sink for metals, the organic matter also generates DOC, which is a water-soluble fraction. This fraction is said to include fulvic acids, which differ from the humic acids in that they have lower molecular mass, a higher concentration of the reactive functional groups and a higher solubility. They can form water-soluble complexes with many metals over a wide pH range and are considered to be the most important organic fraction in terms of transporting metals in soil solution. The organo-metallic complexes formed may maintain the metal ions in solution, which prevents the metal from being converted into insoluble compounds by adsorption or precipitation. However, it is important to note that (i) only part of the fulvic acid is soluble and solubility depends strongly on pH and metal loading, and (ii) other organic compounds, not classified as fulvic acids, also contribute to DOC (Schnitzer, 1986; Alloway & Jackson, 1991; Ross, 1994; Tipping, 2002).

Due to both metal immobilising and mobilising effects by the organic matter, there is no single answer regarding the effects sewage sludge will have on metals in mine tailings. Several studies have shown that metals can be effectively removed from acidic mine leachate by sewage sludge (Peterson & Gschwind, 1972; Edgerton *et al.*, 1975; Pietz *et al.,* 1989; Theodoratos *et al.,* 2000), while other studies have shown enhanced metal mobility (Baham & Sposito, 1983; Harwood *et al.*, 1987; Clemensson-Lindell *et al.*, 1992; Ross, 1994; Fairley *et al.*, 1998).

Table 2. *Selected chemical properties of sewage sludge from the Henriksdal treatment plant (Stockholm) (mean ± standard deviation, n=4) compared with the limits for total metal content in sewage sludge used on agricultural land (Swedish Environmental Protection Agency, 1996).*

Parameter	Henriksdal sewage sludge	Limit
pH	7.8	-----
Tot-S (%)	0.8[a]	-----
Tot-N (%)	4.3[a]	-----
Tot-P (%)	4.0	-----
Tot-C (%)	24.8	-----
P-AL (mg 100 g^{-1})	600	-----
CaO (%)	3.8[a]	-----
Al (mg kg^{-1})	5850 ± 156	-----
As (mg kg^{-1})	3.0 ± 0.1	-----
Cd (mg kg^{-1})	0.67 ± 0.06	2
Cr (mg kg^{-1})	14.4 ±0.7	100
Cu (mg kg^{-1})	539 ± 100	600
Fe (mg kg^{-1})	110 000[a]	-----
Mn (mg kg^{-1})	94.7 ± 6.3	-----
Ni (mg kg^{-1})	12.5 ± 3.6	50
Pb (mg kg^{-1})	18.2 ± 0.6	100
Zn (mg kg^{-1})	267 ± 7	800

Tot: total content; AL: ammonium lactate/acetic acid-extracted (Egnér *et al.*, 1960);
The metals were extracted by 7 M HNO_3; [a]Analysed by Stockholm Vatten (2002).

Although the total amounts of several elements in the solid phase material were similar between sewage sludge and the Aitik mine tailings (Tables 1 and 2), chemical extractability, solubility and plant availability of the metals differed between NPK-treated and sludge-treated tailings (Papers II, III and IV). This will be discussed in the following text.

Chemical extractability

Figure 8 shows the concentrations of some elements found in the most weakly bound fraction, extracted by NH_4NO_3, and in the specifically adsorbed fraction, extracted by NH_4Ac-EDTA, in unoxidised and oxidised samples, with and without sewage sludge application. The fraction extracted by HNO_3, which included 90-99% of the total concentrations of the elements referred to in Figure 8, is not included in the diagram as this fraction was of minor importance for metal uptake in plants, and any effects of sulphide oxidation and/or sewage sludge application on this fraction were not measurable due to its dominance in the tailings (Paper II).

As mentioned before, the NH_4NO_3-extractability of the elements generally increased with time, due to sulphide oxidation. This was observed in both NPK-treated and sludge-treated tailings. A significant treatment effect on this fraction was only found for Zn and Cd, however, and only in the unoxidised tailings, where a higher level of Zn and a lower level of Cd were found in the sludge-treated samples (Figure 8). Element amounts in the specifically adsorbed fraction (extracted by NH_4Ac-EDTA) were generally higher in sludge-treated samples than in NPK-treated in both unoxidised and oxidised tailings. This agreed with other studies showing that adding sewage sludge to soil increases the fraction of metals held in organically bound complexes (Basta & Sloan, 1999; Theodoratus *et al.*, 2000). However, the difference was only significant for As in the unoxodised tailings and for As, Cu and Ni in the oxidised tailings (Figure 8). The generally small difference between treatments in chemical extractability may be related to the presence of phosphates in the NPK-treated plots, which may also have influenced the metal distribution (Hettiarichichi, 1997; Rietra *et al.*, 2001), and to differences in leaching between plots, removing metals from the most soluble fraction.

In Figure 8 it can be noted that the sum of the NH_4NO_3-extractable and the NH_4Ac-EDTA-extractable fractions decreased for Ni in both treatments and for Zn and Cd in the sludge-treated plots during oxidation. Those elements are considered mobile in soils (Kabata-Pendias, 2001) and may have been easily removed from the top layer of the field plots by leaching, after being released through the oxidation process. This agrees with data from the column study showing a high mobility of those elements in both treatments during sulphide oxidation (Paper III). In relation to the total element content, the sum of the NH_4NO_3-extractable and NH_4Ac-EDTA-extractable fractions was highest for Cd (8.6-17.1%) and Pb (16.8-34.5%) (Paper II). It has been found in previous studies that high amounts of Cd in soils occur in the exchangeable fractions (Eriksson, 1989; He & Singh, 1993). Lead is generally not considered mobile in soils (Kabata-Pendias, 2001), but in the tailings this metal probably occurred in sulphides and thus was released in the oxidation processes (Paper II).

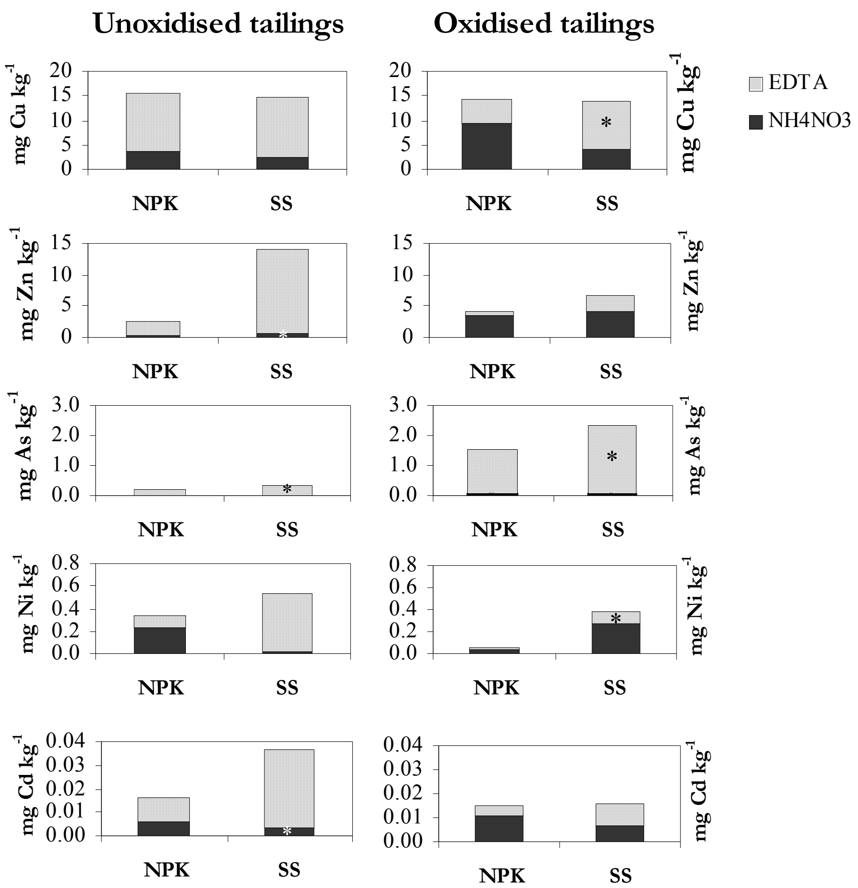

Figure 8. Average concentrations of Cu, Zn, As, Ni and Cd in NH_4NO_3-extracted fraction and NH_4Ac-EDTA-extracted fraction in unoxidised (left) and oxidised (right) Aitik mine tailings from NPK-treated plots and plots treated with sewage sludge (SS). *Significantly (p<0.05) different from the corresponding sample in the NPK-treated plot.

Leaching behaviour

As long as pH was within the range 6.5-7.5, a clear metal mobilising effect of the sewage sludge was observed in the column leaching test (Paper III). Significantly higher concentrations of Al, Cu, Ni, Pb and Zn were found in leachate from sludge-treated tailings under those conditions, compared with untreated tailings. This effect was also observed for Cu in the climate chamber experiment (Paper IV), and was explained by the complexation of metals to DOC leached from the sewage sludge. As leaching proceeded, however, and pH started to decrease in both untreated and sludge-treated columns, pH became the determining factor for metal leaching, irrespective of treatment. On the whole, the effects of sludge on the leaching of all metals studied appeared to be limited, as differences between treatments expressed as leached metal amounts could not be confirmed statistically (Paper III).

Solution chemistry of Cu

Figure 9 shows the effects of sewage sludge on the Cu/pH-relationship found in the column study (Paper III) and in the climate chamber experiment (Paper IV), previously presented for non-sludge tailings (Figure 6). A comparison between the regression equations of the different treatments suggests that sewage sludge addition decreased the dependency of total dissolved Cu on pH. This is probably an effect of a different impact of organic matter in the sludge at different pH values. The sludge increased the amount of total dissolved Cu at high pH, due to the binding to DOC (Papers III and IV). It has been shown that the complexation of Cu by DOC from sewage sludge is greatest at neutral pH (Ashworth & Alloway, 2007). As sulphide oxidation progressed, DOC from sludge-treated tailings decreased, and the binding of Cu to the solid phase organic matter then became more dependent on the Cu concentration in aqueous solution, at least within the pH range 4 - 5 (Figure 9a). At pH values below 4, however, data from the column study suggest that metal immobilising effects of the sludge were less significant (Figure 3 in Paper III).

Although sewage sludge occasionally decreased the concentrations of free Cu under acidic conditions (Figure 2 in Paper IV), it did not significantly moderate the steep increase in free Cu with decreasing pH (Figure 9c). This weak effect of the sludge on free Cu probably depended on the high amount of metals in the sewage sludge product itself (Table 2), Al, Cu and Fe occupying binding sites on the organic matter surfaces, and Cu replenishing the Cu pool in solution.

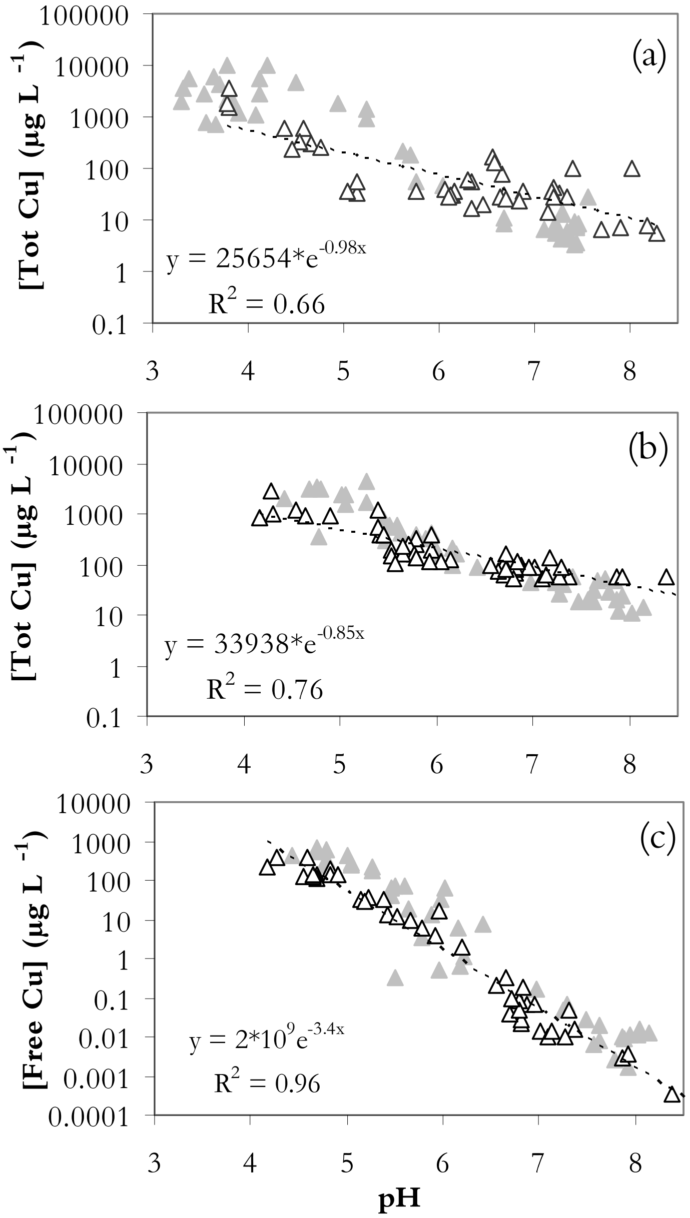

Figure 9. Total dissolved Cu (µg L^{-1}) as a function of pH in solutions from a) columns and b) pots in the climate chamber, and c) free Cu (µg L^{-1}) as a function of pH in solutions from pots in the climate chamber. Open triangles = tailings treated with sewage sludge. Shaded triangles = tailings without sewage sludge. Equations and correlation coefficients of exponential regressions on the data from tailings treated with sewage sludge are included.

5.3 Plant Growth

The nutrient content of the sewage sludge was far above the corresponding levels in untreated Aitik mine tailings (Tables 1 and 2). This resulted in a dense vegetation cover and a high survival of the plants (Papers II and IV), which is consistent with several studies reporting improved growth when using sewage sludge on mine tailings (*e.g.* Pietz *et al.*, 1989; Pichtel *et al.*, 1994; Zabowski & Everett, 1997; Ye *et al.*, 2001). The sewage sludge was superior to the mineral fertiliser in terms of stimulation of biomass production, although the difference between treatments was greater in the field (Figure 1 in Paper II) than in the climate chamber experiment (Table 4 in Paper IV). In NPK-treated tailings the biomass of barley grain was about 50% lower than normal yields of barley in the area. In sludge-treated tailings, however, the yield was similar to the background values (Figure 1 in Paper II). In the climate chamber experiment, a very low root biomass was found in both treatments under acidic conditions, but both root and shoot biomass were consistently higher where sewage sludge had been added to the tailings (Table 4 in Paper IV).

In previous plant selection trials with the Aitik mine tailings it was found that although NPK fertilisation supported good growth at the time immediately after application, the vegetation did not survive after the first growing season unless NPK application was repeated. In sludge-treated tailings, however, the survival was good for several years after a single treatment except for the first plant selection trial (Ledin, 2006). Although the sewage sludge slightly increased the porosity and water-holding capacity of the tailings due to its organic matter content (Paper I), it is likely that it was mainly its strong nutritional effect that promoted plant growth. The organic matter served as a nutrient reservoir, counteracted the nutrient leaching and supplied plants with nutrients in pace with the mineralisation. Wilden *et al.* (1999) found that application of mineral fertiliser caused a short-term (about 1 month) increase of nitrate (NO_3^-) in soil solution, while application of sewage sludge caused a long-term (about 16 months) increase.

5.4 Metal Uptake by Plants

The metal uptake by vegetation in mine tailings is of great concern as it can lead to accumulation in grazing animals. The Aitik deposit may become a significant pasture for reindeer, moose and hares living in the area. These animals are attracted to the open windy area on the deposit, where they can avoid heat and mosquitoes (Figure 10).

Figure 10. Reindeer are frequent visitors to the flat and open tailings deposit, here grazing the grass on one of the vegetation establishment trials on the Aitik mine tailings.
(Photo: Iiris Takala)

Reindeer and moose in particular are consumed by humans, and during the summer months about 40-60% of the reindeer diet is composed of different grass species (Cederlund *et al.*, 1980).

Elevated amounts of metals in plants grown on mine tailings have been reported from mining districts all over the world (*e.g.* Smith & Bradshaw, 1979; Pietz *et al.*, 1989; Hao *et al.*, 2004; Askaer *et al.*, 2008). It is difficult to draw any general conclusions about the effects of sewage sludge on metal uptake by plants grown on soils or mine tailings, as the effects are highly dependent on plant species, biomass production, metal properties and substrate characteristics. Although results showing increased metal levels in plants due to sewage sludge application appear to dominate the literature (*e.g.* Ernst, 1988; Pietz *et al.,* 1989; Sopper, 1993; Hooda *et al.,* 1997; Lan *et al.,* 1998; Singh & Grawal, 2007), some studies also report the contrary (Christensen & Tjell, 1983; Clemensson-Lindell *et al.*, 1992; Theodoratos *et al.*, 2000; Chiu *et al.*, 2005).

High metal solubility generally corresponded to high metal levels in plants grown on the Aitik mine tailings both in the NPK treatment and the sewage sludge-treatment (Papers II and IV). In the field study (Paper II), the amounts of all metals studied were far above background levels in both barley and fescue. Barley contained 175 mg Cu kg^{-1} on NPK-treated tailings and 125 mg Cu kg^{-1} on sludge-treated tailings (Paper II), which exceeded the maximum tolerable Cu level in dry forage for daily intake by cattle (100 mg kg^{-1}, NRC, 1980). Copper amounts in red fescue grown on NPK-treated oxidised tailings in the climate chamber (168 mg kg^{-1}) also exceeded this value (Paper IV) (Figure 11).

Despite indications of higher specific adsorption of some metals in tailings treated with sewage sludge compared with NPK-treatments, significantly higher levels of Al, As, Cr, Cu, Pb and Zn were found in red fescue shoots grown on sludge-treated tailings (Figure 3 in Paper II). In barley plants, however, only Mn and Zn occurred in higher concentrations in the sewage sludge treatment (Figure 2 in Paper II). Slightly higher Cu concentrations in fescue shoots on sludge-treated tailings than on NPK-treated tailings were also found in the unoxidised tailings in the climate chamber experiment (Figure 11), despite similar solution concentrations of free Cu in the two treatments (Paper IV). This promoting effect of the sewage sludge on metal uptake by fescue may be related to soluble metal-organic complexes in the sludge-treated tailings (Wallace *et al.*, 1974; Minnich *et al.,* 1987; McBride, 1989; Zhang *et al.*, 2001). Fulvic acids can promote metal convection and diffusion and thus increase the delivery of metals from the solid phase of the tailings to the tailings solution (Wallace *et al.*, 1974; Zhang *et al.*, 2001). Furthermore, the DOC of the sludge also includes low-molecular weight organic acids (LOAs; $R\text{-}(COOH)_{1\text{-}3}$), which can form metal complexes that make the metals more available to the plants than the metal ion alone. The LOAs are generated through breakdown of organic matter and have been shown to constitute about 8% of the soluble organic carbon in sewage sludge (Baham & Sposito, 1983). The presence of anions of LOAs, especially citrate, malonate, malate and lactate, has been shown to increase the bioavailability of metals (McBride, 1981; Ahumada *et al.*, 2001; Parker *et al.*, 2001; Inaba & Takenaka, 2005). However, although plants are able to take up LOAs (Jones & Darrah, 1992; Molas & Baran, 2004), it is still unclear whether the plants absorb whole metal-LOA complexes or metals in the form of free ions resulting from the dissociation of these complexes in the solution (Molas & Baran, 2004; Inaba & Takenaka, 2005). The uptake mechanisms are probably plant-specific, which may explain the difference in sludge effects on metal uptake between red fescue and barley (Paper II). In previous studies red fescue has been suggested to be able to take up chelated metals (Boswell, 1975; Miller & Boswell, 1978), while barley has been shown to have a lower capacity to take up metal chelates than other plant species (Ebbs & Kochian, 1998).

However, the effects of sludge seemed to vary between tailings with different degrees of sulphide oxidation (Paper IV) (Figure 11). The slightly higher Cu concentrations observed in fescue shoots from sludge-treated unoxidised tailings were not observed in shoots grown on highly oxidised tailings. Instead, about 6-fold lower levels of Cu were found in shoots from sludge-treated tailings compared with NPK-treated tailings under those conditions. Bearing in mind the weak effect of the sewage sludge on Cu in solution, this observation was surprising. However, one should consider the toxic conditions occurring in those tailings. Root growth in the tailings without sewage sludge was almost completely inhibited due to toxic conditions caused by the sulphide oxidation. Surprisingly, shoots were able to grow in those pots despite the damaged root tissue, but a high flow of metals from solution to shoots could be expected due to the limited root biomass. In the sludge-treated tailings root growth was also depressed, but not to the same extent (Table 4 in Paper IV). This effect of the sewage sludge on roots was probably more important for Cu uptake in shoots under those conditions than any sludge effect on Cu chemistry in solution.

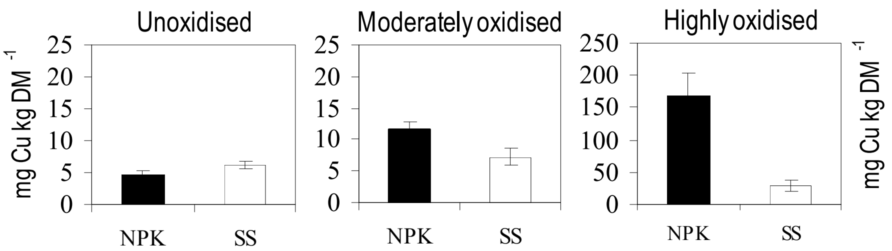

Figure 11. Cu content in shoots of red fescue (*Festuca rubra*) grown in climate chamber, with unoxidised tailings (left), moderately oxidised tailings (center) and highly oxidised tailings (right). NPK = tailings treated with mineral fertiliser; SS = tailings treated with sewage sludge. Note the different scales.

In tailings with a lower degree of oxidation, the Cu content in roots was consistently lower in tailings treated with sewage sludge than in NPK-treated tailings (Figure 3d and 3e in Paper IV). The difference in sludge effects between roots and shoots in those tailings is difficult to explain, but may be related to differences in sludge effects on biomass between roots and shoots. The higher biomass due to sludge application may have caused a dilution effect on Cu level in the plants that was greater for roots than shoots (Table 4 in Paper IV). Another explanation is that metal translocation within the plants was higher in sludge-treated tailings than in NPK-treated. This may be related to the soluble metal-organic complexes. When metals are bound in neutral-charged complexes with organic compounds, their affinity for the negative charges in the cell walls is reduced (White, 1981; Cataldo *et al.*, 1988) and the complexes may therefore be more rapidly transported from roots to shoots if organic matter is present.

Levels of Cu found in red fescue shoots in the field (Figure 3 in Paper II) did not agree with the levels found in any of the corresponding treatments on any of the tailings types used in the climate chamber experiment. There are a number of differences between these two plant studies, including pH conditions, NPK fertilisation, plant growth and climatic conditions, that could explain the different results.

6 Conclusions

This thesis provides physical, chemical and biological perspectives on how sulphide oxidation and sewage sludge application influence mine tailings, with the focus on the first months after oxidation of the tailings.

In relation to the initial objectives formulated it was concluded that:

- From a physical point of view, plants are able to grow on unoxidised tailings, although the coarse texture and the predominance of large pores can cause rapid drying of the tailings and an elevated risk of nutrient leaching from added fertilisers. In oxidised tailings, however, iron hydroxides formed during sulphide oxidation can increase the hardness of the tailings, limiting root penetration.

- From a nutrient perspective, plants are not able to grow in untreated tailings, mainly due to lack of nitrogen. In tailings fertilised with either NPK fertiliser or sewage sludge, however, plants grow well during the initial stage of plant establishment, as long as pH remains non-acidic, *i.e.* in unoxidised tailings or in tailings with a low sulphide level (about 0.1%). Sewage sludge is superior to NPK fertiliser in terms of biomass production and plant survival, due to its high content of both nutrients and organic matter.

- Due to sulphide oxidation processes, the chemical conditions in tailings with a sulphide level of about 1% can change within three months after oxidation has started, *i.e.* during the initial stage of plant establishment. This results in an inhospitable environment for plants due to low pH and increased concentrations of metals in aqueous solution. Cadmium, Cu, Pb and Zn are suggested to be the elements that need most attention in the future management of the Aitik tailings deposit. Compared to other elements, high proportions of those elements were found in the most soluble fractions in oxidised tailings, and their level in solutions increased by 2-3 orders of magnitude as sulphide oxidation proceeded.

- The porosity in the tailings was increased by sludge application in both unoxidised and oxidised tailings. Sewage sludge addition resulted in an increased percentage of large pores (diameter 30-300 μm) and very fine pores (diameter <5 μm) and a slight increase in plant-available water. In the oxidised tailings there is a risk of increased cementation in the presence of sewage sludge or mineral fertiliser.

- Slightly higher pH values were occasionally found in tailings treated with sewage sludge, but in general the buffering effect of the sewage sludge was limited.

- Application of sewage sludge resulted in elevated levels of Zn and lower levels of As and Cd in the most weakly bound fraction of the unoxidised tailings, and increased levels of specifically adsorbed As, Cu and Ni in oxidised tailings, all compared with the NPK treatment. Red fescue grown on sludge-treated field plots contained significantly higher levels of Al, As, Cr, Cu, Pb and Zn compared to the corresponding plots treated with mineral fertiliser.

- In fresh and unoxidised material, leachate concentrations of Al, Cu, Ni, Pb and Zn were higher in sludge-treated than in NPK-treated tailings, due to initially high concentrations of dissolved organic carbon. As leaching proceeded, however, the amounts of Al, Cu, Mn and Ni leached were more closely related to the degree of sulphide oxidation occurring in the tailings than to treatment.

- The effects of the sewage sludge on Cu in solution and plants depended on the degree of oxidation of the substrate. In unoxidised tailings, application of sewage sludge resulted in increased solubility and shoot accumulation of Cu compared with tailings treated with NPK fertiliser, probably due to DOC forming soluble complexes with Cu. Sewage sludge also seemed to promote translocation of Cu to shoots in those tailings. In oxidised tailings, however, slightly lower contents of total dissolved Cu and free Cu were found in solution. Under those conditions considerably lower metal levels were found in fescue grown on sludge-treated than on NPK-treated tailings, probably due to beneficial effects of the sludge on plant growth, moderating the toxic effects caused by the sulphide oxidation. In general, sludge effects on metal uptake in plants appeared to depend on plant growth and metal translocations within plants – factors that can vary widely between species and treatments.

As this thesis shows, sewage sludge is suitable for use as an organic amendment on the Aitik copper mine tailings, due to the plant nutrition effect. However, the growing conditions can change rapidly in tailings containing a sulphide level $\geq$1%. When those tailings are oxidised, the sewage sludge will still have a beneficial effect on plant growth, but its buffering and immobilising effect will not be sufficient to counteract the toxic conditions that develop in the tailings.

7 Future Perspectives

From a metal immobilisation perspective, the possibility of using an organic amendment that is ‘cleaner’ (*i.e.* with a lower content of mainly trivalent metals) than sewage sludge should be considered in the reclamation of the Aitik mine tailings. Peat is a suitable alternative, but repeated additions of mineral fertiliser would then be needed as the nutrient content of the peat is low, limiting the conditions for sustainable growth and long-term survival of the plants. Furthermore, the use of peat would be much less cost-effective than the use of sewage sludge. Alternatively, a combination of sewage sludge and peat could be used.

In order to obtain a sustainable vegetation cover, the best alternative would be a sulphide content in the tailings that is sufficiently low at the time of plant establishment, to avoid a net acidification in the tailings. In that case there would be no need for a strong metal immobilisation caused by sewage sludge addition. In pilot trials, the mining company is investigating the possibilities of reducing the pyrite content in the tailings during the last years of operation, by introducing a scavenger flotation step in the process. That will generate a small amount of a product with a very high pyrite content, which will be managed and deposited separately, and a high amount of tailings with a low content of pyrite, which would create a top layer suitable for plant establishment on the deposit. That layer would be expected to have properties similar to the unoxidised tailings used in Paper IV, *i.e.* a low sulphide content and pH values near 7.0. In such a scenario, the use of sewage sludge instead of mineral fertiliser would result (at least initially) in somewhat increased metal concentrations in the tailings soil solution, and possibly also (for red fescue) an increased uptake and translocation of metals. However, as long as pH remains non-acidic, the metal levels in tailings solution and plants would remain below toxic levels.

This thesis highlights areas that need further investigation. The studies described focused mainly on the first months after exposure of the tailings to air and mixing with the sewage sludge. Further research on the behaviour of metals in tailings that have been stabilised for several years after sludge application is needed to determine the long-term effects of sewage sludge application, *i.e.* as the organic matter decomposes further and the biological activity in the tailings increases. Existing studies on Aitik mine tailings show that although the organic matter decomposes rapidly during the first growing season, around half of it may remain in the tailings after five growing seasons. Increased knowledge is needed on the availability of metals bound in this remaining organic matter. The long-term effects of the sewage sludge on metals are uncertain. One alternative is that the organic matter in the sewage sludge is the major binding agent in the sludge, and that further mineralisation of the organic matter could release metals into more soluble forms. Another alternative is that the microbiological activity will cease with time due to the depletion of degradable humic substances and that metals bound in both inorganic and organic compounds will be maintained at a low degree of bioavailability.

Nutrient dynamics, decomposition processes and the role of micro-organisms in the sludge/tailings mixture were not examined in this work. Studies on the risk of nitrate and phosphorus leaching from sludge-treated tailings should be included in any further assessment of the environmental risks associated with sludge application.

The results presented in this thesis indicate the importance of organic acids on metal uptake by red fescue grown on the tailings. This should be explored in more detail, preferably under more controlled conditions in the absence of oxidative processes. Plant physiological studies on metal complexes occurring in the xylem sap of plants grown in the absence and presence of sewage sludge would contribute to knowledge within this area.

Other sampling methods that provide important complementary information to the lysimeter technique used in this work should be tested, as they could provide a deeper insight into differences in metal chemistry and organic acids between bulk solution and rhizosphere solution.

8 På ren svenska (Swedish Summary)

De flesta gruvorna i Sverige är malmgruvor där man bryter sulfidmalm, som innehåller flera olika metaller, t.ex. koppar, zink, guld och silver. För att anrika metallen krossas malmen till partiklar i sandstorlek och genom en process som kallas flotation kan den önskade metallen koncentreras och transporteras vidare till smältverken. Metallhalterna i malmen är mycket låga, vilket gör att stora mängder malm måste brytas för varje gram koncentrerad metall. Följaktligen produceras stora mängder restprodukter vid metall-utvinningen. Den krossade malmen som blir kvar och fortfarande kan innehålla små mängder sulfider kallas för anrikningssand och pumpas ut på öppna magasin. När anrikningssanden får ligga oskyddat utan växttäcke kan den transporteras av vind och vatten och förorena omgivningarna. Sulfiderna i sanden kan börja vittra, vilket kan leda till att surt lakvatten bildas, med höga halter av metaller. Att efterbehandla gruvavfall med bästa möjliga teknik är därför en viktig framtidsfråga för såväl gruvindustrin som miljön.

Genom att etablera vegetation på magasinet kan sanden bindas och ett fungerande ekosystem återskapas. För att kunna få växter att trivas i den näringsfattiga sanden måste dock näring tillsättas och försurning undvikas. I detta syfte kan avloppsslam användas. Avloppsslam är den restprodukt med hög halt organiska ämnen, som separerats från det kommunala avlopps-vattnet genom sedimentation. Färskt slam innehåller höga halter kol, kväve och fosfor och andra växtnäringsämnen, och genom att använda slammet på gruvavfallsupplag kan dessa ämnen komma till nytta för växterna.

Användning av avloppsslam är dock inte problemfri, eftersom slammet, liksom gruvsanden, innehåller metaller som i för höga koncentrationer är giftiga för växter och djur. Effekterna av att använda slam på anrikningssand måste därför undersökas noga. Den fasta fasen av det organiska materialet i slammet kan fastlägga metallerna till mindre växttillgängliga former, men det finns också en risk för att lösliga organiska föreningar i slammet kan öka metallernas löslighet i sanden och därför leda till ett ökat växtupptag av metaller. På sandmagasin med etablerad vegetation förekommer betande djur, som kan påverkas negativt av växternas metallhalt.

I min avhandling har jag försökt studera anrikningssanden utifrån växternas perspektiv, med avseende på fysikaliska och kemiska förhållanden och hur dessa påverkas av sulfidvittringen och tillsatser av avloppsslam. Målet med studierna har varit att ta reda på hur de kemiska och fysikaliska villkoren för växterna i sanden förändras direkt efter att sanden utsätts för väder och vind, och hur tillsats av rötslam påverkar dessa förändringar. Anrikningssanden har studerats med avseende på textur (storleken på partiklarna), porositet och mängden växttillgängligt vatten, samt metallers förekomstformer och löslighet. Växter som odlats i sanden har studerats med avseende på tillväxt och metallupptag.

Jag fann att i ovittrad sand var både de fysikaliska och kemiska förhållandena relativt goda för växterna, så länge man tillsatte näring till sanden. Utan tillsats av något organiskt material finns dock en risk för att sanden lätt torkar ut och att mineralgödselkväve som sätts till sanden lakas ur på grund av dominansen av sandpartiklar och relativt grova porer. Metallösligheten var låg i den ovittrade sanden. Förhållandena förändrades dock fort efter att sanden utsattes för väder och vind, redan under den första växtsäsongen. Sura förhållanden och hög metallöslighet ledde till hämmad tillväxt och höga halter av metaller i växterna. Järnhydroxider som bildats under försurningsprocessen kittade ihop sandpartiklarna, vilket ökade det mekaniska motståndet för rötterna.

Tillsats av avloppsslam förändrade porstrukturen i sanden och resulterade i en liten ökning av växttillgängligt vatten i slambehandlad sand jämfört med sand utan slam. I vittrad sand tycktes både avloppsslam och mineralgödsel ha orsakat en ökad aggregering och cementering av sanden. Detta kan ha berott på fosfater i båda tillsatserna, som bundits till järnhydroxiderna. Avloppsslammet hämmade inte själva sulfidvittringen, men hade gynnsamma effekter på växternas biomassa, oavsett vittringsgrad. Slameffekterna på metallerna varierade med graden av sulfidvittring. Överlag var den fastläggande effekten av slammet på metaller begränsad och i vissa fall resulterade tillsatsen av avloppsslam i ett ökat metallupptag av växterna. Mängderna metaller som frigjordes under sulfidvittringen var större än slammets buffringskapacitet med beaktande av de mängder slam som är möjligt att tillsätta. En förutsättning för att ett uthålligt ekosystem skall utvecklas på ett slambehandlat sandmagasin är därför att sulfidmängderna i anrikningssanden reduceras till en nivå som inte leder till sura förhållanden.

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Special Appendix (see section 9 for sources)

Supplementary Information about Sulphide Oxidation and Buffering Processes

The sulphide oxidation process can be described by a sequence of reactions (Singer & Stumm, 1970; Kleinmann *et al.*, 1981; Stumm & Morgan, 1996):

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \quad (1)$$
$$Fe^{2+} + 5/2\ H_2O + 1/4\ O_2 \rightarrow Fe(OH)_3\ (s) + 2\ H^+ \quad (2)$$
$$Fe^{2+} + 1/2\ O_2 + H^+ \rightarrow Fe^{3+} + 1/2\ H_2O \quad (3)$$
$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \quad (4)$$

The formation of sulphuric acid and ferric hydroxide (reactions 1 and 2) is spontaneous and leads to a decrease in pH. The formation of acid is a very important factor in the continued weathering of the sulphide minerals. As pH falls, the abiotic oxidation of Fe^{2+} slows down. The bacteria *Thiobacillus ferroxidans*, whose optimum pH for growth is in the range 2-3.5, will then play a significant role in the oxidisation of Fe^{2+} (reaction 3). The oxidation of Fe^{2+} to Fe^{3+} is accelerated by *Thiobacillus ferroxidans* by a factor > 10^6. This allows reaction 2 to continue, producing protons and ferric hydroxide. In the last stage (reaction 4) Fe^{3+} is the major oxidant of the pyrite (Singer & Stumm, 1970; Kleinmann *et al.,* 1981).

The weathering of the sulphide minerals chalcopyrite ($CuFeS_2$) and sphalerite (ZnS) is similar and can be described by the following reactions (Strömberg & Eriksson, 1996):

$$CuFeS_2 + 4\ O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2\ SO_4 \qquad (5)$$
$$ZnS + 2\ O_2 \rightarrow Zn^{2+} + SO_4^{2-} \qquad (6)$$

The dissolution of carbonates, aluminium hydroxide and alumino-silicate (*e.g.* chlorite) can reduce the acidity as shown by the following reactions (Bellaloui *et al.*, 1998):

$$CaCO_3 + 2\ H^+ \rightarrow H_2CO_3 + Ca^{2+} \qquad (7)$$
$$Al(OH)_3 + 3\ H^+ \rightarrow Al^{3+} + 3\ H_2O \qquad (8)$$
$$Mg_5Al_2Si_3O_{10}(OH)_8 + 16\ H^+ \rightarrow 5\ Mg^{2+} + 2\ Al^{3+} + 3\ H_4SiO_4 + 6\ H_2O \qquad (9)$$

In the initial stages of sulphide oxidation the dissolution of calcite, the most soluble of the common carbonate minerals, is favoured (reaction 7). As acid generation continues, and the carbonate minerals are consumed, pH declines until the next pH buffer, $Al(OH)_3$, takes over (reaction 8). Dissolution of $Al(OH)_3$ buffers the pH to values between 4.0 and 4.3. When $Al(OH)_3$ is consumed, pH again declines, favouring the dissolution of $Fe(OH)_3$, resulting in pH values below 3.5. The buffering by alumino-silicates (reaction 9) takes place under all pH conditions, but not until very low pH conditions, when all carbonates and hydroxides are consumed, does the dissolution of the silicate minerals become an important acid-neutralisation mechanism (Blowes & Ptacek, 1994).

Acknowledgements

This work was financed by Boliden Mineral AB and Swedish Geological Survey (SGU), which is gratefully acknowledged. Besides this financial support I have had many people around me who have supported me and encouraged me all the way through during my years as a PhD student.

My deepest thanks go to:

- My main supervisor *Stig Ledin*, who initiated this project and introduced me to the world of Aitik. I have very much enjoyed working with you and I have appreciated your kindness, guidance and encouragement, as well as all our laughs, during all those years. Thank you for always believing in me much more than I did myself. I still hope that the angel didn't fool us, although it fooled Woody Allen!

- My assistant supervisors during the second half of the project; *Dan Berggren Kleja* and *Maria Greger*, for opening new pathways when I thought I was stuck in a blind alley, and for giving me very valuable scientific support. Thank you both for spreading knowledge, enthusiasm and inspiration, and for looking on my work with sharp and bright eyes. *Dan*, thanks for your engagement and brilliance that gave me the strength during those last months, and made it possible for me to complete the last papers. *Maria*, thank you very much for introducing me to 'the metal group', and for giving me valuable knowledge in plant physiological issues.

- My assistant supervisors during the first half of the project; *Jon-Petter Gustafsson, Gustav Sohlenius* and *Johan Ljungberg*. Thanks for very valuable scientific support, advice and comments on my manuscripts.

- *Iiris Takala, Gunnel Nilsson* and *Åsa Sjöblom* at Boliden Mineral AB in Aitik, for following this project with great interest and engagement, and for always being very friendly and helpful.

- The members of the 'Hydrotechnic group' and other former and present corridor neighbours, for taking good care of me, giving me smiles, kindness and help whenever I needed it: *Abraham, Alfredo, Ararso, Aron, Bibbi, Camilo, Elisabeth, Fantaw, Gerardo, Harry, Hasse, Ingmar, Ingrid, Janne, Johan, John, Juan, Kerstin, Liselott, Mats, Osvaldo, Peter, Ragnar, Sixten, Stig, Thomas, Tomas, Urban, Åsa and Örjan.*

- All former and present PhD-students who have shared the dilemmas of being a PhD-student with me. Thank you all for being so nice and friendly, and for introducing joyful moments into my working life.
  In particular I want to mention:
  - *Kristin Boye, Sara Elfstrand* and *Thord Karlsson*, for good friendship, very nice lunches and a lot of support.
  - *Joris van Schaik,* for helping me with many things (*e.g.* the copper ion electrode, the Minteq program and the lovely Acta-Thesis-template) and for spreading a positive and relaxed attitude to the life of being a PhD student.
  - *Pär Wennman,* for help and company in field, and for being a very good PhD partner in the Boliden project.

- All former and present colleagues at the Department of Soil and Environment. I think I have had coffee breaks and/or corridor discussions with almost all of you!
  In particular I want to mention:
  - *Anke Herrmann* and *Mats Linde*, for great support and very valuable comments on the thesis.
  - *Christina Öhman, Gunilla Hallberg, Gunilla Lundberg* and *Lise Gustafsson* for excellent laboratory work.
  - *Ingmar Messing*, for very good talks, and for always listening and understanding.
  - *Ingvar Nilsson, Johan Arvidsson* and *Olle Andrén* for improving the text.
  - *Kerstin Berglund*, for being an excellent Director of PhD studies and corridor neighbour, always willing to answer my many questions.
  - *Ragnar Persson*, for taking very good care of my computer.
  - *Tomas Rydberg*, for cheering me up with the right smiles and calming me down with the right words.

- ‘The metal group’ at the Department of Botany, Stockholm University: *Agneta Göthberg, Beata Dabrowska, Clara Neuschütz, Eva Stoltz, Johanna Nyquist, Maria Greger, Sylvia Lindberg, Tariq Javed, Tommy Landberg* and *Åsa Fritioff*, for very interesting and nice meetings.
  Clara, thanks for good friendship and for being such a supporting and happy person!

- *Mary McAfee*, for excellent work with correcting my English.

- *Mohammad Bigee* and *Agrilab* for kind treatment and excellent laboratory work.

- *Hans Arrendal*, for great support and for giving me the right spirit (the ‘jävlaranamma’) that I needed to finish this thesis.

- A mis amigos en España: *Isabel, Rocío y su familia*, por la hospitalidad y por haberme enseñado su cultura hermosa y fabulosa durante mis estancias en Andalucía.

- My friend *Patrik*, for your great generosity, no matter what, and for being my private ‘therapist’.

- *Ana, Ann* and my cousin *Sara* for being very understanding, listening and caring friends during my toughest days. *Ana*, thanks for your patient daily e-mailing that has meant so much to me.

- My ex-husband *Gustaf,* for support and encouragement during an important part of my life, and for being such a good father to our children.

- My family: *Mamma Birgit, Pappa Robert, Martin & Gabrielle, Henrik & Nettan, Rikard & Karin.* You have all inspired me and supported me, everyone in his or her own way. Thank you *Mamma*, for being the one who introduced me to environmental issues and for always standing by my side no matter what. *Mamma* and *Pappa*, you have always opened many doors for me, without forcing me over any doorstep.

- My wonderful children *Ludvig* and *Klara.* You are the true happiness and love in my life!