Swedish University of Agricultural Sciences
Department of Soil and Environment

The legacy of the mill
– a metal polluted forest soil in Gusum

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Master's Thesis in Soil Science
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SLU, Swedish University of Agricultural Sciences
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Cover: Affected soils and trees, Stångberget, Gusum. May 2010. Photo by author.

Abstract

Soils in a metal contaminated site on Stångberget in Gusum in southeast Sweden were investigated and compared to relatively unaffected soils a few kilometres away. Pollution came from historical release of untreated flue gases from a brass mill. The objective was to find information on how high the metal concentrations are, if metals from the polluted soil affect the surroundings and if the metal contamination affects the microbial community. The soil was investigated using several different methods, such as field XRF measurements, chemical analysis of metal, carbon and nitrogen content, pH, acid neutralizing capacity, texture, soil depth, field leach tests, sequential extraction and microbial functional profiles. The study showed that copper and zinc concentrations were above Swedish Environmental Protection Agency guidelines for less sensitive land use on the entire investigated area. Copper showed the highest concentrations in relation to guideline values, 50 times the guideline in the worst affected sample point, followed by zinc, lead and cadmium, in that order. A pH raising effect caused by the release of metal oxides, that had previously been shown could not be seen and pH on Stångberget was now similar to that of a natural Swedish forest soil. Results could not show that the pH drop had caused increased leachability, instead the leachability was lower than in previous studies. Leaching from Stångberget did not seem to affect metal concentrations in the soil nor be a major source of metals to surrounding soils and waters. Microorganisms from the visibly affected part of Stångberget had an increased specific respiration compared to the reference but the difference between the forested part of Stångberget and the reference area was not as clear even though metal concentrations were severely elevated also in the forested part. The effect on microorganisms could to a large extent be explained by the metal contamination. The size of the bare part of Stångberget had increased over the last 50 years and there was no sign of a decrease.

Sammanfattning

Jord från en metallförorenad skogsmark på Stångberget i Gusum i sydöstra Östergötland undersöktes och jämfördes med en relativt opåverkad jord några kilometer bort. Föroreningarna härstammar från historiska utsläpp av orenade rökgaser från ett mässingsbruk. Målet med studien var att få reda på metallkoncentrationer, om metallföroreningen påverkar omgivningarna och huruvida metallföroreningen påverkar mikroorganismerna i jorden. Jorden undersöktes med flera olika metoder, såsom XRF-mätningar i fält, kemiska analyser av metall-, kol- och kvävehalter, pH, syraneutraliserande förmåga, textur, mäktighet, fältskakförsök, sekventiell lakning och mikroorganismernas funktionella profiler. Studien visade att koppar- och zinkhalterna låg över Naturvårdsverket riktvärden för Mindre känslig markanvändning över hela det undersökta området. Kopparhalterna var högst i förhållande till riktvärdena, 50 gånger riktvärdet i den kraftigast förorenade provpunkten, följd av zink, bly och kadmium, i nämnd ordning. En pH-förhöjande effekt orsakad av metalloxidutsläpp som tidigare uppmätts kunde inte påvisas och pH på Stångberget var nu nära det naturliga i svensk skogsmark. Resultaten kunde inte visa att pH-sänkningen orsakat ökad lakbarhet, lakbarheten var istället lägre än i tidigare studier. Utlakningen från Stångberget tycktes inte påverka metallkoncentrationerna i jorden eller vara en betydande metallkälla för omgivande mark och vatten. Mikroorganismerna från den synligt påverkade delen av Stångberget hade förhöjd specifik respiration jämfört med referensen men skillnaden mellan den beskogade delen av Stångberget och referensen var inte lika tydlig trots att metallkoncentrationerna var kraftigt förhöjda även på den beskogade delen av berget. Påverkan på mikroorganismerna kunde till stor del förklaras av metallföroreningen. Storleken på den kala delen av Stångberget hade ökat sedan 1950-talet och det fanns inga tecken på en vändning mot minskad utbredning.

Stångberget, Gusum

Dec 2009 – May 2010

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Appendices

Field protocols, results in editable format and original protocols from ALS laboratory are archived at Golder Associates AB (project no: 0970100)

1 Introduction

The small community of Gusum arose around the brass mill. For more than 300 years the mill provided its surroundings with work, food and culture. But it also provided more devastating elements, such as the flue gas emissions, which were sent untreated over the surroundings for as long as the mill in central Gusum existed. The result of this heavy contamination is clearly visible when entering the village today - large previously forested areas have lost their vegetation, the bedrock lies bare and the thin soil layers host very few plants and animals. In this thesis one of those ecologically disturbed areas was thoroughly investigated.

1.1 Overall aim

Previous investigations around Gusum have studied soil processes and soil organisms with focus on macro organisms (Tyler, 1984a and others). Little attention has previously been paid to metal chemistry and the scale of investigations has been much larger than the visibly disturbed areas. The chemistry of the metals is the basis to understand uptake, leaching, time-dependent variability etc. Therefore this work focused on a chemical characterization of the soil with special regard to the metals copper, zinc, lead and cadmium since they have shown largest deviations from background and guideline values in previous studies (SGI, 2007, 2008a)[1]. A respiration analysis was also performed to get some information on how the soil chemistry affects microorganisms. Macroorganisms were not studied. Because of economical and time restraints only a limited number of samples could be taken. The investigation should therefore be regarded as a pilot study.

1.2 Problem statement

The study was designed to answer the following question:

- How high are the metal levels (especially of copper, zinc, lead and cadmium) in the soils of Stångberget today, and how much do they vary along a gradient from seemingly normal forest to more or less vegetation free ground?
- How is the polluted soil affecting its surroundings, are the metals being leached?
- Are the metal concentrations affecting the microbial community?

To gain answers to the questions several different components were included in the work. A geochemical and biological characterization of the ecologically disturbed area aimed at identifying contaminants, contamination levels, leachability, specific respiration and microbial functional diversity was performed. For comparison one local little polluted reference area and data from

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[1] Analyses were also performed on arsenic, cobalt, chromium, mercury, nickel and vanadium, but the results are not treated in the report. Data can be found in Appendix C.

previous investigations was used. A literature study including previous investigations in i) the Gusum area and ii) other similarly contaminated areas and iii) basic metal geochemistry was also included in the work.

The study has its focus on one ecologically disturbed forest site close to the former brass mill in central Gusum. The area was chosen since it was assumed to be representative for the other ecologically disturbed sites around the mill.

1.3 Outline

Chapter 2 gives some background information, a summary of earlier work and information about comparative values. Chapter 3 gives of a theoretical basis for the geochemistry, pollutants and soil biology. In chapter 4 the methods used in the study are described and chapter 5 describes the results from the different analysis and investigations. In chapter 6, the results are discussed and finally, chapter 7 concludes the work. The appendices include maps (A) and photos (B) of the sample locations, a summary of the lab results (C) and an extensive summary in Swedish (D).

1.4 Contributions

Most laboratory work was outsourced to professional laboratories (ALS Scandinavia AB and laboratories at Dep. of Soil and Environment, SLU, Ultuna) although some parts of it (pH measurements, MicroResp™ analysis and preparations for the Field Leach Test) were performed by the author. Field work with sampling and field analysis was performed by the author, except for the surface runoff investigations which were planned by Golder Associates AB together with the municipality of Valdemarsvik and performed by Sondera AB. GIS work and drawing of some maps were performed by Malin Sträng at the IM department at Golder Associates AB.

2 Background

2.1 Mill history

Around the 17th century and into the 19th century early industries of Sweden were built around natural resources, such as water, forests and metal ores. The resources were often found far away from towns, which resulted in new self-supporting communities being formed. These small industries, or mills, that totally dominated an area were common up until the 20th century, when many of them were outcompeted by larger industries. The mill in Gusum was established in the 1650s. The area was well suited for a mill, with its vast forests for charcoal, small waterfalls for hydropower and good transports on the Gusum River.

The Swedish industrial revolution started in the mid 1800s and the Gusum brass mill was among the many industries that did well in these years. In about 100 years the mill grew to be the biggest brass mill in Scandinavia, being twice as big as all other brass producers in Scandinavia combined. Figure 1 shows an old picture of the mill property. At the end of the 1960s the site in Gusum village had become too small for the expanding industry and it moved, step by step, to a new location at Gräsdalen, one kilometre northwest of the old mill.

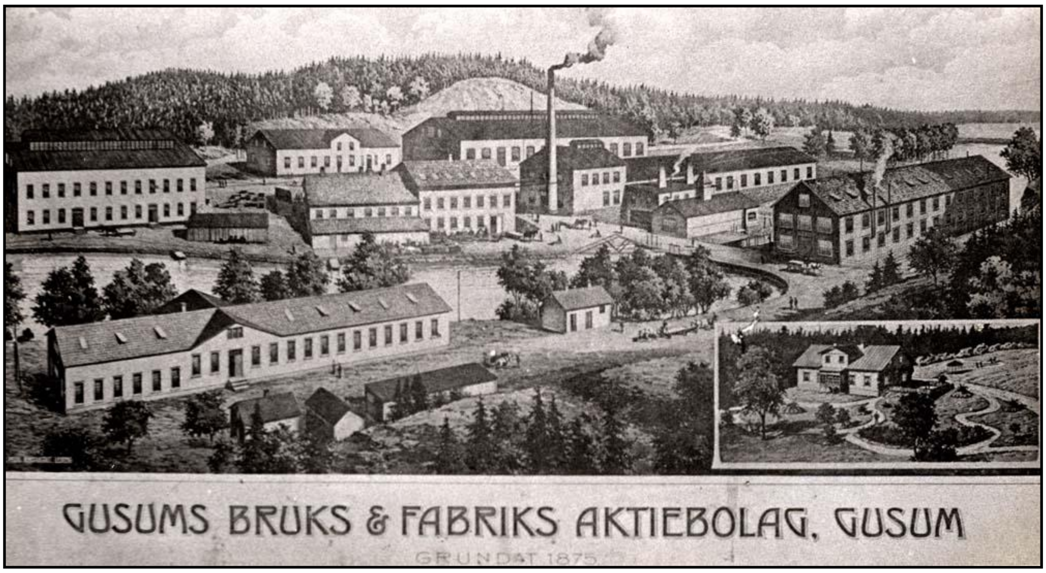

Figure 1. Old picture of the mill property (photo lent by County Adm. Board of Östergötland).

The profitability of the company started to decline during the 1970s. Some dubious decisions by the leadership involving speculation on the English commodity market with factory money and double bookkeeping were the beginning of the end for the more than 300 years old industry. Company assets and parts of the production were sold and in 1988 the Gusum brass mill was declared bankrupt. A complicated investigation started where one of the largest company frauds in Sweden since the Second World War was discovered.

After the bankruptcy the property had several different owners. A combination of neglected maintenance and vandalism made the buildings deteriorate and when the last owner was declared bankrupt in 2007 the county administration board started investigations aiming for a remediation and demolition of the buildings.

Two parts of the mill survived. The new site at Gräsdalen is still run as a secondary brass smelter by Outokumpo Nordic Brass and the German company Voith has run wire cloth production in buildings close to the old mill, but nowadays plastic is used instead of metals. The wire cloth production will be shut down in 2010 (Lindqvist, 2009).

For a comprehensive report on the cultural history of the Gusum brass mill in Swedish see *Kulturhistorisk byggnadsdokumentation Gusums Bruk* by Albin Lindqvist (2009).

2.2 Metal emissions from smelters

The Gusum area is one of few places where metal concentrations in the soil are high but pollution of other substances, such as sulphur, is low (Pettersson, 1994). The reason for this is that the smelting in the area has been secondary (Lindqvist, 2009), using scrap metals of some other metallic source, as raw material. Primary smelters use metal ores as raw material. Metals in ores are often in sulphide form and roasting of these releases large amounts of sulphur to air. The acidifying effect of these emissions is a problem in itself, for both terrestrial and aquatic ecosystems but it also increases the problem with metal contaminations since acidification leads to less metal adsorption to soil and thus to higher mobility and bioavailability (Pettersson, 1994). From secondary smelters, as the one in Gusum, the metals are the major pollutants. Metals from smelters can be released to the surroundings in many different ways; contaminated filling materials can leach to the surroundings, insufficient water treatment can lead to direct release to surface waters and sediments and contaminated flue gases can lead to ground contamination in large areas around the smelters. All these pathways have occurred in Gusum (Eriksson et al., 2009) although only the contaminated flue gases have affected the area of interest in this study.

2.3 Earlier investigations in the area

2.3.1 The Gusum project

The area around the Gusum brass mill was studied already in the early 1970s by researchers interested in the impact of heavy metal pollution on the forest eco system. Gusum was a well suited area for these studies since it was sparsely populated, surrounded by coniferous forests and the only source of pollutants in the area was the brass mill (Tyler, 1984a). For the major part of the more than 300 years that the mill was operating it was a secondary smelter, which means that the emissions of acidic compounds were insignificant and effects of the metals *per se* could be studied (Tyler, 1984b). The project, which took place from the early 1970s until the mid 1980s was called the *Gusum project* and was one of the most comprehensive works of its kind (Tyler, 1984a).

Many reports and articles were written about the research in Gusum. The Swedish EPA report *Metallförorening i skogsmark - biologiska effekter* (Tyler, 1984a) summarizes the results from the soil biological studies. It also gives a listing of earlier reports and publications from the Gusum project.

In many of the articles and reports the ecologically disturbed areas are mentioned (e.g. Rühling, 1983; Tyler, 1974b; Tyler, 1984a; Tyler, 1984b). Undecomposed plant litter and exposed bedrock was seen, and in the areas where the zinc and copper levels were more than 100 times the background level coniferous trees had died and even the most resistant grasses had disappeared (Tyler, 1984a).

Many different organisms were severely affected by the metal pollutions. The studies in the Gusum project showed that the soil enzymatic activity (urease and acid phosphatase) was reduced (Tyler, 1974), phosphatase activity and P mineralization rates (Tyler, 1976) as well as N mineralization rates (Tyler, 1975) were reduced, starch decomposition was inhibited (Ebregt et al., 1977) and soil respiration was reduced (Tyler, 1974; Ebregt et al., 1977). The macro and micro fungal species compositions were strongly affected (Rühling et al., 1984), ground living invertebrates were reduced both in species number and number of specimens per species (Bengtsson et al., 1984) and the moss and lichen vegetations were markedly impoverished (Folkeson, 1984).

In Bergkvist (1986 & 1987) the zinc and copper transports through the Gusum soil was tested in lysimeters. It was found that the flow of copper from the upper five centimetres was almost 500 mg/m^2 and year in profiles collected close to the mills. This was 900 times higher than that of a reference profile. The flow of zinc from the same location was 200 times that of the reference profile, which means almost 10000 mg/m^2 and year from the upper five centimetres.

2.3.2 Governmentally subsidized investigations in Gusum

In 2002 the County Administration Board initiated investigations in the Gusum area, aiming for a remediation of the areas affected by the historical activities (Valdemarsviks kommun, 2009). Since the company that caused the pollution no longer exists, the investigations in Gusum are financed by the Swedish Environmental Protection Agency (SEPA) through the County Administration Board of Östergötland (Eriksson, H., 2009a). The Municipality of Valdemarsvik is remedial principal. Many different parts of the surroundings had been affected by the brass mill; the Gusum River that runs through the area was directly polluted by contaminants such as heavy metals and PCB (Eriksson & Elander, 2007b), filling material contaminated with various metals was spread out on more or less the entire mill property (Eriksson et al., 2009) and untreated flue gases were released over the surroundings to a distance of about 10 km from the mill (Tyler, 1984a) causing severe damage to large areas. The investigations have been divided into three sub areas; *Gusum Mill, Gusum Community* and *Gusum River*.

The main study of the *Gusum Mill* was performed by several different consultancy companies and compiled in a risk assessment and measure proposal by

Hifab AB (2009). High levels of metals and other contaminants were found in filling materials, paint, and plaster and under buildings. These contaminants had also spread to the river through groundwater, erosion, pipes and storm water. In a risk evaluation (Valdemarsviks kommun, 2009c) it was decided on a measure proposal including demolition of all buildings, tanks and pipes and "dig and dump" remediation of the contaminated filling material on large parts of the area. The remediation was initiated with demolition of the buildings in 2010.

The main study of the *Gusum Community* area included an investigation of ground water, soils and foodstuff (SGI, 2008a) and showed that heavy metal levels in the soil were mostly low although high levels of copper, zinc and cadmium where found in some places. Contamination levels in the ground water were low suggesting that ground water was not a major transport route for the contaminants. A risk assessment from environmental medicine perspective (Landstinget i Östergötland, 2007) showed that increased levels of metals (lead, copper, zinc and cadmium) and dioxins where found in some vegetables and mushrooms but at normal consumption this would cause no health risk for healthy adults. Fish and crayfish were still affected by a major PCB spillage in the river in the 1970s, but the levels would cause no health risk if the general guidelines from the Swedish National Food Administration were followed. High levels of metals in soils close to the mill could pose a risk for children with pica behaviour and is also a reason to rinse all vegetables and mushrooms before consumption. The metals' bioavailability for humans was found to be 2 - 27 % of the total concentrations.

Analyses of sediments and water in the *Gusum River* and downstream lakes were compiled in a report by Envipro Miljöteknik (2007). Low levels of metals and organic pollutants were found in the surface waters, but in the sediments the levels of metals and PCB were elevated. Higher levels deeper down in the sediments suggested that the contamination situation has improved.

In the future (up to 2011) the Gusum River and Gusum Community will be further investigated by the municipality of Valdemarsvik. Previous reports can be found on the municipality website (Valdemarsviks kommun, 2009b).

This master's thesis is part of the main study of Gusum Community.

2.4 Guideline values and other comparative values

To understand measured levels of various substances it is useful to compare them to some kind of guideline or background value. In this study results will be compared to different values.

SEPA guideline values are used as a comparison for metal concentrations in soil (Table 1). These include guidelines for two different land uses, sensitive land use (KM, *Känslig Markanvändning*) and less sensitive land use (MKM, M*indre Känslig Markanvändning*). Human exposure to the pollutants is the most important factor when determining guideline values, but environmental factors are also included. The difference between the two guideline values is mainly how much time people spend in the area and how environmental factors are protected. They do not differ for different soil types but focus on the land use. In addition to general guidelines there are also guidelines for different targets, e.g. soil environment. The KM guideline for soil environment aims at protecting 75 % of soil dwelling species and the MKM guideline value aims at protecting 50 % of the species (this does not mean that 25 and 50 % respectively automatically will be harmed. The guideline values are recommendations and not legally binding (NV, 2008b). More information on the guideline values can be found in NV, 2009c.

The Canadian Council of Ministers of the Environment (CCME) has developed several guidelines, including guidelines for the protection of aquatic life (Table 1). Metal levels in leachate from United States Geological Survey (USGS) Field Leach Test, sequential extraction and surface runoff are compared to CCME guidelines (CCME, 2007).

MarkInfo (MarkInfo, 2007a & b) is a database run by Swedish University of Agricultural Science (SLU) covering information mainly on Swedish forest soils and vegetation. From MarkInfo information about average soil pH, nitrogen and carbon concentrations has been gathered.

Background values for metal concentrations in soil have been developed by Swedish Geological Survey (SGU), SLU and SEPA and compiled by SEPA (2009c, Table 1). Those have been used as a comparison to metal concentrations in soil.

Results have, when possible, also been compared to results from previous studies, mainly from the Gusum project and from previous reports from the remediation investigations (see Chapter 2.3).

Table 1. SEPA guideline values, CCME guideline values and background values for copper, zinc, lead and cadmium

	SEPA(4 [mg/kg DM]				CCME(5	SGU(6/SLU(7/SEPA Background
	general		soil processes		[µg/L]	[mg/kg DM]
	KM(1	MKM(2	KM(1	MKM(2		
Cu	80	200	80	200	2-4(3	30
Zn	250	500	250	500	30	70
Pb	50	400	200	400	1-7(3	15
Cd	0.5	15	4	20	0.017	0.2

(1Sensitive land use (2Less sensitive land use (3Depending on water hardness (higher value for harder water) (4 Swedish Environmental Protection Agency (5 Canadian Council of Ministers or the Environment (6 Swedish Geological Survey (7 Swedish University of Agricultural Sciences

3 Theory

3.1 Geochemistry

Many metals can in excessive concentrations cause harm to most organisms and are considered pollutants when spread in the environment from human activities (Giller et al., 1998). They are however also naturally occurring in the nature and in lower concentrations many of them are essential nutrients. Since metals are pure elements they are nonbiodegradable (Walker et al., 2006) but can nevertheless adopt various forms that have various toxicity.

Metals can occur in nature in different species, in water phase or as solids. In water phase the metals can either be dissolved or bound to particles. Dissolved ions are often the dominating species in soil- and groundwaters. They can be either free hydrated ions or dissolved complexes. Metals in soil can precipitate/dissolve or adsorb/desorb and thereby take on (or leave) solid phase.

3.1.1 Complexation and ion exchange

A surface complex is formed between an ion in solution and a reactive group on the surface. A dissolved complex is formed between an ion and a dissolved particle or molecule. Cations often form complexes with the oxygen in either hydroxyl groups or carboxylic groups. Complexation is enabled by electrostatic attraction, which is dependent on the pH value. A high pH gives fewer protons on the particle surfaces leading to more negative charge, and thereby more possibilities for cations to bind. The soils redox potential also has a major influence on which process that will take place (Gustafsson et al., 2007).

Inner sphere complexes are chemically bound to a specific site on the particle. There is no hydration sphere between the ions. In *outer sphere complexes* the hydration sphere that the ion had before it was adsorbed is retained and the ion is electrostatically bound (Figure 2) (Eriksson et al., 2005).

Ion exchange is another form of electrostatic binding, where the ion is not bound to a specific site on the particle (Figure 2). Ions in ion exchange still have their hydration sphere (Eriksson et al., 2005). Because of the distance caused by the hydration sphere the ions are easily exchanged by other ions. Soil particles in little weathered soils almost exclusively have a negative net charge, which means that adsorption of cations in exchangeable form is much more common than that of anions (Gustafsson et al., 2007).

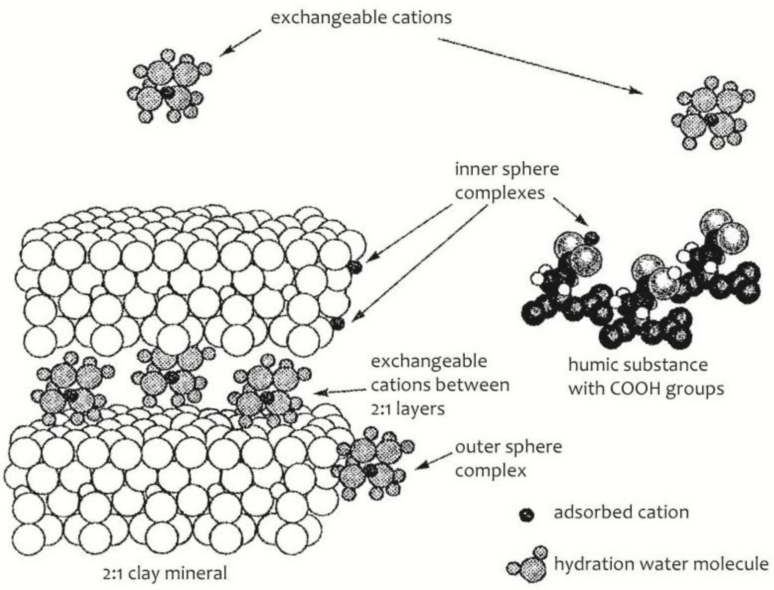

Figure 2. The binding of inner sphere complexes, outer sphere complexes and exchangeable cations to a clay mineral and a humic substance (from Eriksson et al, 2005).

Binding strength varies between different metal ions; some are prone to form the stronger inner sphere complexes and others to form weaker outer sphere complexes. Copper and lead are examples of metals that are prone to form inner sphere complexes, whereas zinc and cadmium more often form outer sphere complexes. The explanation for this lies in the ions affinity towards hydroxyl-, carboxylic and phenolic groups. The strength of the bond is not only determined by the cation but also depends on the anion part of the complex. Complexes with humic substances as the anion part are often the dominating species (Berggren Kleja et al., 2006). Figure 3 shows how the adsorption of copper, lead, cadmium and zinc to a goethite surface varies depending on the pH. When pH drops copper and lead to a large extent remain adsorbed while zinc and cadmium are easily dissolved. This indicate that lead and copper form strong complexes with the oxide surfaces, whereas cadmium and zinc form weaker complexes.

Clay minerals, oxide surfaces and humic substances are soil particles taking part in the adsorption of solutes. They all have a large specific surface area and many reactive sites. Clay minerals and humic substances have a dominance of negative surface charges, leading to adsorption of cations, whereas the positive surface charges of oxides adsorb anions (Gustafsson et al., 2007).

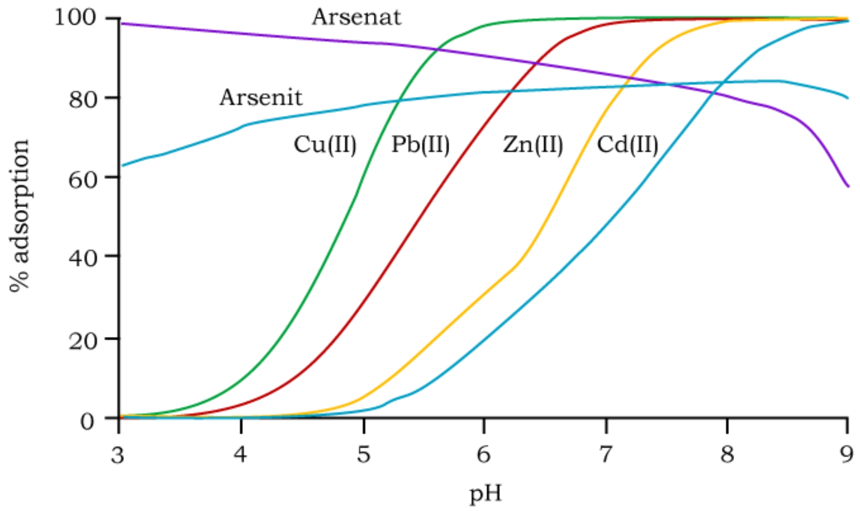

Figure 3. Adsorption of copper, lead, zinc and cadmium to an iron oxyhydroxide (goethite), and its dependence on pH (MiMi, 2003).

Humic substances bind metals at lower pH than oxides, because of the ability to form bi- and tridentate bindings, the many different kinds of active groups in a humic substance and the fact that humic substances always have a negative net surface charge (Berggren Kleja, 2008). Especially some metals, such as copper and mercury can be very tightly bound to humic substances and are not released even at very low pH (pH 2-3). A major source of leaching of those metals is dissolved organic carbon (DOC) which with its attached metals is transported through the soil (Berggren Kleja et al., 2006).

Competing ions, such as calcium and aluminium, are important factors in nature since they adsorb strongly to the same surfaces as the heavy metals. This can lead to a much lower adsorption than what would be the case if the metals where the only adsorbed ions (Berggren Kleja et al., 2006).

It is of major importance if complexes are formed with solid or dissolved particles. Surface complexation with solid particles immobilizes the metals whereas formation of dissolved complexes mobilizes them.

3.1.2 Adsorption

Adsorption is the sorption of a solute to the surface of a solid particle. Adsorption is often the most important mechanism regulating metal mobility in soils. Different species have different ability to sorb to a particle surface (Gustafsson et al., 2007). Equilibrium is maintained through constant adsorption and desorption. Several different mechanisms are involved in the adsorption, *ion exchange* and *surface complexation* being the two most important (Berggren Kleja et al., 2006).

3.1.3 Precipitation

Precipitates can be formed if the ions reach a concentration above the *solubility equilibrium*. Precipitation can regulate the amount of a free metal to a certain extent. However, other processes, such as *complex formation*, also affect it. Presence of complex forming substances, such as humic matter, means that higher concentrations are needed before precipitates are formed. Only free ions affect the solubility equilibrium (Berggren Kleja et al., 2006). *pH* is another important factor determining the degree of precipitation. At high pHs oxides and hydroxides are more easily formed (the hydronium ion concentration being higher). Finally, *reducing environments* can cause very stable sulphur precipitates to form. If oxygen enters the system the precipitates will dissolve leading to a release of metals (Berggren Kleja et al., 2006).

If a metal is precipitated in a polluted soil its concentration in the soil water can remain high long after the contamination has ceased, due to gradual dissolution of the precipitate that keeps its concentration at the equilibrium level until the precipitate is more or less entirely dissolved.

3.1.4 Redox processes

As mentioned earlier redox potential is important for many soil processes, such as precipitation and adsorbtion. The redox state of the soil determines in what phase the metals occur and thereby how easily it is transported through the soil. A change in redox state can result in desorption of previously adsorb ions, leading to increased leachability (Berggren Kleja et al., 2006).

Redox reactions are often very slow. Because of that the reducing and oxidizing form of a substance can co-exist in nature. The reactions are commonly catalyzed by microorganisms (Gustafsson et al., 2007).

3.2 The pollutants

The old Gusum brass mill spread its untreated flue gases over the surroundings for more than 300 years. The gases contained copper and zinc (from the brass production), lead (from button production) and iron (from the years when it was also an iron mill). Surface finishing was performed using cadmium-, chrome-, silver-, nickel- and tin-plating, as well as organic substances. There is no data on how much metal that has been emitted to the soils in and around Gusum, but an estimation by Tyler (1984a) based on the concentrations in the top soil within a radius of 5 km from the mills suggests that more than 400 tonnes zinc, 200 tonnes copper and 10 tonnes lead have been released. The true value is probably higher since a lot of the emissions fell down at a larger distance from the mills and some might have migrated downwards in the soil (Tyler, 1984a).

The smelting and metal production started to move to the new mill in Gräsdalen in the late 1960s. The new mill also contributed to the soil pollution in the area, since flue gas cleaning was not installed until 1981 (Valdemarsviks kommun, 2009).

This section will focus on copper, zinc, lead and cadmium. Copper and lead have many properties that make them behave similarly in soils, as do zinc and cadmium. Therefore they will be discussed in groups.

3.2.1 Copper and lead

Copper is an essential nutrient for plants and animals but at too high levels it is very toxic and can damage the liver, kidneys and immune system. The sensitivity varies a lot between different species (Berggren Kleja et al., 2006).

Copper is strongly adsorbed to several different minerals. Organic compounds form both soluble and insoluble complexes with copper, and therefore its mobility in soils is strongly affected by what kind of organic complexes there is. Copper is also fixed in microorganisms. Copper levels of 150-400 mg/kg can cause poisoning of crops, and levels of 100 mg/kg have been shown to inhibit nitrogen mineralisation and nitrification (Stjernman-Forsberg & Eriksson, 2002). Various microorganisms, *Penicillium* being one of the most well known, can develop resistance to high copper concentrations and accumulate large amounts of the metal (Kabata-Pendias, 2001).

Lead can damage the neurological system, and thus cause learning difficulties and impair the intellectual development, especially for children and foetuses. It can also cause high blood pressure and cardiovascular diseases (Berggren Kleja et al., 2006). Lead has no known biological function (Gustafsson et al., 2007).

Lead is considered as the heavy metal least mobile in soils. Levels of 100 to 500 mg/kg have been reported as toxic, but since soil properties are so important for toxicity it is difficult to give general limit values. Levels of 100 to 500 mg/kg have been shown to inhibit nitrogen mineralisation and nitrification (Stjernman-Forsberg & Eriksson, 2002).

Complexes with DOC are the dominating forms in most waters for both metals. In soils they are strongly bound to organic matter and oxides. At high pH (>7-8) precipitation can occur. At reducing conditions sulphides can be formed. Since the binding to humic substances is so strong the organic matter content in the soil has a major influence on how much the soil can bind. Copper and lead are transported as DOC complexes or bound to small oxide-containing colloids. Because of the strong adsorption both metals tend to accumulate in the top layer and stay in the soil for a very long time. (Berggren Kleja et al., 2006; Gustafsson et al., 2007; Stjernman-Forsberg & Eriksson, 2002).

3.2.2 Zinc and cadmium

Zinc is an essential nutrient for plants and animals. It is part of more than 300 hormones and enzymes in human. The toxic effect on mammals is low, but fresh water organisms can be quite sensitive (Berggren Kleja et al., 2006). Zinc is seldom toxic to plants, but at levels of more than 900 mg/kg and low pH level toxic effects have been seen. Zinc and copper are absorbed in plants by the same mechanisms and therefore zinc has an antagonistic effect on copper (Kabata-Pendias, 2001).

Cadmium is toxic to animals and plants and has no known biological function. It is accumulated in the kidneys and can cause brittle-bone diseases. It is very similar to zinc and therefore has an antagonistic effect by outcompeting zinc on active sites in biologically important molecules (Walker et al., 2006). It is also carcinogenic (Berggren Kleja et al., 2006). Cadmium is more toxic to animals and humans than plants. Cadmium levels of 2.5 mg/kg have been shown toxic to plants, but this is dependent on pH. Inhibition of nitrogen and carbon mineralisation has been reported at zinc levels of 100 mg/kg soil and cadmium levels of 10-100 mg/kg soil (Stjernman-Forsberg & Eriksson, 2002).

Many plants can tolerate relatively high levels of zinc and cadmium, causing an accumulation further up in the food chain. Zinc and cadmium are relatively mobile in soil, but can form complexes with both organic and inorganic compounds (Stjernman-Forsberg & Eriksson, 2002). The mobility depends more on pH, concentration of humic substances and composition of the soil solution than it does for copper and lead. Precipitation can occur at high pH (>7-8). In waters the dominating forms are Cd^{2+} and Zn^{2+} (at low pH) or zinc complexes with DOC (at pH>6). The ions are commonly electrostatically adsorbed to organic material and clay. In soil they bind to organic matter or, at higher pH, to oxides or precipitates as carbonates. At reducing conditions sulphides are formed. The mobility is strongly dependent on pH since solubility increases at lower pH (Berggren Kleja et al., 2006; Gustafsson et al., 2007).

3.3 Soil biology

Soil communities are complex webs of micro- and macroorganisms living in a matrix of minerals and nonliving organic matter (Walker et al., 2006). Soil microorganisms can be highly sensitive to heavy metal pollution. According to Giller et al. (1998) microorganisms may be far more sensitive to heavy metal stress than soil animals and plants. The response to a certain contamination level can however vary a lot due to differences in metal bioavailability and sensitivity of the microorganisms (Giller et al., 2009). As for plants total soil metal concentration is therefore not a good indicator of the effect on organisms (Smolders et al., 2009). Instead the bioavailable fraction is important to find. Unfortunately there is no universally accepted method to assess bioavailable soil metal concentrations (Giller et al., 2009). Many different parameters affect bioavailability, such as pH, clay and organic matter content, iron oxide content and redox potential. Some of these factors are discussed in the geochemistry section of this paper. The pH dependency for solubility and speciation makes pH the most important of the factors but the relative effect of the different factors on bioavailability is not understood today. Microorganisms may furthermore affect the availability of metals by acidifying their closest surroundings or by producing compounds that form complexes with metals (Giller et al., 1998).

Effects on the soil biology in forests can be found already at concentrations three and four times the background value for copper and zinc. Also for lead and cadmium effects have been found at similar deviations from the background. It is therefore possible to assume that changes have occurred in the soil biology in large parts of the Swedish forest soils as a consequence of the general metal pollution (Pettersson, 1994).

An accumulation of undecomposed leaf litter is one of the characteristic features of terrestrial ecosystems heavily contaminated by aerial deposition of metals. The reason for this is, according to Walker et al. (2006), a reduction in invertebrates that feed on plant material and excrete a substrate more easily degraded by microorganisms. The invertebrates' roles as decomposition "catalysts" is a key function in the soil ecosystem since nutrients get locked up in the undecomposed litter without them (Walker et al., 2006).

A strong decrease in the total amount of microbial biomass is also a common sign of a metal polluted soil (Giller et al., 2009). The reason for this is the higher energy costs that microorganisms living in metal contaminated environments have, and lower substrate utilisation efficiency. The ability to utilize different substrates can also be affected. This can be seen as a change in the functional profile of the microbial community. Numbers and types of substrates utilized and the activity levels when using different substrates can give a lot of information on the functional diversity of the community (Zak et al., 1994).

4 Materials and methods

4.1 Area of investigation

Gusum is situated at N 58°16′1′′, E 16°29′8′′ in the municipality of Valdemarsvik, county of Östergötland, in south-eastern Sweden (Lantmäteriet/Metria, n.d.). The old brass mill is located in the centre of the village and the area of investigation in its immediate vicinity, on a small hill, *Stångberget*, which also holds the village water tower. Figure 4 shows an aerial photo of the investigated area and its surroundings and Figure 5 a map of the area.

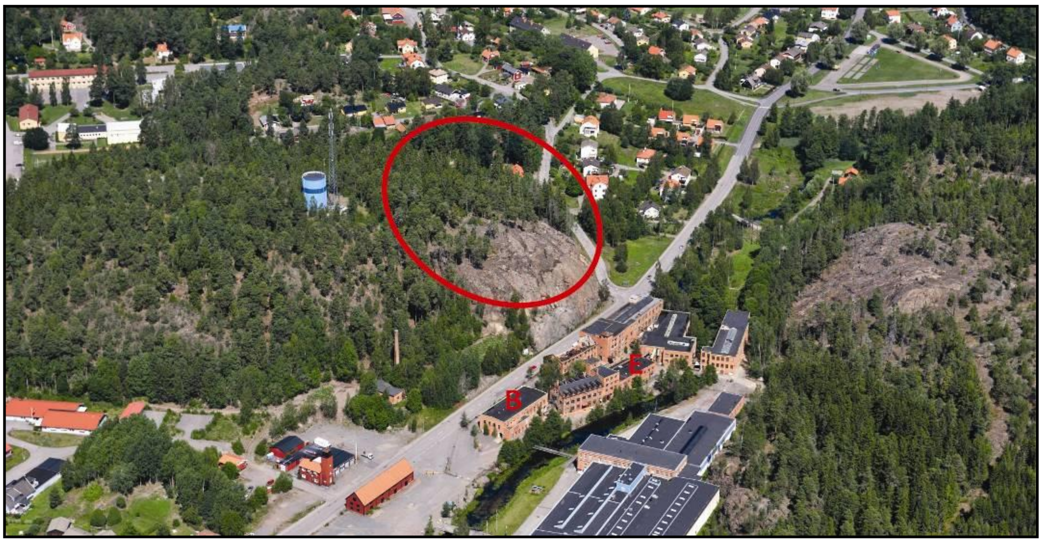

Figure 4. Aerial photo of Gusum, July 2008. The brick buildings in the centre of the photo are the old mill. The smelter was situated in building E 1944-1954 and in building B 1954-1968 (Lindqvist, 2008). Stångberget is the hill to its left and the investigated area marked with red circle on the photo. To the right of the mill another ecologically disturbed area can be seen. (Photo lent by the municipality of Valdemarsvik).

The topography around Gusum is slightly hilly with rock-knobs towering over flat areas. Most of the area is 40-70 m above sea level, with the highest points approaching 100 m above sea level (Tyler, 1984b).

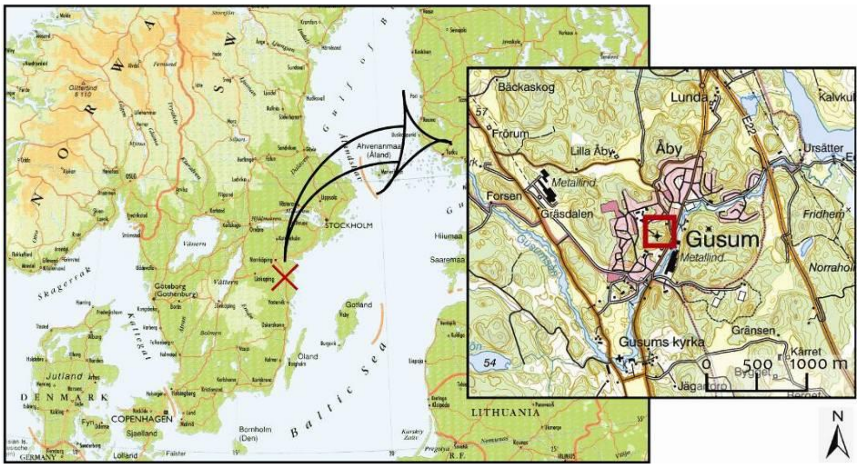

Figure 5. Gusum is situated in Östergötland county, south-eastern Sweden. The area of investigation is in the centre of the village. Figure: H. Almqvist, based on map from Lantmäteriet (© Lantmäteriet Gävle 2010 Medgivande I 2010/0055).

4.2 Reference area

Reference samples were taken from a location 8 km south of the mill (Figure 7).

The area was chosen because of its similarities to Stångberget. It is located in the forest, close to the small village of *Kärnhult*, on top of a steep hill. Soil depths are shallow, as on Stångberget, and the vegetation is similar. Since the prevailing wind direction is west to southwest, an area 8 km south of the mill should only to a very limited extent have been affected by its emissions. No landfills or other anthropogenic disturbances are known in the area. Figure 6 shows two similar hillsides, on the reference area and on Stångberget.

Samples were taken from two parts of the reference area; three samples from a sun exposed part of the hill, close to the hillside, used as reference for the visibly disturbed part of Stångberget which was similarly exposed to the sun, and three samples from a more protected area in the forest, close to a spruce stand, used as a reference for the forested part of the transect on Stångberget (Figure 8).

Figure 6. A steep hill on the reference area (left) compared to the steep hill on Stångberget (right). The hill in the reference area is covered with vegetation whereas the hill on Stångberget lies bare except for a few trees and some undecomposed litter. Photos: H. Almqvist 100414.

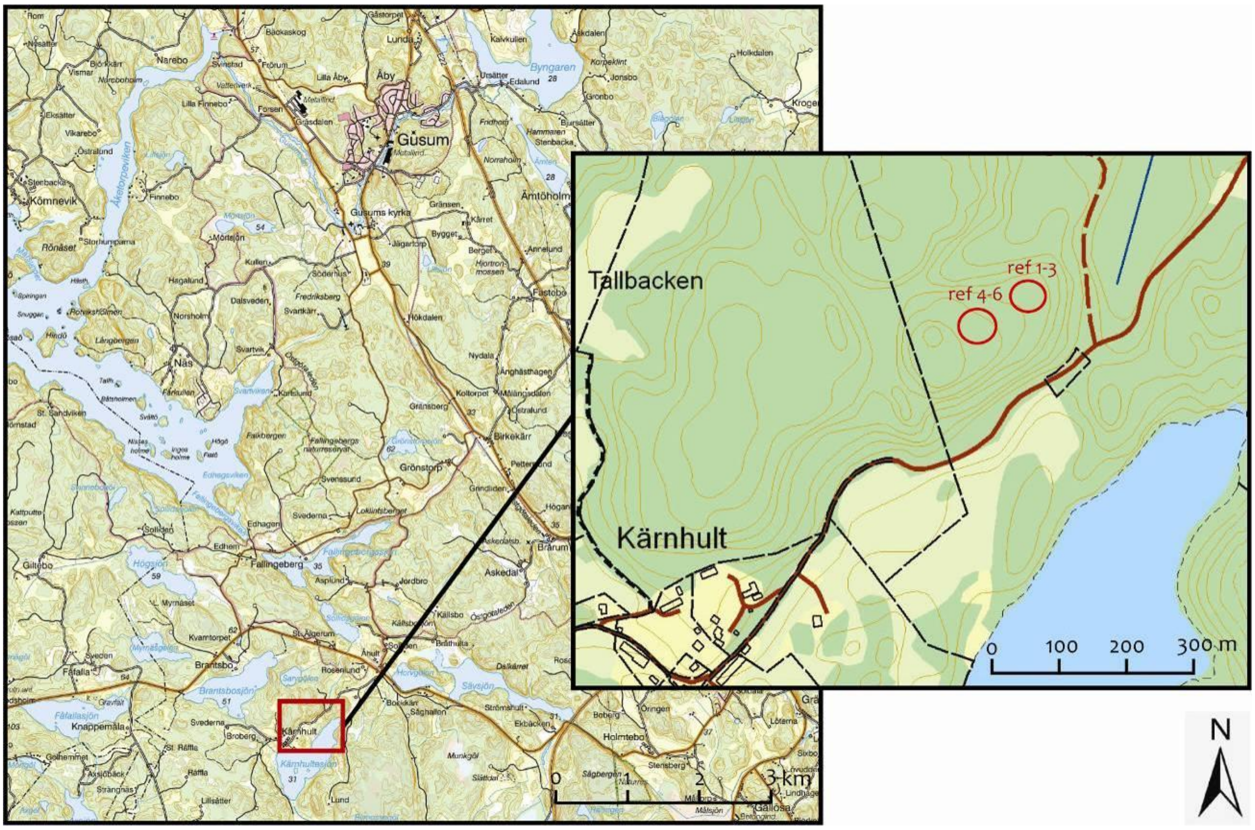

Figure 7. The reference area is located approximately 8 km south of Gusum. The figure also shows approximate locations of sample points. Figure: H. Almqvist, based on maps from Lantmäteriet (© Lantmäteriet Gävle 2010 Medgivande I 2010/0055).

Figure 8. Sun exposed reference area (left), location for samples Ref 1, Ref 2 and Ref 3 and reference area close to spruce stand (right), location for samples Ref 4, Ref 5 and Ref 6. Photos: H. Almqvist 100505

4.2.1 Soils and vegetation

The soils around Gusum are *Dystric* and *Eutric Cambisols* with some *Orthic Podzols* (Troedsson & Wiberg, 1986, see Figure 10). Cambisols are young soils common in areas that have been affected by glaciations. Young parent material and slow soil formation leads to soils where the horizon differentiation is in its initial stage. The material is fine to medium textured and the Cambisols can be good agricultural soils. Together with Cambisols the more coarse-textured Podzols are the most common soils in Sweden. They have an organic top soil (mor layer) over a characteristic pale, leached sub-surface horizon followed by a darker accumulation horizon. Podzols are acidified and have low chemical fertility which makes them unfavourable for cropping. They are often covered with coniferous forests or sometimes heath lands. Many forest soils in the area are Cambisols, because of, among other things, the low precipitation and fine textured soil material. The prefix qualifier *Dystric* indicates a low base saturation and in this area often a forest soil transitional to podzol, whereas *Eutric* indicates a high base saturation. *Orthic* just means that it is a typical Podzol (Driessen et al., 2001).

Pine forests and mixed coniferous forests are the dominating forests in the area and low herbs and grasses are the dominating ground covers (Markinfo, 2007a). Figure 9 shows part of the forest near the reference area. The forest consists mainly of pine and some spruce, and the ground is covered by shrubs, such as bilberry, and mosses.

Figure 9. Typical forest in areas little affected by metal pollution around Gusum. Photo: H. Almqvist 100505.

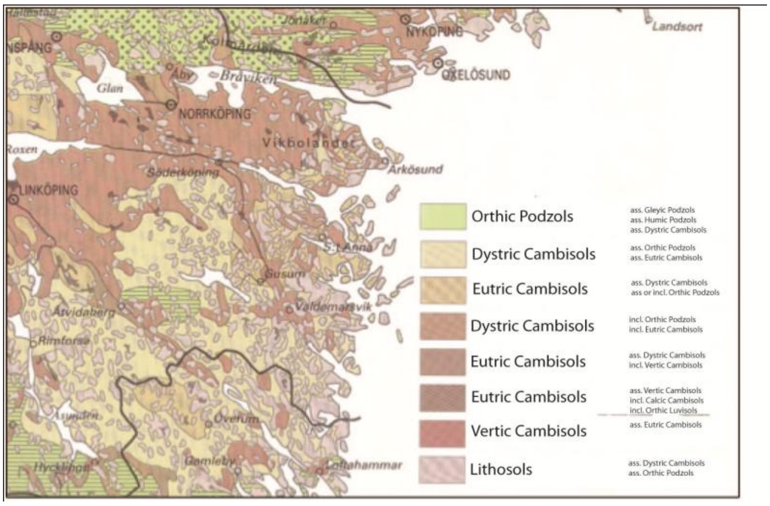

Figure 10. Dominating soil types in eastern Östergötland (from Troedsson & Wiberg, 1986).

4.2.2 Climate

Gusum is situated in a part of Sweden with low precipitation, average annual precipitation is 530 mm. The annual average wind speed is 6.8-8 m/s which is somewhat higher than Swedish average, due to the location close to the coast (the Baltic coast is approx 15 km in easterly direction). The prevailing wind direction is west to southwest, but north-western winds can also occur (SGI, 2008).

4.2.3 Hydrology

The Gusum River has been divided in to 21 sub catchments (Envipro Miljöteknik, 2008). Stångberget is part of two of those catchments, with the dividing ridge line stretching in southeast-north-westerly direction. All sample points for lab analysis are situated in catchment 17. Figure 11 shows the sub catchments of Gusum River.

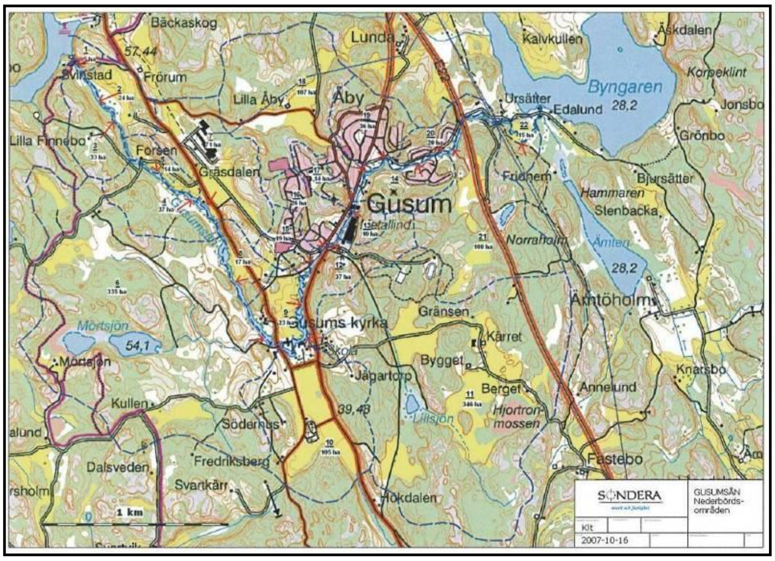

Figure 11. Sub catchments of the Gusum River. Stångberget is in catchments 16 and 17 (Figure: Envipro Miljöteknik, 2008).

4.3 Sampling and sample preparation

XRF measurements were performed in field on April 14 2010. On May 5 2010 samples for metal analysis, carbon/nitrogen, buffering capacity, soil pH, field leach test, sequential extraction, biological and texture analysis were collected from a transect of 150 meters running from the area that the XRF had shown to be highly contaminated and out into the less contaminated area further away from the old mill (Appendix A and Figure 12). At the same time soil depth was measured. Samples were collected from twelve points with a humus drill (Figure 13). From six of the points samples were collected from three layers (0-4 cm, 4-8 cm and 8-12 cm), from the rest only from the top layer (0-4 cm). Several sub samples were taken from each point and soil depth layer and pooled to general samples. The general samples were divided and put in plastic containers (Figure 13). Samples were air dried and sieved to 2 mm. Samples for microbial functional diversity were fresh sieved to 4 mm and preincubated for 20/29 days at 25^{o}C. The top layer soil that were to be analysed for carbon and nitrogen content was fresh sieved to 4 mm, dried and then sieved to 2 mm. Samples for ANC were sieved to 1 mm. Samples for surface runoff were taken on July 27 2010. In Appendix A a table can be found stating which analyses were performed on which samples. Locations of the samples are shown in Figure 12 and in Appendix B photos of the sample points can be seen.

Figure 12. Sample points on Stångberget. Points 1-12 are soil samples and surface runoff a water sample. Figure: M. Sträng, Golder Associates. AB.

Figure 13. Humus drill for soil sampling. The drill consists of a steel serrated plastic tube, which is rotated down into the soil and pulled up with the soil core. Photo: H. Almqvist 100505.

Figure 14. Collecting of soil samples. Photo: H. Almqvist 100505.

4.4 Scanning of the investigated sites with X-ray Fluorescence Analyzer

An X-ray Fluorescence Analyzer (NITON XL3t600 XRF) was used to analyze heavy metal concentrations directly in field. The XRF method is based on emissions of photons from excited atoms. X-rays are emitted from the instrument (Thermo Fisher Scientific, 2009) and when hitting an atom an electron can be ejected from an inner shell creating a vacancy. This is an unstable condition for the atom which is neutralized by the transfer of another electron from an outer shell to the free space. This leads to emission of a photon with an energy content characteristic for the specific element. (Kalnicky and Singhvi, 2001). The XRF instrument detects the emitted photons and transforms the information to a metal concentration in the substrate. Table 2 shows the theoretical detection limits for some elements and Figure 16 an action chart of the XRF.

Table 2. Detection limits (LOD) for NITON XL3t600 XRF measurement instrument [mg/kg DM] (Thermo Fisher Scientific, 2007)

	LOD		LOD
Cu	35	**As**	11
Zn	25	**Se**	20
Pb	13	**Rb**	10
Cd	12	**Sr**	11
Ca	500	**Zr**	15
Sc	400	**Mo**	15
Ti	160	**Ag**	10
V	70	**Sn**	30
Cr	85	**Sb**	30
Mn	85	**Ba**	100
Fe	100	**Hg**	10
Co	260	**Th**	20
Ni	65	**U**	20

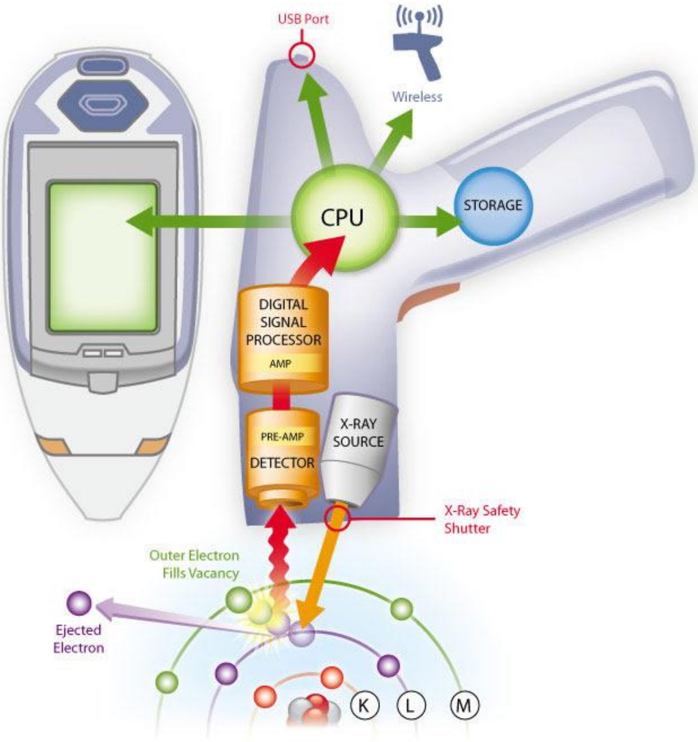

Figure 15. Action chart of Niton XRF instrument (Thermo Scientific, n.d.).

In investigations of contaminated soils the XRF method is mainly used to define the boundaries of the contaminated area and to get a first overview of the contamination level. The exact values from the measurements are thus less important, and can often deviate from those of lab analyses. The accuracy of the results from the XRF measurements depends on several different factors such as the detection limit, resolution of the detector, calibration technique, particle size, homogeneity of the sample and handling of the instrument (Kalnicky & Singhvi, 2001).

Analyses were performed in 47 points on the visibly contaminated area and its vicinity and in five points on the reference location (Figure 16). The screening focused on the transition zone between the visibly contaminated area and soil with ground vegetation, and on the preliminary transect. Each measurement lasted 60 seconds. The locations of the points were established according to the RT90 system using a GPS instrument (Magellan MobileMapper GPS).

Figure 16. XRF measuring in small trial pit at Stångberget. Photo: S. Dahlin 140410.

The results from the XRF measurements were used to determine where the gradient for sampling for lab analyses should be taken.

4.5 Soil analyses

4.5.1 Metal concentrations in soil

Samples were analyzed for metals through acid extraction. To determine the concentrations of As, Cd, Cu, Co, Cr, Fe, Hg, Mn, Ni, Pb, V and Zn the sample was dried at 50°C and dissolved in concentrated HNO_3/H_2O_2 in Teflon bombs in a microwave oven according to the ASTM international standard ASTM D3683. ICP-AES[2] and ICP-SFMS[3] were used to analyze the metal concentrations according to USEPAs standardized analytical methods 200.7 (USEPA, 1994a) and 200.8 (USEPA, 1994b) (ALS Scandinavia, 2009).

4.5.2 Soil depth

Soil depth was measured at the 12 sample points on Stångberget and the six sample points from the reference location. The depth was measured by sticking a metal probe into the soil down to the bedrock at three different points, 50 cm apart, to get an approximation of the soil depth.

4.5.3 Texture analyses

Texture analyses were performed on two soils by the laboratory at the Department of Soil and Environment on SLU, Ultuna.

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[2] Inductively Coupled Plasma Atomic Emission Spectroscopy

[3] Inductively Coupled Plasma Sector Field Mass Spectroscopy

Gravel and stones were sieved from the soil sample using 20 mm (stones), 6 mm (coarse gravel) and 2 mm (fine gravel) sieves. The stones were discarded and not included in the texture analyses, but the gravel was weighed. The finer particles were dispersed to remove any aggregate structure by adding 35% H_2O_2 to oxidize organic matter and 3.3 % $(NaPO_3)_n$ + 0.7 % Na_2CO_3 as dispersing agent. The soil was centrifugated and thereafter the sand fraction was sieved out using a 0.2 mm sieve. The pH was adjusted to pH 8-9 before the finer fractions (silt and clay) were determined using the pipette method.

4.5.4 Soil pH

Soil pH was analyzed on all samples following the Swedish standard SS-ISO 10 390, with the exception that the pore volume was excluded when the soil volume was measured. The soil was suspended in 25 ml of deionised water until the volume was 30 ml. The sample was shaken in a bench top shaker for 5 min and left to settle for two hours before the pH was measured. The sample was hand shaken before the measurement.

4.5.5 Acid Neutralizing Capacity

A solution that resists a change in pH on addition of acid or alkali is called a buffer solution (Tan, 1998). Clay and humic fractions react with added acid or base and decreases the pH change (Tan, 1998). Buffering capacity is an interesting parameter when investigating polluted soils since it can give information about leaching in a longer perspective. If the buffering capacity is low there is a risk that the soil will easily acidify which may increase leachability in the future.

Acid-neutralizing capacity (ANC) was analyzed at ALS Scandinavia in Luleå. Samples were mixed with deionised water to a liquid-to-solid ratio of 10:1 and titrated with HNO_3 until pH 4 was reached.

4.5.6 Carbon and nitrogen content

18 samples from Stångberget and five samples from the reference area were sent to the laboratory at the Department of Soil and Environment at SLU for analysis of total carbon and nitrogen on a CN2000 high temperature furnace (LECO, 2003). Analysis were carried out on a subsample of the sieved soils used for MicroResp determinations whereas analysis of soils from deeper soil layers were carried out on samples also used for metal analyses.

4.6 Metal leachability

4.6.1 USGS Field Leach Test

The United States Geological Survey (USGS) have developed a leaching test to be used in field. The benefits of the test are that it is fast, simple and cost-effective. It was first developed for use on metal mine wastes, but has later been used on various substrates, such as sediments, volcanic ash, forest-fire burned soils and dusts (Hagemann, 2007). It has also been used in pre studies for remediation work on mines in Sweden (e.g. Envipro Miljöteknik, 2009).

The leach tests were performed on dried soil in lab according to Hagemann (2007). 50.0 g of soil was weighed in and mixed with 1.0 L deionised water, to obtain a water-to-solid ratio of 20:1. The mixture was shaken on a bench-top shaker for ten minutes and allowed to settle for twenty minutes. Subsamples were measured for pH. The leachate was then filtered through a 0.45 µm filter, put in plastic containers and sent to ALS laboratory. At ALS samples were analysed for metals using ICP-AES, ICP-SFMS and AFS[4] (leachate). The solid phase was analysed as described in Chapter 4.5.1.

4.6.2 Surface runoff

At July 27, 2010 surface runoff from Stångberget was collected by Sondera AB (Figure 12). The summer had been dry, with only 16 mm of rain between June 15 and July 23. Between July 24 and July 27 58 mm of rain fell. The water was analyzed at ALS Scandinavia in Luleå for metal concentrations, using ICP-AES and ICP-SFMS. The surface runoff analyses are part of a reference investigation in Gusum River and Gusum Community performed to establish a mass balance and for use in future environmental control programs (Golder, 2009).

4.6.3 Sequential extraction

In a sequential extraction different fractions of soil metal are extracted with different solutions in a sequential manner. Since each extraction solution more or less specifically mobilizes a certain fraction in the step where it is added the method can give some information on how the metals are bound to the soil. Standardized leaching tests have been developed (SS-EN 12457-3) and are recommended by e.g. Swedish EPA to use in waste classification, but those tests are often not sufficient for geochemical interpretations. A sequential extraction is more detailed and can give more information. Some criticism on sequential extractions has been published regarding the relatively large overlap between phases that can occur, when some of the extractants extract metals in several of the fractions (Berggren Kleja et al, 2006).

Since sequential extractions are costly it could in this project only be performed on one sample, as a general characterization of a representative strongly polluted soil. Sample 9:1, the top layer of one of the samples from the highly contaminated area, was chosen for this analysis after the metal concentrations at the sites had been established. The sequential extraction was performed by ALS Laboratory in Luleå, Sweden. The method is described in Carlsson et al.

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[4] Atom Fluorescence Spectrometry

(2002) and is a modification of the method described by Hall et al. (1996a, 1996b). Extractants and corresponding metal fractions are shown in Table 3. The extracts were analyzed using ICP-AES, ICP-SFMS and AFS. The sample was analyzed prior to and after the extractions to get total (before extraction) and residual concentration of the elements. For As, Cd, Cu, Co, Hg, Ni, Pb, Sb, S, Se, Sn and Zn the samples were dried at 50°C and dissolved in HNO_3/HCl/HF in a Teflon bomb in a microwave oven according to the ASTM international standard ASTM D3683. Sb and Sn were extracted separately in reversed *aqua regia* (HCl:HNO_3, 3:1). For Si, Al, Ca, Fe, K, Mg, Mn, Na, P and Ti the sample was fused in a $LiBO_2$-melt according to the ASTM international standard ASTM D3682. ICP-AES and ICP-SFMS were used to analyze the metal concentrations according to USEPAs standardized analytical methods 200.7 (USEPA, 1994a) and 200.8 (USEPA, 1994b) (ALS Scandinavia, 2009).

Table 3. Dissolved fractions and extractants in the five steps of the sequential extraction (Carlsson et al., 2002)

Step	Dissolved fraction	Extractant
1	Exchangeable metals (and carbonates)	1.0 M CH_3COONa, pH 5
2	Labile organics (e.g. humic and fulvic substances)	0.1 M $Na_4P_2O_7$
3	Amorphous Fe- and Mn-oxides	0.25 M $NH_2OH\cdot HCl$ in 0.10 M HCl at 60°C
4	Crystalline Fe-oxides (e.g. goethite, hematite and magnetite)	1.0 M $NH_2OH.HCl$ in 25% CH_3COOH at 90°C
5	Stable organics and sulphides	$KClO_3$ in 12 M HCl at 90°C

4.7 Specific respiration and microbial functional diversity

Specific respiration and microbial functional diversity in the soil was measured using a microplate respiration system, MicroResp™. One reason the MicroResp™ system was chosen is that it is not culture based and thereby no extraction and selection among the microorganisms is done, and the whole population can be studied. Instructions in the MicroResp™ Technical Manual (Macaulay, 2009) were followed when performing the test except that soils were sieved to 4 mm instead of to 2 mm.

Soil were put in 96-well microplates and preincubated for eight/ten days. Deep-wells with soils, substrate solutions (Table 4) and detection plates containing indicator gel (Figure 17) were incubated for five hours at 25°C during which time evolved carbon dioxide was trapped in the detection wells. The evolved carbon dioxide reacted with the bicarbonate in the indicator gel during incubation, giving a pH change (Eq. 4.1) which in turn changed the colour of the gel. This colour change was detected by the spectrophotometer.

$$CO_2\,(g) + H_2O + HCO_3 \leftrightarrow 2CO_3^{2-} + 3H^+ \qquad (4.1)$$

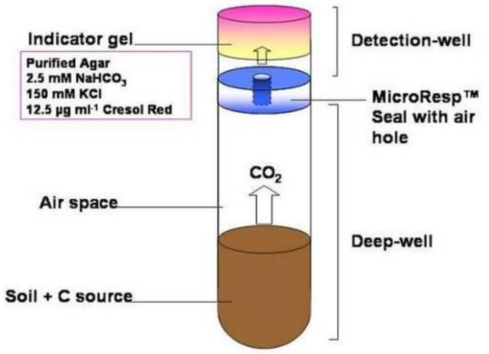

Figure 17. Schematic figure of one well in the MicroResp™ system (Macaulay, 2010).

Table 4. Substrates used in the MicroResp™ experiment

Amino acids	Sugars	Amids	Carboxylic acids	(Water)
L-Alanine	L-Arabinose	N-Acetylglucosamine	Citric acid	(Deionized water)
γ-Aminobutyric acid	D-Fructose		L-Malic acid	
L-Proline	D-Galactose		Ascorbic acid	
L-Lysine-HCl	D-Glucose		α-Ketoglutaric acid	
L-Cysteine-HCl monohydrate	D-(+)-Trehalose dihydrate			

Absorbance data from the spectrophotometer was converted to % CO2 and CO2 production rate using formulas from Macaulay (2009) and calibration curve specific for soil and instrument. Measurements were done in six replicates for each soil and substrate. *Specific respiration* was calculated from the basal respiration, i.e. respiration in soils where only deionised water had been added. Microbial biomass was estimated from the substrate induced respiration (SIR) with glucose as substrate, using an empirically estimated equation from Anderson & Domsch (1978).

$$y = 40.04x + 0.37 \qquad (4.2)$$

where y is biomass C per 100 g soil DM and x is respiration rate in ml CO2 per 100 g soil and hour. ($\varrho_{CO_2(1atm,25C)}=1.799$ kg/m^3) Substrate Induced Respiration (SIR) was calculated by subtracting respiration in soils after water addition from respiration in soils after substrate addition. Microbial functional diversity was evaluated by looking at the functional profiles. Evaluation was performed by researcher Sigrun Dahlin at SLU based on the SIR after addition of the 15 different substrates and the deionised water.

4.8 Statistical analysis

Minitab 16 Statistical software (Minitab, 2010) was used to perform General linear model (GLM) ANOVA analysis on the results. Averages for chemical properties and specific respiration in three subareas were compared using individual samples collected within each subarea as replicates. The subareas were the forested part of Stångberget (represented by samples 1-5), the visibly contaminated part of Stångberget (represented by samples 6-12) and the reference area. For pH, carbon and nitrogen Stångberget was treated as one subarea (samples 1-12).

The GLM analyses were performed on soil metal concentrations, specific respiration, pH, carbon- and nitrogen content and C/N ratio, of the surface soils where nothing else is stated.

Microbial functional diversity was evaluated by discriminant analysis using canonical analysis software (Andersson, 2004). To investigate if the variation between samples could be explained by the canonical metal contamination, correlation analysis of SIR vs. concentrations of copper, zinc, lead and cadmium were carried out. Data from all sample points were used and grouped in three groups; Stångberget sampls 1-7, Stångberget samples 8-12 and the reference samples.

5 Results

5.1 General site properties

5.1.1 Soil depth

The average soil depth in the transect on Stångberget was 19 cm. There was no significant difference between the forested part and the bare part (18 cm vs. 20 cm). The soil depth varied between 0 and 35 cm. On the reference location the average soil depth was 24 cm, varying between 15 and 35 cm.

5.1.2 Texture analyses

Soil texture was determined on two different soils, one from Stångberget and one from the reference location (Table 5). According to a soil-texture triangle the soil on Stångberget was classified as ***loam*** and the reference soil as ***sandy loam***.

Table 5. Texture and Loss on Ignition (LOI) of two soils from the sampled sites [% of mineral soil]. Particle sizes in mm. LOI is a measure of organic matter content

	Clay	Silt			Sand				
		Fine	Medium	Coarse	Fine	Medium	Coarse	Gravel	LOI
	d<0,002	0,002-0,006	0,006-0,02	0,02-0,06	0,06-0,2	0,2-0,6	0,6-2	2.0-20	%
Stång-berget	10	5	11	16	19	14	10	15	16
Ref. area	7	4	14	19	22	26	8	0	19

5.1.3 Soil pH

pH was higher on Stångberget than on the reference location (Figure 18). Average on Stångberget was 4.3 and on the reference location 3.8. pH was generally higher further down in the profile. pH was also measured in leachate from the USGS Field Leach Test (see chapter 4.6). The two methods gave comparable results. Average pH values were significantly different when comparing surface soils on Stångberget and the reference area (p=0.027), but not when comparing lower soil depths (4-8 cm p=0.072 and 8-12 cm p=0.087).

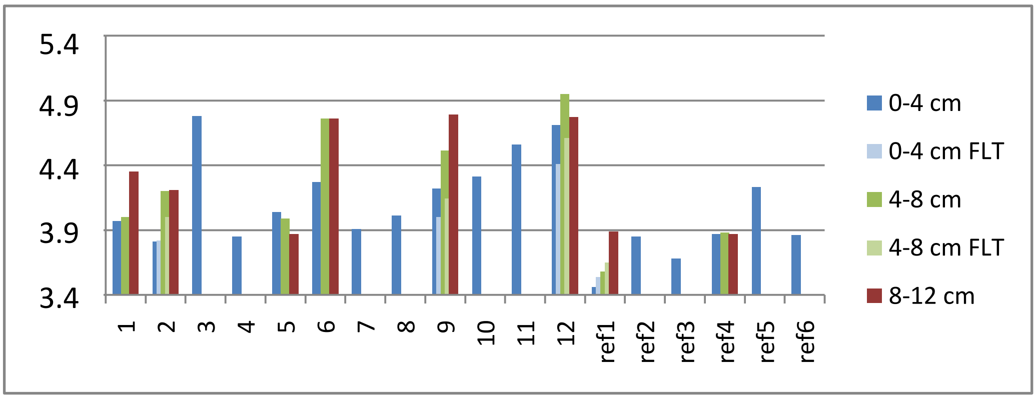

Figure 18. pH of soil solutions from Stångberget and reference area. FLT is pH measured in samples from the USGS Field Leach Test.

5.1.4 Acid Neutralizing Capacity

Acid Neutralizing Capacity (ANC) on Stångberget was low (Table 6). ANC was also measured on two soils from the reference location but the pH was below pH 4, which means that the acid neutralizing capacity that was measured with this method was already depleted.

Only a small amount of acid was needed to make pH drop to 4 indicating a low acid neutralizing capacity (Table 6).

Table 6. Acid Neutralizing Capacity (ANC) of soils from Stångberget [mol H+/kg DM]

	ANC
2:1	0.012
9:1	0.028

5.1.5 Carbon and nitrogen concentrations

Carbon content was between 30 and 50 % for most samples, but a few had a much lower content (Figure 19). Nitrogen content was between 1.0 and 2.0 % for most samples but a few had lower content (Figure 19). No pattern could be seen and there was no significant difference between the subareas (C p=0.15, N p=0.86). The C/N ratio varied between 20 and 44, significantly highest in the reference area and lowest in the visibly affected area (p=0.006). Forest soils often have a ratio of 25-50 in the O-horizon (Eriksson et al., 2005) which means that most samples had a normal C/N ratio.

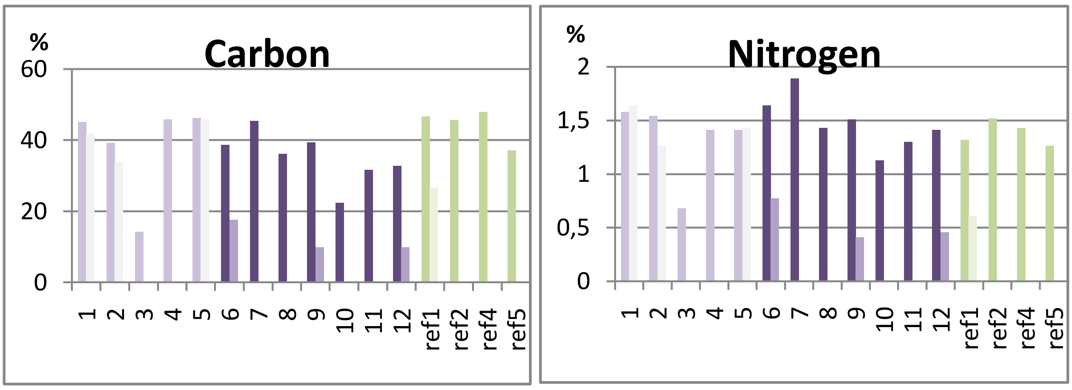

Figure 19. Carbon and nitrogen concentrations [% of dry weight] in the soils from Stångberget and the reference area. Pale purple is from the forested part of Stångberget, purple from the visibly contaminated part and green from the reference area. The left bars on each sample point are samples from 0-4 cm, the right bars samples from 4-8 cm.

5.2 Soil metal concentrations

5.2.1 XRF analyses

Copper and zinc concentrations estimated by the XRF scanning clearly differed between the bare and the forested soil (Figure 20 and Figure 21) where almost all points on bare soil showed levels above MKM. For copper many of the measured points had concentrations even above 10 times MKM and 100 times the reference area. The border zone was situated on top of the hill, so that the area beyond it was somewhat shadowed from the mill by the hill crest, as can be seen in Figure 23. Lead levels were also above MKM in several points (Figure 22). Cadmium data is not shown since all measurements were below detection limit of the XRF.

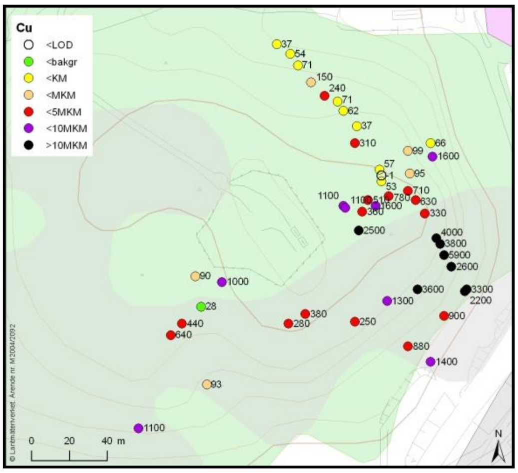

Figure 20. Copper levels on Stångberget, measured with XRF instrument, in relation to background and SEPA guideline values. Background=30 mg/kg DM, KM= 80 mg/kg DM, MKM=200 mg/kg DM. Figure: M. Sträng, Golder Associates AB.

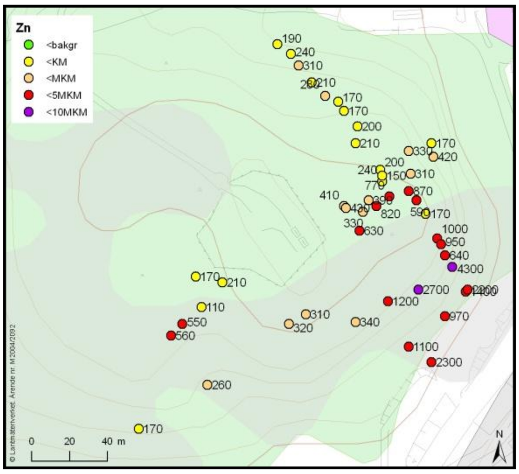

Figure 21. Zinc levels on Stångberget, measured with XRF instrument, in relation to SEPA guideline values. Background=70 mg/kg DM, KM=250 mg/kg DM, MKM=500 mg/kg DM Figure: M. Sträng, Golder Associates AB.

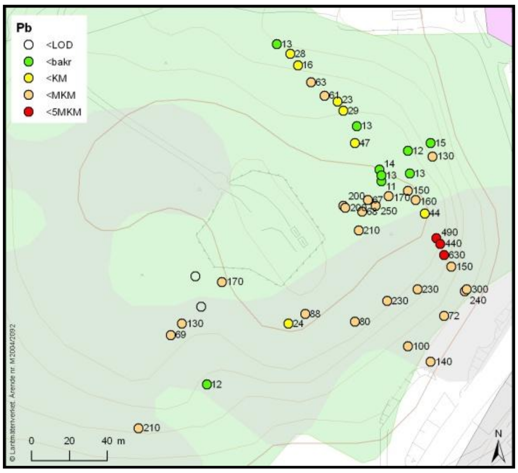

Figure 22. Lead levels on Stångberget, measured with XRF instrument, in relation to SEPA guideline values. Background=15 mg/kg DM, KM= 200 mg/kg DM, MKM=400 mg/kg DM Figure: M. Sträng, Golder Associates AB.

The southern part of the hill had bare soil but live trees. Soils showed high levels of metal pollution (Figure 24 and points 38-57 on Figure 20), but concentrations were about a tenth of those on the area to the northeast, where both the soil was bare and most trees were dead. The crest was not as steep in the southern part, and therefore the shadow effect from the flue gases not as obvious. Because of that the transit between the visibly affected area and the forested area was more gradual than in the northern part of Stångberget.

Figure 23. Transition zone on northern part of Stångberget. The transition was sharp where the hilltop shadowed the ground. Photo: H. Almqvist 100505

Figure 24. Southern part of Stångberget where the trees were alive but the soil was bare. Photo: H. Almqvist 100505

5.2.2 Lab analyses

Copper was the metal showing the highest concentrations relative to the guideline values (Figure 25). On the worst affected point the concentrations were more than fifty times the MKM value (10800 mg/kg DM) and on several other points the levels were 16 to 20 times MKM. The whole hill showed concentrations above the MKM value and concentrations were higher on the visibly affected part than in the forest. On the reference area the concentrations were below the Swedish background value.

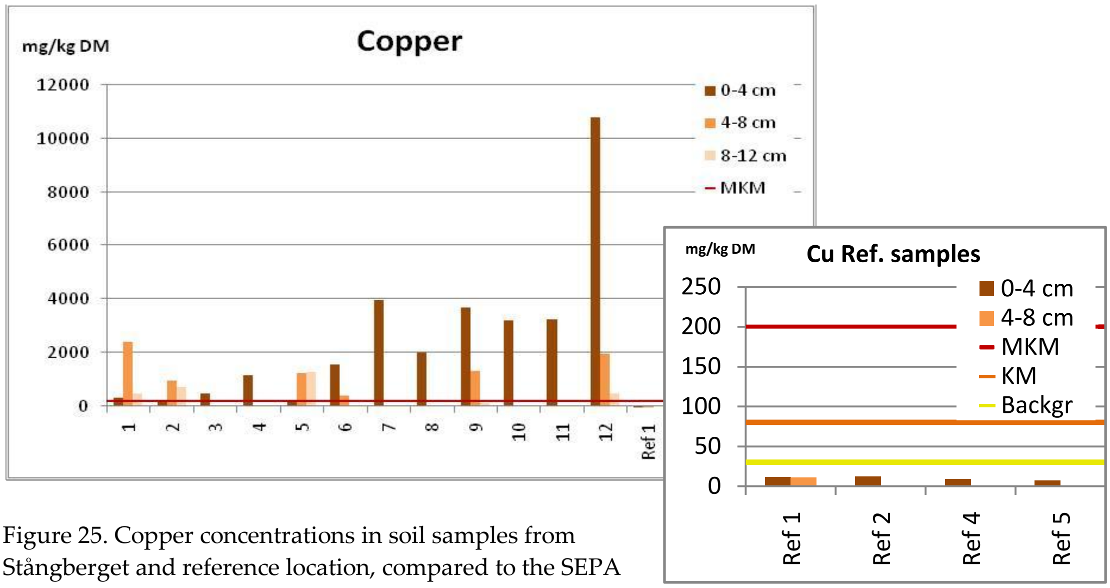

Figure 25. Copper concentrations in soil samples from Stångberget and reference location, compared to the SEPA guideline values for soil environment. (MKM = less sensitive land use, 200 mg/kg DM, KM = Sensitive land use, 80 mg/kg DM Backgr = background value, 30 mg/kg DM).

Nine of the twelve sample points on Stångberget showed zinc concentrations above MKM in one or more soil depths (Figure 26). On the worst affected points concentrations were around 6 times MKM (the highest concentration was 3140 mg/kg DM). On the reference location values were above the Swedish background value.

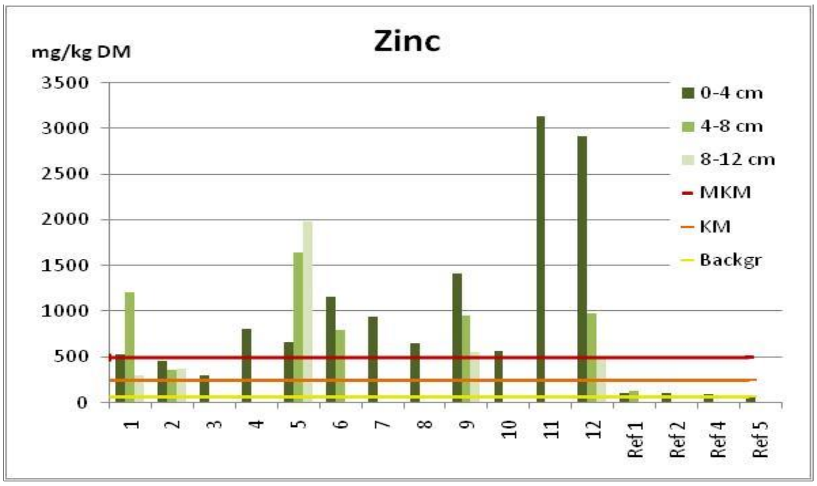

Figure 26. Zinc concentrations in soil samples from Stångberget and reference location, compared to SEPA guideline values for soil environment (MKM = less sensitive land use, 500 mg/kg DM, KM = Sensitive land use, 250 mg/kg DM Backgr = background value, 70 mg/kg DM).

Lead showed values above MKM in five points, the highest one being three times MKM (1140 mg/kg DM) (Figure 27). All concentrations above MKM were from sample points on the visibly affected area. The reference values were quite far above the Swedish background value.

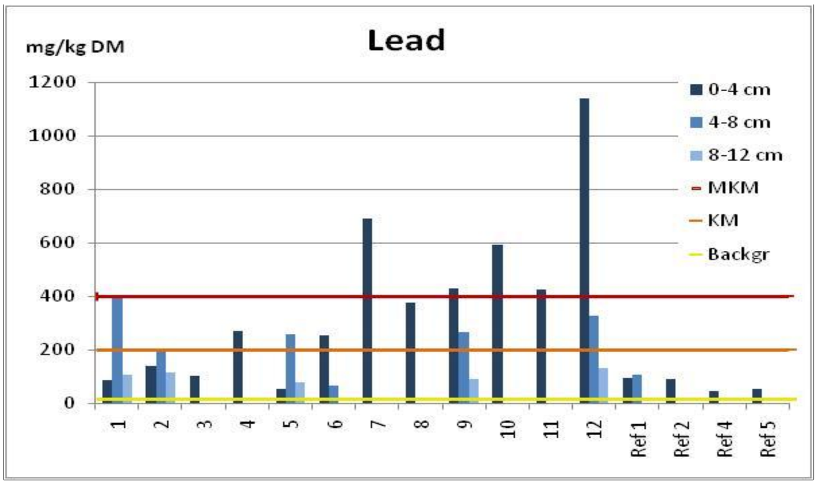

Figure 27. Lead concentrations in soil samples from Stångberget and reference location, compared to SEPA guideline values for soil environment (MKM = less sensitive land use, 400 mg/kg DM, KM = Sensitive land use, 200 mg/kg DM Backgr = background value, 15 mg/kg DM).

All over Stångberget and the reference location cadmium concentrations were below the guideline value for less sensitive land use, but samples from five locations were above the guideline value for sensitive land use (the highest concentration was 13.7 mg/kg DM) and all were above the Swedish background value (Figure 28). Also the reference values were above background.

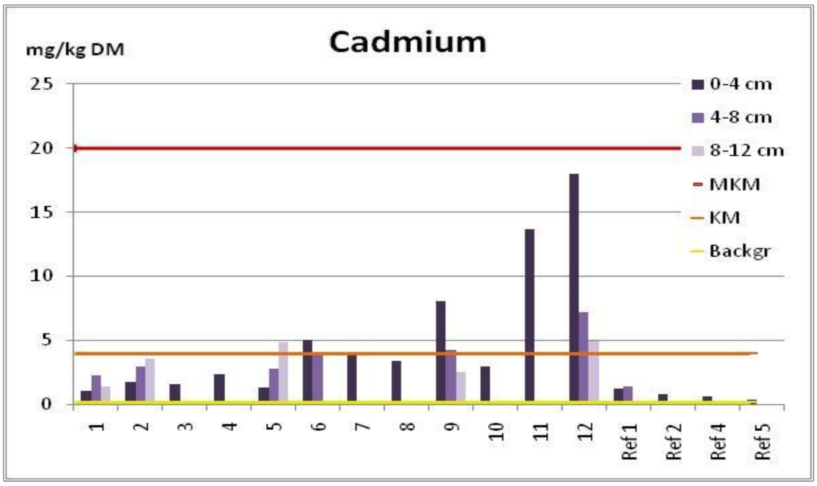

Figure 28. Cadmium concentrations in soil samples from Stångberget and reference location, compared to SEPA guideline values for soil environment (MKM = less sensitive land use, 20 mg/kg DM, KM = Sensitive land use, 4 mg/kg DM Backgr = background value, 0.2 mg/kg DM).

Average concentrations of all metals differed significantly between the reference site, the forested part of Stångberget and the bare part of Stångberget (Cu: p=0.011, Zn: p=0.016, Pb: p=0.003, Cd: p=0.003).

Looking at charts showing metal concentrations at various depths (Figure 29) it is clear that the pattern varies for different metals and different parts of Stångberget. Soils under living vegetation (sample points 1-5) have in general lower concentrations in the 0-4 cm layer than in the 4-8 cm layer. The opposite goes for sample points under bare soil.

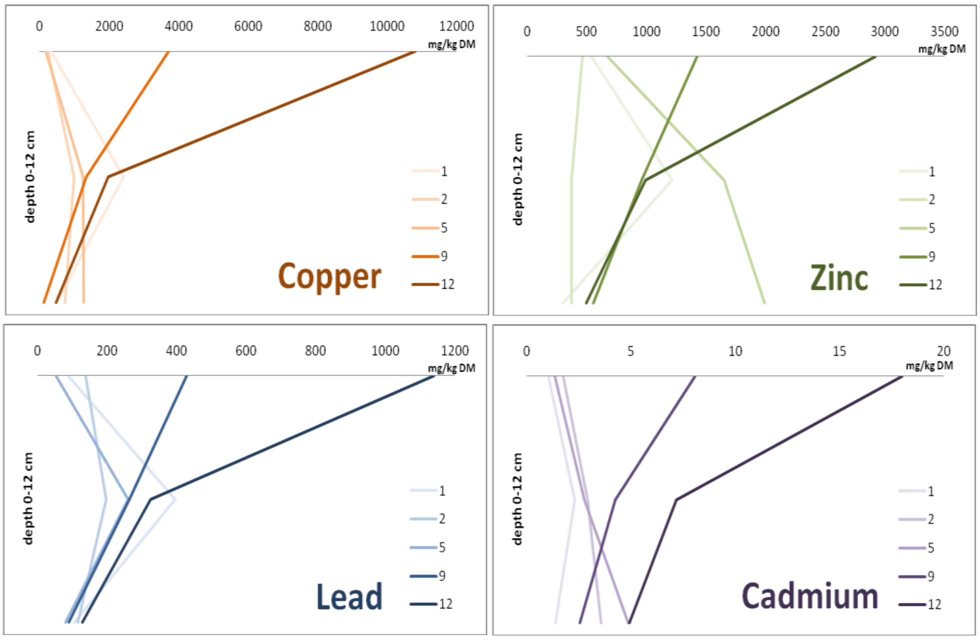

Figure 29. Variation in opper, zinc, lead and cadmium concentration with depth.

5.2.3 Correlation between XRF and lab analysis

The correlation between XRF results and lab analysis is an important factor to know in the event of a remediation. XRF is a useful tool to get an overview of the variation in metal concentration over a polluted area but it is often less accurate about the exact levels. The metal concentrations measured by the XRF instrument were lower than those from the lab analysis in most cases (Figure 30).

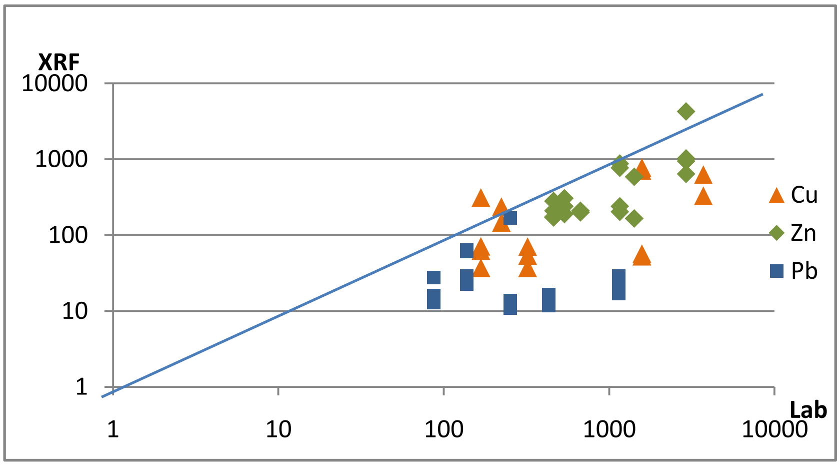

Figure 30. Correlation between results from XRF measurements and lab analysis for copper, zinc and lead concentrations. The blue line indicates perfect correlation [mg/kg DM]

5.3 Leachability

5.3.1 USGS Field Leach Test

Zinc was the metal showing the highest concentrations in the leachate, the highest measured concentration was 1350 µg/L (Figure 31). The copper concentration in the same leachate was 872 µg/L and the lead concentration 11.7 µg/L. Cadmium concentrations was highest in the leachate from sample 12:1, where it was 4.05 µg/L. In general the leachability was higher in the 0-4 cm horizon (named no:1), than in the 4-8 cm horizon (named no:2) and higher on the bare part of Stångberget than on the forested part. The leachability of copper, zinc and lead was higher in 9:1 than in 12:1 even though the total concentrations were higher in 12:1 (see Chapter 5.2.2).

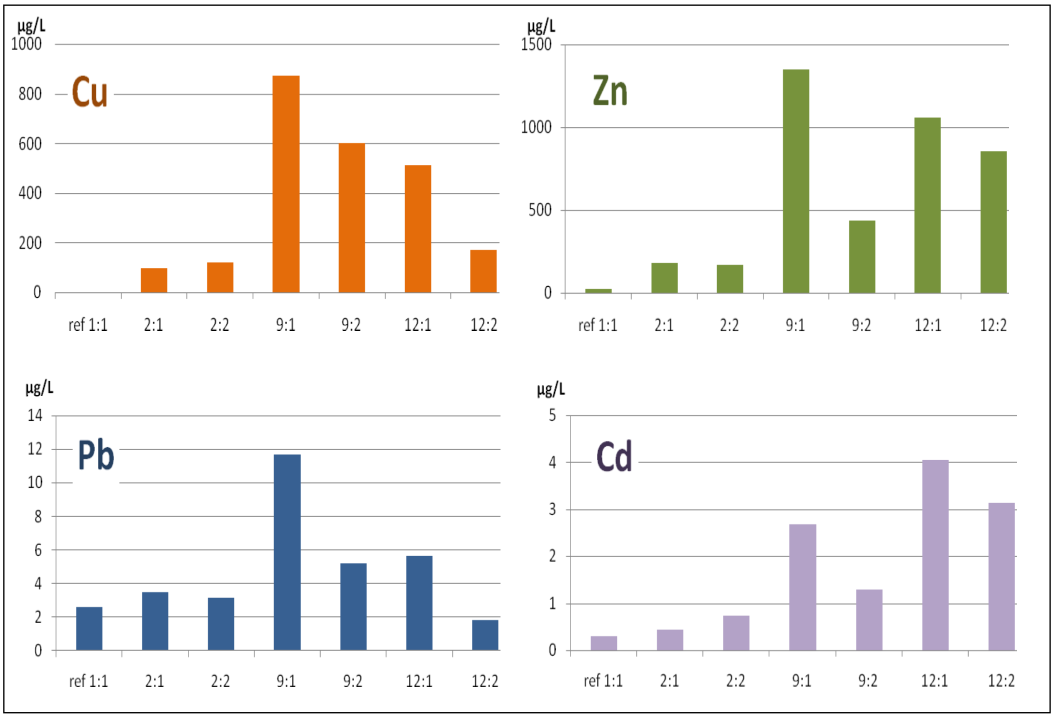

Figure 31. Concentrations of copper, zinc, lead and cadmium, as measured in leachates in the USGS Field Leach Test.

5.3.2 Surface runoff

Zinc showed the highest concentrations also in leach water collected in situ, at 425 µg/L (Table 7). Compared to the total amount of metals in the soil a larger fraction of zinc and cadmium leached than of copper and lead.

Table 7. Concentrations in surface runoff from Stångberget [µg/L]

	Cu	Zn	Pb	Cd
Surface runoff	121	425	0.968	1.06

5.3.3 Sequential extraction

All metals showed the highest concentrations in the first two steps of the sequential extraction, and quite low concentrations in the later steps (Figure 32 to Figure 35). This shows zinc and cadmium were mainly bound as exchangeable metals whereas copper and lead where bound to more equal amounts as exchangeable metals and to labile organics.

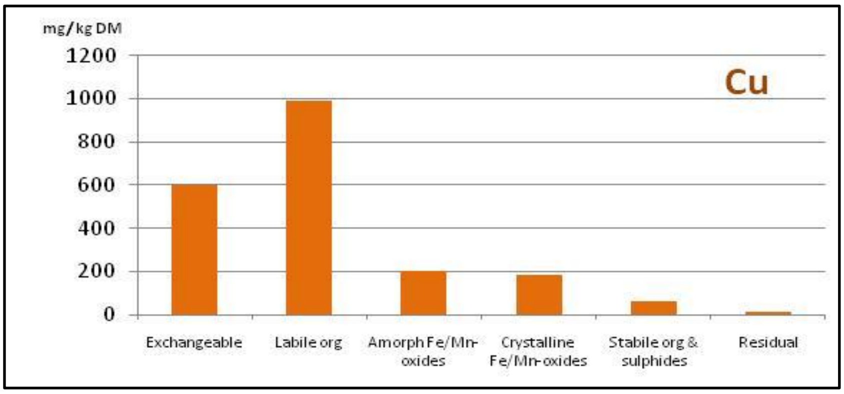

Figure 32. Copper concentrations in different fractions of the sequential extraction.

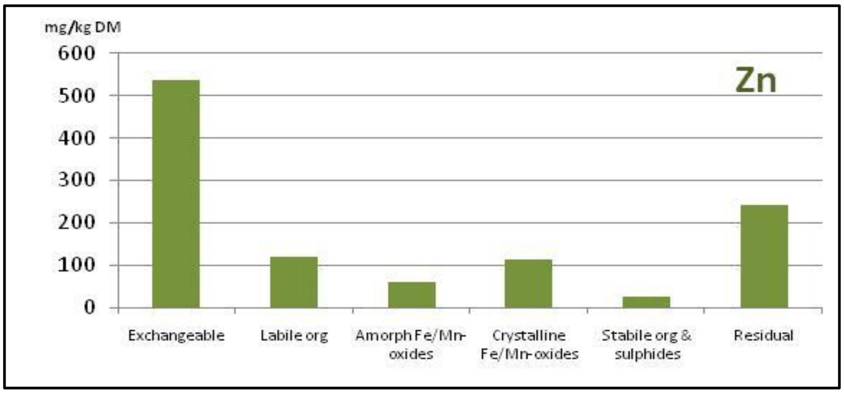

Figure 33. Zinc concentrations in different fractions of the sequential extraction.

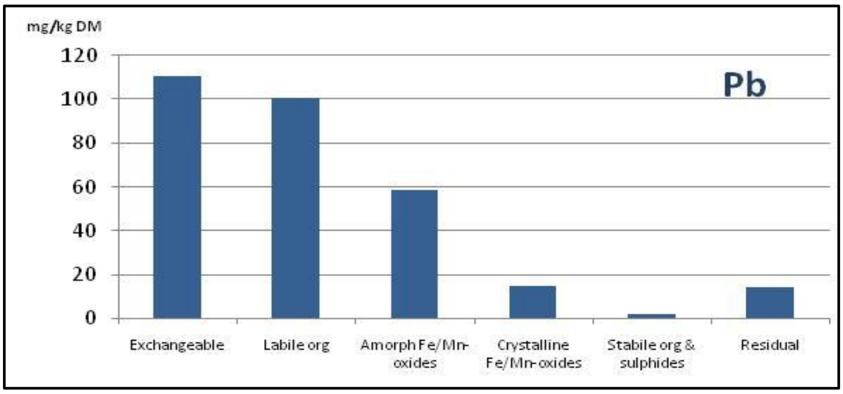

Figure 34. Lead concentrations in different fractions of the sequential extraction.

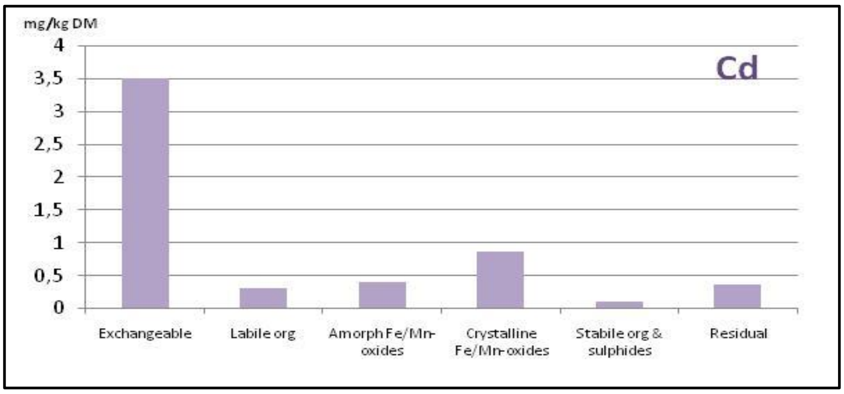

Figure 35. Cadmium concentrations in different fractions of the sequential extraction.

5.4 Effects on the microbial community

5.4.1 Specific respiration

Specific respiration was significantly higher ($p<0.001$) on the visibly contaminated area than the other areas if three possible outliers were omitted from the statistical analysis but not if they were included ($p=0.423$) (Figure 36). Three samples showed specific respiration rates clearly above the rest.

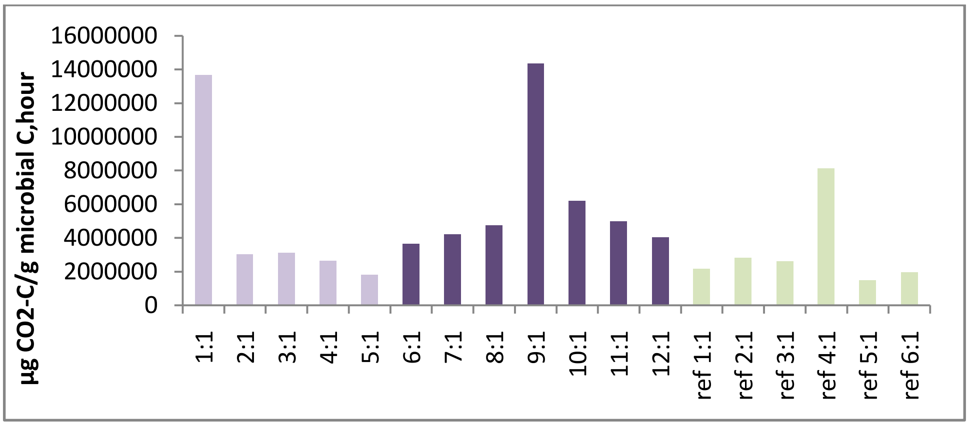

Figure 36. Specific respiration of soils from Stångberget and reference location.

5.4.2 Functional diversity

Discriminant canonical analysis of patterns of the substrate induced respiration (SIR) revealed a clear difference between samples from the forested part of Stångberget (samples 1-7) and samples from the visibly affected part (samples 8-12) (Figure 37). There was also some indication that the reference area and the forested part of Stångberget differed, but the difference was not as clear. Analysis could not discriminate the two subsets of reference soils, i.e. the sun-exposed soil of the pine stand and the shaded soil of the spruce stand (Figure 37). The canonical correlation analysis showed an Eigenvalue of 57 % when running Substrate Induced Respiration (SIR) vs. copper, zinc, lead and cadmium concentrations which shows that the variation to a high degree could be ascribed the metal concentrations. Copper seemed to be the metal affecting the microbial community the most, the Eigenvalue for SIR vs. copper alone was 45 %.

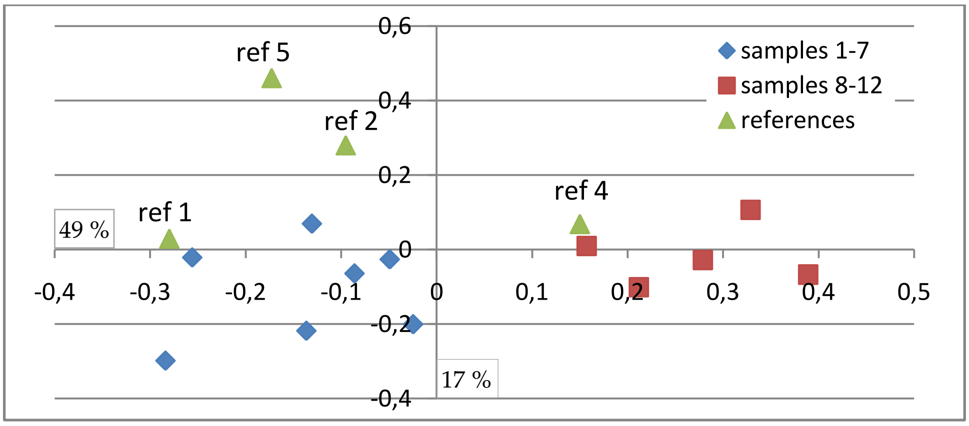

Figure 37. Ordination plot of the first canonical axis produced by CAP analysis of SIR/SOC*h for soils from Stångberget and the reference area. Percentages indicate percentage of variation explained by the axis.

6 Discussion

6.1 Soil pH

Coniferous forest soils normally have a low pH, because of the parent material, the soils capacity to withstand acidification, acid litter and base cation uptake. The general acidification has also affected the soil pH. A mor layer often has a pH below or close to 4 (MarkInfo, 2007). In the reference samples from Kärnhult average pH is 3.8, which is normal for the soil type. On Stångberget the pH is slightly higher, average for the surface layer in the visibly contaminated area is 4.3 and for the forested area 4.1. pH normally increases with depth in a profile because of the pH raising effect of weathering of base cations and less effect of acidification (MarkInfo, 2007).

In the 1980s pH was measured in soils from locations up to 8 km from the mills in Gusum by Tyler (1984) and Bergkvist (1986) (Figure 38). Tyler found a drastic increase in pH towards the mills starting about 1 km away. Bergkvist's results, despite only showing two different distances, points in the same direction, but no such pattern was found in my study. Rühling (1983) and Tyler (1984b) explained the drastic increase by the pH raising effect of the metal oxides. Metals from the mill were emitted as large alkaline particles which caused a pH raise. It seems as though this impact on pH has decreased since the 1980s and that pH in soils on Stångberget has approached that of a typical Swedish forest soil. An increased pH leads to less leaching, so the lower pH in the soil today might be a factor leading to higher leaching of the metals. Tyler measured pH in a KCl solution whereas measurements in this study were made in H_2O. The potassium will compete with the protons for surface sites and thereby cause a lower pH in the soil solution then what would be the case if pH was measured in pure water.

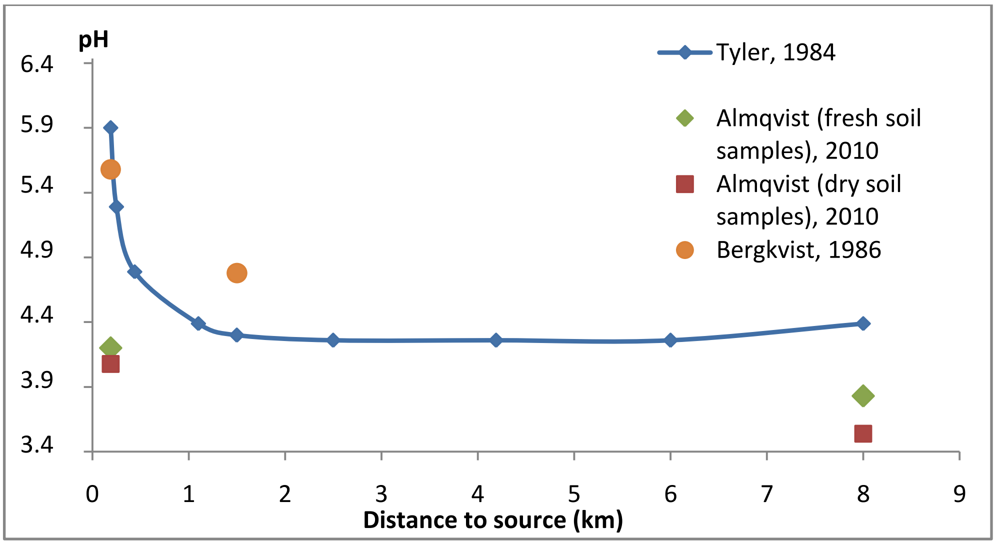

Figure 38. pH as a function of distance from the brass works in Gusum.

6.2 Metal concentrations in soil

Metal analysis both in field and lab showed that the visibly affected part indeed has higher metal concentrations than the forested part of Stångberget. Concentrations of copper, zinc, lead and cadmium increases closer to the old mill. The forested part also has elevated metal concentrations, compared to the reference site, copper and zinc concentrations were above MKM throughout Stångberget. Copper has the highest concentrations compared to guideline values, followed by zinc, lead and finally cadmium. Copper concentrations are well above the levels that cause poisoning and inhibit nitrogen mineralization and nitrification according to previous studies (100-400 mg/kg DM, see Chapter 3.2). Zinc concentrations are above 900 mg/kg DM in ten of the sample points on Stångberget, concentrations that previously has shown to be toxic to plants. Lead concentrations are in the same range as what has shown to inhibit nitrogen mineralization and nitrification (100-500 mg/kg DM) in most cases, and cadmium concentrations are above 2.5 mg/kg DM in most sample points on Stångberget, the level that may be toxic to plants according to previous studies.

On the forested part of Stångberget metal concentrations are lower in the surface layer than further down in the profile. The trees and undergrowth produce new organic matter every year, adding to the mor layer and by dilution gives a surface soil that has lower metal concentrations. On the visibly affected part where the soils are bare no new mor layer has been produced and the highest metal concentrations can be seen in the surface soil. All four metals are strongly adsorbed and thereby move slowly in the soil, which is shown by the generally lower metal concentrations in the 8-12 cm layer. A previous study in Gusum (Bengtsson & Rundgren, 1987) has shown that the metal concentrations decrease drastically with depth in the horizon, being only 30-10 % of what it was in the top 2 cm between 4 and 10 cm. Another explanation to the depth variation could be the organic matter content. The low pH (around pH 4) indicates that the metals are predominantly bound to organic matter which make up 16 % of the soil in the 8-12 cm level and around 40 % in the top soil (Figure 19). On the visibly affected part organic matter content decreases drastically between the 0-4 cm layer and the 4-8 cm layer but it stays more constant on the forested part.

Copper and lead are more strongly adsorbed than zinc and cadmium. That can be seen on Stångberget as copper and lead concentrations are lower in the bottom layer than in the above layers in the profile, in all sample points. Zinc and cadmium on the other hand show the highest concentrations in the bottom layer in some sample points. The low pH suggests that no precipitation has occurred.

A comparison to previous studies (Tyler, 1974, Tyler 1978, Rühling 1983) suggests that the metal concentrations on Stångberget have decreased since the 1970s. Little information on exactly where previous samples were taken makes the results hard to interpret, but samples that are likely to come from Stångberget show copper concentrations of 13 200 – 19 000 mg/kg DM and Zn concentrations of 14 400-25 100 mg/kg DM, all above the maximum concentrations from this study of 10 800 mg/kg DM of copper and 3 140 mg/kg DM of zinc. The reason for this could be that the metal concentrations in the soils have decreased due to leaching to deeper soil layers of out of the soil.

6.3 Leachability

Concentrations measured in leachates from the USGS Field Leach Test gave comparable results to those measured in the surface runoff, which means that the USGS Field Leach Test gives a good estimation of the metal leachability. USGS Field Leach Test and surface runoff gives information on the intensity in leaching at the time of the test. The first step in the sequential extraction gives information on the entire pool of exchangeable metals, i.e. what can be leached. The amount leached momentarily is much smaller than the total amount that can be leached. All methods show that copper and lead are bound more strongly in soil than zinc and cadmium. The sequential extraction shows that copper and lead are found in soil as both exchangeable metals and in complexes with labile organics, whereas zinc and cadmium mainly are found as exchangeable metals.

The amount of metals leaching into the recipient per year can be estimated by multiplying the total infiltrated amount per year over the entire catchment with average concentrations in leachate. An assumption is made, that the average of the samples could represent the whole catchment area which is likely to be an over estimation. The leached amounts found by doing such an estimation can be compared to what is leached from the old mill property itself (Table 8). Leaching in the surface water collected at Stångberget is very low compared to what is leached from the old mill property. Stångberget does not seem to be a major source of metal pollution to the Gusum River compared to other sources in Gusum.

Table 8. Total metal amounts leached from the catchment area per year, according to calculation based on concentrations measured in the Field Leach Test and in surface runoff, compared to the amount that leach from the old mill property according to Eriksson et al. (2009), [kg/yr]

	Field Leach Test	Surface runoff	Mill property
Cu	0.7	0.3	55-560
Zn	1	1	85-430
Pb	0.009	0.003	2-23
Cd	0.004	0.003	0.1-0.4

The fraction of total soil metal content that is leached per year can also be estimated from data on surface runoff and average soil metal concentrations in the visibly disturbed area. Unfortunately the water samples for measurement of metals in the surface runoff by mistake were not taken directly downhill form the area where soils were sampled, which means that concentrations are not directly comparable, but they can give an indication of the fraction leached. The leached fraction is very small compared to the total amount, and it should not influence metal concentrations in Stångberget soils in any considerable way in the short term (

Table 9). The relative magnitude of the fractions leached are in accordance with theory on binding strength; zinc and cadmium leach to a higher extent than the other metals and lead is the metal with lowest relative leaching.

Table 9. Estimated percent of the total amounts of metals in soil that leach from Stångberget in a year

	Zn	Cu	Pb	Cd
% leached in a year (average)	0,09	0,01	0,001	0,04

Metal concentrations measured in previous studies (Tyler, 1974b, Tyler, 1977, Rühling, 1983) were much higher suggesting that a considerable amount of the metals on Stångberget have leached, but if the measured leaching rate is representative only small amounts of metals could have left Stångberget through leaching. Comparing data from a previous leaching study in field lysimeters (Bergkvist, 1986 & 1987) with data from this study shows that the leaching has decreased (Table 10). The reason for this difference is unknown. pH in the area has dropped during the past 30 years and since binding of especially zinc and cadmium, but also to a lesser extent copper and lead, is pH dependent, it is likely that leaching from Stångberget would increase. A possible explanation that it instead has decreased could be that the adsorbed metals with time have formed strong bindings in the soil, which has made them less leachable. That the metals have been transported further down into the soil could be another explanation, but metal analyses suggests that that is not the case on the visibly affected area, since concentrations decrease further down in the profile.

Table 10. Copper and zinc concentrations in leaching waters [µg/L]

	Field Leach Test average	Surface runoff	Lysimeter test (Bergkvist, 1986)
Cu	397	121	904
Zn	675	425	17600
Zn/Cu	1,7	3,5	19

Bergkvist (1986 & 1987) predicted that the zinc/copper ratio would decrease in the soils due to a higher rate of zinc than of copper leaching. Even though the number of samples is not sufficient to statistically conform this it seems as though Bergkvist's prediction was right. The comparison to previous studies also shows that zinc concentrations has decreased much more than copper concentrations.

The concentrations in the leachate can also be compared to guideline values for the protection of water organisms. Most values are above guideline, often far above (Table 11). However, before the leachate from Stångberget will reach water organisms there will be a substantial dilution and the water will probably filter through soils below the hill slope before reaching the river.

Table 11. Concentrations in leachate compared to CCME's guideline values for the protection of aquatic life (CCME, 2007) [µg/L]

	Field Leach Test			Surface runoff	CCME GV
	max	min	average		
Cu	872	101	397	121	2-4
Zn	1350	169	675	425	30
Pb	11.7	1.82	5.17	0.968	1-7
Cd	4.05	0.44	2.05	1.06	0.017

The highest leaching rate according to the USGS Field Leach Test was not correlated to the highest soil metal concentrations. The reason for this is unknown, nothing unusual was noted about the sample point that had the highest leaching.

6.4 Effects on the microbial community

The specific respiration is highest on the visibly affected area. This was expected since microorganisms in a metal contaminated soil will have to spend energy merely on surviving in the polluted environment. Therefore less energy can be spent on producing biomass and the specific respiration (respiration per microbial biomass) will be higher.

Analysis of functional diversity showed that the microorganisms on the visibly affected part of Stångberget clearly differ from the forested part and the reference area. Samples from the forested part could not as clearly be separated from the reference samples, but there was some indication that they differ. The two groups of reference samples (sun exposed and in spruce forest) does not differ systematically, indicating that the difference between the forested and bare part of Stångberget cannot be explained by this factor and that the difference to a large extent is due to metal contamination. That is also confirmed by the canonical correlation analysis, although a large part of the variation is still not explained (see below). The number of reference samples was too small considering the large variation.

Substrate induced respiration (SIR) per gram soil organic carbon (SOC) and hour was used as input for the analysis of the functional profiles instead of the generally used SIR per gram soil and hour. The reason for this was that SOC concentration varied between the sample points, and with it presumably the microbial biomass. As the SIR is dependent on the size microbial biomass calculating SIR/SOC*h was done to minimize the noise of factors that were not to be investigated so that possible variations caused by metal contamination could be seen clearer.

No significant effect of the metal contamination on the microbial community could be seen on the forested part of Stångberget with the used methods, even though the metal concentrations are severely elevated. The specific respiration did not show a significant difference between the forested part and the reference area and the functional profiles only showed a small difference between them. The result was unexpected and could indicate that the microbial community have adapted to the high metal contamination during the many years the microorganisms have lived in the polluted environment. However the metal concentrations in the forested part are so far above guideline values that it is unlikely that microorganisms are not affected by the pollution. Another reason for the results could be that the reference soil was not identical with Stångberget soil (e.g. the soil texture and vegetation was somewhat different). The difficulties of finding good reference soils when performing field experiments is well known (see e.g. Giller et al, 1998), and can, as may be the case here, cause difficulties with interpretations of data. Yet another reason could be that the number of samples was too small to reveal differences between groups with high internal variability.

Sample points 6 and 7 did not follow the same pattern as the other samples from the bare part and were therefore included in the group of samples from the forested part when doing the CAP analysis. Samples 1-5 receive new organic matter every year from the vegetation, whereas the organic matter in samples 8-12 is old, something that is shown by the lower carbon/nitrogen ratio on the bare part of Stångberget. Sample points 6 and 7 might get some new organic matter from the vegetation adjacent to the bare part and therefore behave more like samples under vegetation. If that is the case it is not only the metal concentration in the soil itself that affects the microbial community but also the quality of the organic matter.

One point (9:1) on the visibly contaminated part of Stångberget shows much higher specific respiration than the others. The point corresponds to the sample with the highest metal leaching. Leachability and bioavailability correspond, and sample point 9:1 can therefore be assumed to have the highest concentrations of bioavailable metals among the samples where this was measured, which might be the reason for the high specific respiration. However leaching data is only available for a few sample points, and leaching in the rest of the points is unknown. Samples 1:1 and ref 4:1 also has much higher specific respiration than the others. Sample 1:1 differed from the others in texture, it seemed much drier than it was, and was wetted and then slightly dried again before MicroResp™ measurements, which may have increased the respiration activity of the microbial biomass. Nothing unusual was noted about sample ref 4:1 and the high specific respiration in the sample cannot be explained.

6.5 Vegetation changes with time

The bare part of Stångberget, closest to the old mill, has increased in size since the 1950's according to historical photos (Figure 39). The major increase occurred between the 60's and 2000's. On the photo from 1957 the entire investigated area is forested. In 1968 some bare soil can be seen in the part closest to the old mill and in 1974 the bare part has grown. In the last photo, from 2007, most of the area in the circle is bare. The aerial photos only show if there are trees or not, undergrowth is difficult to see. The flue gas emissions from the old mill ended in the late 1960's when the new area was established in Gräsdalen. This means that most of the trees on Stångberget disappeared after the flue gas emission had stopped. They might have been severely damaged before that, something that is also difficult to see from the aerial photos.

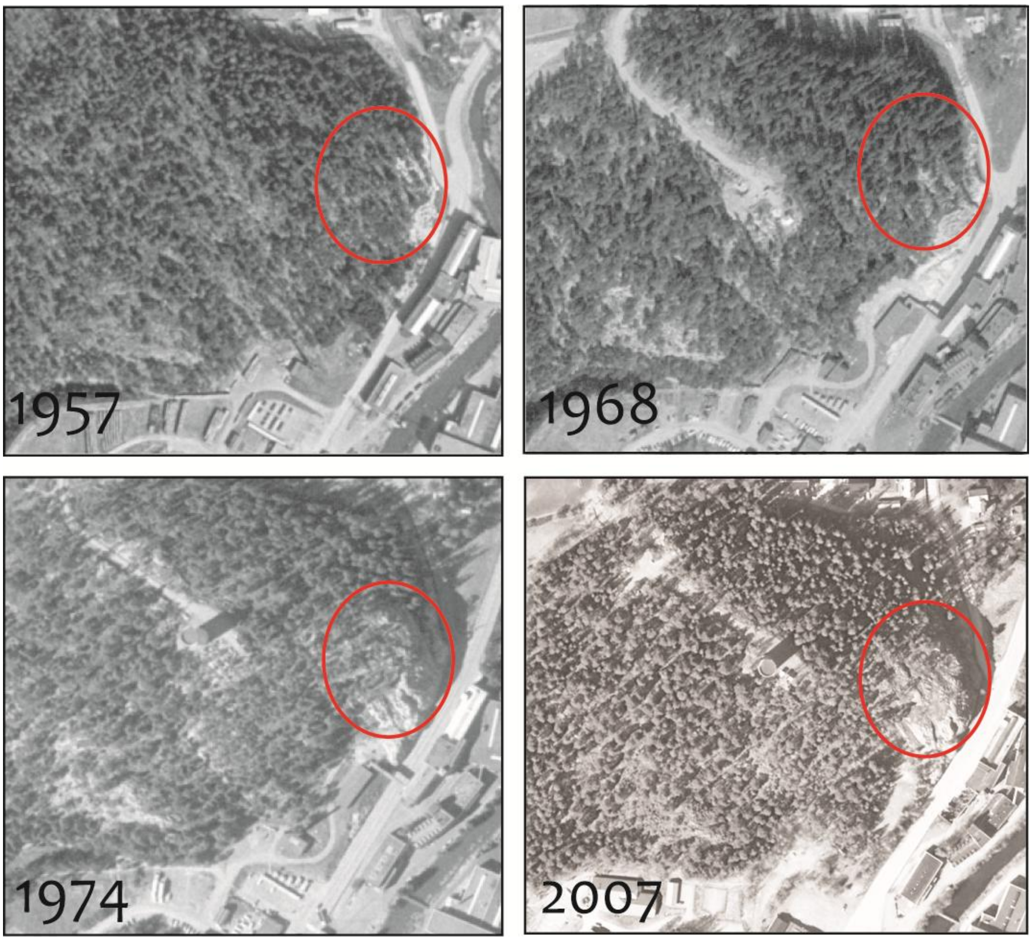

Figure 39. Ortho photos of Gusum from 1957, 1968, 1974 and 2007. Bare part of investigated area in red circle. (Photos from county administration board of Östergötland).

In the future it is not likely that the visibly disturbed area will be naturally remediated at the same rate as has occurred in the forested part (where new mor layer is covering the soil layers with highest metal concentrations) simply because there is no vegetation that can produce new mor. One possibility is that litter from the vegetation near the bare part can fall on adjacent bare soil and thereby produce new mor layer that enables a progressive establishment of new vegetation on the bare part. However this would be a very slow process. The metal concentrations are also so much higher on the visibly disturbed part that it might not be enough with a new mor layer for plants to be able to grow on the soils. The aerial photos do not show that any decrease of the bare part has occurred since the mill was moved.

6.6 Further studies

The need for further studies can be divided into two subareas; research and remediation project.

6.6.1 Further studies from a research point of view

This study should be seen as a pilot investigation and more studies are needed on the soils of Stångberget. More samples to give better certainty of the results is one way of continuing the research. One example where this could be interesting is for the Field Leach Test, where the only two sample points on the visibly affected part showed very varying leachability. By analyzing further samples more could be said about the leachability pattern. The fact that the sequential extraction was performed only on the sample with the highest leachability makes it interesting to test the sequential extraction also on another sample.

In this study the visibly affected, bare part of Stångberget and the part where the forest looks natural with healthy trees and thick undergrowth were investigated. Stångberget also has a third type of nature, in the southern part of the hill, where trees are alive but the undergrowth is missing. It would be interesting to further study that part of the hill. The XRF showed that levels of copper, zinc, lead and cadmium were high also in that part, but no other analyses were performed in this study.

The MicroResp™ analyses would be interesting to follow up, since results were somewhat unexpected. One possibility could be to use other substrates, another to investigate further samples from the reference area.

6.6.2 Fulfillment of goals and further studies needed within the remediation project

In the project plan some goals with the remediation project and a number of questions to be answered are stated (Golder, 2009). One of the goals is that the public should be able to use accessible areas with no health risks. Concentrations of several metals are far above the generic guideline values from SEPA, but to be able to tell if that means that humans are at risk more information is needed. Another goal is that the ecologically disturbed soils should decrease in size. This will not happen naturally on Stångberget and remediation measures are needed to fulfil the goal.

A number of the questions concerning the visibly affected soils are answered in this report, while some further studies are needed to answer others. *Which are the dimensioning elements for soil environment risks?* and *How are the metals spread?* are to a large extent answered, whereas further investigations are needed to answer *How large are the ecologically disturbed areas?* and *Which are the risks with the contaminants for human health and nature? Possible remediation measures* have not been part of the scope of this study but could e.g. be the scope of another thesis project.

A continuation of the study of Stångberget will be to perform a risk assessment. A lot of the information needed can be found in this report, but some further information needs to be obtained. The *source* of risk has been investigated and it is clear that the soil environment is disturbed and that concentrations of the four metals investigated in this study are severely elevated in relation to the generic guideline values from SEPA. There is however no information on who or what that is at risk because of the increased concentrations, and thereby no information on who or what *to protect*. Leaching has been investigated and found to be low but other *transport pathways*, e.g. ground water or dusting, have not been identified, nor quantified. *Protective barriers* have been somewhat investigated, as to how metals are bound in soil, but other barriers could also be investigated.

It is important to find a way of delimiting the area of investigation. In the project plan one of the questions is *How large are the ecologically disturbed areas?*. To be able to answer that one must first decide what to consider as ecologically disturbed. The bare part on Stångberget is clearly ecologically disturbed but whether the forested part is ecologically disturbed is more difficult to answer. Metal concentrations are severely elevated, but microorganisms are not clearly affected and vegetation is growing on the soils. Tools to use to delimit the area can e.g. be guideline values, either generic ones or site specific guideline values, which can be developed using a method from SEPA. Visible investigations, i.e. the visible border between bare and forested soil or other indicators, such as the microbial functional profiles, which have been investigated in this study, can also be used.

When the risk assessment is performed the next step is a measure proposal. Important parts of a measure proposal are to delimit the area and find the volumes that need to be treated. If soils are to be sent to a landfill standard leaching tests are required. To delimit the heavily polluted areas based on metal concentrations XRF measurements in field can be used. Correlation analysis showed that the XRF generally showed lower concentrations than the lab analysis which is something that needs to be considered it the XRF is to be used in further studies.

A *handling plan* for polluted soil volumes will be established as part of the remediation project. Data from this study can be used as inputs.

Other visibly affected areas in Gusum

The other visibly affected areas also need to be investigated, but assuming that the other areas have similar properties as Stångberget the investigations do not have to be as thorough as this study, and background information from Stångberget can be used. XRF measurements supplemented with a few lab analyses could be a good start. Metal concentrations in surface runoff can be a good measure of leaching, if it can be ensured that the water has been in contact with the polluted soil.

7 Conclusions

Metal concentrations on Stångberget were severely elevated for copper, zinc, lead and cadmium. Copper was the metal showing highest values above guidelines, with a concentration 50 times the guideline value for less sensitive land use on the worst affected point. Zinc, lead and cadmium followed, in that order. Copper and zinc showed levels above the guideline value for less sensitive land use over the entire transect. Levels were higher on the visibly contaminated part than on the forested part and metal concentrations followed the sharp visible line between the two sub areas. On the forested part metal levels were lower in the surface than further down in the profile, suggesting production of a new mor layer, covering the worst contaminated soil layers.

A drastic increase in pH close to the mill was shown in earlier investigations, but in this study pH was found to be around 4 which is normal for the soil type. This suggests that the pH raising effect of the metal oxides has disappeared. A pH drop can cause increased leachability of metals. However in this study the leachability tended to be lower than in previous studies, although leachability was measured in few places and no clear conclusions can be drawn. Available data on leachability of metals at Stångberget indicates that the amounts lost annually are small in comparison to the total metal stores in the soil. Data also indicate that leaching from Stångberget is a small source of metals to the Gusum River, in comparison to the old mill property.

Microorganisms in the visibly affected part of Stångberget were affected by the metal contamination, which was shown by an increased specific respiration. The difference between the forested part of Stångberget and the reference area was not as clear, even though metal concentrations in the forested part were severely elevated. The effect on microorganisms could to a large extent be explained by the metal contamination.

Historical orthophotos showed that the visibly contaminated area had increased in size over the last 50 years. There was no sign of a natural decrease of the size of the area in the future which means that remediation measures are needed if the bare part shall decrease in size.

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In the process of writing this thesis valuable input, ideas and help have been offered from several persons. I would therefore like to thank my external supervisor **Henrik Eriksson** (consultant at Golder Associates AB), my supervisors at SLU **Jan Eriksson** and **Sigrun Dahlin** (researchers at Department of soil and environment, SLU), **Annette Källman** (project leader at the Municipality of Valdemarsvik), **Magnus Broström** (Municipality of Valdemarsvik), **Thomas Lerch** (PhD student at Department of chemistry, SLU) and **Ebba Wadstein** (SGI). Thank you!

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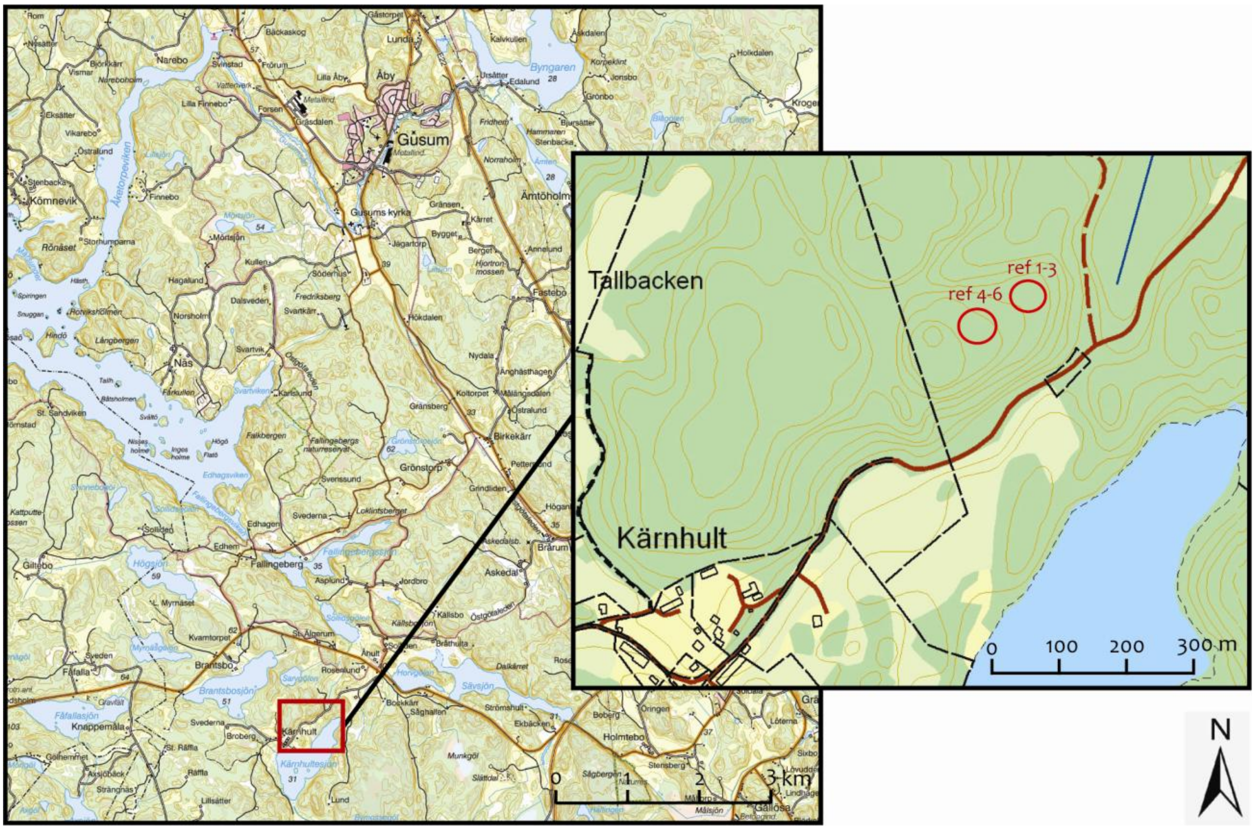
Appendix A:
Sample locations

Stångberget

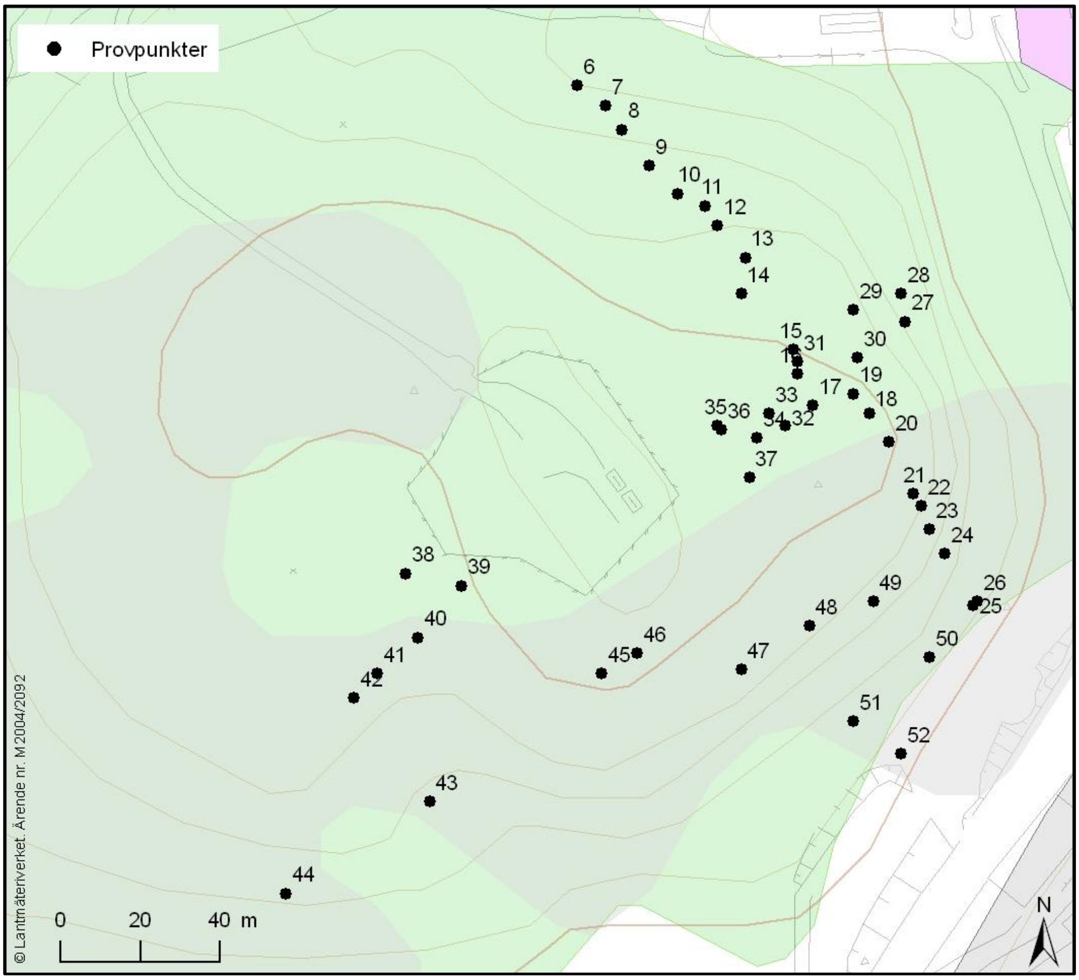
	1			2			3	4	5			6			7	8	9			10	11	12		
	0-4	4-8	8-12	0-4	4-8	8-12	0-4	0-4	0-4	4-8	8-12	0-4	4-8	8-12	0-4	0-4	0-4	4-8	8-12	0-4	0-4	0-4	4-8	8-12
Metals	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x	x	x	x	x
FLT				x	x												x	x				x	x	
Seq. Ex																	x							
MicroR	x			x			x	x	x			x			x	x	x			x	x	x		
ANC				x													x							
C/N	x	x		x	x		x	x	x	x		x	x		x	x	x	x		x	x	x	x	
Texture																			x					
Soil pH	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Depth		x			x		x	x		x			x		x	x		x		x	x		x	

Reference area near Kärnhult



	ref 1			ref 2	ref 3	ref 4			ref 5	ref 6
	0-4	4-8	8-12	0-4	0-4	0-4	4-8	8-12	0-4	0-4
Metals	x	x		x	x	x	x		x	x
FLT	x									
Seq. Ex										
MicroR	x			x	x	x			x	x
ANC	x								x	
C/N	x	x		x	x	x	x		x	x
Texture			x							
Soil pH	x	x	x	x	x	x	x	x	x	x
Depth		x		x	x		x		x	x

XRF measurements sample points

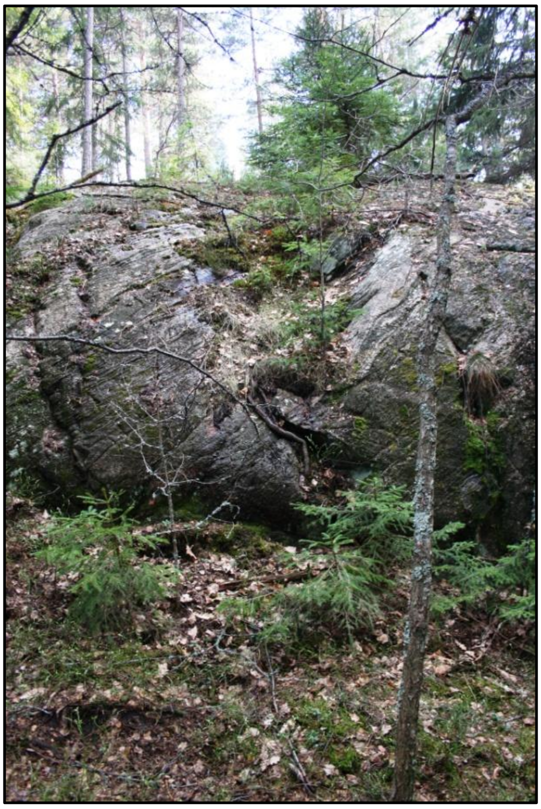


Appendix B:
Photos of sample points

Sample point 1

Sample point 2

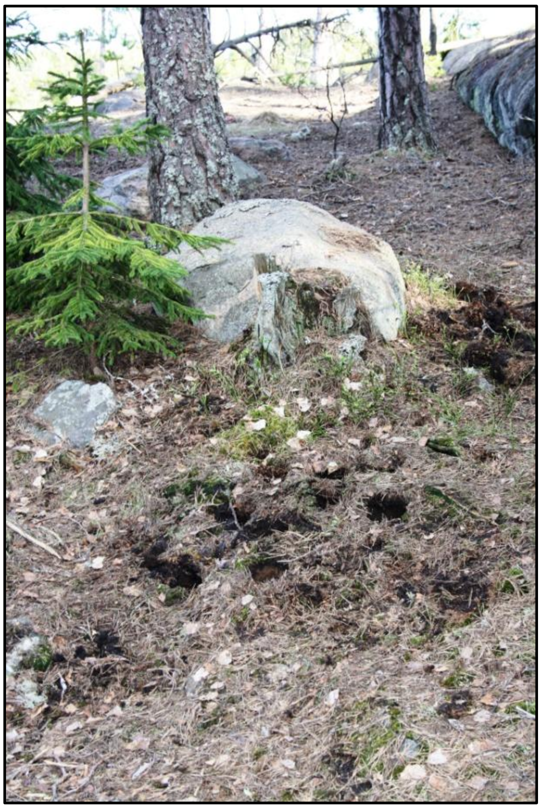
Sample point 3



Sample point 4

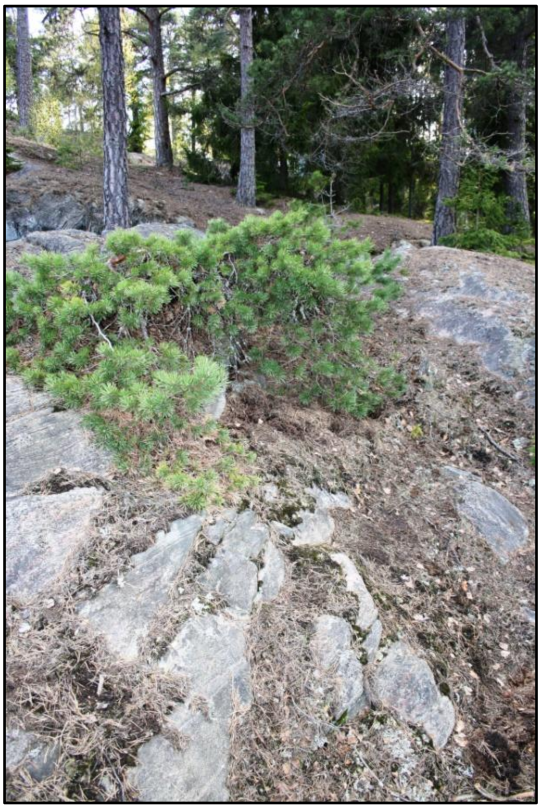
Sample point 5

Sample point 6



Sample point 7

Sample point 8



Sample point 9

(soil core is upside down)

Sample point 10

Sample point 11

Sample point 12

Reference sample point ref 1

Reference sample point ref 2

Reference sample point ref 3

Reference sample points ref 4 – ref 6

Appendix C:
Summary of results from lab analysis

XRF and MicroRespTM excluded

Metals

	Sample no	**1:1**	**1:2**	**1:3**	**2:1**	**2:2**	**2:3**	**3:1**	**4:1**	**5:1**	**5:2**
	Order no	L1008889	L1008889	L1012932	L1009098	L1008889	L1012932	L1008889	L1008889	L1008889	L1008889
%	**TS**	45,4	60,6	70,4	18,4	32,6	28,5	53,6	26,9	26	29,9
mg/kg TS	**As**	0,804	2,63	5,16	1,17	3,89	5,56	3,41	1,86	0,546	2,13
mg/kg TS	**Cd**	1,03	2,29	1,38	1,75	2,92	3,56	1,58	2,32	1,34	2,75
mg/kg TS	**Co**	0,739	2,3	1,91	1,08	2,07	1,63	2,38	1,01	0,5	1,13
mg/kg TS	**Cr**	2,81	8,13	6,62	3,56	11,9	12	9,03	4,8	1,58	4,06
mg/kg TS	**Cu**	322	2410	481	223	989	729	487	1160	168	1250
mg/kg TS	**Fe**	1850	5500	10300	2230	10400	12000	10500	3870	1050	2700
mg/kg TS	**Hg**	0,245	0,419	0,147	0,283	0,326	0,288	0,0987	0,447	0,156	0,318
mg/kg TS	**Mn**	226	189	125	294	73,8	106	139	144	208	77
mg/kg TS	**Ni**	4,78	10,5	4,56	4,71	5,2	4,52	6,86	6,44	3,63	7,28
mg/kg TS	**Pb**	86,8	395	106	138	196	115	102	270	51,4	259
mg/kg TS	**V**	8,44	31,7	21,2	10,4	19,6	16,1	28,7	18,2	4,65	16,5
mg/kg TS	**Zn**	537	1210	299	462	369	371	298	808	672	1650

Metals

	Sample no	**5:3**	**6:1**	**6:2**	**7:1**	**8:1**	**9:1**	**9:2**	**9:3**	**10:1**	**11:1**	**12:1**	**12:2**
	Order no	L1012932	L1008889	L1008889	L1008889	L1008889	L1009098	L1008889	L1012932	L1008889	L1008889	L1008889	L1008889
%	**TS**	25,6	35,4	49,2	33,2	52,2	49,7	46,8	63,5	52,1	42,6	30	47,6
mg/kg TS	**As**	3,27	3,8	3,19	2,6	6,24	10,2	7,98	6,07	5,69	10,5	7,56	7,97
mg/kg TS	**Cd**	4,84	5,05	4,1	3,79	3,38	8,07	4,25	2,54	2,91	13,7	18	7,16
mg/kg TS	**Co**	1,18	1,39	5,19	0,944	3,25	3,3	3,09	3,68	3,4	2,13	5,42	9,06
mg/kg TS	**Cr**	1,98	5,13	12,2	7,66	17,6	18	19,2	21,9	11,3	14,4	16,3	17,3
mg/kg TS	**Cu**	1270	1580	402	3980	2020	3710	1330	112	3220	3240	10800	1970
mg/kg TS	**Fe**	1970	6720	21400	4370	13200	20400	22700	25300	12800	15400	17400	24700
mg/kg TS	**Hg**	0,318	0,243	0,127	0,401	0,239	0,252	0,151	0,073	0,191	0,367	0,571	0,208
mg/kg TS	**Mn**	52,9	438	902	166	388	306	249	284	519	216	739	600
mg/kg TS	**Ni**	6,09	6,2	5,52	9	12,8	13,3	9,99	7,55	11,1	12,8	15,8	9,36
mg/kg TS	**Pb**	79,2	252	63,4	691	374	429	264	89,8	590	424	1140	325
mg/kg TS	**V**	8,27	20,7	29,5	35,9	38,2	42,9	43,4	37,3	50,9	44,1	65,3	41,6
mg/kg TS	**Zn**	1990	1160	802	949	648	1420	959	552	571	3140	2920	987

Metals

	Sample no	**12:3**	**Ref 1:1**	**Ref 1:2**	**Ref 2:1**	**Ref 4:1**	**Ref 5:1**	**MKM**	**KM**	**background**
	Order no	L1012932	L1009098	L1008889	L1008889	L1008889	L1008889	(NV, 2009c)	(NV, 2009c)	(NV, 2009c)
%	**TS**	54,2	26	25,2	26,7	23,4	26,4			
mg/kg TS	**As**	5,23	2,56	2,95	2,6	0,97	1,25	40	20	10
mg/kg TS	**Cd**	4,91	1,25	1,42	0,799	0,631	0,349	20	4	0,2
mg/kg TS	**Co**	9,4	0,681	0,911	0,779	0,509	0,516	35	20	10
mg/kg TS	**Cr**	18,4	2,51	2,26	2,73	1,85	2,3	150	80	30
mg/kg TS	**Cu**	468	11,9	11,4	12,7	8,87	7,3	200	80	30
mg/kg TS	**Fe**	24500	1790	2350	1810	1110	1450			
mg/kg TS	**Hg**	0,0847	0,273	0,279	0,305	0,234	0,258	10	5	0,1
mg/kg TS	**Mn**	466	43,7	27,4	77	199	183			
mg/kg TS	**Ni**	6,59	4,12	4,5	3,67	3,6	3,91	120	70	25
mg/kg TS	**Pb**	129	95,7	107	91,6	44,6	54,9	400	200	15
mg/kg TS	**V**	33,5	6,62	6,27	7,46	4,51	5,55	200	100	40
mg/kg TS	**Zn**	492	112	135	107	99,4	79,2	500	250	70

pH

sample	1:1	1:2	1:3	2:1	2:2	2:3	3:1	4:1	5:1	5:2	5:3	6:1	6:2	6:3	7:1	8:1	9:1
pH	3,97	4,00	4,35	3,81	4,20	4,21	4,78	3,85	4,04	3,99	3,87	4,27	4,76	4,76	3,91	4,01	4,22

sample	9:2	9:3	10:1	11:1	12:1	12:2	12:3	Ref1:1	Ref1:2	Ref1:3	Ref2:1	Ref3:1	Ref4:1	Ref4:2	Ref4:3	Ref5:1	Ref6:1
pH	4,51	4,79	4,31	4,56	4,71	4,95	4,77	3,46	3,58	3,89	3,85	3,68	3,87	3,88	3,87	4,23	3,86

ANC

Sample no		2:1	9:1	Ref 1:1	Ref 5:1
Order no		L1009099	L1009099	L1009099	L1012933
ANC at pH 4,0	mol/kg DM	0.012	0.028	-----	------
pH		4.40	4.85	3.3	3.7

Carbon and nitrogen

Sample no	1,1	1,2	2,1	2,2	3,1	4,1	5,1	5,2	6,1	6,2	7,1	8,1	9,1	9,2	10,1	11,1	12,1	12,2
Tot-C %	45,04	41,81	39,18	33,89	14,17	45,75	46,23	45,76	38,69	17,67	45,36	36,1	39,29	9,885	22,37	31,65	32,74	9,884
Tot-N %	1,58	1,64	1,54	1,26	0,681	1,41	1,41	1,43	1,64	0,773	1,89	1,43	1,51	0,41	1,13	1,3	1,41	0,457
C/N	29	25	25	27	21	32	33	32	24	23	24	25	26	24	20	24	23	22

Sample no	Ref 1.1	Ref 1:2	Ref 2.1	Ref 4.1	Ref 5.1
Tot-C %	46,71	26,68	45,56	47,8	37,09
Tot-N %	1,32	0,61	1,52	1,43	1,26
C/N	35	44	30	33	29

Texture

	Clay		Silt			Sand			
		"Fin mjäla"	"Grov mjäla"	"Fin mo"	Fine	Medium	Coarse	Gravel	LOI
	d<0,002	,002-0,006	0,006-0,02	0,02-0,06	0,06-0,2	0,2-0,6	0,6-2	2.0-20	%
9:3	10	5	11	16	18	14	10	15	16
ref 1:3	7	4	14	19	22	27	8	0	19

Surface Runoff

	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K
Conc in leachate	41,3	0,176	4,98	1,09	1,06	0,153	0,131	121	0,0248	0,0051	<0,4
Unit	µg/l	µg/l	µg/l	mg/l	µg/l	µg/l	µg/l	µg/l	mg/l	µg/l	mg/l

	Mg	Mn	Mo	Na	Ni	P	Pb	Sb	Si	Sn	Sr	Zn
Conc in leachate	0,101	19,1	0,193	0,502	0,735	5,58	0,968	0,299	1,17	0,0608	2,86	425
Unit	mg/l	µg/l	µg/l	mg/l	µg/l	µg/l	µg/l	µg/l	mg/l	µg/l	µg/l	µg/l

USGS Field Leach Test - leachate

	Sample no	**ref 1:1**	**2:1**	**2:2**	**9:1**	**9:2**	**12:1**	**12:2**
	Order no	L1012800	L1012800	L1012800	L1012800	L1012800	L1012800	L1012800
	Filtered	NO	NO	NO	NO	NO	NO	NO
mg/l	**Ca**	0,289	0,668	0,317	1,16	0,715	0,605	0,414
mg/l	**Fe**	0,0903	0,335	0,657	0,137	0,27	0,104	0,0686
mg/l	**K**	4,32	14,2	6,33	3,45	1,43	0,811	0,551
mg/l	**Mg**	0,155	0,253	0,196	0,266	0,155	0,113	0,1
mg/l	**Na**	1,35	0,642	0,401	0,925	0,352	0,161	0,13
mg/l	**Si**	0,323	0,277	0,207	0,265	0,183	0,235	0,252
µg/l	**Al**	349	696	785	276	329	392	262
µg/l	**As**	1,06	0,671	1,25	1,01	1,38	0,5	0,201
µg/l	**Ba**	4,08	10,8	8,75	25,5	10,6	10,2	9,63
µg/l	**Cd**	0,299	0,44	0,739	2,68	1,28	4,05	3,14
µg/l	**Co**	0,154	0,336	0,358	0,399	0,17	0,429	0,224
µg/l	**Cr**	0,197	0,267	0,398	0,262	0,304	0,29	0,204
µg/l	**Cu**	2,43	101	124	872	603	513	171
µg/l	**Hg**	0,0556	0,0339	0,0229	0,0376	0,0278	0,0111	0,0087
µg/l	**Mn**	15	98,9	39,8	83,1	47,5	100	52,2
µg/l	**Mo**	0,326	0,941	0,303	0,481	0,365	0,117	<0,05
µg/l	**Ni**	0,626	1,35	1,15	2,57	1,36	2,1	1,69
µg/l	**P**	2420	4900	1330	1210	568	172	83,4
µg/l	**Pb**	2,58	3,5	3,15	11,7	5,19	5,65	1,82
µg/l	**Sb**	0,237	0,191	0,322	0,487	0,591	0,462	0,341
µg/l	**Sn**	0,0914	0,682	0,245	0,964	0,391	0,12	<0,05
µg/l	**Sr**	3,36	5,21	3,43	6,86	2,61	2,59	<2
µg/l	**Zn**	26	180	169	1350	435	1060	854
	pH	3,54	3,82	4	4	4,14	4,41	4,61

Sequential extraction

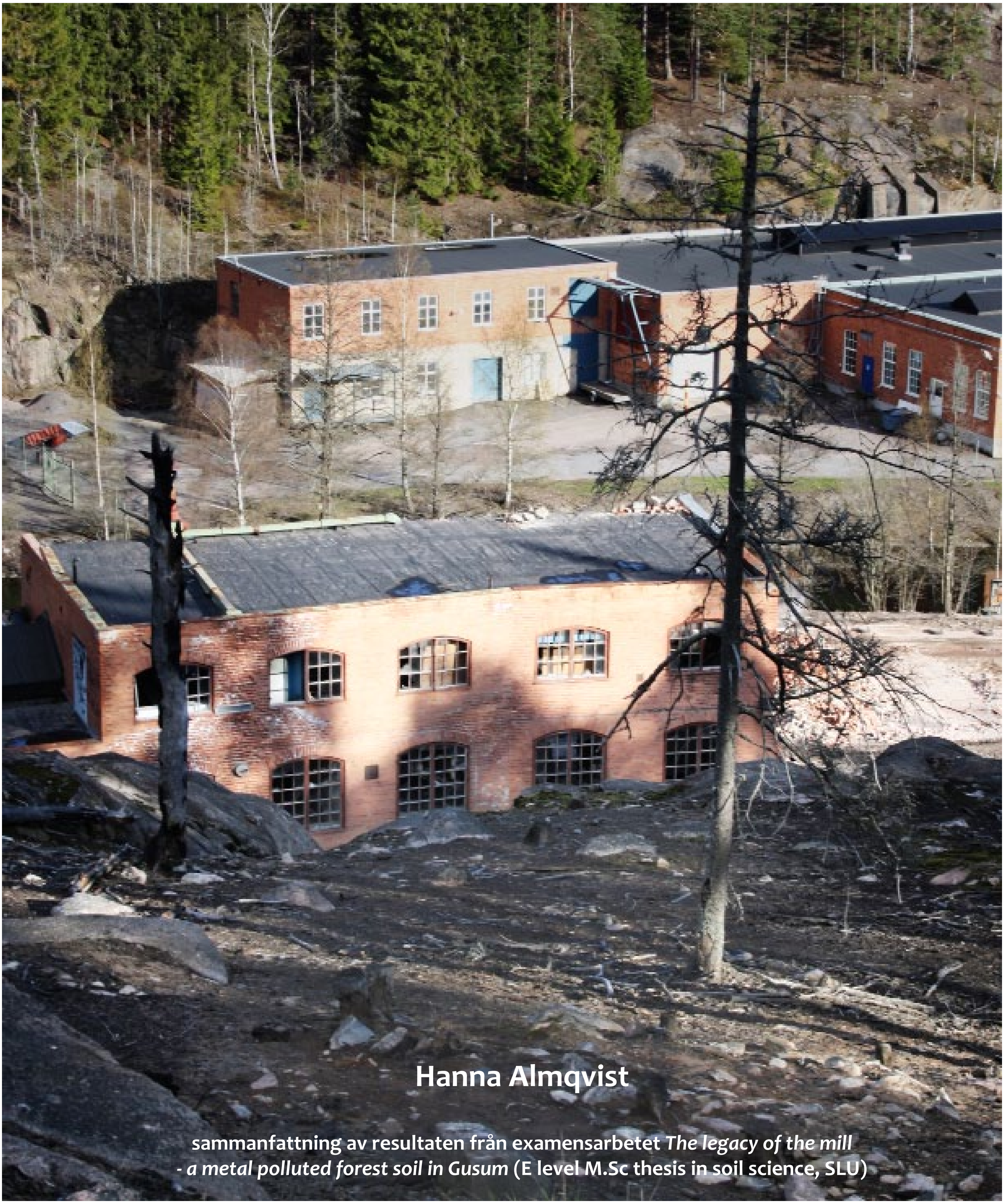
		Before leaching	**After leaching**
	Sample no	**9:1**	**9:1**
	Order no	L1011841	L1011843
%	**TS**	50,9	
% TS	**SiO2**	37,1	52,2
% TS	**Al2O3**	8,26	7,57
% TS	**CaO**	1,22	1,54
% TS	**Fe2O3**	4,48	1,43
% TS	**K2O**	1,44	1,87
% TS	**MgO**	0,659	0,583
% TS	**MnO**	0,0542	0,0271
% TS	**Na2O**	1,2	1,73
% TS	**P2O5**	0,432	0,0338
% TS	**TiO2**	0,342	0,294
% TS	**Summa**	55,2	67,3
% TS	**LOI**	43,3	
mg/kg TS	**As**	10,1	1,07
mg/kg TS	**Ba**	342	348
mg/kg TS	**Be**	1,66	1,31
mg/kg TS	**Cd**	4,96	0,376
mg/kg TS	**Co**	3,92	2,77
mg/kg TS	**Cr**	66,9	66,7
mg/kg TS	**Cu**	1740	13,2
mg/kg TS	**Hg**	0,263	0,0484
mg/kg TS	**Mo**	<6	<6
mg/kg TS	**Nb**	<6	<6
mg/kg TS	**Ni**	17,3	9,92
mg/kg TS	**Pb**	308	14
mg/kg TS	**S**	1040	362
mg/kg TS	**Sb**	1,94	1,54
mg/kg TS	**Sc**	4,36	2,74
mg/kg TS	**Sn**	21,1	7,36
mg/kg TS	**Sr**	95,1	125
mg/kg TS	**V**	69,3	31,1
mg/kg TS	**W**	<60	<60
mg/kg TS	**Y**	9,97	12,2
mg/kg TS	**Zn**	905	242
mg/kg TS	**Zr**	128	173

	Step 1	**Step 2**	**Step 3**	**Step 4**	**Step 5**
Sample no	**9:1**	**9:1**	**9:1**	**9:1**	**9:1**
Order no	L1011842	L1011842	L1011842	L1011842	L1011842
mg/kg TS					
Ca	694,0953	223,7986	78,82905	159,8561	99,91008
Fe	1371,566	7687,481	4106,304	4356,08	1378,759
Mg	88,94395	100,7094	275,1524	511,5396	226,2963
S	198,2536	223,7986	59,94605	314,9166	584,474
Al	1072,315	6557,298	2053,152	1778,399	904,1862
As	0,288444	23,27505	1,291837	2,130083	9,991008
Ba	33,41633	18,01579	11,92926	3,824558	2,257968
Cd	3,49957	0,32227	0,401639	0,879209	0,117394
Co	0,702408	0,597542	0,467579	0,671396	0,392647
Cr	2,527006	6,635628	2,964332	2,805475	5,545009
Cu	602,6576	990,3087	199,6203	186,632	60,4456
Hg	0,000831	0,004879	0,002296	0,087521	0,038665
Mn	130,0909	48,89999	29,13378	30,69238	9,441503
Ni	2,514537	3,356979	2,221001	3,113198	1,568588
Pb	110,5565	100,7094	58,74713	14,86662	1,678489
Zn	536,1575	119,7322	59,34659	112,6986	25,62694

Appendix D: Extensive summary in Swedish

Arvet efter bruket

- en metallförorenad skogsjord i Gusum



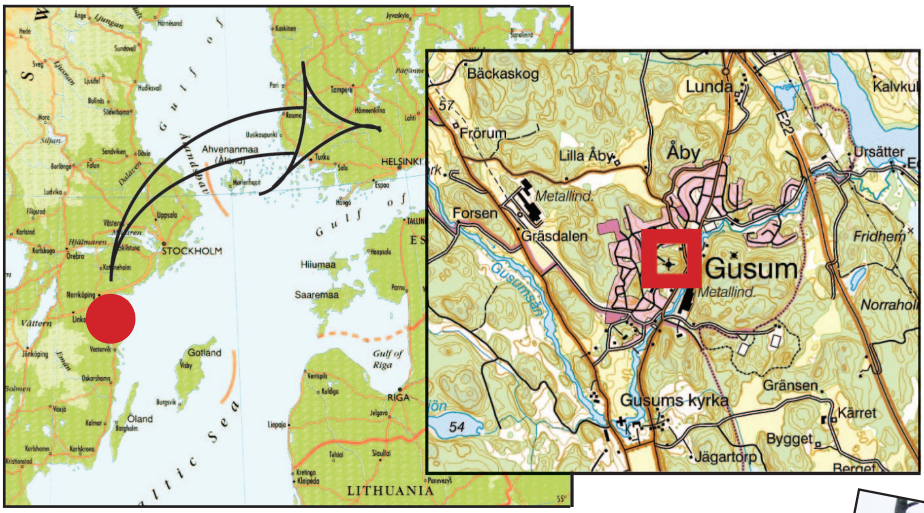
Hanna Almqvist

sammanfattning av resultaten från examensarbetet *The legacy of the mill*
- a metal polluted forest soil in Gusum (E level M.Sc thesis in soil science, SLU)

Gusum är ett brukssamhälle.
I över 300 år försedde mässningsbruket samhället Gusum med arbete, mat och kultur, infrastruktur och föreningsliv. Bruket har flera gånger satt Gusum på kartan; som Sveriges första och största blixtlåsfabrik, som tillverkare av magnifika ljuskronor och miljontals knappnålar och som skådeplatsen för en av Sveriges största ekonomiska skandaler sedan andra världskriget. Och så för de metallförorenade markerna.

De metallförorenade markerna omkring Gusum är resultat av århundraden av rökgasutsläpp. Samtidigt som mässingsbruket byggde upp Gusum orsakade det också stor förödelse genom att rökgaserna från smältugnarna orenade släpptes ut över omgivningarna. Resultatet av denna kraftiga förorening syns än idag när man kommer in i samhället, stora områden som tidigare varit skogsbevuxet har avskogats, berg ligger i dagen och de tunna jordlagren hyser varken växter eller djur. Ett av dessa störda områden finns på Stångberget, ett litet berg mitt inne i samhället. Inom ramen för ett examensarbete i markvetenskap har Stångbergets jordar undersökts. Den här broschyren är en populärvetenskaplig sammanfattning av resultaten från studien.

Stångberget i Gusum.



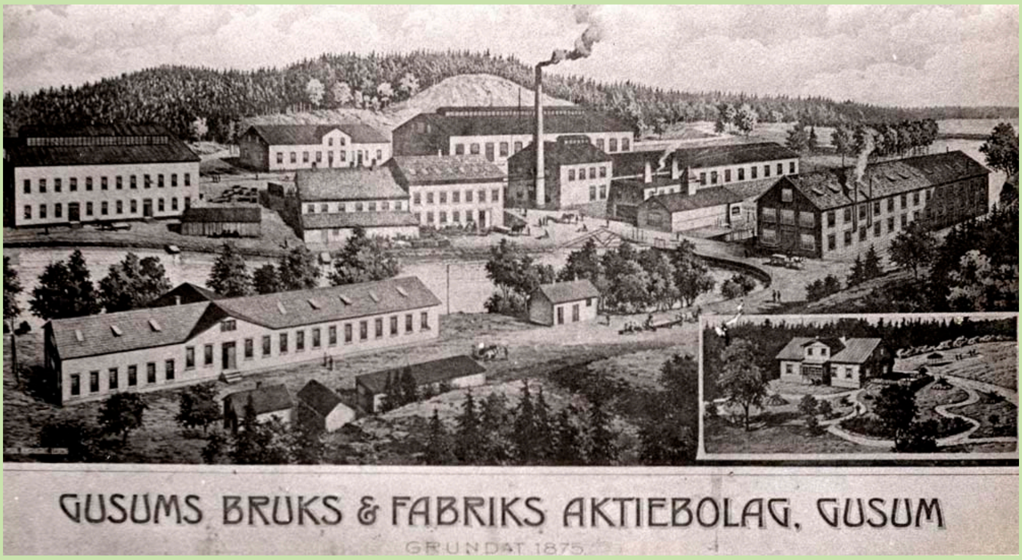
Gusum ligger i Valdemarsviks kommun, Östergötlands län. Mitt i Gusum ligger det gamla mässingsbruket och strax nordväst om bruket ligger Stångberget, som är fokus för denna studie.

Marken på Stångberget bär tydliga spår av metallföroreningen.

Gusums bruk - Tre århundraden av mässingsbruk

Metallindustrin i Gusum grundades på 1600-talet. Området passade mycket bra för ett metallbruk, där fanns stora skogar för träkol, små vattenfall för vattenkraft och bra transporter på Gusumsån. Vid slutet av 1600-talet var Gusums bruk det tredje största mässningsbruket i Sverige och vid sin guldålder var det dubbelt så stort som alla andra mässingstillverkare i Skandinavien tillsammans. Men en minskad svensk konfektionsindustri och avstannande byggindustri gjorde att brukets lönsamhet i slutet av 1900-talet började minska. 1988 förklarades företaget bankrutt.

Bruket hade påverkat sin omgivning på många olika sätt. Gusumsån, som rinner genom bruksområdet, var förorenad med tungmetaller och PCB, förorenat fyllnadsmaterial hade spridits ut över nästan hela bruksområdet och orenade rökgaser hade orsakat allvarliga skador på stora ytor i omgivande marker.



Saneringen av Gusums bruk

År 2002 inleddes undersökningar av föroreningssituationen i Gusum. Eftersom företaget som orsakat föroreningarna inte längre existerar står Naturvårdsverket tillsammans med Valdemarsviks kommun för kostnaderna.

Under 2010 inleddes själva saneringsarbetet med rivning av bruksbyggnaderna.

De förfallna fabriksbyggnaderna är ett numer ett minne blott.

Gusumprojektet

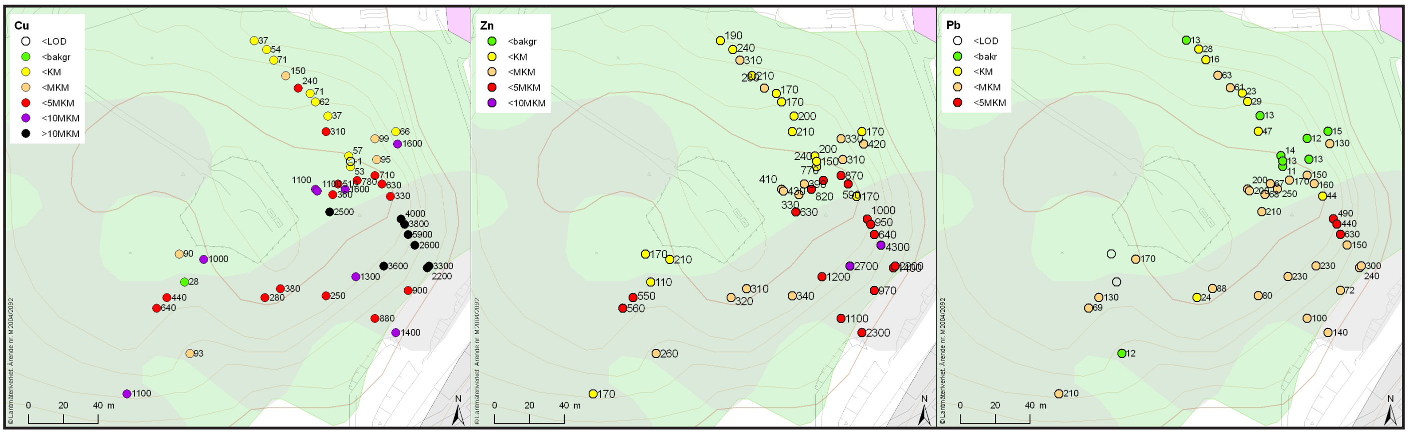
Gusum har länge varit ett välstuderat forskningsobjekt. Redan i början av 1970-talet började forskare studera skogarna kring Gusum. Man ville undersöka hur skogarnas ekosystem påverkas av tungmetaller och Gusum var en perfekt plats att göra det på. Området var glest befolkat, med mycket barrskog omkring och de enda luftutsläppen kom från bruket. Från tidigt 1970-tal till mitten av 1980-talet pågick i Gusum en av dåtidens mest omfattande studier av tungmetallförorenings inverkan på skogsekosystem. Både markprocesser och markorganismer studerades och man såg att många av dessa var kraftigt påverkade av metallföroreningen.

Flera olika analysmetoder för grundlig karaktärisering

Den förorenade jorden på Stångberget har undersökts ingående med hjälp av flera olika analysmetoder, samt teoretiska och geografiska studier. Metallinnehållet i marken undersöktes både med en snabb fältmetod (XRF) och laboratorieanalyser. För att få information om i vilken form metallerna fanns och hur mycket av dem som lakade från marken gjordes en avancerad femstegslakning och enklare fältskakförsök. Regnvatten som runnit genom den förorenade jorden analyserades också. Om mikroorganismerna i jorden var påverkade av metallföroreningarna eller inte undersöktes genom att titta på deras respiration. För att kunna tolka data undersöktes även pH, textur, kol- och kvävehalt samt buffringskapacitet. Historiska flygbilder studerades för att se om det kala områdets storlek förändrats med tiden.

Jordprover togs längs en linje, från det kala området närmast det gamla bruket och vidare bort från bruket in i den skogsbevuxna delen av Stångberget. För jämförelse togs dessutom prov från ett liknande skogsområde som inte var förorenat av metallerna från bruket.

Proverna på Stångberget togs i en linje bort från bruket.



Resultat från XRF-undersökningarna visade att halterna av koppar, zink och bly var kraftigt förhöjda närmast bruket. På kartorna här ovanför är provpunkterna markerade med olika färg beroende på hur förhöjda metallhalterna är. XRF-mätning är snabbt och billigt och därför kunde mätningar utföras i betydligt fler punkter än övriga analyser.

Resultat

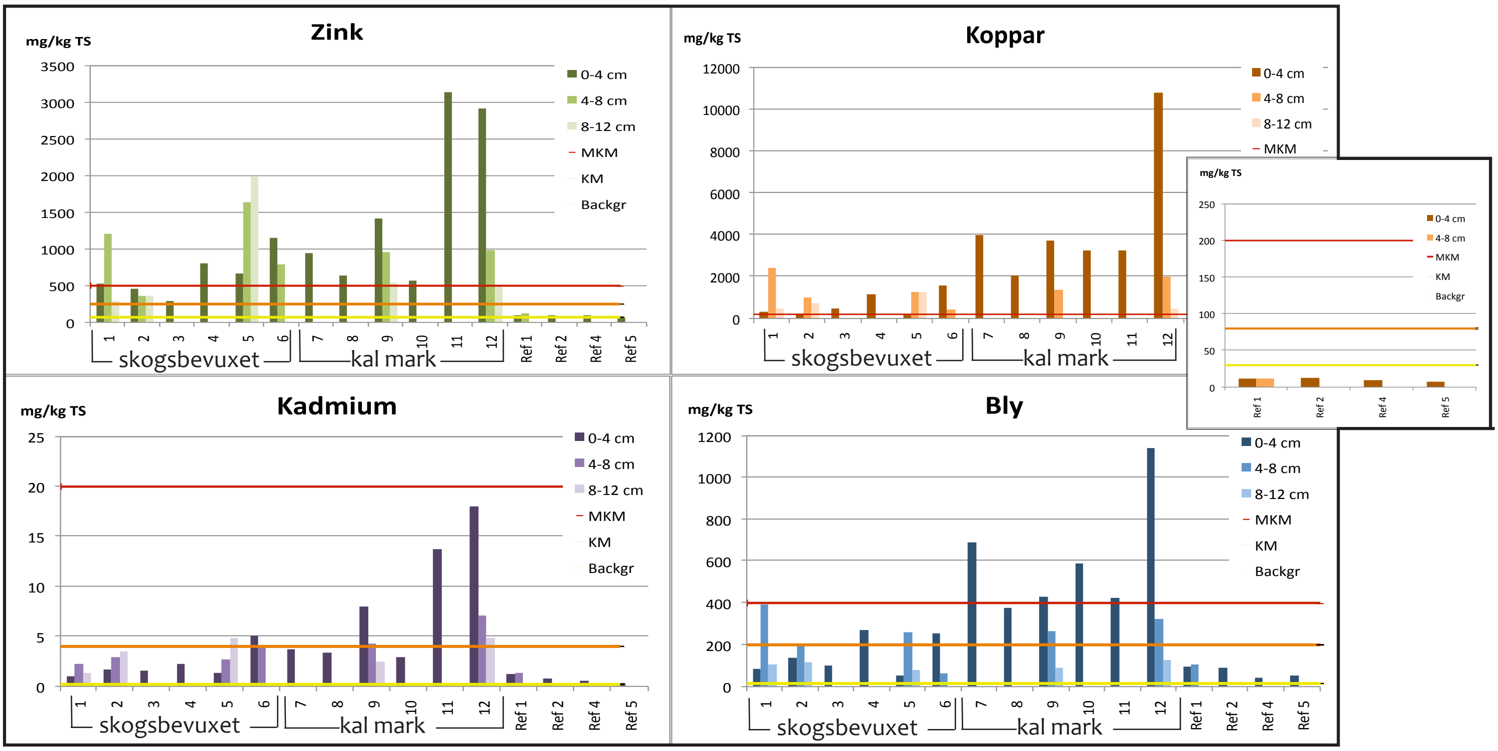
Studien fokuserar på koppar, zink, bly och kadmium, de metaller som tidigare visat sig utgöra störst problem i området.

Cu Zn Pb Cd

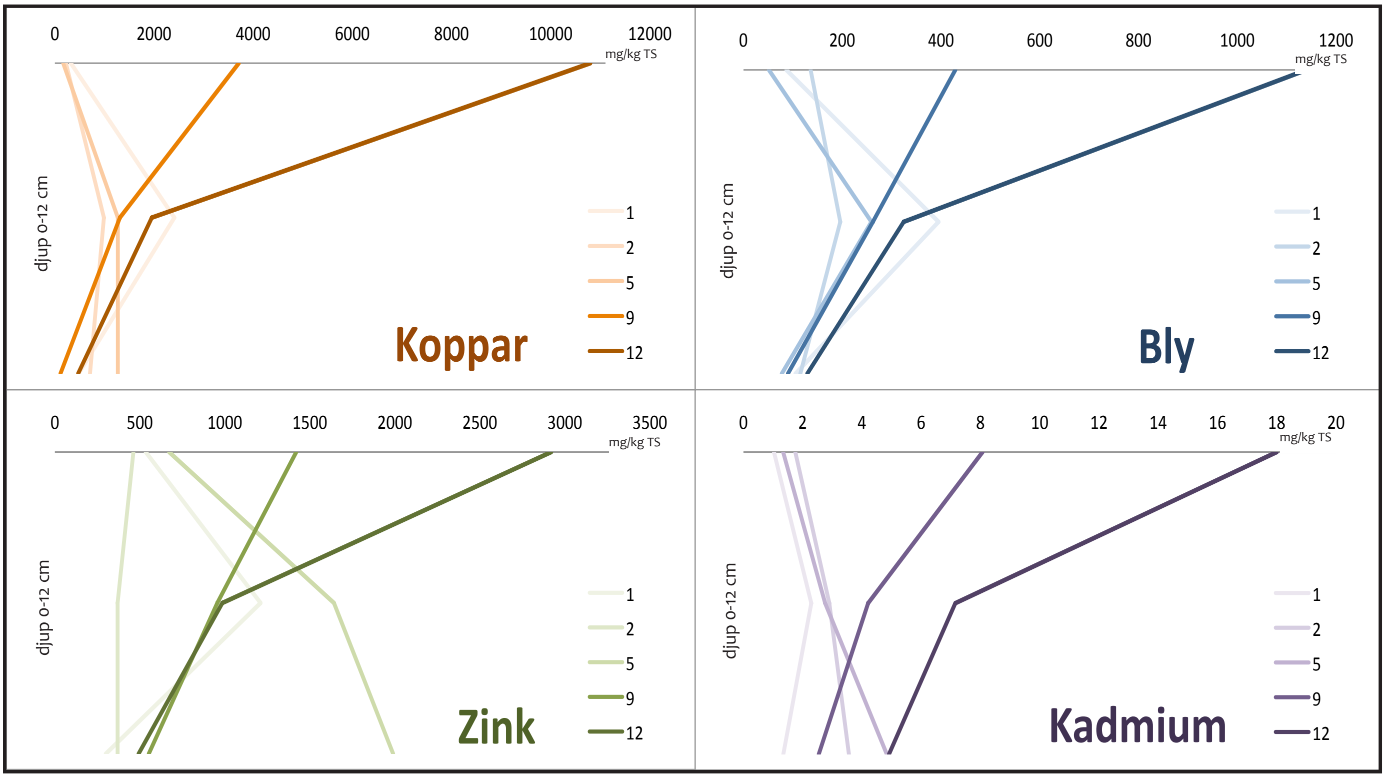
Metallhalter långt över Naturvårdsverkets riktvärden

Metallanalyser i fält och på labb visade att hela Stångberget har kraftigt förhöjda metallhalter. Den kala delen har tydligt högre halter än den skogsbevuxna och halterna ökar ju närmare bruket man kommer. Halterna jämfördes med riktvärden för förorenad mark som Naturvårdsverket satt upp, som skyddar människor och miljö. Det finns två olika riktvärden, ett för mark som människor kan bo på (KM) och ett där man kan bygga kontor och industrier, men där människor inte ska bo (MKM).

Kopparhalterna är allra högst, i den värst förorenade punkten är halten 50 gånger Naturvårdsverkets riktvärde för sån mark där man inte ska bo, över 1 % av jordens vikt är koppar! Även zink- och blyhalterna är över riktvärdet för mark man inte ska bo på, och kadmumhalterna är över det andra, strängare riktvärdet, för mark man kan bygga bostäder på.



Analyser av metallhalterna visar att halterna koppar, zink, bly och kadmium är förhöjda. Allra högst är halterna av koppar, över 50 gånger riktvärdet i det mest förorenade provet! Proverna är tagna från tre olika markdjup (0-4 cm, 4-8 cm ch 8-12 cm). MKM är riktvärdet för mindre känslig markanvändning, områden där man kan bygga kontor och industrier, och KM är riktvärdet för känslig markanvändning, där man kan bygga bostäder. Backgr är den svenska bakgrundhalten.



Metallhalterna varierar med djupet. Där marken är täckt av skog är halterna högst en bit ner i marken, men på det kala området är halterna högst i ytan. 1, 2, och 5 är provpunkter från den skogsbevuxna delen av Stångberget och 9 och 12 är provpunkter från den kala delen av berget.

Gränsen mellan skogen och den kala delen av Stångberget är väldigt skarp.

Höga metallhalter dolda under skogens matta

Metallhalterna varierar med djupet. På den kala delen av Stångberget, där föroreningen är som värst, är metallhalten betydligt högre i ytan än längre ner i marken. När man kommer lite längre bort från det gamla bruksområdet, in i skogen, är mönstret ett annat och metallhalten är istället högst längre ner i marken. Det beror på att buskarna, mossan och träden har producerat barr, löv och annat material varje år. Allt detta material har byggts på lager på lager på jorden och täckt över det kraftigt metallförorenade jordlagret. Man kan säga att jorden har återhämtat sig på naturlig väg.

Något liknande kommer nog inte hända på den kala delen av berget, där inga växter finns som kan producera sånt material.

Olika mönster för olika metaller

Olika metaller beter sig olika i marken. Vissa binder väldigt hårt till olika partiklar i marken och rör sig inte alls, andra följer med regnvattnet till grundvatten och olika vattendrag. Metallerna i denna studie, det vill säga koppar, zink, bly och kadmium, är alla metaller som binder hårt i jorden, men koppar och bly binder ännu hårdare än zink och kadmium. Det kan man se på bilderna över djupvariationen här ovanför. Koppar- och blyhalterna är alltid lägst längst ner i jorden, medan zink och kadmiumhalterna är högst längst ner i några punkter.

Metallhalterna och utlakningen har sjunkit

Metallhalterna i marken på Stångberget var mycket högre när marken undersöktes på 70- och 80-talen. På något sätt har en del av metallerna försvunnit från marken. Ett sätt som föroreningar kan lämna marken är genom utlakning. Det innebär att föroreningen löses upp i regnvatten som infiltrerar jorden och följer med vattnet till grundvatten eller ytvatten. Utlakningen undersöktes på flera sätt men det visade sig att den var låg. På ett år lakade mindre än 0,1 % av zinken i marken, och ännu mindre av de andra ämnena. Utlakningen från Stångberget är nästan obetydlig när man jämför den med utlakningen från det gamla bruksområdet.

Utlakningen undersöktes också på 1980-talet och var högre då än den är nu. Vad det kan bero på att utlakningen minskat vet vi inte riktigt.

En väldigt liten del av de totala metallhalterna på Stångberget lakar ut varje år

	Zink	Koppar	Bly	Kadmium
% utlakat/år	0,09%	0,01%	0,001%	0,04%

Jämfört med det gamla bruksområdet lakar väldigt lite från Stångberget

[kg/år]	Stångberget		Gamla bruksområdet
	Fältskakförsök	Ytavrinning	
Koppar	0,7	0,3	55-560
Zink	1	1	85-430
Bly	0,009	0,003	2-23
Kadmium	0,004	0,003	0,1-0,4

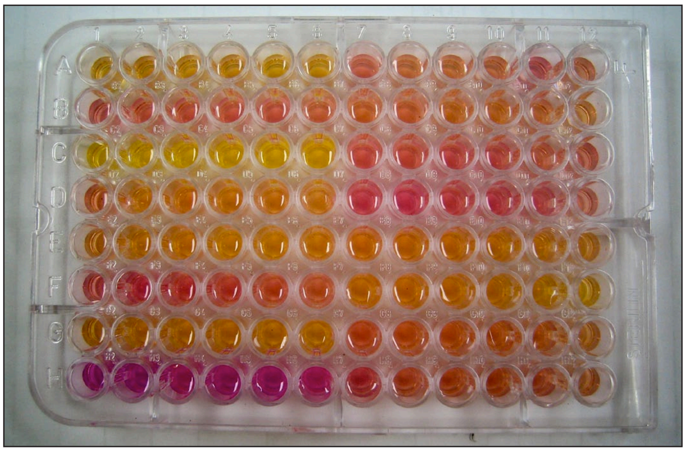
På 1980-talet lakade det mer från Stångbergets jordar än det gör idag

[ug/l]	2010		1986
	Fältskakförsök	Ytavrinning	Lysimeter
Koppar	400	120	900
Zink	680	430	18000

Mikroorganismer lägger stor del av energin på att överleva

Mikroorganismerna på den kala delen av Stångberget, där metallföroreningen är som värst, måste lägga mycket energi på att överleva i jorden och kan därför inte växa lika mycket som mikroorganismer i en oförorenad jord. Därför andas, respirerar, mikroorganismerna där mycket mer i förhållande till sin vikt än kontrollprovets mikroorganismer. Det gick att se när mängden koldioxid som kom från jorden mättes. Jord lades i små mikrobrunnar och ovanpå lades en gelé som ändrade färg när den kom i kontakt med koldioxid.

Det gick att visa att den ökade respirationen till stor del beror på metallföroreningen.



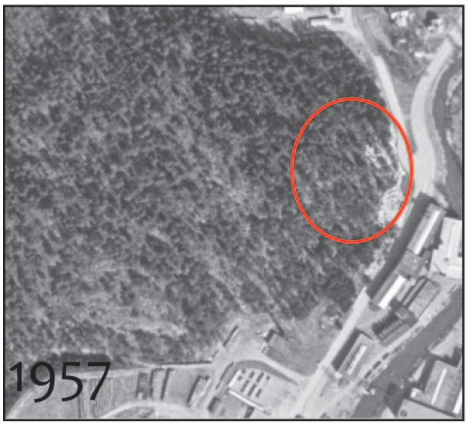
Indikatorgelén ändrar färg när den kommer i kontakt med koldioxid. På så sätt går det att se hur mycket mikroorganismerna andas. MicroResp^{TM} kallas metoden.

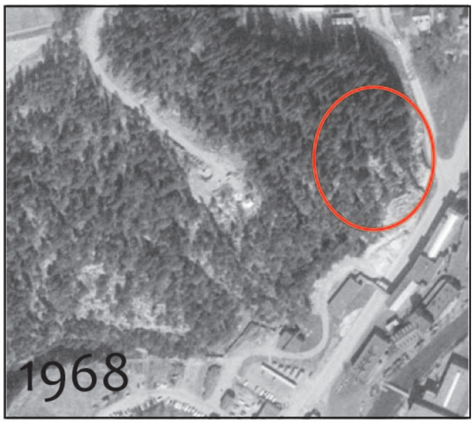
Dåtiden och framtiden

Flygfoton från 1950-, 60-, 70- och 2000-talen visar hur storleken på det kraftigt störda området har förändrats. På flygfotot från 1950-talet finns skog på hela Stångberget. På 1960-talet börjar delar av berget närmast bruket att förlora skogen och på 1970-talet är en större del av berget avskogad. På 2000-talet är ett stort område på berget helt utan både träd och andra växter.

Rökgasutsläppen från det gamla bruket tog slut i slutet av 1960-talet, när verksamheten flyttades till Gräsdalen, ett område en kilometer utanför Gusum. Trots det fortsatte skogsdöden långt senare. Kanske var träden skadade redan långt innan de försvann?

Om inget görs åt de höga metallhalterna i jorden kommer nog det kala området på Stångberget finnas kvar även i framtiden. Flygfotona visar inte att det kala området har minskat något sedan rökgasutsläppen upphörde, snarare tvärtom.





Bruket som en gång var Gusums hjärta och stolthet har nu blivit en skamfläck. I och med rivningen hoppas Gusumborna att punkt ska sättas för det tråkiga kapitlet i samhällets historia. Kanske kan man istället minnas allt gott som bruket förde med sig?

Men de kala klipporna man möts av när man färdas genom Gusum kommer fortsätta vittna om de mörka sidorna av Gusums bruk.

Flygfoton och äldre bild av Gusums bruk: Lst i Östergötland
Övriga foton: H. Almqvist
Kartor: (c) Lantmäteriet Gävle 2010 Medgivande I 2010/0055
GIS-arbete: M. Sträng, Golder Associates AB

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