

Soil Remediation: Metal Leaching from Contaminated Soil through the Modified BCR Sequential Extraction Procedure

Master of Science Thesis in the Master's Programme Industrial Ecology - for a sustainable society

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Department of Civil and Environmental Engineering
Division of Water Environment Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
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Master's Thesis 2012:155

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Examensarbete / Institutionen för bygg och miljöteknik,
Chalmers tekniska högskola 2012:155

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Cover: liquid metal extraction of the third step from bark, clay soil sample and ash sample respectively.

Printed by Chalmers Reproservice / Department of Civil and Environmental Engineering
Gothenburg, Sweden, 2012

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Abstract

Sequential extraction is a useful method of identifying how toxic trace metals bind to soil particles and the strength of these bonds. This is very essential knowledge to reach an efficient soil washing when dealing with remediation of metal-contaminated soil. Sequential extraction uses a succession of extractions on a soil same sample, with extraction liquids expected to promote decreasing mobility of metal fractions from the soil. The sequence selected in this study is a three-step scheme which mainly follows the modified BCR method, but with improvements in the second step. A less toxic and more environmental friendly chemical, ascorbic acid has been used instead of $\text{NH}_2\text{OH}\cdot\text{HCl}$. Four different soil samples from the contaminated sites, Köpmannebro and Österbybruk, were investigated. All metal contaminants were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), but only analysis results of Cr, Cu and Pb were evaluated about their possibilities to leach and potential for recover.

The results show that except for the clay soil, the highest percentage of Cr, Cu and Pb were generally in the residual fraction. The metal contaminants are stable and immobile to leach and contaminate the surrounding ecosystem. Stronger acids will be required to improve the efficiency of the soil washing. Copper is the metal easiest to be extracted from all the soil samples, as the total extractable content can be up to 70% in clay soil. It is more interesting and valuable to recover Cu from the site Köpmannebro, according to the higher occurrence of extractable and soluble Cu compounds found in the clay sample from this site. The potential for Cu recovery is higher from the grinded bark than from the remaining ash after bark incineration. The new improved BCR scheme used in this study can be a good alternative for applying the sequential extraction method. The results and findings in this study can also serve as a good guideline for remediation activities on-site at other saw mill and forest industry contaminated sites in Sweden.

Key words: *sequential extraction, metals, copper, chromium, lead, modified BCR, contaminated soil, soil washing*

Acknowledgements

First, my heartfelt gratitude goes to my thesis supervisors, Karin Karlfeldt Fedje and Ann-Margret Strömvall. I highly appreciate their patient supervision, constant encouragement, and warm relationship throughout this study. Under their support, I am confident that my thesis is a meaningful work to improve the environment towards sustainability.

I feel very much grateful to Mona Pålsson, for her kindly and patient help in the lab. Her practical experimental tips, beaming smile and communication of Swedish culture impressed me a lot. Warm thanks also to Jesper Knutsson and Sebastien Rauch, for the generously help in preparing ICP-MS samples, and the cooperation with Bei Gao as well.

I also would like to thank all the friends that I have met in Chalmers. The kind and benign teachers and classmates make my two-years life in Sweden impressive. Deep gratitude to my parents also, thanks for their wholehearted support. Without their support and encouragement, this study would have not been possible.

QIANYU LI

Gothenburg

October 2012

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1. Introduction

1.1 Background

Soil is comprised by air, water, organic matter, living organisms and mineral particles (Commission of the European Communities, 2006), see *Figure 1*. Among these structural ingredients, different minerals are active structures that can bind to heavy metals (McBride, 1989). The typical minerals in soil can be quartz (SiO_2), calcite (CaCO_3), feldspar (KAlSi_3O_8) and mica ($\text{K}(\text{Mg}, \text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$) (Donahue, 1977).

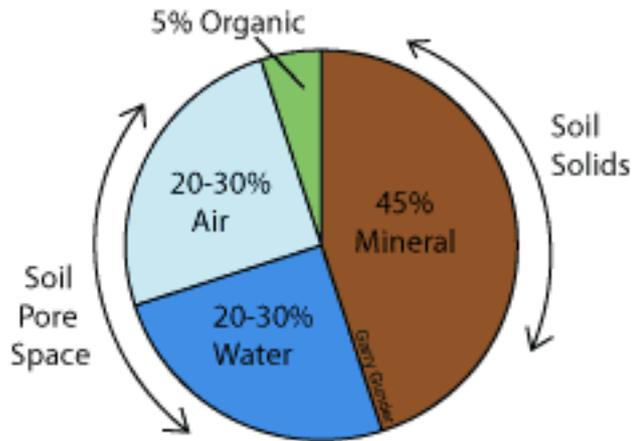


Figure 1. Natural soil composition (Commission of the European Communities, 2006)

Generally, contaminants in the soil are chemically attached to or physical trapped into soil structure particles. Soil can be considered as a sink for contaminants entering the environment, independently of if the contamination derives from air pollution, water pollution or soil pollution itself. The latter comes from various agricultural and industrial activities e.g. agriculture use of fertilizers and pesticides, fossil fuel combustion, mining waste, and landfill leaching.

Potential harmful contaminants have been accumulated in the upper soil during thousands of years, starting from the mining for hematite and later for copper. Soil-contamination problem was revealed in Europe until the 19th century, and got worse due to the technology development in the 20th century. Till the year of 2006, there are 3.5 million potentially contaminated sites existing in Europe (Commission of the European Communities, 2006), accounting for €5.2 billion for remediation cost. Consequently contamination has been ranked as one of the seven threats for the EU thematic soil strategy (European Commission, 2012), mainly contributed by metals and polycyclic aromatic hydrocarbons (PAHs). If focusing on Sweden, toxic trace metals are regarded as one of the offenders of soil contamination, see *Figure 2* (Färnkvist & Österlund, 2005). In terms of their mobility and bio toxicity on living ecosystem, removing metals from soil is an essential task.

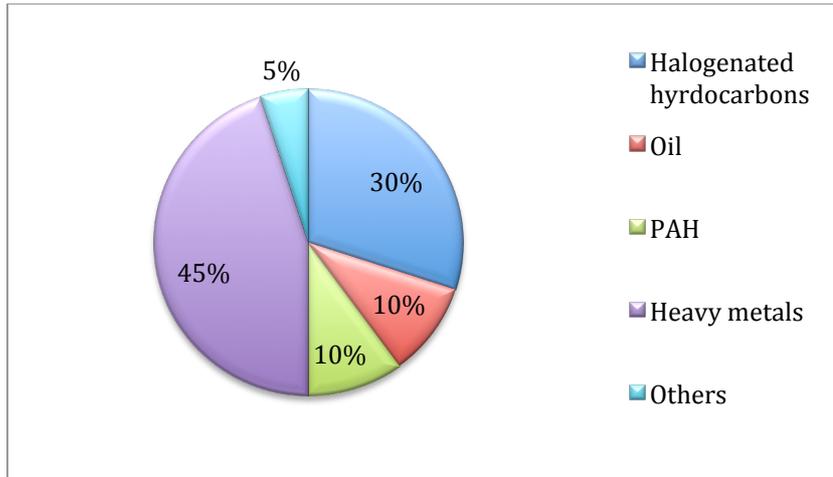


Figure 2. Distribution of common contaminants in Sweden (Färnkvist & Österlund, 2005)

1.2 Aim and specific goals

The aim of this master's thesis work is to modify and test the modified BCR Sequential Extraction Procedure (SEP) for leaching and potential recovery of metals by soil washing from different contaminated soil. The specific goals are to:

- through measurement of the total content of metals in three different soil samples, identify the specific major contaminants in each sample respectively.
- adjust and modify the BCR sequential extraction procedure, by avoid using toxic chemicals.
- characterize metal contaminants by measurement of metal concentrations of each leaching fraction in different soil and ash samples, in order to predict their solubility and the degree of soil washing treatment.

The results from this diploma work will serve as a guide for helping to select the optimal leaching agents for remediation of polluted sites by soil washing, where the aim is to extract the maximum amount of metal pollutants. In addition, this will provide information for coming studies, which aims at developing new remediation methods as a result of making the decontamination of polluted site more profitable.

Four different samples were investigated in this study, from two contaminated sites in Sweden: Köpmannebro and Österbybruk. Although all trace metals were analyzed by ICP-MS, only chromium (Cr), copper (Cu) and lead (Pb) were evaluated in this study.

2 Theory

2.1 Remediation technologies

The aim of soil remediation is to purify and revitalize soil. There are numbers of technologies employed in the process of soil remediation, sorting by in-situ vs. ex-situ or physical vs. chemical mechanism. Among these, the most commonly used techniques are isolation, removal, phytoextraction and soil washing.

Isolation of metal pollutants has been traditionally involved for the sake of lowering the risk of spreading the contamination. The immobilization and local binding based on solidification/stabilization (S/S) technology were used generally (USEPA, 2000). Solidification is a physical procedure that encapsulates the contaminants in a solid matrix, while the stabilization applies chemical reactions to secure pollutants. But none of them remove the heavy metals from the contaminated media, which remains task for further monitoring of metals. Thus this treatment is not considered as a permanent remediation anymore.

Removing polluted soil to a permitted landfill site is also not a good permanent environmental solution, as costly to remove and dispose the soil. Additionally, under the overall consideration, this treatment just transfers the problem to another media rather than solving it.

Phytoextraction is a more “green” way to remediate as it follows the harvest and removal of specific plants. The plants used for phytoextraction should have an abundant root system and be metal tolerant, such as *Thlaspi*, *Urtica* or *Chenopodium*, in order to absorb metal contaminants. There are two approaches included in phytoextraction method, namely continuous or natural phytoextraction and chemically enhanced phyroextraction (Lombi, 2001). Both of these means less negative impact on ecosystem, but require the longest treatment duration among these four common applied methods.

Soil washing is a method using chemical or physical processes to separate metals from the soil. It is one of the few permanent ways to solve soil contamination, but lack of specific extraction agents and the possible side effect of the extraction solution are two key problems for its application. This thesis work tries to give some suggestions for agent selection.

2.2 Soil washing

From the sustainable and environmental point of view, soil washing is considered as a permanent alternative to S/S and landfilling. Soil washing is a volume reduction treatment process and the polluted soil particles are dealt with in either of three ways, physical separation, chemical extraction or a combination of these two, see *Figure 3*.

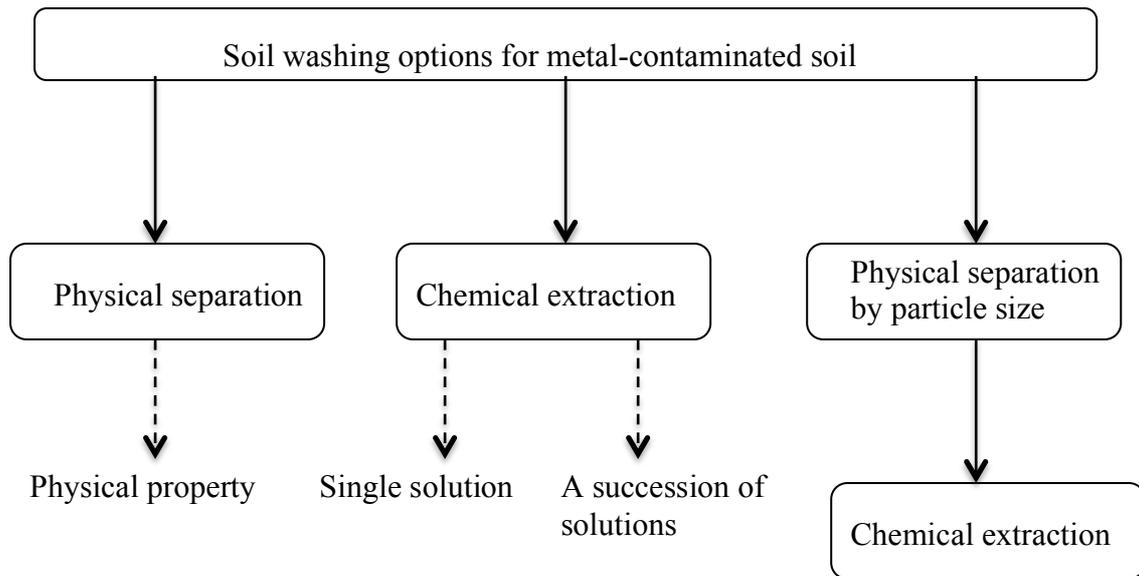


Figure 3. Schematic diagram of typical options used in soil washing

Physical soil washing, which is also named physical separation, utilizes certain physical characteristics, such as particle grain size, settling velocity, specific gravity, surface chemical behavior or magnetizability, to separate the contaminated soil particles from the bulk soil part. In general, the operation of physical separation is based on the approach used in mining and mineral processing industry, with single or associated participation of mechanical screening, hydrodynamic classification, gravity concentration, froth flotation, magnetic separation, electrostatic separation and attrition scrubbing on each sample (Dermont, 2008). However Wuana showed that physical soil washing only performed cost effective when the soil is sandy and granular, while for the clay and silt the volume reduction is less than 35% (Wuana, 2011). However, the silt and clay part are more risky binding to contaminants than sand and gravel portions (Office of Solid Waste and Emergency Response, 2001). Consequently, chemical solutions are needed to separate soil matrix more completely.

Chemical soil washing is a method that utilizes a water-based system to dissolve the contaminants in the soil into solutions. It is a metal solubilization process that is applicable for contaminants ionic formed with soil proportions. Unlike physical separation which is only applicable on the particulate forms like discrete particles or sorbed metal forms (Dermont, 2008).

Generally, the employed aqueous chemical reagents can be water acids, alkalis, salts, reducing agents or complex forming agents (Wuana, 2011). Referring to *Figure 4*, the principle under removing metals from soil with acid solution is that firstly, the water-based solution can dissolve metal contaminants; then the added protons (H⁺) can react with soil surface function groups including Al-OH or COOH groups and enhance the desorption of metal cations via ion-exchange reaction. With the pH value decreasing, the ion exchange can be replaced by dissolution of metal compound itself or soil mineral components like Fe-Mn oxides which contain metal contaminants. With the high leaching efficiency, acid extraction also cause problems changes of soil

structure, up to 50% loss of soil, acidification of the processed soil and remaining strong acidic wastewater. As alternative diluted acid agents containing chloride salts will not significantly acidify the soil. Consumption of leaching agents depends on the degree of soil matrix co-dissolution, and treatment of the remaining leaching agents will be easier in the salt solutions than in acid solutions. The chelating agent should have an ability to form stable metal complexes, and doing less damage to soil structures makes it better in comparison with use of acidic solutions. On the contrary, using chemical reducing agents aims to convert metals to a more soluble form. The reducing agents are generally used for dissolve the Fe-Mn oxides. Generally, whether use several different chemicals together or just single reagent is mainly dependent on the properties of specific studied site.

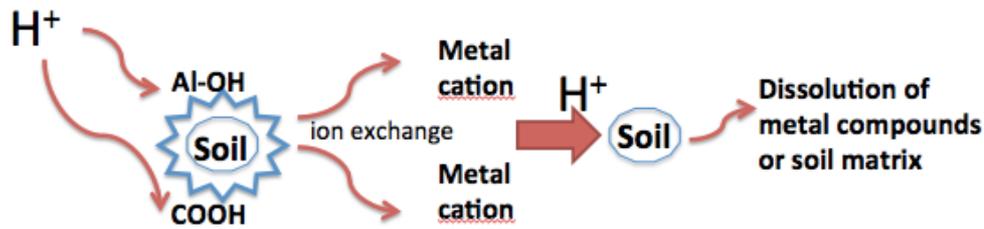


Figure 4. Mechanism of chemical extraction using acid solution

The effectiveness of soil washing, especially of the chemical extraction, depends very strongly on the selection of appropriate leaching agents that requires coinciding with the dissolution of contaminant species in the soil. Thus, the detailed information about metal-contaminants concentrations are of importance before conducting soil-washing treatment. It is helpful to identify if the metals can be separated by the remediation methods and the strength of the leaching agents, especially when using chemical extraction.

2.3 Sequential extraction

To indicate metal toxicity to living organism in soil, information of the total content of heavy metals only is insufficient. Because it is the solubility that makes metals mobile in the environment, thus bioavailable for plants to uptake, then via the food chain consumed by animals and accumulated in mans' body. The reactivity (including solubility, toxicity or bioavailability) varies with speciation or fractionation of metals in soil instead of the total amount (Cottenie, 1980). Speciation describes the distribution between metal species in soil, and fractionation is the identification of the fractions that bind metals in the soil matrix (Nieboer, 1999). The strong soluble species (fraction) will have a higher mobility, which are more toxic for plants and animals/human (Lund, 1990). Therefore, investigations of metal speciation and fractionation in soil are more essential and relevant indicators for describing metal characteristics rather than total content. In this study it is the metal fractionation that is investigated by sequential extraction procedures (SEPs).

Sequential extraction procedures is an analytical multi-step approach for the fractionation of trace metals in soils, sediments and sludge samples according on their chemical nature (Tessier, 1979). The theory behind SEP is a succession of chemical extractions applied to the same soil sample, with a decreasing mobility of the metals from after each following fraction.

The increasing interests of having available information about the solubility and mobility of metals in soil, water or sediment can be traced back to the year of 1967. Chester and Hughes (1967) first released their method on investigating the soil matrix phase with which metals were associated and the strength of the bond involved. The most widely utilized sequential extraction protocol is the Tessier procedure (Tessier, 1979). It is a five-step method, separating metal-contaminants into five fractions: the exchangeable fraction, the carbonatic fraction, the reducible (bound to Fe-Mn Oxides) fraction, the oxidizable (bound to organic matter) fraction, and residue fraction. Later on, numerous of researches modified the procedure developed by Tessier. In terms of different purpose and performance, the schemes of SEP range from 3-step up to 9-step: Salomons and Forstner (1984) divided the reducible fraction of Tessier's procedure into easily reducible fraction and moderately fraction; Ma and Uren (1995) added EDTA to the exchangeable step in order to remove sorbed metal avoiding impact on carbonates dissolution; Hullebusch et al. (2005) largely based on the Tessier procedure except skipped the oxidize step.

However, as these procedures differ in the sequence of extraction and in the condition of operation, the major drawback of the Tessier and its adjustments is the difficulty of comparing and evaluating the reliability of results obtained from various procedures and in various labs. Some research has criticized the widely used Tessier scheme. Tipping et al. (1985) reported the problem of reabsorption during extraction, where metal is initially released by the reagent but then reprecipitated back to the solid phase again Rauret et al. (1989) and Pfeiffer et al. (1983) found different concentrations of fraction depending upon the solid to solution ratio that low ratios would lead to severe effects.

In the 1990's, a group of experts who worked under the European Commission for the framework of BCR, Community Bureau of Reference (now named Standards, Measurement and Testing Program) proposed a standardized sequential extraction procedure named BCR® SEP (a registered trademark of the European Commission), in terms of worldwide acceptance (Ure, 1993). It is a three-step process developed for fractionation of trace elements with stated leaching agent and operation. It is similar to Tessier's scheme, but the BCR procedure combine the exchangeable-step and carbonate-step together into the first fraction (exchangeable fraction). To increasing reproducibility of the BCR procedure as a standard protocol, a group of European experts adapted the second step of the origin BCR SEP by increasing concentration of the used chemical from 0.1mol to 0.5mol and adding a fixed amount of concentrated HNO₃ adjusting the pH value in 1.5 during the process. This is called the modified BCR SEP (Rauret S. , 1999).

Table 1. Overview of the modified BCR SEP scheme (copper as example)

Step	Materials	S/l ratio (g/ml)	Condition	Fraction	Possible compounds
1	0.11mol/l HAc	1:40	Shaking 16 hours, 22±5 °C	Exchangeable	CuCl ₂ , CuCO ₃ , CuSO ₄
2	0.50mol/l NH ₂ OH·HCl	1:40	Adjust pH in 1.5, shaking 16 hours, 22±5 °C	Reducible	CuS
3	8.8mol/l H ₂ O ₂	1:10	Shaking 1 hour, 22±5 °C; 1 hour water-bath at 85±2 °C; further heating with below 3 ml volume	Oxidizable	Copper binds with organic matter
	8.8mol/l H ₂ O ₂	1:10	Heating 1 hour at 85±2 °C, volume below 1 ml		
	1.0mol/l NH ₄ Ac	1:50	Shaking 16 hours, 22±5 °C		
4				Residue	Copper silicates

Table 1 demonstrates the detailed information of each step in modified BCR SEP. In the first step, the exchangeable fraction, the metal-contaminants in the soil surface will be released through weak electrostatic interaction or ion-exchange reaction. The extracted metal species are also very sensitive to the pH change. Therefore, the potential metal fraction recovered in this step/condition can be metal carbonates, metal chlorides, metal sulfates and etc. (Gleyzes, 2002). Therefore the reagent used in the first step should be electrolytes in aqueous solution and as metals associated with carbonates are susceptible to pH change, acetic acid is generally selected in this fractionation analysis.

In the second step, metal ions associate with the iron and manganese oxides. The release of metals is achieved through the dissolution of a fraction of the soil using reducing agents which control the Eh. Hydroxylammonium chloride (NH₂OH·HCl) is the one used in the BCR procedure. Because one of the studied sites has used numerous copper sulfates, it might be copper sulfide released in this fraction.

Then in the third step, metals could be comprised in various forms of organic matter, and in sediment and soil in the complex polymeric material (humic substances). Being in an oxidizing system, soil organic substances have the potential to be degraded, causing the release of the sorbed metals. Hydrogen peroxide (H₂O₂) is the most frequently used oxidizing reagent and recommended in the BCR protocol (Gleyzes, 2002).

After the three steps, the solid is called the residual fraction, which contains primary and secondary minerals binding metals into their crystal lattice, like silicate compounds. Thus strong acids are required to destruct the crystal structure. In BCR, aqua regia is in use (Gleyzes, 2002).

2.4 Experimental scheme

All chemical reagents applied in modified BCR SEP are common in laboratory work, except NH₂OH·HCl. The Swedish Environmental Protection Agency (EPA) do not recommended to use it unless necessary, because it is very toxic to the natural environment and human health during its usage and after-use deposit. Therefore there is a need to find alternatives for metal extraction of contaminated Fe and Mn minerals.

The candidate extractants should be a reducing reagent and has the ability to attack the different crystalline forms of minerals containing Fe and Mn. The most common used solutions are oxalic acid (H₂C₂O₄), sodium dithionite (Na₂S₂O₄) and ascorbic acid (Filgueiras, 2002). Because oxalic acid is light sensitive and sodium dithionite will add sulfides causing extra reaction with other substances (Pickering, 1986), the ascorbic acid is chosen as reducing reagent in this study. According to Shuman's work, if the aimed metal is copper, using ascorbic acid can reach the same extracting efficiency (Shuman, 1982). For the sake of impact on environment, ascorbic acid is the "greenest" one within these four choices, since it is the major constituent of vitamin C.

However, the exact procedure about how the ascorbic acid is applied is not clearly written in Shuman's paper. Through comparing the structural formula of NH₂OH·HCl and ascorbic acid, referring to *Figure 5* and *Figure 6*, it was decided to use 0.2mol/l ascorbic acid in this work. Referring to *Figure 5* and *Figure 6*, NH₂OH·HCl acts as a reducible agent because it has an amino group in its structure, while ascorbic acid has a hydroxyl group. Although both of these two chemicals have only one reducible functional unit in their structure, in ascorbic acid there is a carbonyl making the hydroxyl more oxidized, which means to achieve the same reducible effect, the used dose of ascorbic acid should be smaller than NH₂OH·HCl. Therefore, the second step of the experimental scheme employed in this study will be the use of a 0.2mol/l ascorbic acid instead of 0.5mol/l NH₂OH·HCl in the modified BCR SEP.

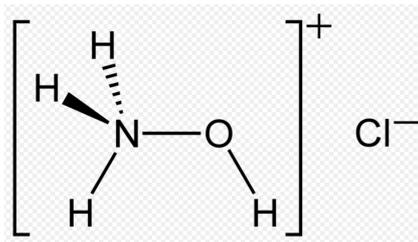


Figure 5. Structural formula of NH₂OH·HCl

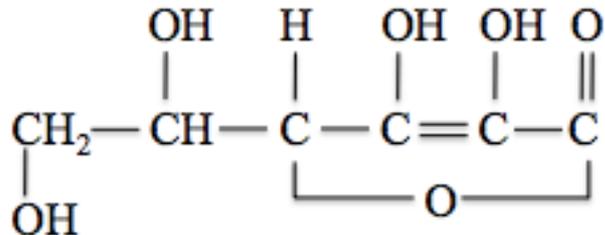


Figure 6. Structural formula of ascorbic acid

2.5 The evaluated metals

Although there are twenty metals analyzed by ICP-MS, only Cr, Cu and Pb are chosen as representatives for discussing the metal mobility and contamination.

2.5.1 Copper

Copper (Cu) has been in use at least 10,000 years and is in a wide application from conductor of heat and electricity to corrosion resistant and antimicrobial (Cameron, 1992). It is found naturally in sandstones and in minerals, but the significant increasing concentration of copper in soil is distributed to fertilizer and pesticide usage, wood production, municipal waste, and industrial emission. In the rural soil, the average concentration of copper is 2 to 100ppm (Schulte, 2004). This brown metal can bind strongly with the organic proportion of soil or the clay minerals, and copper can also be released as its monovalent state Cu(I) or divalent state Cu(II) after aerobic or anaerobic reaction. As a nonrenewable natural resource, copper ore is finite that the desired demand outpaced the supplication. According to International Copper Study Group (ICSG), in 2012, there will be a 250,000 tons' deficit as supply growth continues to lag demand growth (International Copper Study Group (ICSG), 2010).

2.5.2 Chromium

Chromium (Cr) was first used by human beings 2000 years ago in China. Nowadays it is marked as one of the world most strategic and critical metals, due to its good corrosion resistant performance and hardenability. To produce stainless steel, nonferrous alloys and alloy steel are its three dominant applications. The natural source of Cr is chromite (FeCr_2O_4) which chromium presents as trivalent form Cr(III) and the range of its content varies from 7 to 150ppm (Jankiewicz, 2005). The occurrence of certain amount of Cr(VI) in soil is a symbol that artificial contamination has happened through industrial activities, such as leather production which generates solid residues including high quantity of Cr(VI) in soil. Hexavalent chromate compounds are more dangerous to ecosystem than trivalent chrome, due to its high solubility which makes it readily taken up by organisms (Chen, 1998). The reduction of Cr(VI) to Cr(III) can be occurred under acid condition (Reyes-Gutiérrez, 2007). According to KPMG report in 2012, the demand of chrome ore is assumed to increase 4.82% in the next five years (Fossay, 2012).

2.5.3 Lead

Lead has also been used thousands years ago, cause its worldwide distribution and stability, while the modern industry now more make use of its highly density and corrosion resistance property. Lead (Pb) normally presents in soil at the surface and organic matter (less than 10 ppm) (Jawarsky, 1978), combined with other elements such as the ore galena (PbS), cerussite (PbCO_3), anglesite (PbSO_4), and crocoite (PbCrO_4). Its content in earth crust ranges from 10 to 30ppm (USDHHS, 1999). The general form of lead is in divalent state, which is capable of exchanging other elements, like calcium, strontium, barium and potassium in soil (Jawarsky, 1978). It's heard from International Lead and Zinc Study Group (ILZSP), that global Lead demand is forecasted to have a 4.8% rise to 10.78 million metric tons (Mmt) in 2012 (International Lead and Zinc Study Group (ILSZG), 2012).

3 Experimental

3.1 Sampling

There are three different soil samples investigated in this thesis work, and they were sampled from two contaminated sites respectively in Sweden. Both original bark sample and clay sample derived from Site Köpmannebro but in different soil layer, while the sandy sample came from Site Österbybruk.

Site Köpmannebro was a wood-manufacturing factory 100 years ago that applied copper sulfate against fungal growth, so copper should be found in a high concentration here. Still nothing grows on this site indicating high concentrations of metal contamination. Site Österbybruk was a more integrative industrial area having various factories that lead to a more complex soil contamination with several metals involved in.

In Köpmannebro, the surface soil up to 10cm deeper were sampled as the A1 sample and the soil which was in the 50-80cm layer was collected as A2 sample; In Österbybruk, the B1 sample was sampled from the surface up to 10cm depth as well, see *Figure 7*. After collection, all samples were kept in refrigerator at 4°C until needed.

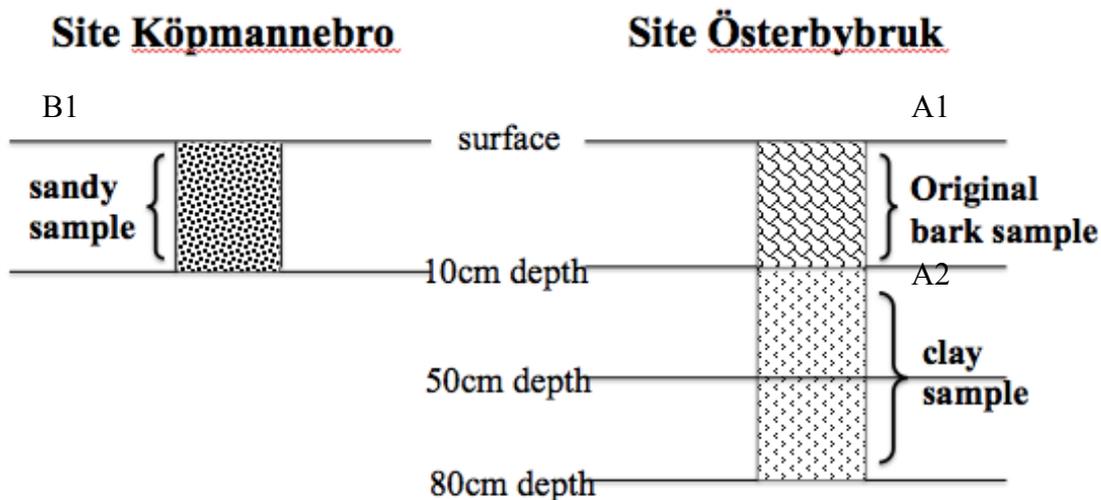


Figure 7. Soil samples from the contaminated sites

3.2 Pretreatment

3.2.1 Mixing

First of all, in order to get a homogeneous sample, A1 and A2 sample were entirely mixed respectively in a bowl, but by avoid to destroying sample particles. It should be noted that the A3 sample was already mixed in this case, see *Figure 8*. All mixed samples were stored at 4°C prior to chemical analysis.

3.2.2 Drying

All samples, including A1, A2 and B1, needed to be oven-dried at 80°C until the weight was stable and unchanged, see *Figure 8*. The drying time depended on the

amount of soil sample and the type of the sample. All dried samples were placed in a desiccator to cool down and for storage.

3.2.3 Extra process for bark sample

Additionally, the relevant big particle size of the original bark sample would make difficulties for extraction, in terms of the experimental dose (only 0.5 gram). Therefore, it was needed to disaggregate the sample particles into pieces. This study employed two pretreatments both grinding and incineration, but only for the A1 sample, then named the incinerated ash as A1_a sample, see *Figure 8*. The aim of it was to qualify whether the leaching from the resulting ash would have more copper extracted.

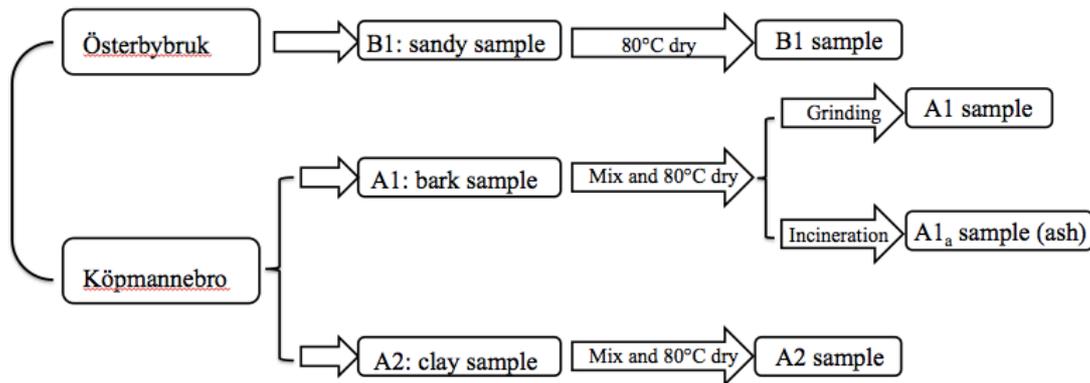


Figure 8. The four analyzed subsamples

Consequently, after 80°C drying, half of the dried A1 sample was picked up for grinding and then sieved to a particle size below 2 mm; while the rest half amount of dried A1 sample was incinerated in furnace at 860°C, see *Figure 8*. The degree of this temperature is settled under a tradeoff between being close to 1000°C in real industry to avoiding metal volatilization.

3.3 Details of sequential extraction procedure

The certain sequential extraction method used in this thesis work is mainly accomplished on the modified BCR, but with some improvement on the second step. The specific procedure employed in this study is illustrated in *Figure 9*.

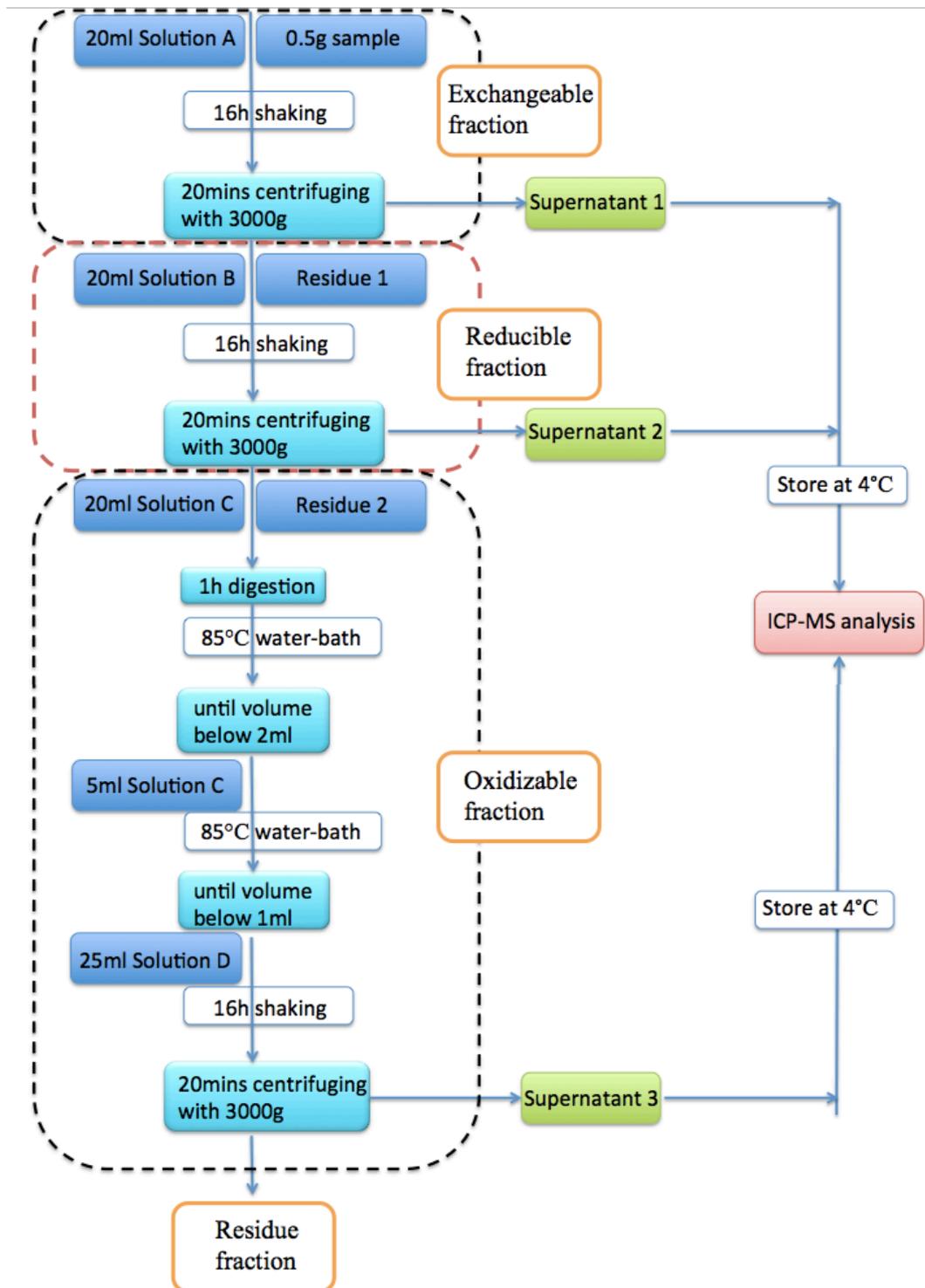


Figure 9. Detailed experimental schemes

Step 1: 20 ml of 0.11mol/l acetic acid (Solution A) was added to 0.5 g of soil sample in a 50 ml centrifuge tube, then kept it in reciprocating shaker for 16 h at 22±5 °C. This step follows what is regulated in the modified BCR scheme.

Step 2: 20ml of freshly prepared 0.2mol/l ascorbic acid (Solution B) was added to the residue from Step one in the centrifuge tube and did the mechanical shaking for 16

hours at 22 ± 5 °C. This step is the adjustment of the modified BCR scheme in this study.

Step 3: the third step was a little bit complicated that could be divided into three procedures. First of all, 10 ml of 8.8mol/l hydrogen peroxide (Solution C) was added carefully to the residue from Step two. Then digested at room temperature for 1 h with occasional manual shaking. Continued the digestion at 85 ± 2 °C in a water-bath, until the volume reduced to below 2ml. Secondly, it was time to add a further aliquot of 10 ml of Solution C and heated at 85 ± 2 °C again. Not until the volume of liquid was less than 1ml, did 50 ml of 1.0mol/l ammonium acetate (Solution D) was added to the tube. Again, shook mechanically for 16 hours at 22 ± 5 °C.

For each step, the speed of reciprocating shaker was 30 ± 10 rpm. After extraction of each fraction, the after shaking tube was then centrifuged at 5000 rpm (3000 gravity) for 20min in terms of separating the liquid phase and solid phase. Then the supernatant was collected by pipet and stored at 4°C refrigerator for later ICP-MS analysis. The remaining solid was used as reactant for the next step.

All the chemicals used in this experiment were of analytical grade or better and the deionized water used for preparing reagent was from a Millipore Milli-Q3RO/Milli-Q2 system. And all the subsample was analyzed in duplicate.

Attention:

- It also needed to notice that no delay should occur between the addition of the extractant solution and the beginning of shaking.
- To make the shaking more sufficient, laid down the tube in the shaking machine during shaking.
- Although using the rinse water can avert excessive solubilization of solid matter, this thesis work aimed to find a new remedy of the least conceivable soil losses. Thus a compromise was made to apply the supernatant-removed residue directly to the next step, without 15 minutes washing with deionized water.

3.4 ICP-MS

In this study, concentrations of various metal fractionations from different samples were determined using Inductively Coupled Plasma Mass Spectrometer (ICP-MS), which all were conducted by ALcontrol Laboratories. In ICP-MS, plasma is applied to atomize and ionize the sampled elements, thus the species are identified by their mass-to-charge ratio. Comparing with other analytical tools, ICP-MS has a lower detection limit (better than sub ng/L) suiting for trace metals analysis under a wide dynamic range (Rosen, 2004).

4 Results and dissuasions

4.1 Total amount of metals

Although the entire general trace metals (as As, Ba, Cd, Mo, Se and etc.) were analyzed by ICP-MS, only Cr, Cu and Pb were evaluated and assessed. Comparing with the MKM (Swedish Environmental Protection Agency for short) guideline value with total amount of metals from ICP-MS results, it is clear that there is a more complex contamination in Site B (Österbybruk), referring to *Table 1*. In Site Österbybruk, the concentration of Ba, Co, Cr, Mo and Ni are all exceeding the limitation regulated in the MKM guideline. However in Site A (Köpmannebro), the contamination is simply due to copper, because it is the only metal which has the exceeded amount. Copper in A2 (clay) mainly came from the surface of this site (A1 bark sample) through leaching, and it is therefore reasonable that the concentrations of copper are higher in the A1 bark sample than in the clay sample. Lead is considered as a good representative for toxic metals, in terms of its high risk in even a very low level of exposure or uptake, chromium may also be toxic in low concentrations and is also an indicator of artificial activities.

Table 2. ICP-MS results of metal total content

Element	B1 Acid leaching (mg/kg DW ¹)	A1 Total content (2012) (mg/kg DW)	A2 Acid leaching (mg/kg DW)	MKM ² Guidelines (mg/kg DW)
As	27	4	3	25
Ba	1010	89	75	300
Cd	0,2	0,4	0,3	15
Co	1300	2	3	35
Cr	2067	16	12	150
Cu	105	20000	7600	200
Mo	4033	2	-	100
Ni	963	13	7	120
Pb	203	66	13	400

4.2 Enrichment factors

The incineration temperature in this study was up to 860°C, so it could make the A1bark turn into ash, called the A1_a sample. Assuming that there is no metal loss during the incineration, and that all the mass reduction is due to the combustion of organic matters in the original bark sample. Then the concentration of metals in the A1_a sample will increase. According to the equation showed in *Table 2*, the ideal enrichment factor is calculated to five, which indicates the metal content in the A1_a sample increase five times higher than it is in the A1 sample. In fact, it is obvious that all the enrichment factors of Cr, Cu and Pb are smaller than five, see *Table 2*. It demonstrates that the set incineration temperature of 860°C is too high for the bark sample, especially for chromium which even half amount of it is volatilized by the high temperature (comparing with the ideal enrichment factor as 5, it is only 2.2 in fact).

¹ DW: dried weight

² MKM: Less sensitive ground from Swedish Environmental Protection Agency (Naturvårdsverket)
The red data means exceed the guideline.

Table 2. Metal enrichment factors after incineration

$\text{Ideal enrichment factor} = \frac{\text{weight of dried bark sample}}{\text{weight of ash after incineration}} = \frac{3.12g}{0.63g} \approx 5$					
Elements	TA* in bark sample (µg/g)	TA in ash sample (µg/g)	Equation	Enrich. Factor (EF)	Result
Cr	16	35	$EF = \frac{TA_{ash}}{TA_{bark}}$	2.2	< 5
Cu	20000	74000		3.7	
Pb	66	250		3.8	

*TA: total amount

4.3 Results for soil and ash samples

All the data obtained from ICP-MS of each sample and fraction are classified by metal contents and compared with the total amount respectively. Thus the final results are manifested by percentage.

4.3.1 B1 sandy soil sample

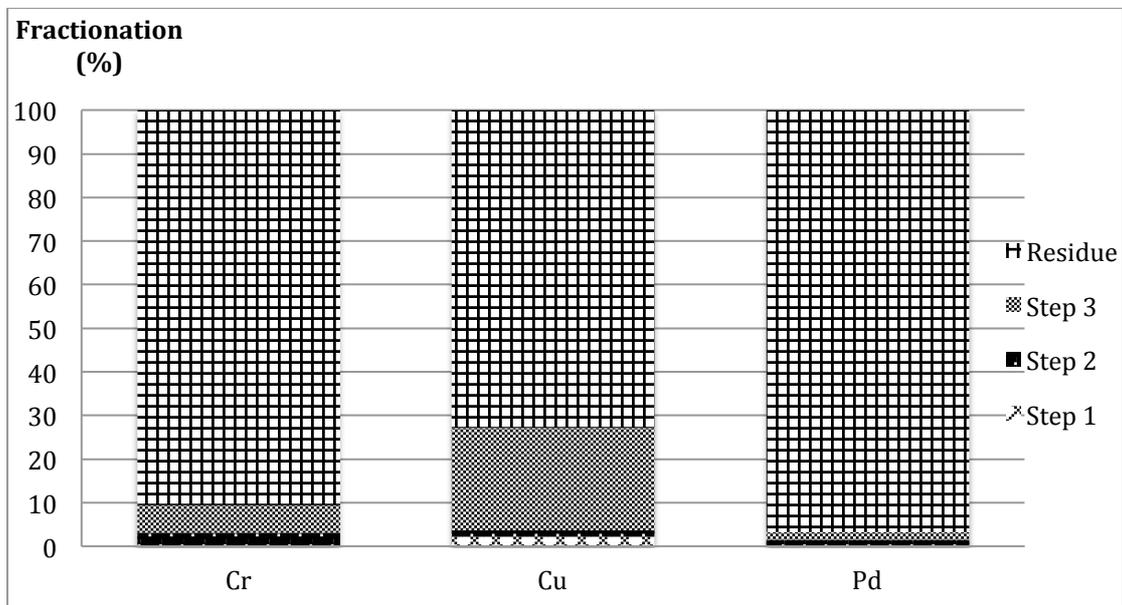


Figure 10. Metal fractionation distribution of B1 sandy sample

According to Figure 10, the dominant fractionation for chromium, copper and lead in the B1sandy soil is the oxidizable fraction occurring in the third step. The total extractable amount of these three metals account to 6.3%, 23% and 1.7% respectively. Meanwhile, the most extractable metal is copper with around 30% removed after three steps; lead is difficult to leach from the sequential extraction procedure; only 3% can be recovered.

4.3.2 A2 clay soil sample

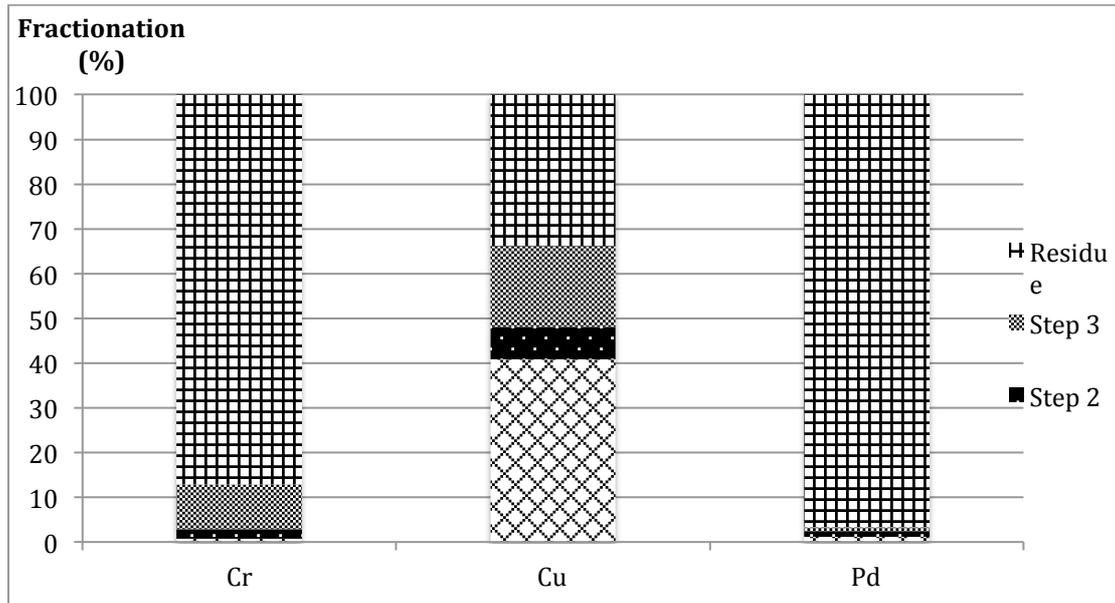


Figure 11. Metal fractionation distribution of A2 clay sample

The compounds of chromium and lead in the clay soil sample are stable and hard to be released, see *Figure 11*. The total extractable metals content remain in the same level as in the B1 sandy soil sample. But the result change dramatically of copper distribution because the dominant fraction turns to be the exchangeable fraction. This indicates that the only use acid solution can recover the majority of copper in the clay sample. Additionally, almost 70 percentages of total copper species in clay sample are extractable prior to residue fraction. In Andersen's paper which used the modified BCR SEP, the rate of total extractable copper is around 50% in clay samples and 80% of them is in the reducible fraction (Andersen, 2002). In contrast to Andersen, the adjusted procedure employed in this study works well and even has a higher removing rate. The difference can also be due to other parameters, as the various pretreatment on sample, the different reduction potential of tested sample or the different pH condition of soil sample.

4.3.3 A1 bark soil sample

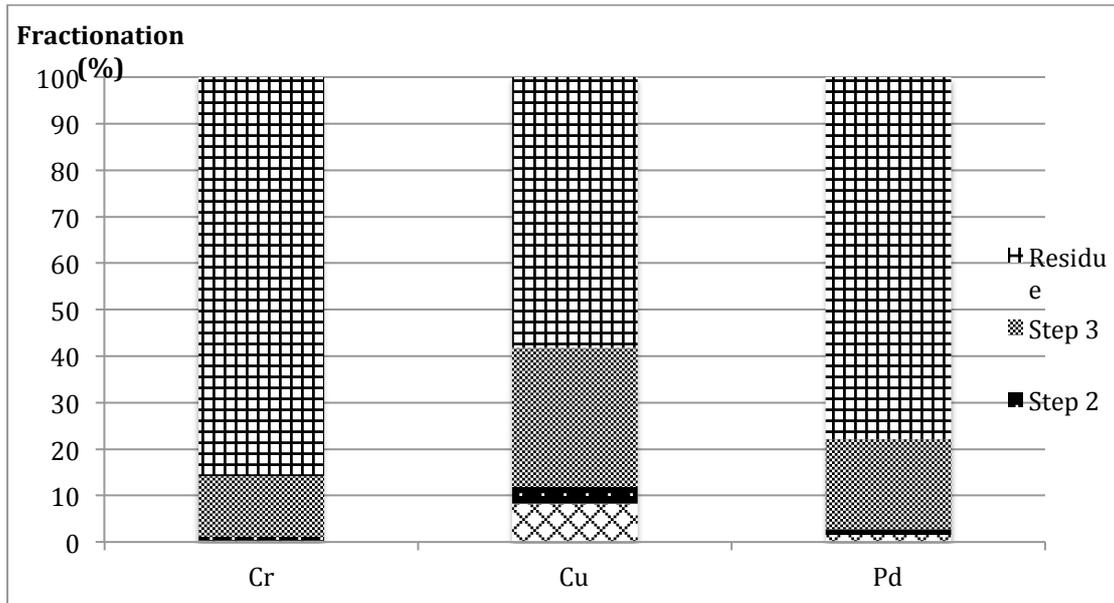


Figure 12. Metal fractionation distribution of A1 bark soil sample

According to the results presented in *Figure 12*, the significant difference is that more lead is in the extractable fractions in the A1 sample. All the metals in this sample are strongly bounded to soil particle that the oxidizable fraction generated from the third step is the dominant fraction for all these three metals (Cr is 13%, Cu is 30% and Pb is 19%), and the overall leachable metal amount is not very high (the highest is copper around 42% after three steps). Comparing with the results from Davidson (1999) which applied the modified BCR SEP for a bark sample and got 60% of extractable copper, this study obtained similar results in bark sample. Both in Davidson and this study, the leachable copper compounds are more in the oxidizable fraction. This can again manifest the sequential extraction scheme used in this thesis work has the same efficiency as the modified BCR SEP dose (Davidson, 1999).

4.3.4 A1_a ash sample

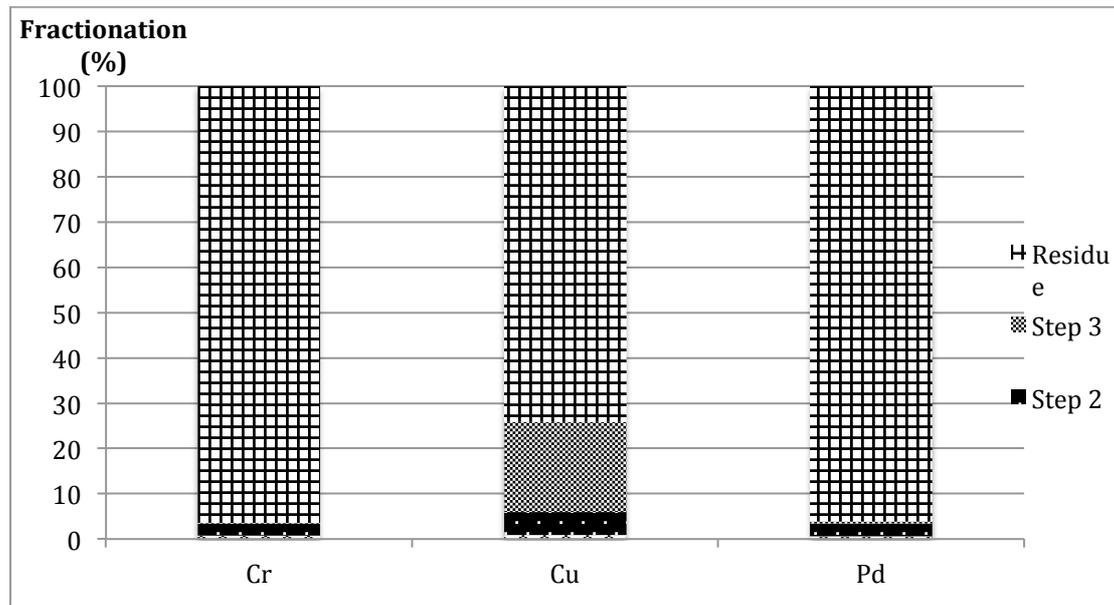


Figure 13. Metal fractionation distribution of A1_a ash sample

According to the results, see *Figure 13*, the dominant fractionation in the A1_a sample turns to be the reducible fraction which is generated from the second step (both 3% of Cr and Pb are in this fraction). For copper, the oxidizable fractionation remains the most easily leached with around 20%. In the B1 and A2 sample, copper is still the most extractable metal (but only around 26% after the whole three steps), and both chromium and lead are difficult to be recovered with less than 4% removing rate.

4.4 Copper distributions in each sample

Comparing the results illustrated in *Figure 10* and *Figure 13*, copper is the easiest extractable one among these three metals from all samples. The total leaching rate after the 3-step extraction can reach 67%, while the highest rate for lead is less than 25%, and for chromium is only 15%.

Figure 14 summarizes the performance of copper in various samples. These sequential extraction results are very valuable and reasonable, as the consequent distributions of Cu in the A1 and A2 sample are well connected with the site history. Both of them has a relevant higher proportion of extractable fractionation, because they are both sampled from the same site which has used a mass of copper compounds, but in different layer as illustrated in *Figure 7*. During year's of leaching, copper can be released via ion exchange reaction and penetrate to the deeper layer where the A2 clay soil sample is collected. Thus the soluble and easy leached compounds, like copper sulfate (CuSO₄), copper carbonate (CuCO₃) or copper chloride (CuCl₂), is most in the A2 clay sample rather than in the A1 bark sample; the oxidizable fractionation which is hardly released naturally are more found in the A1 bark, which appears in the third step in sequential extraction procedure after using some oxidant.

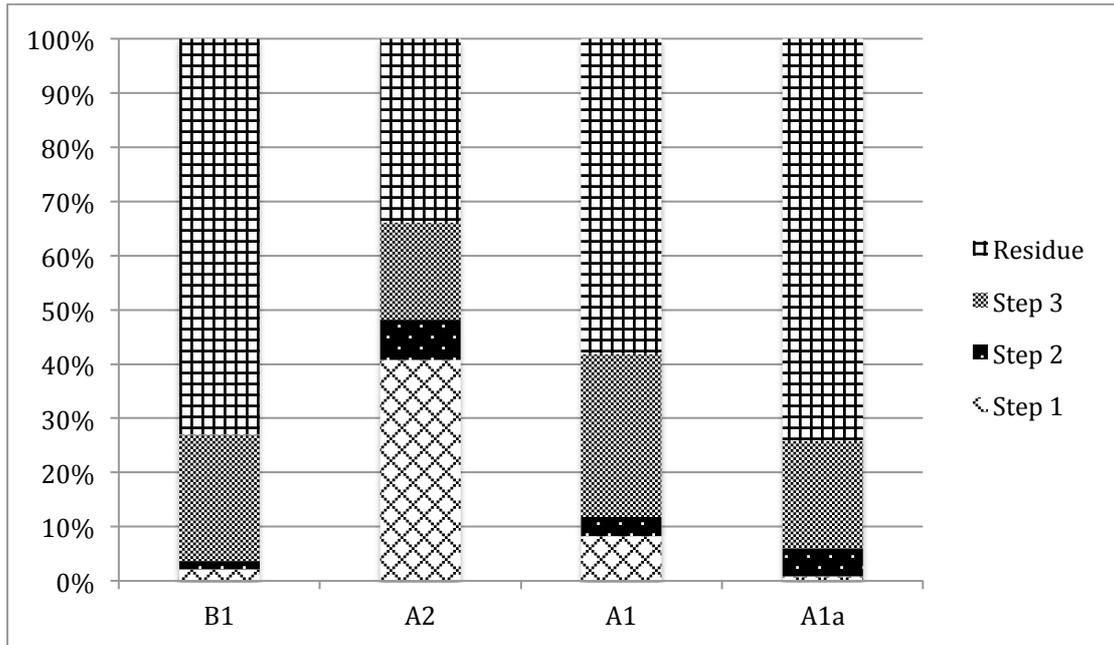


Figure 14. Copper solubility in different soil samples

Additionally, the results of the A1 bark sample and A1_a ash sample in *Figure 14* can illustrate the influence of combustion on the metal distribution in soil. Both of them belong to the same original bark sample, except various pretreatment, grinding and incineration respectively. It is apparent that incineration can change the distribution that converts metals to more stable fraction, since more copper is present in the residual fraction in the A1_a ash sample. The XRD results can prove this in another side. It is said that copper oxide (CuO) is the major compound in the A1_a ash sample which copper is already in its highest state (Cu²⁺). While the chemical used in the third step of this study is hydrogen peroxide (H₂O₂), functioning as an oxidant that cannot dissolute CuO. Consequently, during incineration some copper compounds convert to CuO and appear in the residual fraction.

5 Conclusions

For the pretreatment of bark sample, grinding seems to be more adaptable than incinerated to ash. From the results it is obvious that incineration decreases the solubility of metals in soil, which not only reduces the extraction efficiency but also transform fractionation distribution.

For these four soil samples, the highest percentage of Cr, Cu and Pb are generally in the residual fraction, except in the clay soil sample where the majority of copper pollutants occur in the exchangeable fraction. This result indicates that metal contaminants in both of these two sites are stable and immobile, so the potential risk to the surrounding ecosystem will not increase. To solve the contaminated problem of these sites permanently, the trade-off between soil loss and soil cleaning is important.

Additionally, this thesis work is not totally following the modified BCR procedure by using the ascorbic acid instead of $\text{NH}_2\text{OH}\cdot\text{HCl}$. The results obtained in this scheme are similar with earlier studies results which applied the modified BCR procedure; it can be concluded that the experimental scheme applied in this study is effective. More experiments with the modification of reaction condition are recommended to strengthen the findings in this study.

Copper is the most leachable metal in all samples, and site Köpmannebro is more interesting to treat with soil washing than Site Österbybruk, because higher amount of metals can be extracted, and more soluble fractions appear in bark and clay sample which are both from site Köpmannebro. Additionally, it is recommended using grinding to pretreat the bark sample instead of high temperature incineration for the best potential of Cu recovery.

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Appendices

Appendix A: Chemical solution preparations

Solution A (acetic acid, 0.11 mol/l): Dissolve 3.3022 gram acetic acid under fume cupboard to 500ml volumetric flask. Then fill up this flask with distilled water to obtain an acetic acid solution of 0.11M

Solution B (ascorbic acid, 0.2 mol/l): Dissolve 4.4033 gram ascorbic acid in a 250ml volumetric flask with distilled water, and make up to volume with distilled water aiming to get the 0.1M ascorbic acid solution. Remember to cover with tinfoil and keep under 4°C storage.

Solution C (hydrogen peroxide, 8.8 mol/l): Add 67.4072ml pure hydrogen peroxide into a 250ml volumetric flask, using distilled water to fill up it and dilute it to the concentration of 8.8M.

Solution D (ammonium acetate, 1.0 mol/l): Dissolve 38.54 gram ammonium acetate in 500ml volumetric flask with 300ml distilled water. Adjust pH value around 2.0 with 0.1 degree fluctuation by using HNO_3 and fill it up with distilled water.

Pay attention to that all reagents used are of analytical-reagent grade or better.

Appendix B: Primary mass weight data about oven drying.

	Sample	Origin/g	Final/g	Reduction/%
A1	80°C dried	20	3.12	15.6
	860°C incineration	3.12	0.63	20.2
A2	80°C dried	18.52	12.16	65.7
B1	80°C dried	17.91	15.47	86.4

Appendix C: Primary ICP-MS results of trace metals

Elem.	Sandy						Clay						Bark						Ash					
	Step 1		Step 2		Step 3		Step 1		Step 2		Step 3		Step 1		Step 2		Step 3		Step 1		Step 2		Step 3	
	S11	S12	S21	S22	S31	S32	C11	C12	C21	C22	C31	C32	B11	B12	B21	B22	B31	B32	A11	A12	A21	A22	A31	A2
As	0,13	0,14	3,5	5,8	0,15	0,14	0,03	0,03	0,1	0,11	0,49	0,073	0,32	0,3	0,46	0,49	0,79	1	2,7	2,8	0,67	0,69	0,23	0,26
Ba	27	44	34	48	74	70	2,8	2,9	3,8	3,8	1,4	1,5	1,7	1,7	3,1	3,2	6,1	5,6	0,8	0,68	14	11	33	36
Cd	0,02	0,02	0,09	0,12	0,06	0,079	0,01	0,01	0,0021	0,0021	0,0043	0,0029	0,057	0,054	0,022	0,023	0,02	0,021	0,024	0,026	0,056	0,056	0,0038	0,0037
Co	63	54	170	230	49	49	0,057	0,05	0,014	0,013	0,037	0,033	0,38	0,35	0,1	0,11	0,11	0,1	0,031	0,029	0,16	0,15	0,01	0,0099
Cr	0,56	0,57	25	37	55	75	0,047	0,045	0,13	0,12	0,59	0,61	0,022	0,02	0,066	0,06	1,1	1	0,13	0,12	0,49	0,48	0,024	0,021
Cu	1,2	1,1	1,3	<0.2	8,6	16	1500	1600	250	310	680	680	790	860	350	370	3100	2900	330	300	2000	1800	7100	7600
Pb	0,11	0,13	1,2	1,6	1,3	2,2	0,07	0,078	0,074	0,095	0,048	0,061	0,52	0,52	0,39	0,4	6,4	6,4	0,96	0,63	3,5	3,3	0,64	0,67
Mo	1,8	1,7	130	200	110	140	-	-	0,037	0,021	-	-	0,0049	0,003	0,03	0,03	-	-	0,18	0,18	-	-	-	-
Ni	33	31	120	150	47	36	0,13	0,12	0,049	0,048	0,14	0,15	2	1,9	0,69	0,71	0,9	0,84	0,14	0,14	1	1,1	0,084	0,083
Se	<0.01	<0.01	0,03	0,05	0,033	0,07	0,019	0,018	0,031	0,029	0,22	0,24	0,011	<0.01	<0.01	<0.01	0,56	0,51	0,59	0,59	0,11	0,11	0,029	0,03
Sr	2,2	2,7	0,74	0,84	0,54	0,48	-	-	0,19	0,21	-	-	2,7	2,8	1	1,1	-	-	16	18	-	-	-	-
V	0,48	0,45	71	82	4,6	8,4	0,33	0,3	0,53	0,51	1,1	1,2	0,099	0,09	0,16	0,16	1,6	1,4	1,1	1,1	7,5	7,3	0,031	0,026
Zn	7	8,2	11	14	2,8	5,3	0,91	0,92	0,21	0,2	<0.5	<0.5	12	14	6,1	6,6	4,4	4,2	0,72	0,86	4,5	4,8	<0.12	<0.11