Soil Washing: Optimization of Acid Leaching of Copper from Contaminated Soil

Master of Science Thesis in the Master Degree Programme, Chemistry and Bioscience

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Abstract

Contaminated soils are a problem all around the world. Only in Sweden it is estimated that there is 80 000 contaminated sites. The most common remediation technique is excavating and landfilling, thus just shifting the problem to a new location. Another problem with this technique is that possibly valuable contaminants, most commonly metals, are lost. A more sustainable soil treatment would be chemical soil washing with recovery of the contaminants, i.e. washing the soil with liquid; in this case acidic process water.

In this study the aim was to leach copper from heavy contaminated soil and bark, from two sites in Sweden: Björkhult and Köpmannebro. The washing media used was acidic process water from the flue gas cleaning process in a municipal solid waste incineration plant. The leaching process was optimized with the parameters L/S-ratio and leaching time, and further on with evaluation of possible benefits with stepwise leaching. The optimal settings where then used for batch experiments and includes two leaching steps followed by a washing step where Milli-Q water is used instead of the process water leaching agent.

The leaching experiments were successful extracting more than 90% of the initial copper concentration in the one-step leaching. The best parameters were proved to be L/S 10 with a leaching time of 30 minutes. The two-step leaching, only involving the ash samples, gave a higher extraction yield allowing for a cheaper disposal method of the ash.

The results show a good leaching of copper, but also that the cleaned soil still has contaminants above the Swedish guidelines for non-hazardous soils. The key to solve this probably lies in improving the washing step and by this enable a less expensive alternative for landfilling the soil residue. The leaching itself will be hard to improve further since it already gives an almost total leaching of copper and therefore could be used for recovery and this should be seen as an environmental advantage.

Key words: Contaminated soil, acidic soil leaching, soil wash, copper

Jordtvätt: Optimering för sur lakning av koppar i förorenad jord

Examensarbete inom masterprogrammet Chemistry and Biosciences

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Sammanfattning

Förorenad mark är ett problem över hela världen. I Sverige uppskattas att det finns 80 000 förorenade områden. Den vanligaste metoden för omhändertagande är att gräva upp och deponera den förorenade jorden. Denna lösning förflyttar dock bara problemet till en ny plats: deponin. Ytterligare ett problem är förlusten av eventuellt värdefulla föroreningar, vanligtvis metaller. En mer hållbar jordreningsmetod är kemisk jordtvätt där de värdefulla föroreningarna återvinns. Jordtvätt innebär att man tvättar jorden med en vätska och i denna studie har surt processvatten använts.

Målet för denna studie var att laka ur koppar från starkt förorenad jord och bark från två olika områden i Sverige; Köpmannebro och Björkhult. I denna studie användes surt processvatten, från rökgasreningen vid den kommunala avfallsförbränningen vid Renova, som lakningsvätska. Lakningsprocessen optimerades med avseende på två parametrar: L/S-kvot och lakningstid. Optimeringen fortsatte genom att utvärdera eventuella fördelar med stegvis lakning. De optimala parametrarna användes sedan för batchexperiment vilka inkluderade två lakningsteg följt av ett tvättsteg där Milli-Q vatten användes istället för processvatten.

Lakningsexperimenten var framgångsrika i vilka mer än 90% av den initiala koncentrationen extraherades när ett lakningssteg användes. De bästa parameterinställningarna från dessa försök var L/S 10 med en lakningstid på 30 minuter. Tvåstegslakning utvärderades bara för askproverna, för vilka de gav ännu högre lakningsutbyte jämfört med ett lakningssteg. Detta medför eventuellt en billigare deponikostnad för askan.

Resultaten visar att processvattnet har mycket goda lakningsegenskaper för de aktuella jord- och askproverna, men också att den tvättade jorden fortfarande har metallhalter som överstiger de svenska riktlinjerna för brukbar jord. Lösningen på detta problem ligger med stor sannolikhet i att förbättra tvättsteget för att billigare deponeringsalternativ ska bli aktuella. Lakningsteget är dock i sin nuvarande form svår att förbättra med nära total urlakning av koppar, vilket i sig bör ses som en miljömässig fördel då kopparen kan tillvaratas.

Nyckelord: Förorenad jord, sur jordlakning, jordtvätt, koppar

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1. Introduction

In 2008 the Swedish Environmental Protection Agency (SEPA) estimated that there are 80 000 potentially polluted sites in Sweden (SEPA, 2009a). This is one of the main obstacles to achieve the environmental goal ”A non-toxic environment”, one of the 16 environmental objectives set by the Swedish government to be accomplished by 2020 (SEPA, 2013). The process is now in an inventory phase where all of the potentially polluted sites are divided into classes according to the origin of the pollution, normally depending on what type of industry that exist/existed, the degree of pollution and the toxic effect. This is a very time consuming work but the ambition is that the inventory phase should be finished by 2013. The process is obstructed by the fact that new polluted sites are identified and formed continuously (SEPA, 2009a, Ohlsson et al., 2011).

Parallel to the inventory phase the intervention process is running, which is when the actual remediation of the contaminated sites occurs. This is a very time consuming and costly process. In 2008 250 million SEK was distributed to the different counties administration boards for their remediation of contaminated sites (SEPA, 2009a). This corresponds to 970 ongoing investigations and 170 interventions during the same year (SEPA, 2009b).

The pollution situation at the different sites differs widely. The SEPA has calculated the distribution between different pollutants based on the top 216 prioritized sites in 2008, as seen in Figure 1.1.

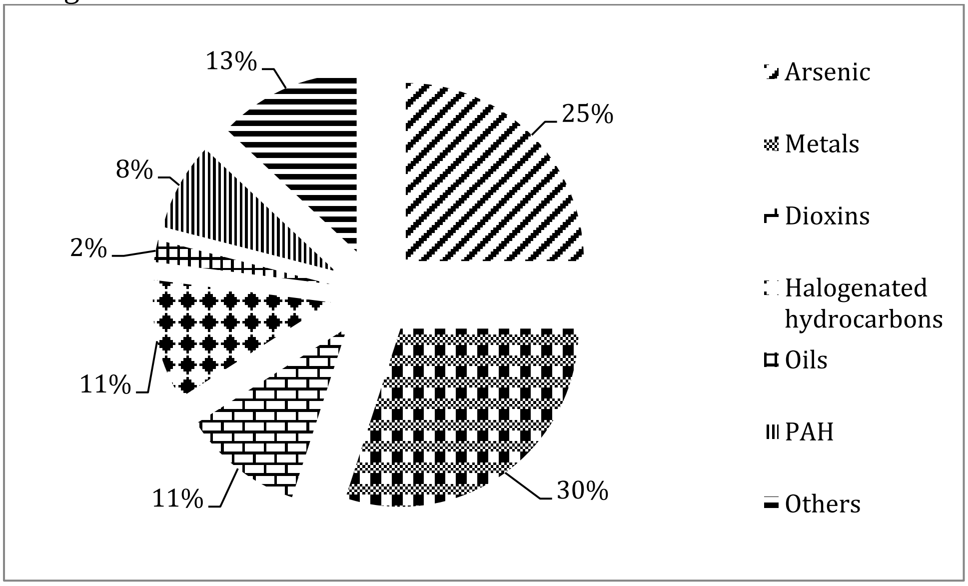

Figure 1.1. The estimated distribution of pollutants in contaminated sites in Sweden (SEPA, 2009a).

Metal and arsenic contamination contributes to about 55% of the total pollution. Metals are a natural part of the ecosystem, but here their levels are elevated. Elevated metal amounts can be directly toxic to organic life as well as indirect, pointing to that metals are non-biodegradable and thus accumulates in biological tissue.

1.1. Aim and objectives

The main aim with this thesis work is to optimize the soil washing process for contaminated soil and ash from bark as well as evaluate the possibility of recovering copper. The specific goals are to:

- Investigate the parameters L/S ratio, leaching time and the possible advantages with two-step leaching by several leaching experiments.
- Measure the success of the leaching by the amount of leached copper, the amount left in the solid residue but also how stable the soil residue is to further leaching as this is equally important.

The samples that is used for experiments consist of clay soil and bark from the polluted site Köpmannebro south of the Swedish city Mellerud and Björkhult close to the Swedish city Kisa. Both of these sites are heavily contaminated with metals, foremost copper, from the former wood processing industry. The bark samples are be incinerated before leaching due to its high organic content, which makes it illegal at landfill, but also since previous studies indicate that the copper becomes more accessible with incinerated samples (Tateda, 2011, Karlfeldt Fedje et al., 2013).

As leachate, acidic process water from the flue gas cleaning process of the municipal waste incineration at Renova in Gothenburg, Sweden is be used. After optimization the cleaned soil is evaluated in terms of quality compared to the Swedish guidelines for landfill and contaminated soils. Depending on the degree of contamination, soils are divided into two different categories KM, “känslig markanvändning”, and MKM, “mindre känslig markanvändning”. The KM is less contaminated soil, which do not apply any boundaries for what kind of activities or buildings that can reside in the area. The MKM corresponds to more contaminated soil, which restricts the area to be used for industry, offices and other activities where people for example only spend their working hours. The KM and MKM limitations for Cu are 80 and 200 mg Cu per kg soil, as comparison the soil in Köpmannebro has measured values as high as 51600 mg Cu/kg soil (Kemakta, 2012).

The aspiration of the project is to find a remediation method for contaminated soil, where large amount of the copper can be recovered and reused. Due to the very acidic process water’s effect on the soil samples, the intention for these samples are not to be used as soil again but rather as construction material and thereby avoiding the landfill alternative.

1.2. Limitations

This project will focus on the leaching of copper although other metal contaminants will be measured to some extent. The focus will also be on the specific site at Köpmannebro even but the optimal settings from this site will be evaluated for the Björkhult site as well. The optimization will be set on using the acidic process water from the flue gas cleaning of municipal waste from Renova and Milli-Q water as leachates.

1.3. Main research questions

- What settings of L/S ratio and leaching time give the best leaching of Cu from the contaminated soil of Köpmannebro?
- Is it an advantage to perform the leaching in one more step?
- Are the pollution levels of the cleaned soil below the Swedish limits for toxic waste? If not, are the soil and ash matrixes stable enough to prevent heavy leaching of contamination to the surroundings?

2. Theory and background

2.1. Remediation methods

Different pollutions need different methods of remediation. This report focuses on the remediation of metal-contaminated soils. This process is complicated, mainly because of three facts:

A. The contamination is seldom homogenous; the metals are unevenly distributed in the soil.
B. Metals are non-degradable and cannot be destroyed.
C. The large variation of the forms the metals exist in as ions, salts etc., as well as the variation in soil matrixes. This yields multiple interactions as bonding, partitioning, chemical reactivity, mobility etc., between the soil and the metal contamination that derives from the soil characteristics as particle size, cat-ion exchange capacity, pH, mineralogy, organic content, and the form of the metal (Dermont et al., 2008).

The by far most common soil remediation technique in Sweden, as well as internationally, is soil excavating and landfilling. This is due to tradition, availability and economic reasons (Ohlsson et al., 2011, Dermont et al., 2008). The problem with this method is that it does not primarily solve the underlying issue, rather relocate the problem because it does not remove the contamination from the soil; just shift the contaminated soil to a different location even though the potential leaching is controlled within the landfill.

Dermont et al., 2008, gives a review of the existing techniques for remediation of metal contaminated sites, and divides them into two main groups: stabilization/isolation of metals and extracting metals. Each of these main groups can be further divided into off site and on site techniques, thus excavation and landfilling, where the contaminated soil is dug up and relocated to a landfill and the contaminated site is refilled with clean soil, are examples of ex situ stabilization/isolation techniques.

Other stabilization/isolation techniques except from excavation are;

- Stabilization/solidification: Stabilization and solidification neither remove the contaminants, rather covers them. Solidification is to physically encapsulate the contaminated soil e.g. bitumen, fly ash or cement are injected to the soil (Mulligan et al., 2001). This can be done either on site or after the soil have been moved; the latter more common. In stabilization different chemicals are used to stabilize the contaminants, thus reduce their mobility. Often the chemical is a liquid monomer that polymerize (Mulligan et al., 2001). The main advantages of these methods are their relatively low costs though problems can occur if the soil for example has a lot of clay or oily patches, which obstruct the mixing procedure.
- Vitrification: Vitrification is similar to stabilization/solidification in the way that the contaminants are not removed. Instead of using encapsulation or stabilizing media it uses thermal energy. Electrodes are inserted in the soil and a glass or graphite frit is placed on the ground. This frit initiates the vitrification process where the minerals in the soil are melted due to the high induced current. The soil is then allowed to cool off at which point an encapsulating glassy material is formed by the inorganic compounds. Successful vitrification solutions exist for arsenic, chromium and lead contamination, but problems concerning clay rich soils that lower the efficiency still exist. Other problems are the hazards with toxic gases that could be released during the process, the uncertainty in the vitrified end products leaching qualities that still has

to be monitored and the high cost since the method is highly energy demanding. However this could be a suitable method for large masses of contaminated soils in shallow depths (Mulligan et al., 2001).

- Chemical red/ox: This is a chemical treatment used to detoxify the contaminated soil. It is especially applicable for reducing highly toxic Cr(VI) to less toxic Cr(III) or oxidizing As(III) to less toxic As(V) or to adjust pH in acidic or basic soils (Mulligan et al., 2001). This method is commonly used prior stabilization/solidification to lower the toxicity. The major disadvantage of chemical treatment is that it is in need of chemicals that could be both hazardous and expensive (Dermont et al., 2008).
- Phytostabilization: Phytostabilization is a technique based on certain plants ability to accumulate heavy metals. Implantation of such plants can thereby remediate contaminated sites although the method is limited to root deep contamination and the remediation has to be monitored during a long period of time. When the soil is remediated the plants has to be taken care of as toxic waste. Advantages is that except the remediation of the contamination on site the plants also prevent erosion, hence preventing that the contamination is spread to ground water (Dermont et al., 2008, Mulligan et al., 2001).
- Monitored natural attenuation: This is the non-treatment option which might be relevant where any action might lead to enhanced spread of contamination or the costs exceeds the benefits. However, this demands continuous observations assuring no high toxic compounds leaks to the surrounding environment.

The main advantage with the stabilization/isolation techniques is that they work for a wide variety of soils and metals compared to extracting techniques. The drawbacks are many; most important is that it is not a sustainable solution because the contaminants are not removed from the soil. There is also a lack of research of the long-term stability of the stabilized material, which means that the contaminated site or the landfill has to be monitored for a long time period. Other problems are that the excavated area needs to be refilled with clean soil as well as that the cement based solidification significantly increase the volume if it is sent to landfill.

Therefore the extracting techniques have a promising future. Not only because the cleaned soil sometimes can be used as soil once again but also because there is a possibility of recovering the metals. Examples of extracting techniques are;

- Physical separation: Physical separation is a good method when the contaminant is dominant in one of the particle fractions. Equipment to perform the physical separation varies from hydro cyclones, fluidized beds or flotation, all these well-known methods from the ore industry. Another method is magnetic separation that uses the magnetic qualities of many metals (Mulligan et al., 2001).
- Chemical soil washing: When using soil wash the contaminated soil is excavated and washed with various agents in either reactors or as heap leaching. Ideally the cleaned soil is clean enough to be returned afterwards. Several different leaching agents have been used, such as inorganic acids, organic acids, chelating agents or combinations of earlier mentioned. Earlier test soils have showed that the method is most efficient with sandy soils i.e. less than 10-20% clay and organic content (Mulligan et al., 2001).
- Soil flushing: Soil flushing is quite self-explanatory, a solution is flushed through the soil via infiltrations systems, surface trenches or horizontal/vertical drains and leachate collected at the bottom (Dermont et al., 2008). The technique is based on the possibility to solubilize the contaminants and is preferably applied on soil with high water permeability (Mulligan et al., 2001). The solution could vary depending on the

type of contaminant, but most commonly used is water with or without additives. Water being more environmentally friendly alternative since additives such as chelating agents and surfactants could have a negative effect on the environment. (Dermont et al., 2008). Soil flushing is quite similar to soil wash and is preferable if all of the contaminated water can be collected at the site. Is this not the case soil washing is the better choice

- Biological extraction: Is similar to soil washing but with biological agents as bacteria or algae used instead of earlier mentioned chemical agents (Dermont et al., 2008). Biological extraction has not yet been used in any big scale remediation but successful lab trials have been performed.
- Electro kinetics: Electro kinetics involves passing a low electric current through the soil; the current makes the positive ions move to the cathode and negative ions move to the anode (Mulligan et al., 2001). This method is most efficient with saturated soils since water enhance the conductivity of the soil.

There are some problems with the existing extraction techniques that stem from the earlier mentioned problem with a large variety of soils as well as with the economical sustainability (Dermont et al., 2008).

2.2. Sites used in this study

2.2.1. Köpmannebro

In Långö, south of the city of Mellerud in Dalsland Sweden, there was a wood processing industry for telephone poles in the beginning of the 20th century. The processing was made according to the Boucherie method, which involves injecting blue vitriol into the timber and let it soak until saturation (de Vougy, 1856). Then the timber were decorticated and limbed and the bark was left at the site, leading to accumulation of contaminated bark at the site. Blue vitriol is a rest product from mining with sulfuric ores, and consists of one Copper(II)sulfate molecule that is crystalline bonded to five water molecules [$CuSO_4{\cdot}5H_2O$].

This industry resulted in the highly contaminated site of 8000 m^2, were still no vegetation exist (Kemakta, 2012). The core study performed by Kemakta, commissioned by Dalsland’s office of environment, concludes that the copper content is elevated in all of the soil layers, with 70% of the samples showing levels corresponding to toxic waste. The study suggests several different treatment alternatives as landfilling or solidification. None of the suggested treatments will recover the Cu from the site, which is the main goal with this project. Therefore the site is fitting for this study, to determine if there is a method to actually recover the large amounts of copper.

Figure 2.1. The contaminated area at Köpmannebro (Kemakta 2009).

As seen in the Figure 2.1, the bark is not degraded to a high degree. The bark layer reached from the surface to as deep as 1-1.5 m under which the clay layer could be found.

2.2.2. Björkhult

The other site investigated is Björkhult, situated on the south shore of the lake Verveln close to the city Kisa in Östergötland, Sweden. From 1916 to 1944 there was a wood processing industry for telephone poles, similar to the one earlier described at Köpmannebro. The site is approximately 7000 m^2, but differs from Köpmannebro in the case of vegetation. At Björkhult the natural fauna seems to have recovered well, as seen in Figure 2.2, and there are a lot of trees, grass and bushes which could be an effect of the different soil characteristics observed at the two sites. This might be due to that the site has been covered with soil from an external site since there is a well-defined soil layer above the bark.

Figure 2.2. The contaminated area at Björkhult.

The soil at Björkhult also differs from the Köpmannebro site. There were three well defined soil layers: 0-10 cm depth consisted of sandy soil, 10-30 cm of a partly degraded bark layer and below 30 cm a red soil, more fine grained than the soil in the top layer.

More than the observations of different soil characteristics made at the different sites, there is also a known difference of the dominating soil classes in different parts of Sweden. As seen in Figure 2.3 the dominating soil class at Köpmannebro is Leptosol while it is Arenosol at Björkhult.

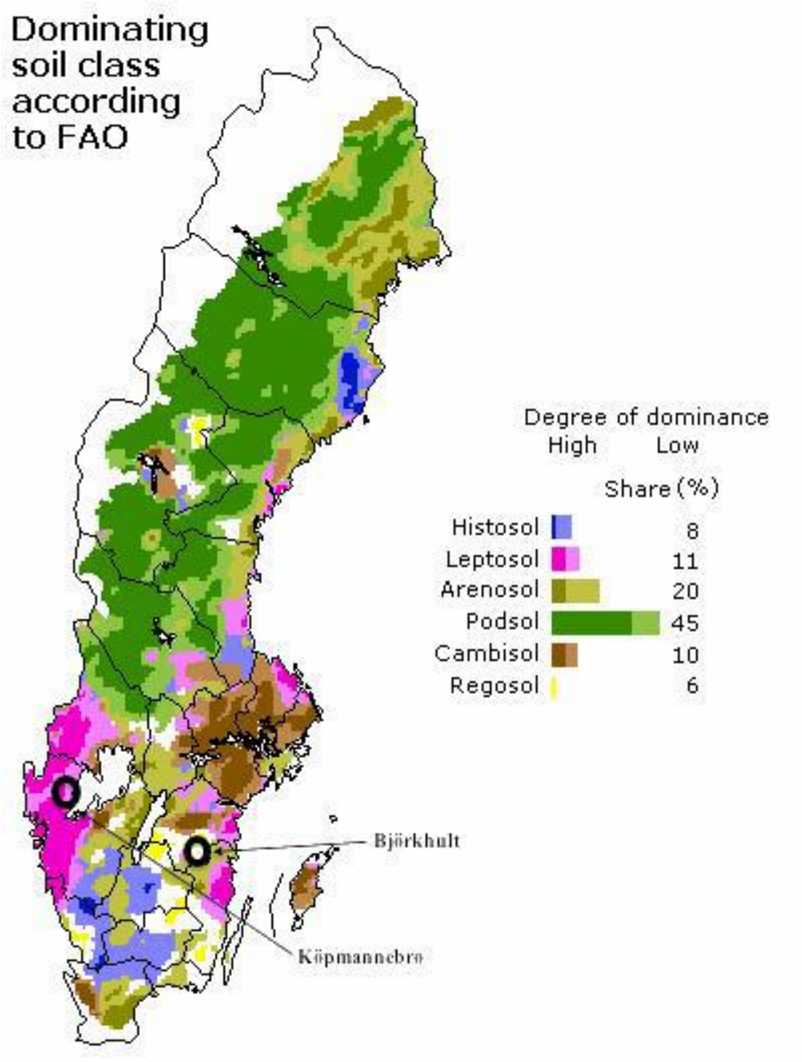

Figure 2.3. The dominating soil classes in Sweden according to FAO (Markinfo, 2006)

2.3. Criteria for contaminated material

2.3.1. The KM/MKM-criteria

The Swedish government has set up 16 environmental objectives to ensure a sustainable environment in Sweden. Among these objectives is "A non-toxic environment". The agency responsible for these is the Swedish Environmental Protection Agency (SEPA). The problem is seen in a long time perspective, 100 to 1000 of years ahead. When come to risk analysis and planned use for a site it is hard to see more than 100 years ahead, but the SEPA tries to make the demands higher to ensure risks in the future. (SEPA, 2009c)

The land use is divided into two main groups, sensitive land use and less sensitive land use. The sensitive land use is for an area where the quality of the soil does not limit the possibilities of land use. All groups of humans are out of harm no matter how much time they spend there and most of the ecosystems, water and ground water systems included, are protected (SEPA, 2009c). The less sensitive land use is for areas where the quality of the soil does limit the possibilities. The risk analyses of these soils recommend that grown-ups should not spend more than normal working hours there whereas children and elderly people should not spend time there regularly. This less sensitive land use is for example offices, industries or roads. The contamination limits are set so that water and ground water systems are protected in a distance of 200 m. The actual limits can be seen in Table 2.1.

The mobility of contaminants is strongly dependent on the surrounding soil, pH and the chemical form of the contaminant. The general guidelines for sensitive and less sensitive land use are set to not underestimate leaching of contaminants. In some cases a site-specific risk analysis can be appropriate. These site specific limits should be set from leaching tests as well as from comparing the existing content in soil and ground water. The site-specific limits are not in any case intended to increase the allowed limits, rather the opposite, to decrease limits if increased risks are suspected.

Table 2.1. Limits for sensitive land use; MK and less sensitive land use; MKM

Substance	**KM [mg/kg TS]**	**MKM [mg/kg TS]**
As	20	40
Pb	200	400
B	7	20
Ba	160	260
Cd	4	20
Co	10	15
Cr	90	150
Cu	75	160
Sb	30	50
Se	1	5
Zn	300	450
Be	20	40
Hg	5/10	10/20
Mo	10	25
Ni	75	150
V	100	200

2.4. Incineration

Several studies have been done regarding chemical soil washing but none about leaching metals from bark. A problem with performing “soil wash” on bark is the requirements of high L/S-ratios owing to the barks high absorption ability and the high amount of organic matter that can form strong bonds with metals (Thomas et al., 2013). A way to overcome this is to incinerate the bark to ash, which not only accumulate the metal contamination to a smaller mass but also burns the organic compounds and thereby releasing strongly adsorbed metals from the complexes.

Another advantage with incineration is that contaminated bark, due to its high organic content, is illegal for landfilling (SFS 2001:512). This is due to volatilization of the organic compounds at 473-773 K depending on the compound properties. Most industrial combustion of biomass is usually done at 1073 K or higher to assure a complete burnout of CO (van Loo, 2008).

2.4.1. Ash

The in biomass, such as bark, the ash-forming part is salts bound to the carbon backbone of the organic compounds. However, since the bark to some extent is mixed with the underlying soil, the ash-forming fraction will also come from mineral particles from the surrounding soil. The ash can be divided into two fractions; the heavier part is called bottom ash which is the part left on the grates consisting of sintered ash particles and impurities such as stone or sand and the fly-ash which is coarser particles precipitated during the second combustion or in the multi-cyclones and particles that precipitates later in the flue gas cleaning, often in the electrostatic filter (van Loo, 2008). The amount of metals and salts in the bottom ash varies from metal to metal. Volatile metals like Hg, Cd, Pb and Zn are for example often accumulated in the fly ash (Hong, 2000, Nurmesniemi, 2007, van Loo, 2008).

The ratio between the fractions depends on several factors; type of incineration, excess air ratio, fuel type, continuous or batch combustion to mention a few. A general rule is that the fly ash-ratio increase with fluidized-bed combustion compared to fixed bed combustion. In this study a larger fraction of bottom ash would be preferred since it is this fraction that will be studied in the leaching optimization and thereby all the copper that goes with the fly ash is lost. The ratio of copper content between fly ash and bottom ash differs amongst studies from 10-90% of the copper in the bottom ash (Sander 1997, van Loo, 2008).

2.4.2. Industrial combustion

The bark in this study was incinerated in batches with smaller furnaces due to the small amount of sample and to generate a pure bark ash. However, a large-scale solution would probably involve an industrial scale continuous furnace because of the large amount of bark. Only at the site in Köpmannebro it is estimated to be more than 6500 ton contaminated bark (Kemakta, 2012). The most common combustion techniques are grate combustion or fluidized-bed combustion. The facility at Sävenäs has four furnaces of the fixed bed combustion-type, which is the method that will be simulated in this study.

In grate combustion furnace, such as those at Sävenäs, the fuel is carried into the furnace on moving grates supplying a homogeneous and even amount of fuel to assure a complete and smooth combustion. A primary air supply is introduced from below with a low flow avoiding turbulence that would lead to a release of fly ash and unburned particles. The flue gases from the primary combustion rises to a secondary combustion chamber where it is mixed with fresh air and often recirculated flue gas, so called secondary air, for a complete combustion of hazardous gases such as NO_x (van Loo, 2008).

The next step is the cleaning procedure. This is not of importance concerning the combustion of the bark but since it does concern the process water, thus is still of interest in this study. In the cleaning procedure the fly ash in the flue gas, from the second combustion, are removed with an e.g. electrostatic filter. This filter is an electric field, where the fly ash can be removed due to the ions it contains. The flue gas then passes through wet scrubbers, which consists of several water curtains that dissolves dust, acidic gases (mostly hydrochloric and hydrofluoric acid), mercury and other heavy metals from the gas. This solution is the process water that will be used in the leaching experiments and its characteristics vary with what is being incinerated (Renova, 2010, van Loo, 2008).

2.5. Copper

Copper exist, naturally in the environment, the average content is about 50g/ton in the earth's crust. Copper commonly occurs as sulfide ores, e.g. $CuFeS_2$ (90%), but also as oxide ores, e.g. Cu_2O, (9%) and as pure copper (1%). In the primary copper producing industry it is mainly the sulfide ores that is used, although a large part of the produced copper comes from recycled materials (Elding et al., 2012).

Half of the amount of produced copper is used in the electric component industry where its excellent conductivity is highly valued. Other industries that use copper are engineering industry (21%), building industry (11%), household articles (10%) and transport industry (8%) (Elding et al., 2012). New materials have started to compete with copper in many of the common usages, this have accelerated the development of new copper materials with improved qualities (Elding et al., 2012).

Copper is essential for probably all living organisms, but it can also be toxic with elevated copper concentrations for many organisms. Vascular plants can be afflicted with shortage of chlorophyll and many funguses' microbial digestion cease when copper concentrations are elevated. Animals are sensitive for copper concentrations both above and below normal. A lack of copper can cause diarrhea and anemia while an excess of copper causes cramps and hepatitis B (Elding et al., 2012).

3. Method

The work process of the project was divided into two parts; first a literature study of the latest progress in the field of soil washing, as well as on other treatment techniques, and second a laboratory part, where leaching experiments were performed. The initial part of the project emphasized on the literature study; what methods had been used earlier and what were their advantages and disadvantages.

The laboratory part began when a suitable experimental setup could be established based on earlier research studied in the literature part. The analyses were done with eg spectrophotometer, ICP-MS (inductively coupled plasma mass spectrometry) and ICP-AES (inductively coupled plasma atomic emission spectroscopy).

3.1. Leaching experiments

The experimental part consisted of the experiments performed to optimize the leaching process. The soil and bark samples collected from Köpmannebro and Björkhult were dried and, in the case of the bark, incinerated to ash before the leaching trials. To optimize the leaching procedure different L/S-ratios, time of leaching and step-wise leaching were evaluated. A schematic overview of the experimental procedure can be seen in Figure 3.1.

3.1.1. Sampling

The soil and bark samples were collected from Köpmannebro and Björkhult, which both have been heavily contaminated with Cu due to earlier wood processing in the area (Kemakta, 2012, SEPA, 2009a). Samples were collected at the same spots previously was identified as Cu hot-spots (e.g. Kemakta, 2012, Arnér, 2011) and at specific depths with shovels in stainless steel. The samples were stored in PP-bottles at 4^{o}C before preparation.

In Köpmannebro the bark layer reached from the surface to as deep as 1-1.5 m under which the clay layer could be found. At Björkhult the soil profile was different and consisted of additional layers: 0-10 cm sandy soil, 10-30 cm bark layer and beneath 30 cm depth there were a red soil more fine grained than the sandy soil. Other differences between the sites were the total absence of vegetation in Köpmannebro, while it grew both grass and trees in the contaminated areas in Björkhult.

3.1.2. Sample preparation

The sample preparation involved a drying step where the bark and soil samples were dried in an oven (Memmert U15) at 80^{o}C until their weights were stabilized, approximately 1.5 day for the soil samples and 2-3 days for the bark samples. During the first 2 hours of the drying step the soil was mixed a couple of times to prevent it from becoming a stiff solid cake that would need grounding prior to the leaching experiments. After drying the samples were kept dry in desiccators until leaching tests or, in the case of the bark samples, until the incineration step.

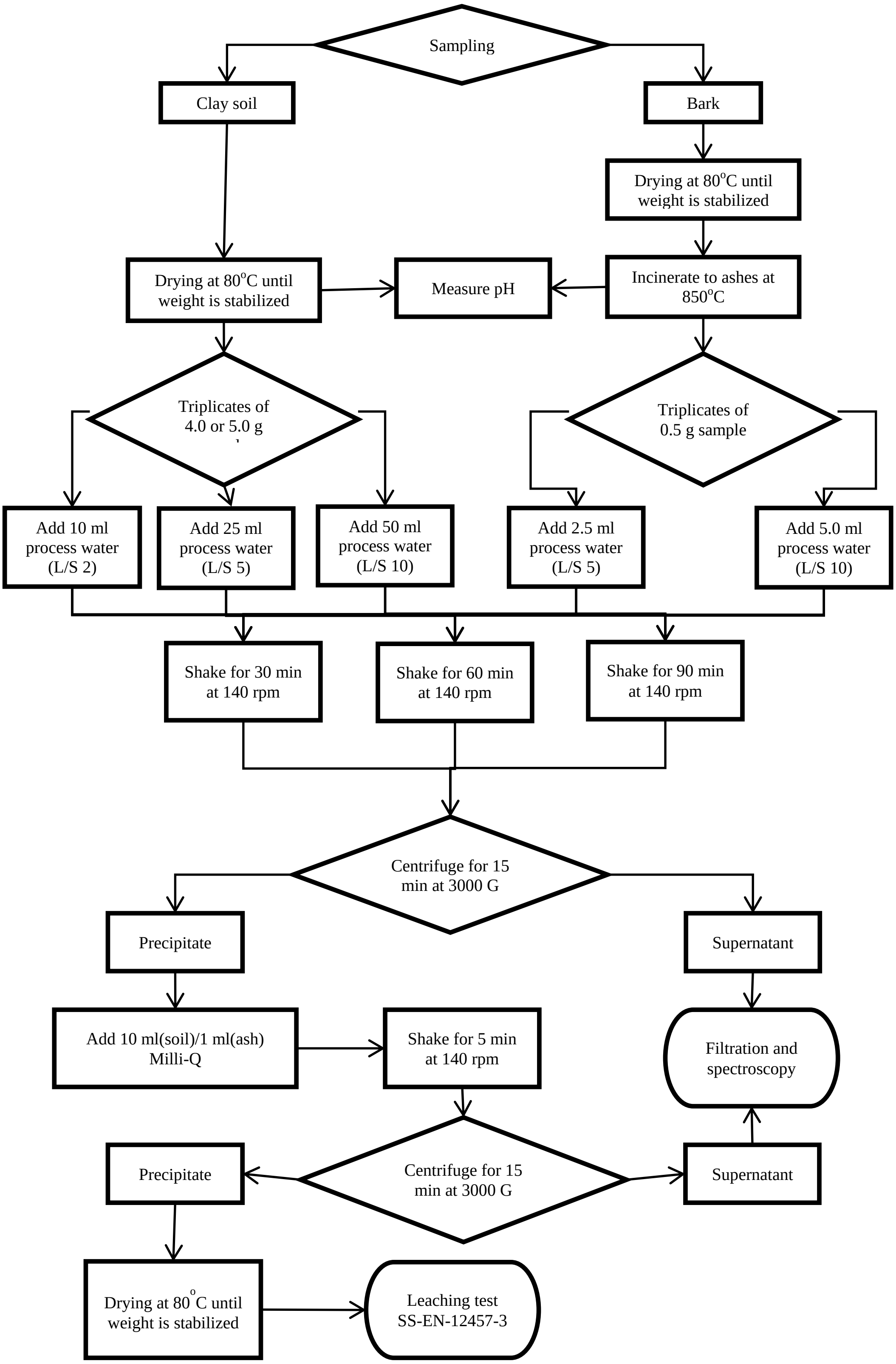

Figure 3.1. Flowchart for the laboratory work for the one-step-leaching

The incineration step was performed due to the low availability of copper, high absorption of leachate and high organic content in the bark samples. The organic content is of importance due to regulations regarding landfill of organic matter. According to the Environmental Code it is illegal to deposit organic material (SFS 2001:512). In addition earlier studies have shown that the copper is easier to leach from ash than from bark. This might be due to strong interactions between organic compounds and copper (Karlfeldt Fedje et al., 2013, Tateda, 2011).

Two different furnaces were used for the incineration process: a Carbolite Furnaces CSF 1200 and a destruction furnace typ-D 200. The Carbolite Furnace CSF 1200 is an ordinary furnace where natural convection heats the sample. This oven was available in the lab and used for incineration both with reducing and oxidizing conditions. Both of the incineration processes began with grounding the bark so the largest particles were >0.5cm. To reach reducing conditions the grounded bark was placed in crucibles with caps, to minimize the access to air, while the incineration with oxidizing conditions the bark was spread in a thin layer (max 4mm thick) on a plate. In both cases the samples were then incinerated at 850°C for 6 hours and afterwards stored in desiccators until further tests. The temperature for incineration was set to 850°C due to earlier studies and that large scale biomass furnaces often operate at this temperature (van Loo, 2008).

Early analysis showed that the copper were much more accessible (see section 4.2.) when the bark was incinerated in oxidizing conditions but then the bark to ash ratio was very low. Therefore, as well as to mimic the real process conditions, bark from Köpmannebro was incinerated at Renova in their destruction furnace typ-D 200. The temperature was the same as with the Carbolite Furnace CSF 1200. The difference between the ovens is generally that the destruction furnace applies heat by blowing hot air on the bark which resembles a large scale furnace where a steady air flow is injected from below to ensure oxygen supply but also increases the amount of fly ash. This showed to decrease the ash to bark ratio even more, but since it probably mimic a large scale process better than the lab oven, ash mixed in a 50/50 ratio from both ovens were used for further analysis.

3.1.3. Leaching procedure

The Cu leaching is the principal part of this project and the process was to be optimized. To extract copper from the soil and ash samples, process water from Renova's waste-to-energy incineration plant in Sävenäs was used as leachate. More specifically the process water is a byproduct from the washing step of the flue gas and has acidic properties (pH≈0.5) that makes it a promising leachate both from a chemical and economical perspective. The process water was analyzed with ICP-AES according to section 3.2.3.1.

The dried soil, 4 or 5 g, and bark, 0.5 g, samples were weighed in 50 ml respectively 15 ml PP-bottles. The process water was then added to the test tubes according to the specific L/S-ratio, 2, 5 and 10 ml per gram. The test tubes were then kept in a reciprocating shaker (Julabo SW-20C) for the allotted time of the leaching procedure: 30, 60 and 120 min. The soil from Köpmannebro was also tested with longer leaching times, 18 and 24 h, due to earlier studies suggested that soil had a slower release of metals than ash (Yip, 2008, van Benschoten, 1997). Each soil sample was done in triplicates, while the ash samples were, to some extent, done in duplicates due to shortage of sample.

The leachates were separated from the soil or ash through centrifugation, which thereby terminated the leaching process. The centrifugation was done in a Sigma 4-16 at 3000 G for 15 minutes. The supernatants were decanted and filtered using paper filters, pore size 6 µm and a funnel (soil samples) or, due to the small amount of sample, filtered with a syringe and glass microfiber filter, pore size 1.6 µm (ash samples). The pH-values of the filtered supernatants were measured with Universal indicator from Merck to determine if acidification was necessary. As none of the samples had a higher pH than 2, no acidification was made. The supernatants were stored at 4°C pending further analysis.

The solid residues were washed with Milli-Q after the centrifugation. At first an L/S-ratio of 5ml per gram solid sample was used but it was later, after the one-step optimization, changed to 2ml per gram in order to minimize the volume of contaminated water. The samples were washed for 5 minutes in the reciprocal shaker (Julabo SW-20C), and then centrifuged at 3000 G for 15 minutes to terminate the washing step. The washing supernatant was filtered and its pH was measured with the same procedure as with the leaching supernatant. The remaining solids from the washing step were dried at 80^{o}C, until its weight had stabilized, and was then stored at 4^{o}C awaiting further analysis. The final weight of the dried solids was noted to be able to approximate the matrix degradation of the ash and soil.

3.1.4. Step-wise leaching

After evaluating the one-step leaching the optimization continued with a two-step leaching to investigate if this further improved the leaching. The leaching experiments showed that a high L/S-ratio was most effective; thus L/S-ratio 10 was used for all the two-step leaching experiments. The leaching time had no significant importance according to earlier experiments (see section 4.2.1.); therefore short leaching times were chosen: 15+15min, 15+30min and 30+30min. The leaching method was the same as in the one-step leaching, except that after decanting of the leaching supernatant from the first step, the leaching was repeated once more before the washing step.

3.1.5. Batch leaching

The optimal leaching parameters were used for a larger sample amount, 20-30g depending on available sample. These batch experiments where performed in the same way as the previous experiments.

3.1.6. Leaching test for depositing

To determine if leached ash and soil samples could be used as a resource instead of being landfilled, a downscaled SS-EN-12457-3 leaching test was performed. The dried pre- and post-leaching soil and ash samples were leached with Milli-Q, first for 6 h with L/S-ratio 2 followed by 18 h with L/S-ratio 8. During the leaching the samples were continuously shaken with a reciprocal shaker (Edmund Bühler 7400 Tübingen SM25) and then centrifuged to separate the leachate from the soil/ash. The volume of the decanted leachates were measured and filtered; then stored at 4°C awaiting analysis with ICP-AES.

3.2. Methods for metal analysis

The analysis of the leachates was the principal indicator if the leaching of the samples had succeeded or not. Selected leachates were sent to a commercial and certified laboratory for external analysis of metal concentrations, as was also done with the original soil and ash samples. To select the significant samples, not having to send all of them for external analysis due to high costs and delay of results, a spectrophotometric measurement of the Cu^{2+} concentration in the filtered supernatants from the leaching and washing steps were made (see section 3.2.1).

3.2.1. Analysis of Cu content in leachates and washing water samples

To get a fast estimation of the degree of success of the copper leaching tests, a semi quantitative spectrophotometric analysis of the leachates and the washing waters were done. This analysis measures the absorption at 610 nm, where the $[Cu(NH_3)_4]^{2+}$-complex has an absorption maximum. The conversion of all present Cu^{2+}-ions to $[Cu(NH_3)_4]^{2+}$-complexes was made by adding NH_3 in excess according to the method in Norin 2000.

To quantify the amount of $[Cu(NH_3)_4]^{2+}$ in the samples, a standard curve was made. For this 9.99 g $CuSO_4*5H_2O$ was dissolved in Milli-Q and diluted to 100.0 ml. From this solution 5.0 ml was further diluted with Milli-Q to 100.0 ml. From this solution five standard samples were made with 5.00, 10.0, 15.0, 20.0 and 25.0 ml of the copper solution. Next 5.0 ml of 5 M NH_3 was added to each sample as well as to a reference sample without any copper solution. These standard and reference samples were diluted to 50ml with Milli-Q, corresponding to 0, 2, 4, 6, 8 and 10 mM. After analysis of these samples, a standard curve for the absorption of $[Cu\ (NH_3)_4]^{2+}$ concentrations ranging 0-10 mM could be made according to Lambert-Beer law.

$$Abs = \varepsilon * c * l$$

To prepare the samples from the leaching experiments for the spectrophotometric analysis V_{sample} ml (specific values can be found in Table 3.1) from the leachate samples was mixed with V_{NH3} ml of 5 M NH_3 and diluted to V_{tot} ml with milli-Q. The differences in volumes when diluting different samples were due to the great variance in copper content between for example the leachate from the ash and the one from the soil. The turbidity of these diluted samples were then measured and, if necessary, diluted even further if the absorbance was higher than 600 or precipitation was found. The concentration of NH_3 was kept at 0.5 M independent of V_{sample} and V_{tot} for all samples to be comparable with the reference sample.

Table 3.1. Volumes for the dilution of leachate and wash water as preparation for spectrophotometric analysis.

ml	Soil	Ash	
	Leachate & washing water	Leachate	Washing water
V_{sample}	4.0	1.0	0.4
V_{NH3}	2.5	2.5	1.0
V_{tot}	25	25	10

3.2.2. Analysis of metals in solid soil, bark and ash samples

The soil, bark and ash samples were sent for external analysis to determine the total elemental content (see appendix II for results). The external lab prepared the dried samples for analysis according to standardized methods where the elements were dissolved using different methods depending on the material of the sample. The ash samples were dissolved according to the standardized methods ASTM D3683 and ASTM D3682 before analysis. For the bark and soil the same two methods were used. The samples was dissolved in Teflon containers using concentrated HNO_3 and H_2O_2 for analysis of As, Cd, Cu, Co, Hg, Ni, Pb, B, S, Se and Zn, or melted with $LiBO_2$ and then dissolved in HNO_3 for Ba, Be, Cr, Mo, Nb, Sc, Sr, V, W, Y and Zr. The exception was for analyzing tin (Sn) in soil samples where Aqua regia in reversed proportion was used for dissolution. The metal concentrations in the corresponding liquids were analyzed using ICP-MS.

3.2.2.1. ICP-MS

A very common analytical method is ICP-MS which was used to analyze the solids for elemental composition. The principle of an ICP-MS (Figure 3.2) is that the sample is converted into an aerosol by either a nebulizer or a laser, depending on whether the sample is a solution or a solid (Thomas, 2004).

The aerosol is then injected into the ICP-torch that consists of argon plasma controlled by an electromagnetic field created by a RF-generator. In the ICP-torch the aerosol is evaporated giving very small solid droplets of sample. These are in turn vaporized into a gas, and finally through collision with argon electrons, atomized and ionized (PerkinElmer, 2004).
After the sample is converted into single atom ions they are lead through two metal plates, called the sampler and the skimmer cone, in what is called the interface region. These cones have centered holes and thereby block the ionized beam that is not centered. The cones also facilitate the pressure drop, from 101.3 kPa at the plasma torch to 200 Pa in the interface region, and finally as low as 10^{-4} Pa in the analyzer region.

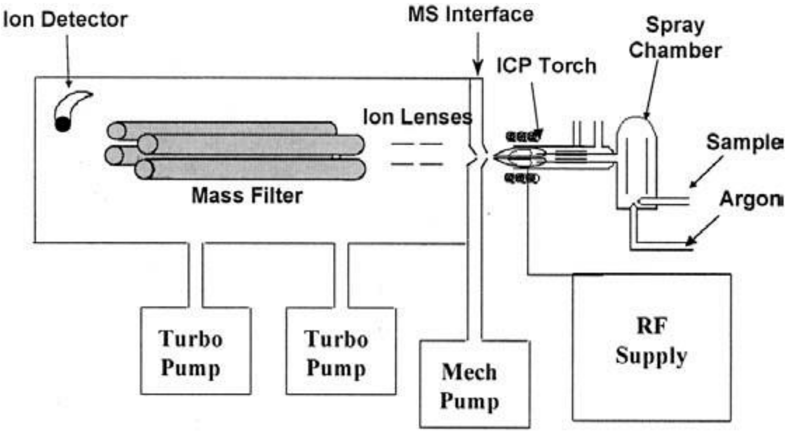

Figure 3.2. Schematic view of ICP-MS (Thomas, 2004)

In the analyzer region ions are first focused by ion optics, i.e. electromagnetic fields, before reaching an analyzer such as quadrupole or Time-of-Flight depending on what instrument is being used. In the analyzer the atom ions are detected depending on their M/Z-ratio and give both qualitative and quantitative measurement of the atoms present in the sample (Thomas, 2004).

3.2.3. Analysis of metals in original process water and selected leachate and wash water samples

The metals in the process water, leachates and wash water were quantified using ICP-AES (see appendix I for results). The samples were prepared by digesting in 7 M HNO_3. Even though the sample already is a solution, this is to break any complexes present. This preparation procedure is according to the standard SS 028150-2 while the analysis is done according to SS-EN ISO 17294-2:2005.

3.2.3.1. ICP-AES

Another analytical method similar to ICP-MS is ICP-AES, which was used to analyze the liquid samples. The method relies on the fact that atoms emits energy at specific wavelength when returning to ground state. The sample has to be a solution to be analyzed with ICP-AES and due to the low detection limit often diluted as well. The first steps of the ICP-AES are very similar to ICP-MS (see section 3.2.2.1.) where the sample is sprayed into an argon gas flow to create an aerosol. This aerosol is then injected into the plasma torch were the sample is vaporized, atomized and ionized using a radio frequency generator. In this part it is of importance that the whole sample is converted to plasma since atoms in ground state would absorb wavelength from excited atoms of the same elements and thereby lowering the sensitivity of the method (Levenson, 2001).

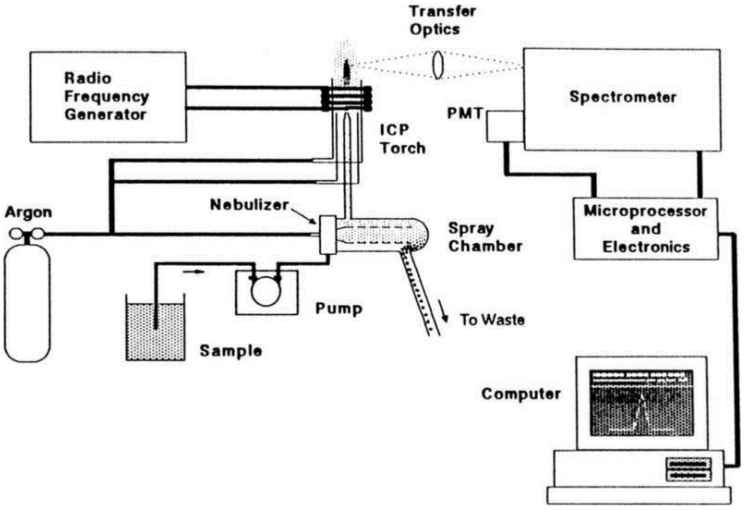

Figure 3.3. A schematic view of an ICP-AES, (Levenson, 2001)

Thereafter the similarities end since it is the light emitted from the plasma torch and not the individual ions, as is the case for ICP-MS that is analyzed. The light from the plasma torch is, through diffraction grating, refracted in different wavelengths and detected by photomultiplier tubes. The specific wavelength of different elements makes it possible to detect up to 40 elements simultaneously (Levenson, 2001).

3.2.4. Measurement of pH of soil samples

The pH of the soil and ash samples was measured according to the method in Bergil and Bydén 1995. The soil samples were prepared by air-drying 15 g until the weight had stabilized. Then 100 ml Milli-Q was added and the samples were mixed on a reciprocating shaker for 1 h. The samples were then stored over night for sedimentation of heavier particles. The next day pH was measured using a WTW pH-electrode SenTix 81 with a WTW Multi 350i.

3.3. Experimental Design

Due to the large amount of results from the leaching experiments, the experimental setup was designed according to a factorial design with two factors; leaching time and L/S-ratio, with 3 respectively 2-3 levels. Each leaching parameter was performed in triplicates (some exceptions for ash samples due to low samples amount) to assure a more robust design.

To get a better overview of the result ANOVA (analysis of variance) was used. Foremost to determine which parameters, if any, was significant but also if there was any interaction between the factors.

4. Results and discussion

This study was conducted with the intention to optimize the leaching of copper from soil and bark ash. Many of the results are promising although the heterogeneity of the samples sometimes makes it rather hard to conclude the success of the process. As for example more than 100% copper has been extracted in some of the leaching experiments even though accumulation from the process water and weight loss is included. Moreover the metal amount is higher in some ash samples than the initial content of the bark. The heterogeneity of the samples is probably a major source of error. Although the very small sample amount for the experiments as well as the small samples sent for total amount analysis.

4.1. Initial metal concentrations in soil, bark and ash

The metal concentrations from the solid samples from Köpmannebro, according to the ICP-MS analysis, where compared with earlier studies (Kemakta, 2012), Table 4.1. Some of the values are rather consistent but most differ by at least 50%, which stresses the fact that the samples are far from homogeneous. However given the large variance in earlier studies, where a tenfold difference or more is not unusual between the lowest and highest amount, the difference between earlier studies and this one is not that remarkable. More importantly the copper amounts are equivalent.

Table 4.1. Comparison of this study's measured metal concentrations with an average from earlier studies.

mg/kg		As	Ba	Cd	Co	Cr	Cu	Hg	Ni	Pb	V	Zn
Soil	Average	0.7	79	0.10	4.8	8.6	1250	0.20	6.2	11	19.8	26
	This study	0.6	497	0.03	2.2	41.5	1090	<0.04	3.1	8	44.4	14
Bark	Average	1.8	47	0.30	1.1	2.8	13700	0.30	3.3	57	3.3	74
	This Study	2.0	109	0.27	1.2	3.9	11300	0.06	3.5	31	6.7	44

In Table 4.2 the complete results from the total amounts analyses are presented. The yellow and red marked values are those that exceed the values for KM (sensitive land use) and MKM (lesser sensitive land use) respectively, for further information concerning MK and MKM (see section 2.3.1.). The copper is, as expected, the major contamination although barium has high enough amounts to be a problem as well. Other exceeding values are those of the ash samples, for which excessive accumulation of metals during incineration is expected, further discussed in chapter 4.1.1. Due to the high degree of contamination it is not likely that these samples will be below the MKM-limit even after leaching.

Table 4.2. Metal concentrations in all solid samples compared with MK and MKM limits. All concentrations are from the ICP-MS analysis with an uncertainty of 20-25%. Levels above KM is marked in yellow while those above MKM is marked in red.

mg/kg	Soil		Bark		Ash				KM	MKM
	Köpmannebro	Björkhult	Köpmannebro	Björkhult	Köpmannebro			Björkhult		
					Renova	Oxidizing	Reducing			
As	0.59	0.28	2.0	7.8	<3	11	5.2	22	10	25
Ba	500	860	110	620	430	930	520	2300	200	300
Be	1.4	1.9	0.12	0.67	<0.5	1.5	1.2	1.5		
Cd	0.032	0.014	0.27	0.095	0.15	1.3	<0.1	0.27	0.5	15
Co	2.2	0.25	1.2	0.94	2.3	7.5	3.9	2.2	15	35
Cr	42	25	3.9	9.0	71	50	23	24	80	150
Cu	1100	720	11000	15000	19000	130000	43000	110000	80	200
Hg	<0.04	0.055	0.062	0.37	<0.01	<0.01	<0.01	<0.01	0.25	2.5
Mo	0.29	0.22	0.25	0.30	3.1	2.4	1.9	1.4	40	100
Nb	9.0	5.9	0.42	7.0	5.4	8.8	<5	6.4		
Ni	3.1	0.25	3.5	2.6	21	26	15	7.9	40	120
Pb	7.9	3.2	31	39	61	360	91	150	50	400
S	76	<50	570	510	2700	4900	1900	2400		
Sc	7.7	1.9	0.56	1.2	<1	5.9	3.4	2.9		
Sr	190	200	30	95	130	230	110	260		
V	44	9.7	6.7	7.0	12	38	22	15	100	200
W	1.2	0.73	0.58	0.58	<50	<50	<50	<50		
Y	17	5.4	2.3	6.9	2.9	19	33	8.0		
Zn	14	3.5	44	36	1500	260	26	160	250	500
Zr	230	110	5.7	42	13	150	22	95		

4.1.1. Effects on metal concentrations from the incineration

As mentioned earlier, the fact that the ash samples have high metal concentration is not surprising. What is striking though is that some of the metals present in high concentrations are considered volatile and would have been more likely to accumulate in the fly ash. The metals in question are e.g. cadmium (Cd), lead (Pb), and zinc (Zn), where lead exceeds the KM-limit for all samples (Table 4.2). However, as mentioned earlier the ratio between bottom ash and fly ash depends on several factors and with this incineration method these metals have clearly accumulate in the bottom ash. In Table 4.3 the percentage of the metals in the bark that is staying in the bottom ash is presented.

As shown in Table 4.3, the percentages of metals left in the ash has quite reasonable values for cadmium (Cd), lead (Pb) and zinc (Zn) as the amount often is around 50% or below, which proves that most of the metals are enriched in the fly ash and the high amount in Table 4.2 is mostly due to the high amounts in the bark. The exceptions are the lead content in the ash incinerated at oxidizing conditions and the zinc content in the ash incinerated at Renova, which probably are due to heterogeneity in the samples. The ash from Björkhult tends to have higher content for all metals, which probably is because of the higher content of sand in the bark which is to high extent unaffected by the incineration and then releases adsorbed metals from its surface in the preparation step for the ICP-MS-analysis and thereby raises the levels for this sample.

Table 4.3. Percentage of the barks metal content still left in the ashes after incineration.

% metal left in ash	Köpmannebro			Björkhult
	Renova	Oxidizing	Reducing	
As	10	51	44	85
Ba	28	81	83	110
Be	29	120	170	67
Cd	3.8	46	6.5	84
Co	13	61	57	71
Cr	130	120	100	78
Cu	12	112	66	210
Hg	1.1	1.5	2.8	0.80
Mo	88	92	130	140
Nb	90	200	210	27
Ni	42	73	74	89
Pb	14	110	51	110
S	34	81	57	140
Sc	12	99	100	69
Sr	31	74	66	80
V	13	54	58	62
Y	8.7	80	250	34
Zn	240	56	10	130
Zr	17	250	68	68

Further on, other trends seen in Table 4.3 are the low percentage of metals in the ash incinerated at Renova compared to the other ashes. The major reason for the low accumulation in the bottom ash is most likely that the heat is applied through a feed of hot air. This airflow increases the amount of particles following the flue gas i.e. increases the amount of fly ash and thereby the accumulation of metals in it.

4.2. Results from the copper leaching optimization

An unexpected problem that occurred in the beginning of the project was the difficulties with incineration of the bark. The bark-to-ash ratio was extremely low, below 1%, and in order to increase the amount of bottom ash incineration with reducing surroundings was tested, i.e. incineration in crucibles with lids.

However, in the first leaching optimization of ash with the samples incinerated under reducing conditions the deficiencies of this preparation method such as incomplete combustion as well as lower leaching became obvious after a few initial test runs. An indication of incomplete combustion was that part of the ash sample was floating after centrifugation, which suggests presence of organic matter. This was later confirmed when the ash incinerated under reducing conditions had a LOI (loss on ignition) of 46.6% whereas the other ash samples had none (see Appendix II). A visual analysis suggested that the amount of leached copper was lower compared to from the ash incinerated under oxidizing conditions, in which' leachate samples were deep blue compared to the pale blue color of the ones from the ash incinerated under reducing conditions. Therefore the optimization continued with ashes incinerated at oxidizing conditions, both at Renova and in the lab, in a 50/50 mixture.

4.2.1. Optimization of leaching from ash samples from Köpmannebro

The optimization process started off with a series of one-step leaching experiments, where the parameters L/S-ratio and leaching time were varied for the contaminated soil and incinerated bark from Köpmannebro. In order to minimize the usage of process water L/S-ratios of 2 and 5 for both soil and ash were used. However, initial experiments indicated that an L/S-ratio of 2 was too low for ash samples since the entire leaching agent volume was adsorbed by the sample. Instead L/S-ratio 10 was included in the experimental set-up. As the results later will show L/S-ratio 10 was preferable; therefore the experimental set-up was extended to include L/S-ratio 10 for the soil samples as well.

Each sample was made in triplicate and the amount of copper measured with spectrophotometry. Measured copper content in the leachate was adjusted by subtracting the initial copper content in the process water: in order to get a better approximation of the amount of contaminant leached. In Figure 4.1 the results from these optimization experiments are presented; the results are normalized on the basis of the highest amount of leached copper to get an easy overview of the different parameters' effects. As seen in Figure 4.1 the L/S-ratio 10 leached 50% more copper than the L/S-ratio 5, while trends connected with the leaching time are less pronounced.

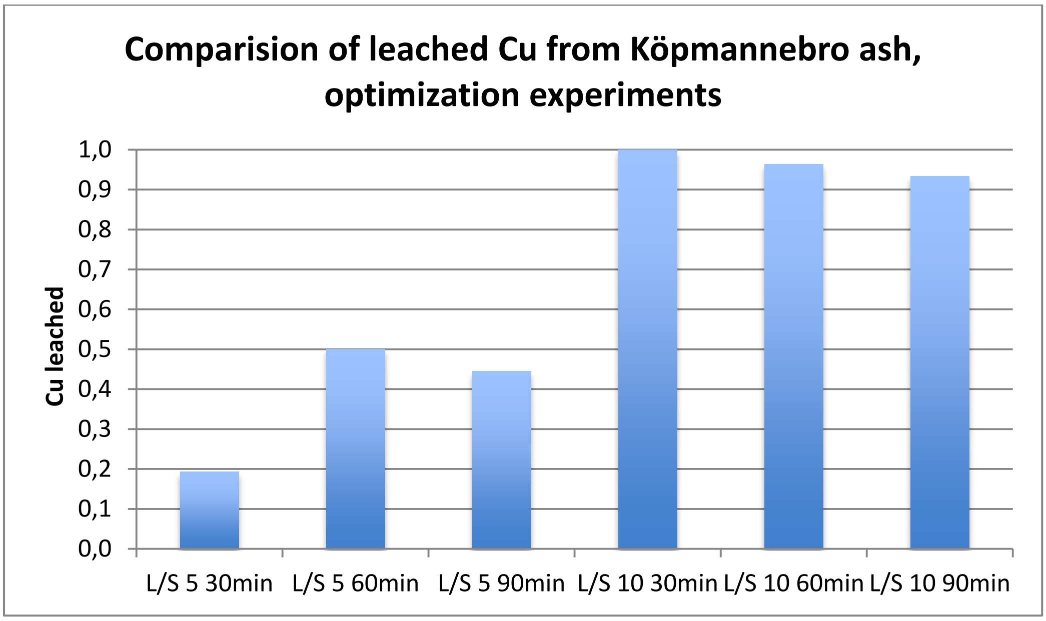

Figure 4.1. Amount of Cu leached with different parameter settings with ash from Köpmannebro. Normalized results with basis on the largest amount of leached Cu. All results mean of triplicate samples analyzed with spectrophotometry. Note that the results are corrected for the amount of copper present in the process water.

The washing water from the optimization experiments was analyzed by spectrophotometry as well. These results were not corrected regarding the initial copper content in the process water because in contrast to the leachate analysis, it is interesting to know the total amount of copper released, in the washing water. The washing water is interesting in order to determine how much weakly bound metal the sample can leach out and by this estimate how the sample would behave at a landfill. As can be observed in Figure 4.2 no obvious trend is evident.

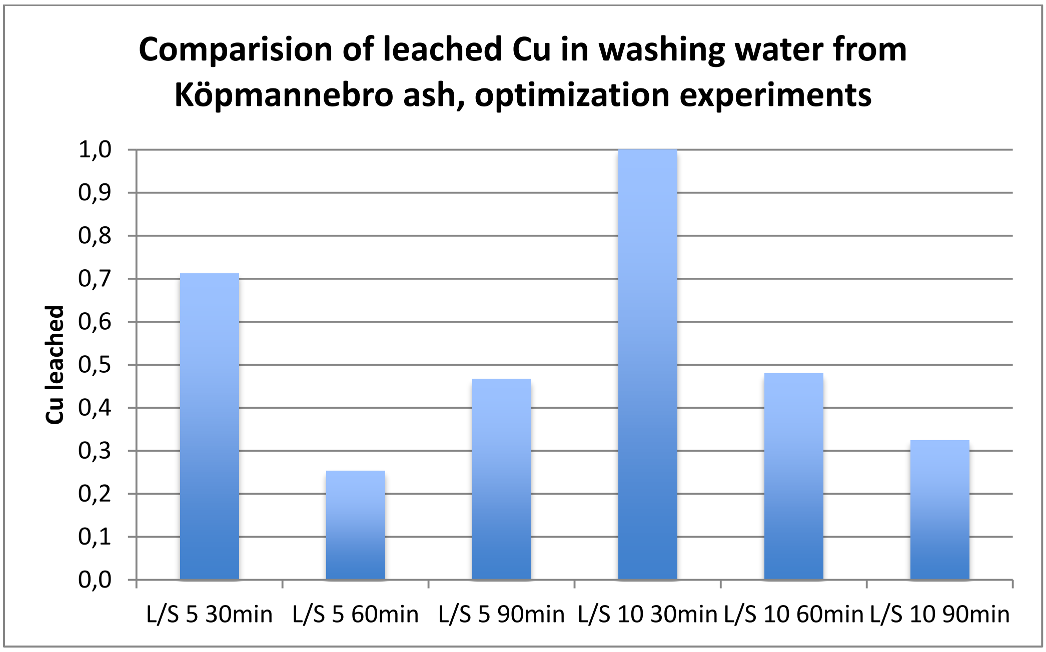

Figure 4.2. Amount of Cu in the washing water from the different leaching experiments with ash from Köpmannebro. Normalized results with basis on the largest amount leached Cu. All results mean of triplicate samples analyzed with spectrophotometry. Note that the results are not corrected with the amount of copper present in the process water used as leaching agent pre washing.

Figure 4.1 and 4.2 show the comparison between the results of the different parameter settings, but the actual amounts of copper removed are important.

In Table 4.4 the amount of copper per kg solid content ash is presented as well as the remaining amounts of copper in samples after leaching. As seen the amount of copper added by the process water is insignificant compared to the initial amounts in the samples, but is important to consider since the process water could vary in future trials. An interesting result is the amount of copper left in the sample that has been leached for 30min with L/S 10, as it is negative. This is due to the measuring insecurity of the spectrophotometric analysis as well as the external lab's measuring insecurity with the initial copper content. The heterogeneity of the samples is also a source of error, since only one solid ash sample, from each type of incineration, was sent for external analysis and the ash used in the experiments could vary in copper content compared to these samples.

The values of remaining copper are low, if you calculate the percentage of copper removed it is close to 100%, however the remaining content still has to be evaluated to determine if it is low enough for non-hazardous or hazardous landfill or if more treatment is needed (see section 4.3.).

Table 4.4. Amount of copper per mass unit of solid content ash in the different steps of the leaching process.

	m Cu leached per m ash, spectroscopy [mg/kg TS]	initial Cu content, extern analysis [mg/kg TS]	total amount of Cu added via process water, external analysis [mg/kg TS]	m Cu in washing water per m ash [mg/kg TS]	amount of Cu left in the samples [mg/kg TS]
L/S 5 30min	14900	79400	15	1630	62900
L/S 5 60min	36700	78200	15	570	40900
L/S 5 90min	33700	77800	15	1050	43100
L/S 10 30min	78100	80200	31	2330	-209
L/S 10 60min	73300	78500	30	1084	4140
L/S 10 90min	71900	79200	30	741	6560

To empower our conclusions on which were the optimal parameters, an ANOVA (statistical analysis of variance) was made of the leachates' copper content according to the spectrophotometric analysis. The results from the ANOVA (Table 4.5) clearly indicate that the only parameter with significant effect (p-value < 0.05) is the L/S ratio as suggested by the plot in Figure 4.1. Concluding the significance of L/S-ratio, the optimal setting of L/S-ratio 10 was used for the succeeding optimization process for ash samples. When determining which leaching time to proceed with the reasoning was, since it was insignificant for the amount of copper leached; shorter time is preferable, especially in large-scale processes, therefore leaching time 30min was chosen.

Table 4.5. ANOVA of the optimization experiments of ash from Köpmannebro.

ANOVA	**SS**	**df**	**MS**	**F**	**F_{table}**	**p-value**
Leaching time	482	2	241	0.60	3.89	0.56
L/S	14900	1	14900	37.25	4.75	0.000053
Interaction	978	2	489	1.22	3.89	0.33
Error	4810	12	401			
Total	21200	17				

4.2.2. Optimization of leaching from soil samples from Köpmannebro

Similar to the ash samples, optimization experiments were made with the soil samples from Köpmannebro. The initial experimental set-up was extended with L/S-ratio 10 since it was successful with the ash samples; hence both L/S-ratio and leaching time had three levels. As in the case of the ash samples, all leachates were evaluated by spectrophotometry. The spectrophotometric analysis was unfortunately non suitable for the soil samples because soil particles dyed the leachates resulting in a too high absorption. However it was assumed that the error due to the coloring remaining after filtration was equal for all of the samples and therefore the results were still accurate for conclusions regarding optimization. The spectrophotometric results were compensated regarding the initial copper content of the process water before evaluation. In Figure 4.3, where the results have been normalized on the basis of the highest amount of copper removed, it is evident that the L/S 10 is superior to lower ratios while as for the ash no obvious trend for leaching time could be deduced.

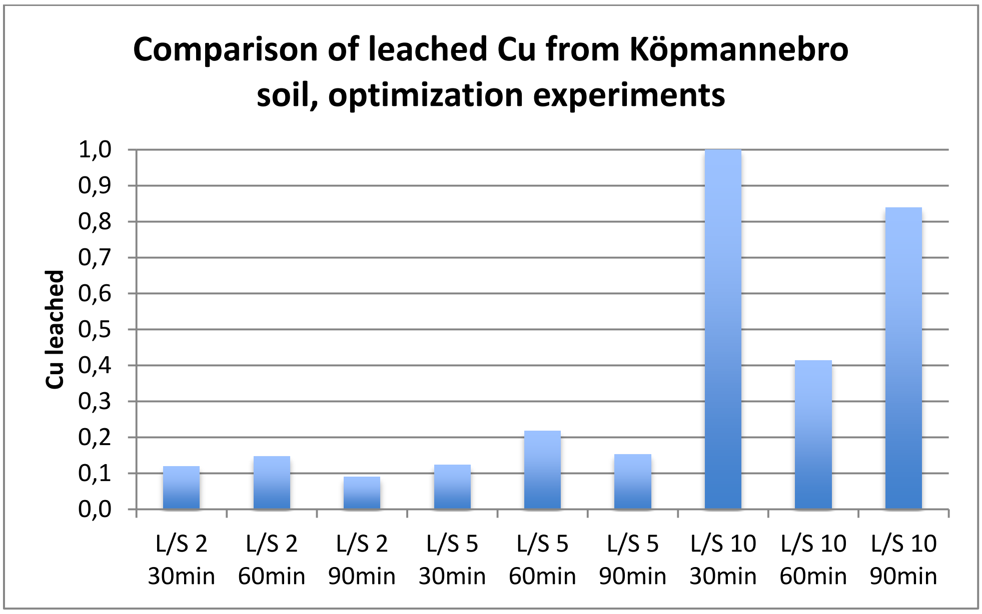

Figure 4.3. Amount of Cu in leachates from the different leaching experiments with soil from Köpmannebro. Normalized results with basis on the largest amount leached Cu. All results mean of triplicate samples analyzed with spectrophotometry. Note that the results are corrected with the amount of copper present in the process water used as leaching agent.

The washing water from the soil samples was also analyzed with spectrophotometry. The results shown in Figure 4.4. are not compensated regarding the initial copper content in the process water. In difference to the corresponding results for the ash samples a trend can be seen for the soil's washing water. It is clear that a higher L/S ratio during leaching results in a less contaminated washing water.

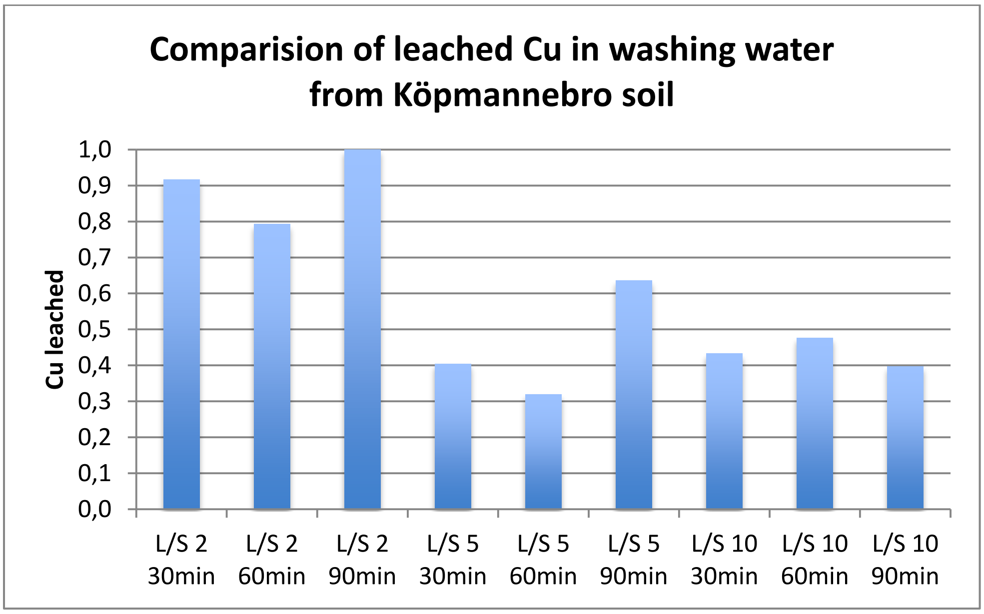

Figure 4.4. Amount of Cu in washing water from the different leaching experiments with soil from Köpmannebro. Normalized results with basis on the largest amount leached Cu. All results mean of triplicate samples analyzed with spectrophotometry. Note that the results are not corrected with the amount of copper present in the process water used as leaching agent pre washing.

A similar table as Table 4.4 for the ash was made for the soil, here (Table 4.6) the disadvantages with using spectrophotometric analysis is obvious because almost all of the results are showing a more than 100% removal of copper. In addition to the unsuited method of analysis the heterogeneity issue is the same as for the ash.

Table 4.6. Amount of copper in all of the leaching process steps for soil from Köpmannebro.

	amount of Cu leached per mass of soil, spectroscopy [mg/kg TS]	initial Cu content, extern analysis [mg/kg TS]	total amount of Cu added via process water, external analysis [mg/kg TS]	amount of Cu in washing water per mass of soil, spectrophotometry [mg/kg TS]	amount of Cu left in the treated samples [mg/kg TS]
L/S 2 30min	1010	1090	6	212	-123
L/S 2 60min	1250	1090	6	183	-335
L/S 2 90min	759	1090	6	231	106
L/S 5 30min	1050	1090	15	93	-34
L/S 5 60min	1840	1090	14	74	-812
L/S 5 90min	1300	1090	14	147	-340
L/S 10 30min	8480	1090	29	100	-7460
L/S 10 60min	3510	1090	29	110	-2500
L/S 10 90min	7120	1090	29	92	-6090

Even though the amounts of copper removed probably are deceptive concerning actual copper contents, the results are still assumed to be comparable and therefore an ANOVA was made for the results. The statistical analysis (Table 4.7) of soil leachates concluded the same as for the ash leachates; the only significant parameter is L/S-ratio (p-value < 0.05). Since the L/S 10 had the superior leaching ability it was chosen as the L/S-ratio to move forward with, and as for the leaching time the same reasoning as with the ash samples was made; shorter time is better and 30min was chosen.

Table 4.7. ANOVA of the optimization experiments of soil from Köpmannebro.

ANOVA	**SS**	**df**	**MS**	**F**	**F_{table}**	**p-value**
Leaching time	67100	2	33500	1.27	3.89	0.316
L/S	1350000	2	677000	25.62	4.75	0.0000054
Interaction	277000	4	69300	2.62	3.89	0.069
Error	476000	18	26400			
Total	2170000	26				

4.2.3. Two-step leaching

The washing water of the ash samples still contained much copper and therefore the optimization process continued with studying if a two-step leaching could further improve the amount copper removed in the leaching process. Three different combinations were tested for the ash samples; 15+15min, 30+15min and 30+30min all with an L/S-ratio of 10. All the samples consisted of an approximate 50/50 mixture of ash incinerated at Renova and ash incinerated at the lab under oxidizing conditions and was made in duplicates. The leachates were then analyzed with spectrophotometry; the results are presented in Figure 4.5 where the results once again are normalized on the basis of the highest amount of copper removed. As seen in the figure the 30+30min seems to be the best option. Another interesting observation of the results is that a considerable amount of copper is leached in the second step, which indicates an advantage with a two-step process.

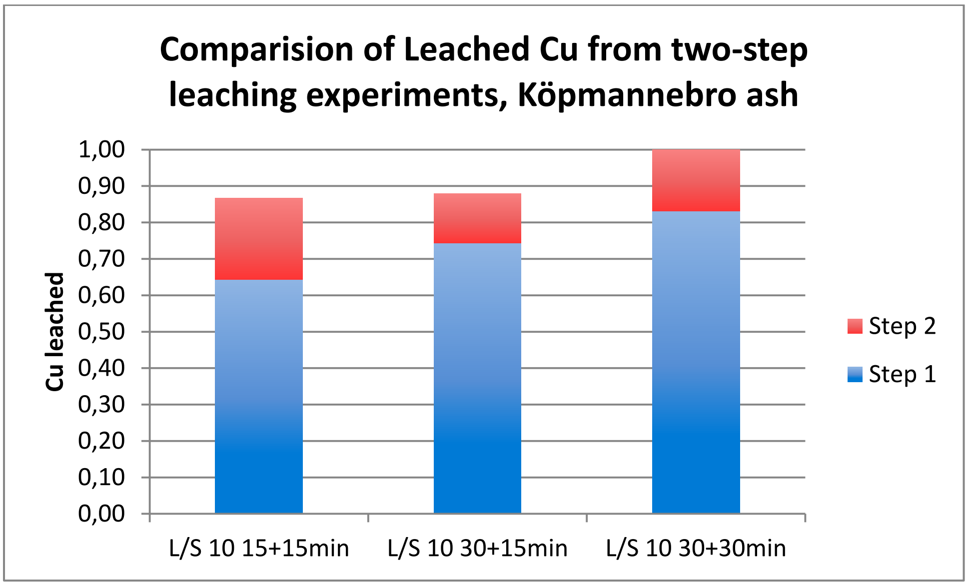

Figure 4.5. Amount of Cu in leachates from the different two-step leaching experiments with ash from Köpmannebro. Normalized results with basis on the largest amount leached Cu. All results mean of duplicate samples analyzed with spectrophotometry. Note that the results are corrected with the amount of copper present in the process water used as leaching agent.

The washing water from the two-step leaching experiments was also analyzed with spectrophotometry. As can be seen in Figure 4.6 the two-step leaching with at least one step of 30min show lower amounts of copper than the experiment with only two 15min steps.

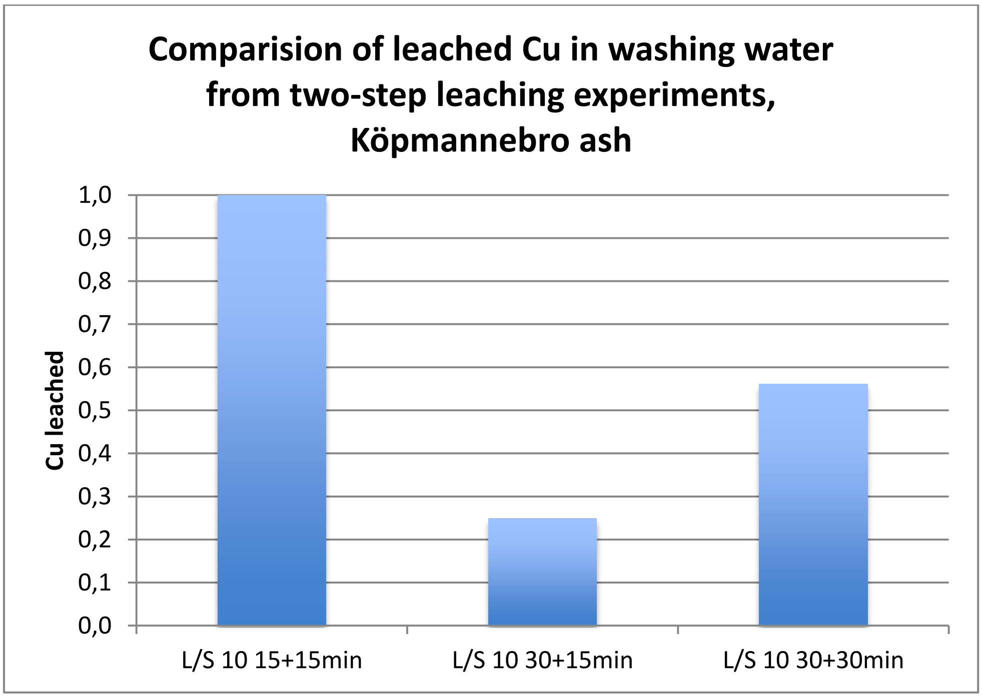

Figure 4.6. Amount of Cu in washing water from the different two-step leaching experiments with ash from Köpmannebro. Normalized results with basis on the largest amount leached Cu. All results mean of duplicate samples analyzed with spectrophotometry. Note that the results are corrected with the amount of copper present in the process water used as leaching agent pre washing.

When the actual amounts of copper removed are calculated the problems with the spectrophotometric analysis is obvious since all of the experiments show a more than 100% removal of copper, as seen in Table 4.8. However we believe that the results are still comparable relative each other, which gives an indication of 30+30min being the optimal leaching time.

Table 4.8. Amount of Cu in the different steps in the two-step leaching.

	amount of Cu leached per mass of ash, spectroscopy [mg/kg TS]	initial Cu content, extern analysis [mg/kg TS]	total amount of Cu added via process water, external analysis [mg/kg TS]	amount of Cu in washing water per mass of ash [mg/kg TS]	amount of Cu left in the treated samples [mg/kg TS]
L/S 10 15+15min	85200	78900	30	71	-6390
L/S 10 30+15min	85400	78200	50	17	-7170
L/S 10 30+30min	103000	79600	30	40	-23900

As earlier mentioned 30+30min leaching seems like the best option by the results presented in Figure 4.5. An ANOVA was made on the results to see if this conclusion was statistically significant as well (Table 4.9). This was not the case, which could be the result of too few replicates, but due to the limited amount of sample no further experiments were made. Concluding the results from the two-step leaching 30+30min was determined to be best and to use this setting for further experiments with ash samples.

Table 4.9. ANOVA of two-step leaching results

ANOVA	SS	df	MS	F	F_{table}	p-value
Leaching time	332	2	166	0.222	3.89	0.804
Error	2240	3	746			
Total	2570	5				

4.2.4. Batch experiments

After the two-step leaching experiments it was determined to continue with 30+30min leaching with an L/S-ratio of 10 for ash samples, while only one step leaching of 30min for soil samples. The next step was to try these optimal conditions on a larger sample size, a batch sample. The spectrophotometric analysis was only used to compare the results, and its qualitative accuracy was doubted. In addition to this it was only suitable for analyzing the copper content while other metal content also is of interest in investigating the success of the method. Unfortunately the leaching exceeded 100% for some samples (Table 4.8) even with the external analyses. Explanations to this are probably the heterogeneity of the materials in addition to the uncertainty of the external analysis.

In Figure 4.7 the result from the batch experiments of ash is presented. The leachates contain much copper than both the process water and the washing water from both Köpmannebro and Björkhult ash. This means that the copper content in the process water is negligible as well as that most of the removable copper is actually removed by the leaching. A difference can be seen between the two sampling points; the second leaching step is of much more importance for Köpmannebro ash compared to Björkhult ash.

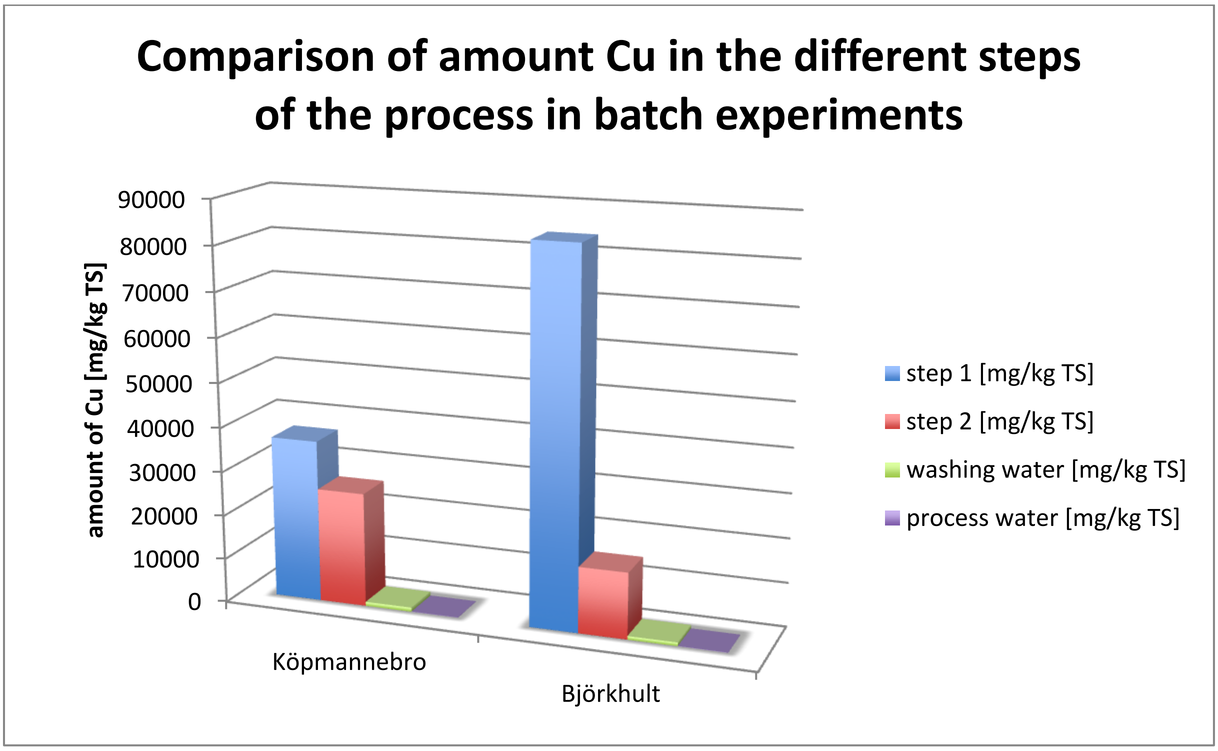

Figure 4.7. Results from two-step leaching batch experiments of ash from Köpmannebro and Björkhult. Both batches being leached for 30+30min with L/S-ratio 10. The copper content for both steps of leaching, the washing water and the leaching agent being presented in mg of Cu leached per solid mass of ash.

When comparing the leached amount of copper with the initial content in the ash a problem appear and for the Köpmannebro ash the removal is more than 120%. This could, as described earlier be due to the heterogeneity of the ash. Interesting to see is that the Björkhult ash, which only was incinerated by one method, has a more believable result, which indicates that future research should use only one method, which is more efficient for consistent results. Another way of handling this problem could be to send both untreated and treated ash for external analysis.

Table 4.10. Amounts of Cu in the different steps in the batch leaching experiments of ash from Köpmannebro and Björkhult.

	step 1 [mg/kg TS]	step 2 [mg/kg TS]	washing water [mg/kg TS]	process water [mg/kg TS]	initial Cu content [mg/kg TS]	Amount of Cu left in the samples [mg/kg TS]
Köpmannebro	36700	25900	939	63	51600	-11800
Björkhult	84000	15000	820	58	107000	7300

In Figure 4.8, the result of batch experiments of the soil is presented. As seen for both soils most of the removable copper is extracted in the leaching step and as with the ash, the process water's copper content is insignificant compared to the amount in the leachate.

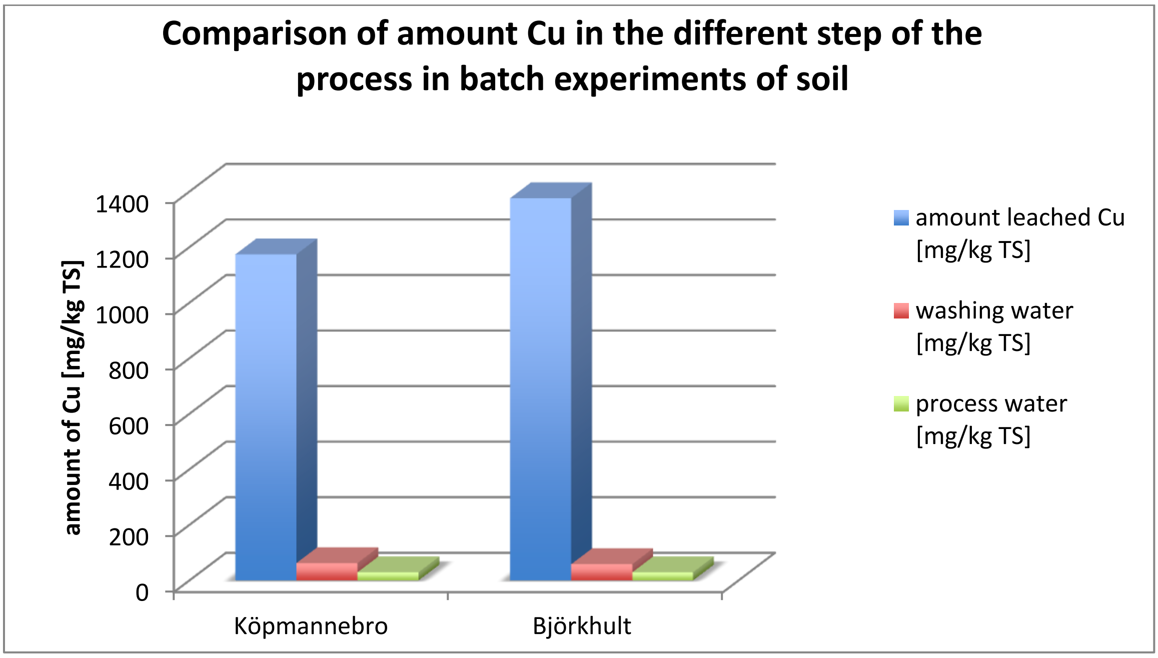

Figure 4.8. Batch leaching of soil, 30min with L/S 10. Results based on external analysis of both soil and leachate and are corrected regarding the initial copper content in process water.

When looking into the actual contents in the leachates the same problem as with the Köpmannebro ash occurred, i.e. more than a 100% removal. This could be due to the insecurity of the analysis or that the external lab analyzed only the fine-grained particles of the soil while the leaching experiments leached the whole particle size distribution.

Table 4.11. Amounts of Cu in the different steps of batch leaching experiments of soil.

soil batch experiments	amount leached Cu [mg/kg TS]	washing water [mg/kg TS]	process water [mg/kg TS]	initial Cu content [mg/kg TS]	Amount of Cu left in the samples [mg/kg TS]
Köpmannebro	1170	62	29	1090	-117
Björkhult	1380	58	29	719	-686

4.2.5. Long leaching time

Some earlier research suggests a much longer leaching time to efficiently release metals from soil (Udovic, 2012). Therefore 18h and 24h-leaching time were tested as well. The results presented in Figure 4.9 illustrate that the percentage copper leached decreases with longer leaching time if you compare 18h with 24h. The difference between 18h and 30min is negligible if you look at the scale of the axis since if you put the difference in numbers it is less than 100mg/kg TS. With this in mind the advantages with a 30min treatment time compared to 18h is obvious and the decision for 30min is easy. As seen later, when comparing the content of other metals in the leachates, the longer leaching time have the disadvantage of other metals from the process water accumulating in the soil, something that is avoided to a greater extent with 30min leaching.

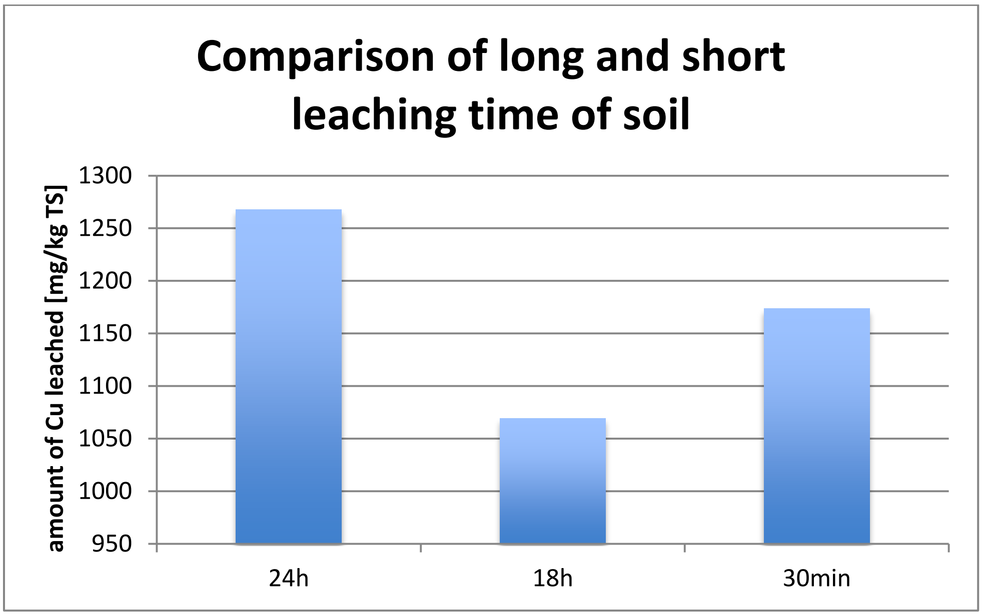

Figure 4.9. Percentage of Cu leached from soil from Köpmannebro. Each analysis for a collected sample from triplicates, all corrected regarding the initial copper content in process water.

4.2.6. Comparison one step leaching versus two-step leaching

To get confirmation of our optimization, leachate from an experiment with L/S 5 and 30min leaching time with ash from Köpmannebro was also sent for external analysis. As seen in Figure 4.10 it is evident that the optimal leaching parameters' yield greatly exceed the L/S 5, 30min leaching's yield. This confirms the importance of both the two-step leaching and high L/S-ratio for the ash.

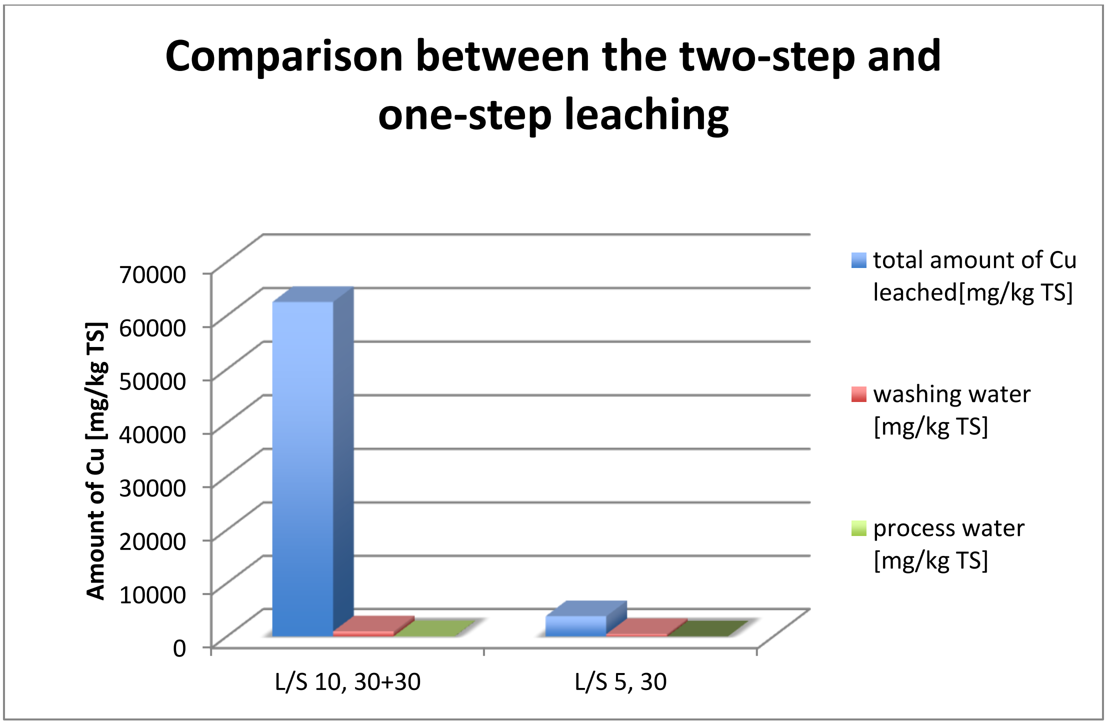

Figure 4.10. Comparison between L/S 5 30min leaching with L/S 10 30+30min leaching of ash from Köpmannebro.

4.2.7. Washing water

The same error in the spectrophotometric analysis due to coloring occurred for the washing water samples, but the same assumption of the error being the equal for all samples was drawn. When converting the amounts of copper in the washing waters to percentage of initial content soil it is easy to believe that since the percentage is higher for soil than ash so is the copper content. This is a faulty conclusion since the initial copper content is so much lower in the soil hence the actual copper content in the washing water of soil samples is actually lower than the washing water of ash samples. In Figure 4.11 the amount copper per mass unit of dry content sample is presented and it is easy to see that all of the soils washing waters have less copper than the ash washing waters. The improvement in cleaner washing water for two-step leaching compared to one-step for the ash samples is also easy to see.

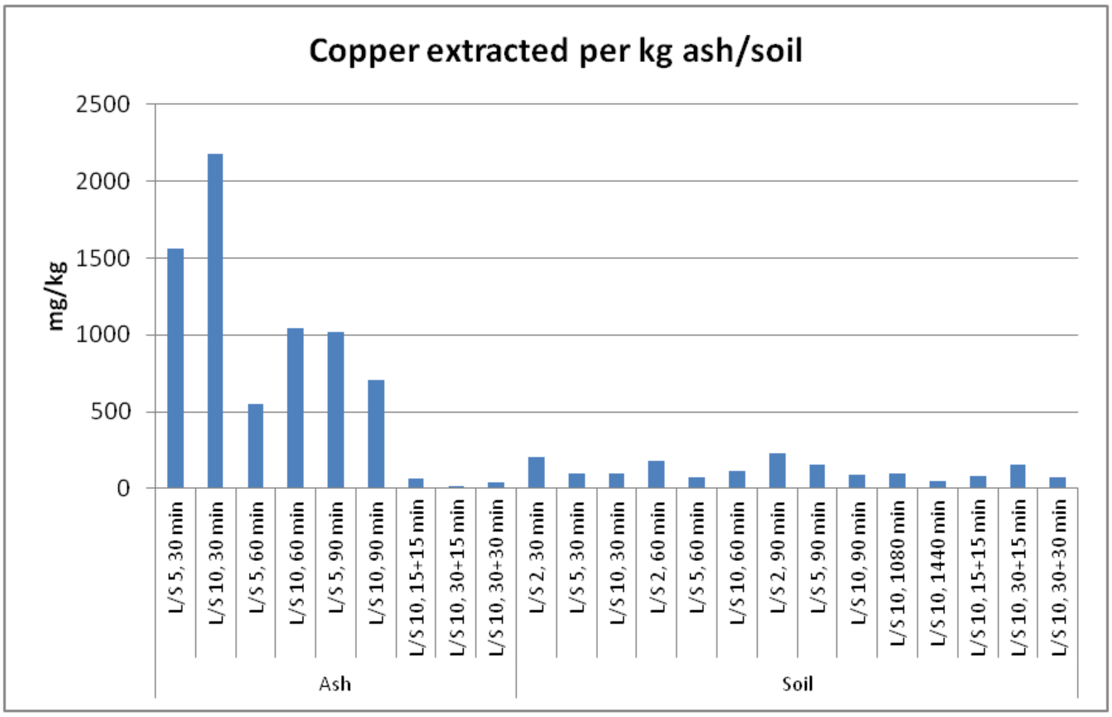

Figure 4.11. Amount of Cu per kg of sample in washing waters of soil and ash samples.

4.3. Handling and after-treatment of the leached soil and ash

The main aim with this master thesis was to extract as much copper from the soils and ashes as possible. However the handling of the leached soil and ash is of great importance as well since disposal of these could be costly depending on how polluted they are. As described in chapter 2.3.1 there are mainly two different criteria (KM/MKM and leaching test SS-EN12457-3) on how to handle the soil and ash dependent the degree of contamination.

For the KM/MKM-criteria the total amounts in the material are measured. Since no quantification of metals in the leached soil and ashes were made the values used are calculated from the initial and the leached amounts. This leads to some negative concentrations due to the heterogeneity of the samples but still gives a hint of the actual amount remaining.

The other criteria is leaching e.g. the SS-EN12457-3 leaching test where the water-leachable amount from the material is measured, to predict how much that will leach to the surroundings at a landfill. Both of these analyses are based on the quantification made with ICP-MS and ICP-AES.

4.3.1. The KM/MKM-criteria

As been discussed earlier the leaching of copper has succeeded to a great extent, which also can be seen in Table 4.11 and 4.12. In regards of the KM/MKM-criteria for copper all samples can be considered safe for reuse except the ash from Björkhult. However 93 % of the copper has been removed from this sample, which still is a success considering reuse of the copper. For some of the samples more than 100% of the copper was extracted which is mostly due to the heterogeneity of the sample. More sample would have been needed for a more precise result but the trend support the success of the copper extraction.

Table 4.11, Calculated metal concentrations in the leftover of the soil/ash samples compared to the KM/MKM-limits. Values marked with yellow is above KM and red is above MKM. These values can be compared with Table 4.1 from before leaching. The values are compensated with the weight loss from the leaching.

mg/kg	Soil				Ash		KM	MKM
	Köpmannebro			Björkhult	Köpmannebro	Björkhult		
	30 min	18 h	24 h	30 min	30+30 min	30+30 min		
As	0,5	1,3	1,2	0,1	0,4	<1	10	25
Ba	494	491	492	872	1051	2583	200	300
Be	1,4	1,4	1,4	1,8	1,3	1,6		
Cd	<0,5	<0,5	<0,5	<0,5	<0,5	0,10	0,5	15
Co	1,9	1,1	1,3	0,1	4,8	2,3	15	35
Cr	42	41	41	25	115	27	80	150
Cu	<1	7,31	<1	<1	<1	8249	80	200
Mo	0,5	0,5	0,5	0,3	1,6	0,8	40	100
Ni	2,6	1,4	1,8	0,1	<1	<1	40	120
Pb	<1	15,2	8,1	7,2	4,3	138,3	50	400
Sr	194	194	194	206	15	240		
V	44	41	42	9	23	11	100	200
Zn	<1	90	15	38	<1	<1	250	500

A longer leaching time for soil leads to uptake of arsenic from the process water, which can be seen in Table 4.12 where the total percentage extracted is negative. In this case, the levels of arsenic (As) is far below the limits but if the process water would have higher arsenic concentration this could be a problem. In earlier studies the arsenic levels of the process water has been twice as high and due to the fluctuation in the material incinerated it could be higher. Unlike for the soil the process water extracts almost all arsenic from the ash samples. This is of importance since the initial levels in the ash were above the guidelines (see section 4.1.) and indicates that the process water could be used to clean ashes from arsenic in addition to copper.

Other metals that were enriched, i.e. got a negative value in Table 4.12, in the soil by the process water were molybdenum (Mo), lead (Pb) and zinc (Zn). Molybdenum was enriched in all of the soil samples although, as with arsenic, far below the guidelines. When it comes to lead and zinc it is hard to draw any conclusion, as the sample from Köpmannbro leached for 18 hours and the one from Björkhult enriched these metals, while the sample from Köpmannebro that has been leached for 30 minutes and 24 hours have very different results. The enrichment of metal contaminations in the soil was as mentioned noticed at low levels which due to the insecurity of the results makes it hard to prove but it is still an important trend to be aware of in further studies. Worth mentioning is that the ash samples do not have any uptake from the process water from any of the quantified metals.

Table 4.12. The percentage of metal removed from the samples in the leaching experiments. A negative value means that there has been an uptake from the process water to the sample.

% metal removed	Soil				Ash	
	Köpmannebro			Björkhult	Köpmannebro	Björkhult
	30 min	18 h	24 h	30 min	30+30 min	30+30 min
As	10	-116	-102	56	96	108
Ba	3	3	3	1	11	1
Be	2	3	3	6	20	6
Cd	676	424	312	2077	131	69
Co	15	49	40	48	38	8
Cr	1	4	4	2	14	2
Cu	113	99	116	199	123	93
Mo	-57	-60	-58	-38	74	49
Ni	17	55	44	47	431	1269
Pb	169	-87	0	-118	99	19
Sr	1	1	1	0	95	17
V	4	9	8	13	43	37
Zn	282	-520	0	-972	391	140

Even though the leaching succeeded in extracting all or most of the major contaminant, i.e. copper, the barium (Ba) levels are still too high for all samples to be regarded as KM or MKM (see Table 4.11). This is much due to the process waters inefficiency to extract barium (generally around 3.0 %). This is not that of a problem for the ashes since these got other contamination that prevents them from this usage but as Ba is the only element in soil residue exceeding the guidelines it would have been a major success if it could be extracted and the soil could be returned to the site and thereby removes the need of other filling material (for comparison with initial concentration see Table 4.1).

Other results of interest from Table 4.11 and 4.12 are the successful extraction of cadmium (Cd) and lead (Pb) from the ash from Köpmannebro. These levels where initially over the MKM-limit (see section 4.1.) but was reduced below the KM-limit after leaching. This was not the case for the ash from Björkhult where the process water only managed to extract 18% lead compared to 99% for the ash from Köpmannebro. This might be due to that the lead is adsorbed on the sandy soil existing in the ash sample from Björkhult (the layers were not as divided as for Köpmannebro) since lead otherwise is rather easy to extract from ash with acidic leachate (Ohtsubo et al., 2004).

Finally the chromium (Cr) amount is initially below the KM-limit but has increased after the leaching. This is not due to any uptake from the process water but rather due to the ashes weight loss during leaching. The weight loss (presented in Table 4.13) for the Köpmannebro ash is so high that metal levels that are initially close to the limits risk breaking them if the leaching was not successful of the particular metal. In this study however this only applies to chromium for the ash sample from Köpmannebro. This loss of solid material is also one reason why the ash from Köpmannebro still have high amount of contaminations compared to total mass after leaching since it loses more than half of its weight.

Table 4.13, The weight percentage of how much solid material that is lost in the leaching and washing step.

Köpmannebro		Björkhult	
Ash	Soil	Ash	Soil
51,4	2,1	11,9	4,1

4.3.2. The results from SS-EN12457-3 leaching test

The result from the EN-leaching test (Table 4.14) gives an indication of how to handle the disposal of soil and ash. However not all of the contamination (can be found in NFS 2004:10) was analyzed so the recommendation of methods of disposal are only made regarding the metals presented in Table 4.14. This discussion will focus on the copper content since it is the main substance in this thesis eventhough there are also other metals (e.g. Zinc (Zn) and selenium (Se)) contributing to exceeding the guidelines the copper concentration raises the risk grade even higher than the zinc or selenium concentration alone.

Table 4.14. Metal concentration in the water leachates after shake test (SS-EN12457-3). Green marked values is those within the non-hazardous waste limit, yellow marked is those within the hazardous waste limit and the red marked is those above the hazardous waste limit.

	mg metal/kg soil or ash	As	Ba	Cd	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Se	Zn
	Köpmannebro 30+30 min	0,04	2,9	0,11	0,04	1019		0,04	0,76	0,02		0,07	50,2
A	Köpmannebro 30+30 min, no wash	0,04	3,5	0,24	0,07	2440		0,03	1,84	0,12		0,14	94,7
S	Köpmannebro 30 min	0,04	2,2	0,00	0,11	11		0,18	0,11	0,04		0,22	1,1
H	Björkhult 30+30 min	0,01	7,9	0,02	0,03	752		0,03	0,08	0,22		0,05	3,7
	Björkhult 30 min	0,11	10,6	0,05	0,28	3043		0,28	0,28	0,24		0,56	7,1
	Köpmannebro 30 min	0,01	1,4	0,03	0,12	78		0,03	0,55	0,07		0,05	7,6
S	Köpmannebro 18h	0,01	1,3	0,03	0,10	51		0,03	0,51	0,07		0,05	7,2
O	Köpmannebro 24h	0,01	1,1	0,02	0,09	39		0,03	0,40	0,06		0,05	5,6
I	Köpmannebro untreated	0,03	0,5	0,00	0,03	52		0,03	0,03	0,15		0,05	0,4
L	Björkhult 30 min	0,01	1,6	0,02	0,03	66		0,03	0,10	0,08		0,05	3,3
	Björkhult untreated	0,02	0,5	0,00	0,03	41		0,03	0,03	0,06		0,05	0,3
	Upper concentration limits												
	Inert waste	0,5	20	0,04	0,5	2	0,01	0,5	0,4	0,1	0,06	0,1	4
	Non-hazardous waste	2	100	1	10	50	0,2	10	10	10	0,7	0,5	50
	Hazardous waste	25	300	5	70	100	2	30	40	50	5	7	200
	Above hazardous waste	>25	>300	>5	>70	>100	>2	>30	>40	>50	>5	>7	>200

4.3.2.1. Results of the EN-leaching of the ash samples

All of the ashes, except for the one leached in one step for 30 minutes, are well above the limits for needing be handled at sites for hazardous waste. The fact that all of the samples exceed limits for hazardous waste is not that surprising due to the extremely high initial amount of copper. However, it is somewhat suprising that the Köpmannebro ash leached once for 30 minutes has so low copper values compared to the other samples especially as the same sample has a lower copper yield in the actual leaching test. Logically it should have more Cu left in the ash complex than other more successfully leached samples (chapter 4.2). This is mainly due to that a higher L/S-ratio was used during the washing step for the first experimental trials. At first L/S 5 was used but was later lowered to L/S 2 due to wanting to minimize the water amount. A washing step with L/S 2 was used for all samples in Table 4.14 except for the Köpmannebro ash leached for 30 minutes. Another probable explanation is that the process water has not been given enough time to destroy the ash matrix and thereby weakened the metal-to-ash bonds. The heterogeneity of the samples is also a likely contributor to the low copper concentration although a far smaller source of error.

Another important remark in the results from the EN-leaching is the importance of the washing step. The ash sample from Köpmannebro leached in two steps; 30+30min, was tested both pre and post washing. Comparing the results it is noted that the pre washing sample leached twice the metal amount or higher for most of the metals analyzed compared to the post washing sample. Even though the washing step seems to be of importance in the leaching process, the copper values are still ten times the limit for being treated as hazardous waste. However, comparing these results with the one for Köpmannebro ash leached for 30 minutes has only 1% of the earlier mentioned. This is below the non-hazardous waste limit and is probably most due to the more extensive washing step for this sample (L/S 5 instead of L/S 2 as mentioned earlier). This suggest clearly that the washing step is insufficient and needs to be improved by a higher L/S-ratio and perhaps a longer washing time.

The results of the ash samples from Björkhult indicates that the two-step leaching substantially improves the leaching since all of the analyzed metal concentration has been lowered compared to one step leaching. However, similar to the ash samples from Köpmannebro, the copper concentration after washing is still far from being acceptable as hazardous waste which once again might be due to an insufficient washing step.

4.3.2.2. Results of the EN-leaching of the soil samples

The soil samples have much lower metal concentrations compared to the ash samples. All of them fulfill the requirements, regarding the analyzed metals, to be deposited at landfills for hazardous waste. Two of the samples even comply with the limits of non-hazardous waste. One of them is the soil sample from Köpmannebro, which has been leached for 24 hours. Compared with the other Köpmannebro soil samples, leached for 30 minutes and 18 hours the amount of all quantified metals leached in the EN-test decrease with longer leaching time. Since the amount of copper removed in the process water leaching is approximately equal for these samples (chapter 4.2) this suggest that longer leaching time fixate the metals left in the soil matrix stronger with time. This is consistent with the results in Table 4.12 where fixation of metals to the soil can be seen as accumulation from the process water to the soil.

The untreated soil samples from both sites had lower release of metals than the samples leached with process water for 30 minutes. This indicates that the process water, as intended, weakens the metal to soil bonds. Although the washing step has to be improved to remove more of the weakly adsorbed metals left in the soil for the method to be even more efficient. This could be done by extending the washing step, use a higher L/S-ratio for this step or using a sequential/multiple steps washing.

Another conclusion from Table 4.2 and 4.14 is that the process water increases the amount of zinc in the soil. This might be due to ion exchange between the process water and the soil/ash matrix. While the untreated soil samples have 0.3 respectively 0.4 mg zinc per kg soil the treated soil samples has zinc contents above 3 mg per kg soil. The amount of zinc in the soil is not alarming, but indicates that process water can increase the toxicity of the soil. This is an important effect to be aware of since the metal content of the process water differs depending on what is being incinerated at Sävenäs.

In continuous trials other contaminants, which might accumulate even more in the soil, could be present in a higher concentration which would result in a treated soil that need a more expensive disposal method than the untreated one. However it is important to remember that this is only at very low concentrations and only looking at the limits it is still better to treat the soil than to send it for landfill untreated even though some metals accumulate and some are left more easily leachable after treatment.

4.3.3. The KM/MKM-criteria versus SS-EN12457-3 leaching test

These results are somewhat contradictory since it is barium (Ba) that is the major concern regarding the KM/MKM-criteria while it got very low values in the leaching test. This however is probably due to it is hard fixated to the matrix and will not be a problem leaching to the surroundings even though it is present in very high amounts.

Even more contradictory is however the high levels of copper (Cu) that is extracted in the leaching test while the levels should be very low, according to the KM/MKM-calculations. This is probably due to that the KM/MKM-values are not measured but calculated from the initial amounts in the solids and the concentrations in the leachates and washing waters. Unfortunately this makes the results from the leaching test more reliable than those for the KM/MKM-guidelines which, except for the barium levels, yields positive results concerning reuse of the soil.

5. Conclusions

The overall result from the copper leaching with acidic process water is promising for both sites in the regards of extracting copper for reuse purposes. However when it comes to the amount still left in the leached samples the ash from Björkhult still has too high levels of copper after leaching to be below the MKM-limit. This is a problem even though the process water has managed to extract more than 90% of the copper.

The copper levels after leaching is only a problem for the ash from Björkhult, but all of the samples have far too high levels of barium to be acceptable for reused as KM and even as MKM. The barium levels are high but it seems as it still very stable in the sample. This has been proven both in the leaching trials with process water and in the SS-EN12457-3 leaching test.

The ash on the other hand has too high levels and leach too much, not only regarding barium but for other metals as well, which might lead to a handling somewhat more costly. This however might be solved using a more extensive washing step, which is proven to be of great importance in the SS-EN12457-3 leaching test. As of now the amount of easily leachable metals has increase in many samples but with a better washing step it could prove to be a good decontamination technique.

Another important remark is the accumulation of metals from the process water to the soil. In this study it did not lead to any hazardous levels of the accumulated metals. However, due to the variations in the content of the process water this might prove to be a problem for further studies.

6. Further research

For continued study within the this field of research it would be of major interest to improve the washing step. This has been concluded to be insufficient in the regards of removing easy leachable metal contaminations still left after leaching with process water. A longer washing step with a higher L/S-ratio might give rise to cheaper ways of disposal or even reuse.

Another point of interest is the up scaling of the process. This especially applies to the mixing and separation part where shaking and centrifugation is used in this study. Both of these methods are impractical and uneconomical if not impossible to use for a large-scale process. The mixing could be solved by for example stirring but the separation could prove more difficult since it is of importance to remove as much process water as possible as this increase the levels of contaminations in the soil or ash if not removed.

To solve the up-scaling cooperation with companies working with full scale soil washing can be of interest since there already exists mobile solution for soil wash. These method utilizes primarily water as leachate but the possibility to include a step for process water could be interesting to look into due to the high leaching yield achieved in this study (Svevia).

Finally the results from extracting arsenic from ash with process waters suggest another field of interest for the method. This is very interesting since arsenic is not only a wide spread contamination but is often used in similar wood processing methods instead of blue vitrol. This vastly increases the number of sites of interest.

7. References

Arnér, M., Erjeby-Florell, S., Land, M. (2011) *Delrapport Huvudstudie – Föroreningssituationen, riskbedömning och behov av riskreduktion.* Stockholm, WSP Environmetal (Rapport 10104614)

van Benschoten, J.E., Matsumoto, M.R., Young, W.H. (1997) Evaluation and Analysis of Soil Washing for Seven Lead-Contaminated Soils. *Journal of Envionmental Engineering.* Vol. 123(3), pp. 217-224.

Bergil, C., Bydén, S. (1995) *Mäta försurning – Undersökningar av mark och vatten.* Limmared, Institutionen för tillämpad miljövetenskap vid Göteborgs universitet.

Dermont, G., Bergeron, M., Mercier, G. and Richer-Laflèche, M. (2008) Metal-Contaminated Soils: Remediation Practices and Tratment Technologies. *Pract. Period. Hazard. Toxic Radioact. Waste Manage.* 12, SPECIAL ISSUE: Metals Removal, pp. 188–209.

Elding L-I., Sundberg R., Granström B., Lundh B., Germund T.(2012) Koppar *Nationalencyklopedin.* http://www.ne.se/lang/koppar (13 Nov. 2012)

Hong, K-J., Tokunaga, S., Kajiuchi, T. (2000) Extraction of heavy metals from MSW incinerator fly ashes by chelating agents. *Journal of hazardous materials.* vol 75, nr 1, pp 57-73.

Karlfeldt Fedje, K., Yilling, L., Strömvall, A-M. (2013) *Remediation of Metal Contaminated Sites through Enhanced Soil Washing ─ Evaluation of Leaching Methods*.

Kemakta, (2012), *Kompletterande huvudstudie för förorenad mark vid f.d. stolpimpregnering på Långö, Köpmannebro*, Mellerud kommun, Ar 2012-06, Stockholm.

Leleyter, L., Rousseau, C., Biree, L., Baraud, F. (2012) Comparison of EDTA, HCl and Sequential Extraction Procedures, for Selected Metals (Cu, Mn, Pb, Zn), in Soils, Riverine and Marine Sediments. *Journal of Geochemical Exploration,* vol. 116-117, pp. 51-59.

Levenson, R. (2001) *More Modern Chemical Techniques.* [E-book] London: Royal Society of Chemistry.

Lin, Y-T., Chien, Y-C., Liang, C. (2011) A Laboratory Treatability Study for Pilot-Scale Soil Washing of Cr, Cu, Ni and Zn Contaminated Soils. *Environmental Progress & Sustainable Energy.* vol. 31(3), pp. 351-360.

van Loo, S., Koppejan, J. (2008) *The Handbook of Biomass Combustion & Co-firing.*Cihppenham: Earthscan.

Markinfo (2006) *Dominating soil class according to FAO.* http://www-markinfo.slu.se/eng/soildes/jman/faodom.html (19 april 2013)

Mulligan, C.N., Yong R.N., Gibbs B.F. (2001) Remediation technologies for metal-contaminated soils and groundwater: an evaluation. *Engineering Geology,* vol. 60, pp. 193-207.

Norin, R. (2000) *Elementär Kemisk Laboratorieteknik*. Revision 4. Ljungsbro: OKP-litteratur.

Nurmesniemi, H., Pöykiö, R., Kuokkanen, T., Rämö, J. (2007) Chemical sequential extraction of heavy metals and sulphur in bottom ash and in fly ash from a pulp and paper mill complex. *Waste management & research.* vol 26, pp 389-399.

Ohlsson, Y., Berggren-Kleja, D., Stark, M., Haglund, K. (2011) *Förorenade områden - Inventering av effektivitetshinder och kunskapsbehov*, SGI-V620, Linköping

Ohtsybo, M., Li, L. Y., Yamaoka, S., Higashi, T. (2004) *Geoenvironmental Engineering: Integrated Management of Groundwater and Contaminated Land, Proceedings of the Conference.* June 28-30, 2004, Stratford-upon-Avon.

PerkinElmer, (2004), *The 30-Minute Guide to ICP-MS,* http://www.perkinelmer.com/PDFs/Downloads/tch_icpmsthirtyminuteguide.pdf (14 Nov. 2012)

Renova (2010) *Från Avfall till Ren Energi - Effektiv och miljöanpassad förbränning på avfallskraftvärmeverket i Göteborg*. http://www.renova.se/Global/pdf/Fran_avfall_till_ren_energi_full_web.pdf (4 Mar. 2013).

Sander, M-L., Andrén, O. (1997) Ash from Cereal and Rape Straw Used for Heat Production: Limiting Effect and Contents of Plant Nutrients and Heavy Metals. *Water, Air and Soil Pollution*, vol 93, nr 1-4, pp 93-108.

SEPA (2009)*, Lägesbeskrivning av efterbehandlingsarbetet i landet 2008,* Diarienr 642-175-09 Rf, Stockholm.

SEPA (2009b) *Naturvårdsverkets årsrapport 2008*. Stockholm. ISBN 978-91-620-8378-6.

SEPA (2009c) *Riktvärden för förorenad mark modellbeskrivning och vägledning.* Bromma. ISBN 978-91-620-5976-7.

SFS 2001:512. *Förordning om deponering av avfall*. Stockholm, Miljödepartementet.

Sienkiewicz-Cholewa, U., Stanislaw, W., Nowak-Winiarska, K. (2012) Practicability of 1 mol HCl as an Extractant for Determination of Cu and Zn in Contaminated Soil. *Fresenius Environmental Bulletin.* vol. 21(9a), pp. 2839-2843.

Skogsjö, E. (2008) *Lägesbeskrivning av Efterbehandlingsarbetet i Landet 2008.* Stockholm: SEPA. (Dnr 642-175-09 Rf).

Svevia. Mobil jordtvätt - renar jorden på plats. *Svevia – Marksanering*. www.svevia.se/download/18.ba20a681324e1e9b3d80006004/SVEVIA-Jordtvatt_LU.pdf (16 Apr 2013)

Swedish Environmental Protection Agency (2013) *The Environmental Objectives System*. http://www.swedishepa.se (25 Jan. 2013)

Tateda, M., Suzuki, S., Kim, Y., Athapattu, B.C.L., (2011) "Behavior of Cu, Pb, and Zn in Ash druing the Endothermic Burning of Mixed Industrial Wastes", *Journal of Enviromental Protection,* vol. 2, nr. 5, pp. 489-501.

Thomas, R. (2004), *Practical Guide to ICP-MS*. New York, Marcel Dekker

Thomas, T.J., Madhu, G. (2012) Removal of Copper and Nickel from Aqueous Solutions Using Natural Adsorbents. *Pollution Research*. vol. 31, nr. 4, pp. 687-691.

Udovic, M., Lestan, D. (2012) EDTA and HCl Leaching of Calcareous and Acidic Soils Polluted with Potentially Toxic Metals: Remediation Efficiency and Soil Impact. *Chemosphere.* vol 88, pp. 718-724.

de Vougy H. (1856) Dr. Boucherie's patent process for preserving wood from decay. *Journal of the Franklin Institute*. vol. 62, pp.1-4.

Yip, T.C.M., Tsang, D.C.W., Ng, K.T.W., Lo, I.M.C. (2008) Empirical Modeling of Heavy Metal Extraction by EDDS from Single-Metal and Multi-Metal Contaminated Soils. *Chemosphere.* vol. 74(2), pp. 301-307.

Appendix I. ICP-AES results for liquid samples

µg/l	1	2	3	4	5	6	7	8	9	10
Al	8000	1200	141860	6500	10250	<1152	130000	3600	150000	4000
As	<3,6	1,3	15,8	<1,0	<25,0	<0,3	1,4	<1,0	1,1	<1,0
Ba	298	290	744	260	1250	<1250	610	<50	710	51
Be	<9,1	<2,5	<5,8	<2,5	<62,5	<7,6	4,1	<2,5	7,3	<2,5
Pb	9	<1	51	3	<25	<3	28	3	40	1
Cd	58,2	2,7	111,6	4,5	<2,5	<0,3	16,0	0,8	12,0	0,5
Co	35,6	3,6	118,6	6,1	<6,3	<0,8	170,0	7,8	29,0	2,0
Cu	472727	33000	1093023	56000	4500	879	38000	1800	30000	1800
Cr	9,1	2,5	25,6	2,5	62,5	7,6	58,0	2,5	3,2	2,5
Li	145	<25	149	<25	<625	<76	180	25	66	<25
Mn	4000	380	18837	940	525	73	4100	200	1100	58
Mo	<9,1	<2,5	<5,8	<2,5	<62,5	15,2	<2,5	<2,5	<2,5	<2,5
Ni	305,5	33,0	814,0	45,0	<62,5	<7,6	260,0	14,0	39,0	3,8
Se	<18,2	<5,0	53,5	<5,0	<125,0	<15,2	<5,0	<5,0	<5,0	<5,0
Ag	7,3	<0,5	176,7	1,6	35,0	<1,5	3,4	<0,5	0,8	<0,5
Sr	727	120	3023	230	<625	<76	200	<25	140	<25
Tl	<18,2	<5,0	<11,6	<5,0	<125,0	<15,2	<5,0	<5,0	<5,0	<5,0
U	<1,8	<0,5	<1,2	<0,6	<2,5	<1,5	1,1	<0,5	0,5	<0,5
V	<9,1	<2,5	<5,8	<2,5	<62,5	<7,6	15,0	<2,5	<2,5	<2,5
Zn	22909	1700	41860	2300	625	<76	3700	180	<1600	67

µg/l	11	12	13	14	15	16	17	18	19	20
Al	10000	<380	<25333	645	140000	3600	120000	2800	5000	4600
As	1,9	<1,0	<66,7	<1,3	1,5	<1,0	1,3	<1,0	4,3	2,2
Ba	1300	690	<3333	658	540	<50	460	<50	63	<50
Be	<2,5	<2,5	<166,7	<3,2	3,6	<2,5	3,2	<2,5	<2,5	<2,5
Pb	110	4	107	9	38	1	35	1	14	15
Cd	9,1	0,5	22,0	1,4	15,0	0,7	13,0	0,5	0,3	0,1
Co	7,5	0,7	<16,7	0,4	150,0	7,8	130,0	5,6	0,8	0,7
Cu	380000	12000	1533333	85161	24000	1400	21000	990	13000	3700
Cr	2,5	2,5	166,7	3,2	45,0	2,5	45,0	2,5	2,5	2,5
Li	<25	<25	<1667	<32	260	<25	250	<25	<25	<25
Mn	2400	180	1267	142	4300	230	3600	190	190	50
Mo	<2,5	<2,5	<166,7	<3,2	<2,5	<2,5	<2,5	<2,5	<2,5	<2,5
Ni	30,0	3,9	<166,7	<3,2	240,0	14,0	210,0	11,0	3,2	<2,5
Se	7,2	<5,0	<333,3	<6,5	<5,0	<5,0	<5,0	<5,0	<5,0	<5,0
Ag	25,0	1,0	49,3	10,1	2,7	<0,5	0,8	<0,5	<0,5	<0,5
Sr	1500	160	<1667	168	280	<25	260	<25	41	<25
Tl	<5,0	<5,0	<333,3	<6,5	<5,0	<5,0	<5,0	<5,0	<5,0	<5,0
U	<0,5	<0,5	<33,3	<0,6	1,3	<0,5	1,4	<0,5	1,7	1,2
V	<2,5	<2,5	<166,7	<3,2	30,0	<2,5	52,0	<2,5	16,0	14,0
Zn	1600	110	3600	194	3400	190	3000	150	83	29

µg/l	21	22	23	24	25	26	27	28	29	30
Al	1300	18000	21000	820000	340000	150000	96000	52000	26000	150000
As	<1,0	1,9	230,0	660,0	260,0	33,0	2500,0	360,0	44,0	230,0
Ba	63	<50	820	5200	2100	990	1300	1500	1600	2000
Be	<2,5	<2,5	<2,5	15,0	4,1	<2,5	10,0	3,2	<2,5	4,8
Pb	<1	7	10000	21000	12000	1800	11000	11000	4100	11000
Cd	0,2	0,1	280,0	340,0	270,0	37,0	290,0	280,0	43,0	290,0
Co	2,3	0,9	14,0	130,0	28,0	8,1	29,0	17,0	4,2	39,0
Cu	5100	3900	2900	3400000	2400000	440000	8400000	1500000	410000	120000
Cr	2,5	2,5	93,0	840,0	170,0	110,0	110,0	110,0	17,0	140,0
Li	<25	<25	33	570	75	<25	60	36	<25	64
Mn	460	110	4000	20000	5000	1000	6900	4500	1100	4900
Mo	<2,5	<2,5	29,0	190,0	66,0	7,7	90,0	36,0	<2,5	12,0
Ni	<2,5	<2,5	83,0	6600,0	2500,0	260,0	9400,0	680,0	250,0	120,0
Se	<5,0	<5,0	24,0	140,0	47,0	9,3	73,0	24,0	7,9	52,0
Ag	<0,5	<0,5	40,0	17,0	21,0	0,6	31,0	29,0	2,4	24,0
Sr	<25	<25	540	13000	2200	550	4300	1100	470	670
Tl	<5,0	<5,0	8,2	<5,0	<5,0	<5,0	9,6	8,2	<5,0	8,3
U	<0,5	<0,5	1,1	49,0	16,0	2,3	47,0	6,4	3,2	38,0
V	<2,5	8,4	28,0	720,0	120,0	39,0	530,0	69,0	28,0	170,0
Zn	27	<25	53000	430000	93000	17000	66000	59000	16000	55000

µg/l	31	32	33	34	35	36	37	38
Al	72000	560000	120000	240000	17000	260000	130000	6100
As	28,0	240,0	27,0	160,0	8,5	170,0	240,0	29,0
Ba	710	1700	460	2400	210	2400	1000	650
Be	<2,5	13,0	3,3	6,5	<2,5	6,5	4,9	<2,5
Pb	1700	9300	1600	9200	530	10000	2900	140
Cd	58,0	300,0	49,0	290,0	18,0	290,0	61,0	9,1
Co	36,0	25,0	5,7	120,0	8,2	100,0	31,0	4,2
Cu	31000	140000	29000	110000	7400	130000	730000	85000
Cr	59,0	140,0	27,0	260,0	9,0	240,0	180,0	9,5
Li	66	43	<25	170	<25	160	110	<25
Mn	1600	5400	990	6600	470	6300	6600	850
Mo	<2,5	20,0	<2,5	11,0	<2,5	12,0	29,0	<2,5
Ni	76,0	90,0	24,0	250,0	18,0	220,0	1300,0	460,0
Se	9,4	30,0	6,0	60,0	<5,0	55,0	46,0	<5,0
Ag	1,5	40,0	2,1	43,0	0,6	40,0	1,6	<0,5
Sr	150	580	110	710	57	710	3500	540
Tl	<5,0	8,6	<5,0	8,9	<5,0	9,0	<5,0	<5,0
U	11,0	15,0	3,6	51,0	3,1	51,0	16,0	<0,5
V	130,0	140,0	61,0	430,0	30,0	400,0	250,0	15,0
Zn	10000	48000	8100	45000	3000	53000	66000	12000

The samples with respective number

1. EN-leaching, Köpmannebro, ash, batch: 30+30 min, L/S 10, step 1
2. EN-leaching, Köpmannebro, ash, batch: 30+30 min, L/S 10, step 2
3. EN-leaching, Köpmannebro, ash, innan tvättstep, batch: 30+30 min, L/S 10, step 1
4. EN-leaching, Köpmannebro, ash, innan tvättstep, batch: 30+30 min, L/S 10, step 2
5. EN-leaching, Köpmannebro, ash, 30 min, L/S 10, step 1
6. EN-leaching, Köpmannebro, ash, 30 min, L/S 10, step 2
7. EN-leaching, Köpmannebro, soil, batch: 30 min, L/S 10, step 1
8. EN-leaching, Köpmannebro, soil, batch: 30 min, L/S 10, step 2
9. EN-leaching, Björkhult, soil, batch: 30 min, L/S 10, step 1
10. EN-leaching, Björkhult, soil, batch: 30 min, L/S 10, step 2
11. EN-leaching, Björkhult, ash, batch: 30+30 min, L/S 10, step 1
12. EN-leaching, Björkhult, ash, batch: 30+30 min, L/S 10, step 2
13. EN-leaching, Björkhult, ash, 30 min, L/S 10, step 1
14. EN-leaching, Björkhult, ash, 30 min, L/S 10, step 2
15. EN-leaching, Köpmannebro, soil, 18 h, L/S 10, step 1
16. EN-leaching, Köpmannebro, soil, 18 h, L/S 10, step 2
17. EN-leaching, Köpmannebro, soil, 24 h, L/S 10, step 1
18. EN-leaching, Köpmannebro, soil, 24 h, L/S 10, step 2
19. EN-leaching, Köpmannebro, untreated soil, step 1
20. EN-leaching, Köpmannebro, untreated soil, step 2
21. EN-leaching, Björkhult, untreated soil, step 1
22. EN-leaching, Björkhult, untreated soil, step 2
23. Filtrered process water
24. Köpmannebro, ash, batch: 30+30 min, L/S 10, step 1
25. Köpmannebro, ash, batch: 30+30 min, L/S 10, step 2
26. Köpmannebro, ash, batch: 30+30 min, L/S 10, washing water
27. Björkhult, ash, batch: 30+30 min, L/S 10, step 1
28. Björkhult, ash, batch: 30+30 min, L/S 10, step 2
29. Björkhult, ash, batch: 30+30 min, L/S 10, washing water
30. Köpmannebro, soil, batch: 30 min, L/S 10, leachate
31. Köpmannebro, soil, batch: 30 min, L/S 10, washing water
32. Björkhult, soil, batch: 30 min, L/S 10, leachate
33. Björkhult, soil, batch: 30 min, L/S 10, washing water
34. Köpmannebro, soil, 24 h, L/S 10, leachate
35. Köpmannebro, soil, 24 h, L/S 10, washing water
36. Köpmannebro, soil, 18 h, L/S 10, leachate
37. Köpmannebro, ash, 30 min, L/S 5, leachate
38. Köpmannebro, ash, 30 min, L/S 5, washing water

Appendix II. ICP-MS results for solid samples

		Soil		Bark	
ELEMENT	SAMPLE	Köpmannebro	Björkhult	Köpmannebro	Björkhult
DM	%	99,6	99,6	94,4	96,6
Ash 550°C				7	42,3
SiO2	% DM	68,3	75,6	1,87	25,7
Al2O3	% DM	12	12,5	0,709	5,3
CaO	% DM	1,77	0,772	0,773	0,454
Fe2O3	% DM	2,51	1,12	0,461	2,03
K2O	% DM	2,36	4,21	0,116	1,62
MgO	% DM	0,599	0,097	0,0645	0,095
MnO	% DM	0,0392	0,0162	0,0105	0,014
Na2O	% DM	2,56	2,68	0,0833	0,999
P2O5	% DM	0,042	0,0143	0,102	0,175
TiO2	% DM	0,522	0,168	0,0172	0,154
Total	% DM	90,7	97,2	4,2	36,5
As	mg/kg DM	0,588	0,278	2,02	7,79
Ba	mg/kg DM	497	863	109	616
Be	mg/kg DM	1,37	1,91	0,119	0,673
Cd	mg/kg DM	0,032	0,0144	0,267	0,095
Co	mg/kg DM	2,17	0,253	1,18	0,94
Cr	mg/kg DM	41,5	25	3,86	9,02
Cu	mg/kg DM	1090	719	11300	14900
Hg	mg/kg DM	<0.04	0,0549	0,0616	0,371
Mo	mg/kg DM	0,291	0,222	0,247	0,299
Nb	mg/kg DM	8,97	5,87	0,417	6,99
Ni	mg/kg DM	3,11	0,251	3,49	2,61
Pb	mg/kg DM	7,94	3,22	30,8	39,1
S	mg/kg DM	76,2	<50	569	512
Sc	mg/kg DM	7,66	1,91	0,564	1,23
Sr	mg/kg DM	192	202	29,9	94,8
V	mg/kg DM	44,4	9,7	6,67	7,03
W	mg/kg DM	1,18	0,725	0,581	0,582
Y	mg/kg DM	16,6	5,37	2,3	6,92
Zn	mg/kg DM	14,2	3,49	43,8	35,7
Zr	mg/kg DM	225	113	5,66	41,6

		Ash			
		Björkhult	Köpmannebro		
ELEMENT	SAMPLE		Renova	Oxidizing	Reducing
DM	%	100	90,1	100	99,8
SiO2	% DM	56,7	8,44	54,2	22,7
Al2O3	% DM	10,8	4,63	10,3	5,75
CaO	% DM	1,31	26,2	4,47	2,09
Fe2O3	% DM	4,39	1,81	3,98	2,95
K2O	% DM	3,54	6,9	2,73	1,62
MgO	% DM	0,24	1,67	0,714	0,386
MnO	% DM	0,0342	0,0131	0,0735	0,0458
Na2O	% DM	2,51	7,33	2,03	1,09
P2O5	% DM	0,363	29,3	0,551	0,273
TiO2	% DM	0,17	0,859	0,361	0,175
Total	% DM	80,1	87,2	79,4	37,1
LOI 1000°C	% DM	-------	-------	-------	46,6
As	mg/kg DM	22,4	<3	10,8	5,18
Ba	mg/kg DM	2290	433	928	519
Be	mg/kg DM	1,53	<0.5	1,46	1,18
Cd	mg/kg DM	0,269	0,146	1,3	<0.1
Co	mg/kg DM	2,24	2,25	7,49	3,85
Cr	mg/kg DM	23,8	71,2	49,9	23,1
Cu	mg/kg DM	107000	19200	133000	43200
Hg	mg/kg DM	<0.01	<0.01	<0.01	<0.01
Mo	mg/kg DM	1,4	3,12	2,37	1,89
Nb	mg/kg DM	6,43	5,36	8,78	<5
Ni	mg/kg DM	7,85	20,8	26,8	14,9
Pb	mg/kg DM	150	61,2	360	91,4
S	mg/kg DM	2370	2730	4850	1870
Sc	mg/kg DM	2,87	<1	5,85	3,39
Sn	mg/kg DM	18,7	33,1	18,5	14,5
Sr	mg/kg DM	256	133	231	114
V	mg/kg DM	14,8	12,4	38	22,3
W	mg/kg DM	<50	<50	<50	<50
Y	mg/kg DM	7,97	2,86	19,3	32,6
Zn	mg/kg DM	158	1520	256	25,5
Zr	mg/kg DM	95,1	13,4	146	22,3

Appendix III. Spectrophotometric results for the ash samples from Köpmannebro

type of sample [LF=leaching fluid, WF= washing fluid]	date	L/S quote	leaching time [min]	m renova ash [g]	m own ash [g]	Abs step 1	Abs step 2
LF I	2013-01-17	5	30	0,2524	0,262	0,117	
LF II	2013-01-17	5	30	0,245	0,2507	0,136	
LF I	2013-01-17	10	30	0,2374	0,2543	0,514	
LF II	2013-01-17	10	30	0,2387	0,2518	0,549	
LF I	2013-01-17	5	90	0,2606	0,2507	0,245	
LF II	2013-01-17	5	90	0,2626	0,2519	0,606	
LF I	2013-01-17	10	90	0,2502	0,2521	0,555	
LF II	2013-01-17	10	90	0,2516	0,2471	0,34	
LF I	2013-01-18	5	60	0,2538	0,259	0,565	
LF II	2013-01-18	5	60	0,262	0,2455	0,252	
LF I	2013-01-18	10	60	0,251	0,256	0,442	
LF II	2013-01-18	10	60	0,2461	0,2476	0,344	
LF III	2013-01-22	5	30	0,2558	0,2507	0,325	
LF III	2013-01-22	10	30	0,2518	0,2514	0,383	
LF III	2013-01-22	5	60	0,2633	0,2516	0,595	
LF III	2013-01-22	10	60	0,2661	0,2452	0,604	
LF III	2013-01-22	5	90	0,2618	0,249	0,442	
LF III	2013-01-22	10	90	0,255	0,262	0,471	
LF I	2013-01-25	10	15+15	0,2597	0,2474	0,291	0,112
LF II	2013-01-25	10	15+15	0,2485	0,2579	0,504	0,164
LF I	2013-01-29	10	30+15	0,1542	0,1517	0,237	0,048
LF II	2013-01-29	10	30+15	0,156	0,149	0,301	0,04
LF I	2013-01-30	10	30+30	0,2489	0,2509	0,612	0,111
LF II	2013-01-30	10	30+30	0,2586	0,266	0,442	0,117
LF	2013-02-04	10	30+30	20,1	7,2	0,251	0,151
WF I	2013-01-17	5	30	0,2524	0,262	0,021	
WF II	2013-01-17	5	30	0,245	0,2507	0,043	
WF I	2013-01-17	10	30	0,2374	0,2543	0,05	
WF II	2013-01-17	10	30	0,2387	0,2518	0,043	
WF I	2013-01-17	5	90	0,2606	0,2507	0,031	
WF II	2013-01-17	5	90	0,2626	0,2519	0,027	
WF I	2013-01-17	10	90	0,2502	0,2521	0,023	
WF II	2013-01-17	10	90	0,2516	0,2471	0,021	

type of sample [LF=leaching fluid, WF= washing fluid]	date	L/S quote	leaching time [min]	m renova ash [g]	m own ash [g]	Abs step 1	Abs step 2
WF I	2013-01-18	5	60	0,2538	0,259	0,016	
WF II	2013-01-18	5	60	0,262	0,2455	0,019	
WF I	2013-01-18	10	60	0,251	0,256	0,026	
WF II	2013-01-18	10	60	0,2461	0,2476	0,019	
WF III	2013-01-22	5	30	0,2558	0,2507	0,017	
WF III	2013-01-22	10	30	0,2518	0,2514	0,012	
WF III	2013-01-22	5	60	0,2633	0,2516	0,007	
WF III	2013-01-22	10	60	0,2661	0,2452	0,016	
WF III	2013-01-22	5	90	0,2618	0,249	0,002	
WF III	2013-01-22	10	90	0,255	0,262	0,004	
WF I	2013-01-25	10	15+15	0,2597	0,2474	0,012	
WF II	2013-01-25	10	15+15	0,2485	0,2579	0,019	
WF I	2013-01-29	10	30+15	0,1542	0,1517	0,011	
WF II	2013-01-29	10	30+15	0,156	0,149	0,011	
WF I	2013-01-30	10	30+30	0,2489	0,2509	0,022	
WF II	2013-01-30	10	30+30	0,2586	0,266	0,02	

*Date is included to determine which standard curve is to be used.

Appendix IV. Spectrophotometric results for the soil samples from Köpmannebro

type of sample [LF=leaching fluid, WF= washing fluid]	date	L/S quote	leaching time [min]	m soil [g]	Abs step 1	Abs step 2
LF I	2012-12-11	2	90	5,0169	0,061	
LF II	2012-12-11	2	90	5,0983	0,211	
LF III	2012-12-11	2	90	4,7183	0,028	
LF I	2012-12-11	5	90	5,2913	0,018	
LF II	2012-12-11	5	90	5,2384	0,117	
LF III	2012-12-11	5	90	5,393	0,081	
LF I	2012-12-12	2	60	4,9212	0,166	
LF II	2012-12-12	2	60	5,0027	0,161	
LF III	2012-12-12	2	60	5,1443	0,163	
LF I	2012-12-12	5	60	4,9477	0,097	
LF II	2012-12-12	5	60	5,0637	0,102	
LF III	2012-12-12	5	60	5,1549	0,093	
LF I	2012-12-13	2	30	4,7771	0,054	
LF II	2012-12-13	2	30	5,0818	0,299	
LF III	2012-12-13	2	30	4,9536	0,043	
LF I	2012-12-13	5	30	5,2643	0,011	
LF II	2012-12-13	5	30	5,0011	0,089	
LF III	2012-12-13	5	30	4,5944	0,06	
LF I	2013-02-01	10	30	4,0104	0,176	
LF II	2013-02-01	10	30	4,0455	0,219	
LF III	2013-02-01	10	30	3,9617	0,28	
LF I	2013-02-01	10	60	3,9943	0,073	
LF II	2013-02-01	10	60	3,998	0,146	
LF III	2013-02-01	10	60	4,0466	0,068	
LF I	2013-02-01	10	90	4,0334	0,305	
LF II	2013-02-01	10	90	4,0556	0,083	
LF III	2013-02-01	10	90	3,9994	0,184	
LF I	2013-02-07	10	1440	4,0327	0,15	
LF II	2013-02-07	10	1440	4,0104	0,347	
LF III	2013-02-07	10	1440	4,0245	0,12	
LF I	2013-02-07	10	1080	4,0238	0,107	
LF II	2013-02-07	10	1080	4,0086	0,095	
LF III	2013-02-07	10	1080	4,0487	0,085	

type of sample [LF=leaching fluid, WF= washing fluid]	date	L/S quote	leaching time [min]	m soil [g]	Abs step 1	Abs step 2
LF	2013-02-11	10	30	20,0358		
LF I	2013-02-13	10	30+30	5,0406	0,055	0,043
LF II	2013-02-13	10	30+30	5,0781	0,044	0,023
LF III	2013-02-13	10	30+30	5,0501	0,047	0,024
LF I	2013-02-13	10	30+15	5,0176	0,086	0,031
LF II	2013-02-13	10	30+15	4,9973	0,052	0,022
LF III	2013-02-13	10	30+15	5,0188	0,043	0,029
LF I	2013-02-14	10	15+15	4,9861	0,058	0,05
LF II	2013-02-14	10	15+15	4,9808	0,066	0,026
LF III	2013-02-14	10	15+15	4,9701	0,063	0,032
WF I	2012-12-11	2	90	5,0169	0,012	
WF II	2012-12-11	2	90	5,0983	0,012	
WF III	2012-12-11	2	90	4,7183	0,011	
WF I	2012-12-11	5	90	5,2913	-0,002	
WF II	2012-12-11	5	90	5,2384	0,004	
WF III	2012-12-11	5	90	5,393	0,022	
WF I	2012-12-12	2	60	4,9212	0,013	
WF II	2012-12-12	2	60	5,0027	0,005	
WF III	2012-12-12	2	60	5,1443	0,01	
WF I	2012-12-12	5	60	4,9477	0,006	
WF II	2012-12-12	5	60	5,0637	0	
WF III	2012-12-12	5	60	5,1549	0,005	
WF I	2012-12-13	2	30	4,7771	0,01	
WF II	2012-12-13	2	30	5,0818	0,011	
WF III	2012-12-13	2	30	4,9536	0,011	
WF I	2012-12-13	5	30	5,2643	0,005	
WF II	2012-12-13	5	30	5,0011	0,007	
WF III	2012-12-13	5	30	4,5944	0,002	
WF I	2013-02-01	10	30	4,0104	0,016	
WF II	2013-02-01	10	30	4,0455	0,016	
WF III	2013-02-01	10	30	3,9617	0,017	
WF I	2013-02-01	10	60	3,9943	0,019	
WF II	2013-02-01	10	60	3,998	0,019	
WF III	2013-02-01	10	60	4,0466	0,015	
WF I	2013-02-01	10	90	4,0334	0,017	
WF II	2013-02-01	10	90	4,0556	0,014	
WF III	2013-02-01	10	90	3,9994	0,015	

type of sample [LF=leaching fluid, WF= washing fluid]	date	L/S quote	leaching time [min]	m soil [g]	Abs step 1	Abs step 2
WF I	2013-02-07	10	1440	4,0327	0,017	
WF II	2013-02-07	10	1440	4,0104	0,013	
WF III	2013-02-07	10	1440	4,0245	0,015	
WF I	2013-02-07	10	1080	4,0238	0,015	
WF II	2013-02-07	10	1080	4,0086	0,013	
WF III	2013-02-07	10	1080	4,0487	0,015	
WF	2013-02-11	10	30	20,0358		
WF I	2013-02-13	10	30+30	5,0406	0,022	
WF II	2013-02-13	10	30+30	5,0781	0,015	
WF III	2013-02-13	10	30+30	5,0501	0,017	
WF I	2013-02-13	10	30+15	5,0176	0,038	
WF II	2013-02-13	10	30+15	4,9973	0,032	
WF III	2013-02-13	10	30+15	5,0188	0,017	
WF I	2013-02-14	10	15+15	4,9861	0,014	
WF II	2013-02-14	10	15+15	4,9808	0,02	
WF III	2013-02-14	10	15+15	4,9701	0,023	

*Date is included to determine which standard curve is to be used.

Appendix V. Spectrophotometric results for the ash samples from Björkhult

type of sample [LF=leaching fluid, WF= washing fluid]	date	L/S quote	leaching time [min]	m ash [g]	Abs step 1	Abs step 2
LF I	2013-02-01	10	30	0,4933	0,140	
LF II	2013-02-01	10	30	0,5045	0,153	
LF III	2013-02-01	10	30	0,4951	0,148	
LF I	2013-02-07	10	30+30	0,5026	0,200	0,050
LF II	2013-02-07	10	30+30	0,4944	0,166	0,048
LF III	2013-02-07	10	30+30	0,5027	0,162	0,051
WF I	2013-02-01	10	30	0,4933	0,047	
WF II	2013-02-01	10	30	0,5045	0,040	
WF III	2013-02-01	10	30	0,4951	0,064	
WF I	2013-02-07	10	30+30	0,5026	0,011	
WF II	2013-02-07	10	30+30	0,4944	0,009	
WF III	2013-02-07	10	30+30	0,5027	0,007	

*Date is included to determine which standard curve is to be used.

Appendix VI. Spectrophotometric results for the soil samples from Björkhult

type of sample [LF=leaching fluid, WF= washing fluid]	date	L/S quote	leaching time [min]	m soil [g]	Abs step 1	Abs step 2
LF	2013-02-11	10	30	30,008		
LF I	2013-02-15	10	30+30	3,9936	0,233	0,038
LF II	2013-02-15	10	30+30	4,0171	0,197	0,025
LF III	2013-02-15	10	30+30	3,993	0,195	0,048
WF I	2013-02-15	10	30+30	3,9936	0,009	
WF II	2013-02-15	10	30+30	4,0171	0,007	
WF III	2013-02-15	10	30+30	3,993	0,006	

*Date is included to determine which standard curve is to be used.

Appendix VII. Standard curves for the spectrophotometric analysis

date	mM $CuSO_4$	Abs	equation
2013-01-17	2	0,108	Abs=0,1023*[$CuSO_4$]+0,0111
	4	0,221	
	6	0,321	
	8	0,42	
	10	0,52	
2013-01-23	2	0,101	Abs=0,1037*[$CuSO_4$]-0,0015
	4	0,206	
	6	0,312	
	8	0,413	
	10	0,516	
2013-01-24	2	0,102	Abs=0,1036*[$CuSO_4$]-0,0002
	4	0,207	
	6	0,312	
	8	0,417	
	10	0,515	
2013-01-25	2	0,097	Abs=0,1047*[$CuSO_4$]-0,0069
	4	0,202	
	6	0,309	
	8	0,413	
	10	0,515	
2013-01-30	2	0,109	Abs=0,1034*[$CuSO_4$]+0,0084
	4	0,219	
	6	0,32	
	8	0,419	
	10	0,526	
2013-02-07	2	0,108	Abs=0,1039*[$CuSO_4$]+0,0033
	4	0,213	
	6	0,31	
	8	0,42	
	10	0,524	
2013-02-08	2	0,106	Abs=0,1049*[$CuSO_4$]+0,0015
	4	0,212	
	6	0,315	
	8	0,423	
	10	0,525	

date	**mM $CuSO_4$**	**Abs**	**equation**
2013-02-14	2	0,11	Abs=0,1015*[CuSO4]+0,0089
	4	0,214	
	6	0,311	
	8	0,415	
	10	0,517	
2013-02-15	2	0,104	Abs=0,1010*[$CuSO_4$]+0,0032
	4	0,205	
	6	0,307	
	8	0,407	
	10	0,508	
2013-02-18	2	0,105	Abs=0,1011*[$CuSO_4$]+0,0037
	4	0,206	
	6	0,307	
	8	0,407	
	10	0,51	
2013-01-29	2	0,108	Abs=0,1041*[$CuSO_4$]+0,0077
	4	0,218	
	6	0,326	
	8	0,421	
	10	0,527	

Appendix VI. Calculations for spectrophotometric results

m_{wet} = the wet mass [kg] of soil or ash sample
DS% = Dry Matter, the percentage of sample left after drying at 105°C
m_{dry} = the dry mass [kg] of soil or ash sample

$$m_{dry} = m_{wet} * \frac{DS\%}{100}$$

Abs = the absorbation measured by the spectrophotometric unit
$[CuSO_4]_{spec.}$ = the $CuSO_4$ concentration [mM] in the diluted spectrophotometric sample
k, m = coefficient from the linearization of the standard curve samples (see appendix V)

$$[CuSO_4]_{spec} = \frac{Abs - m}{k}$$

$[CuSO_4]$ = the $CuSO_4$ concentration [mM] of the original sample of leachate or washing water
V_{sample} = the volume [l] of original sample in the diluted spectrophotometric sample (see table 3.1.)
V_{tot} = the total volume [l] of the spectrophotometric sample (see table 3.1.)

$$[CuSO_4] = \frac{[CuSO_4]_{spec} * V_{tot}}{V_{sample}}$$

$m_{Cu,leached}$ = the mass of leached copper per mass soil or ash [mg/kg]
$V_{leachate}$ = the volume of leachate or washing water that was added for the current step
M_{Cu} = the atomic mass for copper

$$m_{Cu,leached} = \frac{[CuSO_4] * V_{leachate} * M_{Cu}}{m_{dry}}$$

$Cu\%_{leached}$ = the percentage of leached copper regarding the initial concentration
$m_{Cu,initial}$ = the initial mass of copper per mass soil or ash [mg/kg]

$$Cu\%_{leached} = \frac{m_{Cu,leached}}{m_{Cu,initial}}$$

The $m_{Cu,initial}$ was measured with ICP-MS (see appendix II). However since the ash samples of Köpmannebro consisted of two kinds of ash $m_{Cu,initial}$ had to be calculated for these samples.
$m_{Cu,Ash,Kp}$ = the mass of copper per mass of ash mixture
m_{oxi} = the mass of ash incinerated under oxidizing conditions
$m_{Cu,ini,oxi}$ = the initial mass of copper per mass of ash incinerated under oxidizing conditions
$DS\%_{oxi}$ = Dry matter for the ash incinerated under oxidizing conditions
m_{renova} = the mass of ash incinerated at Renova
$m_{Cu,ini,Ren}$ = the initial mass of copper per mass of ash incinerated at Renova
$DS\%_{Ren}$ = Dry matter for the ash incinerated at Renova

$$m_{Cu,Ash,Kp}\,\frac{m_{oxi}*\frac{\mathrm{DS\%_{oxi}}}{100}*m_{Cu,ini,oxi}+m_{Renova}*\frac{\mathrm{DS\%}_{Ren}}{100}*m_{Cu,ini,Ren}}{m_{oxi}*\frac{\mathrm{DS\%_{oxi}}}{100}+m_{Renova}*\frac{\mathrm{DS\%}_{Ren}}{100}}$$