Initial studies of the recovery of Cu from MSWI fly ash leachates using solvent extraction

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Highlights:

- Acidic process waste water could leach ≥90% of Cu from ~~contaminated~~ polluted soils.
- Incineration of ~~contaminated~~ polluted soils with high organic content reduces metal leaching.
- After one leaching step the soil residue metal content exceeds Swedish guidelines.

Remediation of Metal Polluted Hotspot Areas through Enhanced Soil Washing —Evaluation of Leaching Methods ~~Remediation of Metal Contaminated Sites through Enhanced Soil Washing — Evaluation of Leaching Methods~~

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Abstract

Soil washing offers a permanent remediation alternative for metal ~~contaminated~~ polluted sites. In addition, the washed out metals can be recovered from the leachate and re-introduced into the social material cycle instead of landfilled. In this paper, soil, bark and bark-ash washing was tested o~~f~~n four different ~~kinds of~~ metal ~~contaminated~~polluted soil and bark samples from hotspots at former industrial sites. Six~~using 6~~ different leaching agents; HCl, NH_4Cl, lactic acid, EDDS and two acidic process waters from solid waste incineration~~.~~, ~~is~~ were tested, discussed and evaluated. For the soil washing processes, the final pH in the leachate strongly influences the metal leachability. The results show that a pH<2 is needed to achieve a high leaching yield, while <50 w% of most metals were leached when the pH was higher than 2 or below 10. The acidic process waste waters were generally the most efficient at leaching metals from all the samples studied, and as much as 90–100 w% of the Cu was released from some ~~soil~~ samples. Initial experiments show that from one of these un-purified leachates, Cu metal (>99% purity) could be recovered. After a single leaching step, the metal contents of the soil residues still exceed the maximum limits according to the Swedish guidelines. An additional washing step is needed to reduce the contents of easy soluble metal compounds in the soil residues. The overall results from this study show that soil and bark-ash washing followed by metal recovery is a promising on-site permanent alternative to remediate metal ~~contaminated~~polluted soils and to utilize non-used metal resources. ~~However, more research is needed to develop an efficient and solid treatment method; this is currently underway.~~

1. Introduction

More than 80,000 sites that may be ~~contaminated~~polluted due to earlier industrial activities are known in Sweden, and about 2 million potentially ~~contaminated~~polluted sites have been identified in Europe and in the United States (Dermont et al. 2008a, SEPA 2009a). Metals are the main problem at about 50% of these sites. Contrary to many organic pollutants, metals cannot be destroyed and are non-degradable. For this reason, metal ~~contaminated~~polluted soils must always be treated and remediated to decrease the risks of pollution. Consequently, the need for metal remediation technologies is enormous. The most commonly used metal remediation method is to excavate, transfer and landfill the ~~contaminated~~polluted soil and replace it with new, clean material (Dermont et al. 2008a, Shammas 2009). Techniques such as solidification/stabilization (S/S) are often applied prior to landfilling to decrease the potential leaching of metals (Dermont et al. 2008a, Shammas 2009). However, this treatment does not reduce the amounts of pollutants in the materials and metals may leach out in the longer term. In addition, metals are removed from the material cycle, resulting in the loss of valuable resources.

An alternative to landfilling is soil washing. Soil washing is used commercially in both Europe and the Unites States and can be carried out on site (Dermont et al. 2008b). A recent example is the remediation of the Olympic Park site in London in 2012, where more than 800,000m^3 of soil ~~contaminated~~polluted with e.g. oil and Pb was treated (Douglas 2009). Soil washing can be based on either physical separation, like magnetic fractionation or size separation, on chemical leaching, or on a combination of both. Water is often used as leaching agent, but it is also

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common practice to use stronger leaching agents like acids or complex forming ligands such as EDTA (Bisone et al. 2012, Labanowski et al. 2008, Laporte-Saumure et al. 2010, Moon et al. 2012, Moutsatsou et al. 2006, Tandy et al. 2004, Voglar and Lestan 2013). The selection of leaching agent depends on e.g. the properties of the contaminants at each specific site and on the remediation goal, i.e. the acceptable levels of the pollutants in the soil after remediation.

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Generally, the costs for soil washing are comparable with those for techniques like S/S and electrokinetics and much lower than for vitrification (Shammas 2009). ~~Vitrification means that the soil matrix is transferred into a glassy material through heating, something which requires a lot of energy and is therefore associated with high costs.~~ Soil washing offers another important opportunity to reduce the overall costs: through the potential recovery of the released metals. The leachate generated from the enhanced soil washing is rich in pollutants and can act as a source for metal recovery. This is not much studied and the washing procedures currently applied focus on metal removal, as it has this far not ~~has~~ been economically favorable to recover metals from waste materials like ~~contaminated~~ polluted soils and ashes. However, there is one example of a leaching based profitable metal recovery process from ~~municipal solid~~ waste incineration ~~(MSWI)~~ ash. In Switzerland, the world´s first commercial full-scale plant where high purity Zn (99.9%) is recovered from ~~MSWI~~ waste fly ash has recently been started up (Schlumberger and Bühler 2012, Schlumberger et al. 2007). In another study, based on laboratory experiments on the recovery of Cu from ~~MSWI~~ waste fly ash, it was shown that 90% of the Cu could be selectively recovered and that this treatment could potentially be more profitable than the

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way in which ash is usually handled, i.e. landfilling (Karlfeldt Fedje et al. 2012, Karlsson et al. 2010). In the study by Karlsson et al (2010), the Cu content in the ash was about 0.8%, and earlier studies on sites used for wood preservation show that Cu concentrations of 0.5% or higher are common (Dermont et al. 2008b, Shammas 2009). As a comparison, the Cu content in a workable Swedish mine is 0.3% (Boliden AB 2011). The world stocks of metals like Cr, Cu and Zn are at or near historically low levels and are predicted to last about 15, 40 and 20 years, respectively (Stenzel et al. 2011). Consequently, ~~I~~it is ~~likely~~ plausible that metal prices will increase in the near future, as the virgin resources are finite and there is a great demand for metals. ~~The world stocks of metals like Cr, Cu and Zn are at or near historically low levels and are predicted to last about 15, 40 and 20 years, respectively (Stenzel et al. 2011).~~

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In this lab-scale study, soil, bark and bark-ash washing with various leaching agents is used for leaching of metals, and its potential as a method to remediate highly metal ~~contaminated~~polluted soil and bark samples is tested. The metal leaching properties and the solid residues of soil samples taken at different ~~contaminated~~polluted sites with different pollution situations are studied using the various leaching agents. The aim is to maximize the metal release, with particular focus on Cu and Cr, and to produce a metal rich leachate from which valuable metals can be recovered by e.g. electrolysis.

2. Material and methods

2.1 Soil samples

Soil samples with different characteristics and degree of contamination from two sites- Långö in western Sweden and Österbybruk in eastern Sweden- were used in this study. Both sites are strongly ~~contaminated~~polluted with metals. The first site (Långö=A) was historically used for wood preservation, using $CuSO_4$ according to the Boucherie method (Vougy 1856). Based on results from sampling and chemical analyses in previous studies, representative samples of bark and soil were collected from a hotspot with a high metal content; A1 is a bark sample from the surface ~~level~~ horizon (0–10 cm depth) and A2 is a soil sample from a depth of 50–100 cm. Both samples are mixtures of several sub-samples taken from the bark and the soil, respectively.

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The second site (Österbybruk=B) has been used within the iron and steel industry since the late 16th century. More recently, the area has also been used as e.g. a car breaker´s yard and for wood processing. Based on previous investigations on this site, a hotspot with high concentrations of several metals was chosen, and a representative surface horizon soil sample was collected, i.e. B1.

2.1.1 *Pre-treatment of the soil samples*

All samples were dried at 80°C (100 %DS) until a constant weight was achieved. The pure soil samples i.e. A2 and B1 were directly cooled down in desiccators before being stored in air-tight containers until used, while ~~T~~the bark ~~in the A1~~ sample was cut into smaller pieces using an automatic mixer. Part of the bark was thereafter stored until further analyses (A1), ~~and part of the sample~~ while the other part of the sample was incinerated ~~at 860°C~~ for 10h to form an ash sample (A1a). This incineration step was done in order to reduce the organic content of the bark and to increase the potential Cu release. The incineration temperature used was 860°C and chosen to avoid vaporization of Cu compounds. All samples were cooled down in desiccators before being stored in air-tight containers until used. No pre-treatment using e.g. grain-size fractioning to generate highly polluted and less polluted fractions of the soils was done due to too small sample volumes.

2.2 Leaching agents

For the leaching experiments, four chemically different leaching agents known to effectively leach metals from natural materials like soils were chosen for this study; 0.01M HCl, 8M NH4Cl adjusted to pH 10 to enhance amine complex formation, 1M lactic acid, and 0.1M EDDS ((S,S)-Ethylenediamine-N,N-disuccinic acid tri sodium salt) adjusted to pH 7 to especially enhance Cu and Pb leaching. The leaching agents and their concentrations were chosen based on literature research (Lo et al. 2011, Moon et al. 2012, Schöning and Brümmer 2008). In addition, two highly acidic process waste waters “a” and “n” (pH around 0) were used. These process waters came from two different places in the wet flue gas cleaning processes after waste incineration and therefore contained metal ions and high concentrations of chlorides. The concentrations of different ions in the process waters vary naturally depending on e.g. the conditions during the incineration process and the kind of waste used, but representative concentrations of the most common ions are given in Table 1. Today these acidic waters are purified through precipitation processes of the toxic metal ions and small particles. Thereafter the metal sludge is landfilled, while the clean water is released to the recipient.

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2.3 Leaching experiments

2.3.1 Sequential extraction

The modified three-step BCR method is proposed by the commission of the European communities Bureau (BCR) as the European standard method for sequential extraction schedules (Rauret 1999). In brief, the leaching steps are first; acetic acid (exchangeable ions), second; hydroxyl ammonium chloride (reducible fraction) and third; H_2O_2 + ammonium acetate (oxidizable fraction). ~~This method was used to predict the mobility of As, Ba, Co, Cr, Cu, Mo, Ni, Pb, V and Zn in the original samples. However, due~~Due to toxicity the hydroxyl ammonium chloride solution ($NH_2OH{\cdot}HCl$) originally used in the second step was exchanged for non-toxic ascorbic acid (0.2 M). It has been shown that ascorbic acid has the same metal extraction efficiency as hydroxyl ammonium chloride, especially in the case of Cu (Shuman 1982). This method was used to predict the mobility of As, Ba, Co, Cr, Cu, Mo, Ni, Pb, V and Zn in the original samples. All experiments were carried out in triplicates.

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2.3.2. Enhanced batch leaching

In each experiment, 0.5 g soil was leached in airtight plastic containers using 5 mL of either of the chosen leaching agents (liquid-to-solid ratio (L/S) of 10). The leaching time was set to 2 hours with continuous shaking at 140 rpm. After leaching, the soil-liquid-mixture was centrifuged for 15 minutes at 3000G (gravity). The supernatant was transferred to a new container and acidified before being stored in a refrigerator until analyzed. The ash residue was washed for 5 minutes with continuous shaking using 5 mL ultrapure water (18.2 MΩ/cm^2).

Thereafter, the mixture was centrifuged for 15 minutes at 3000G and the ash residue was dried and stored in airtight containers until used. All leaching experiments were carried out in duplicates.

2.4 Analytical methods

In order to measure metal content in the original soil samples, two commonly used digestion methods were chosen, based on the sample characteristics. Due to its high organic content, sample A1 was completely dissolved following the procedure in ASTM D3683 (As, Cd, Co, Cu, Hg, Ni, Pb, S and Zn) and ASTM D3682 (Al, Ca, Fe, K, Mg, Na, P, S, Si, Ti, Ba, Cr, Mn, Mo, Sb, Se, Sn, Sr and V). The methodology in the ASTM D3683 was also used to analyze the total metal content (Al, Sb, As, Ba, Pb, P, Fe, Cd, Ca, K, Cu, Cr, Hg, Mg, Mn, Mo, Na, Ni, Sr, S, Ti, V and Zn) in A1a, while A2 and B1 were digested using the standardized procedure SS 028311. All analyzes were carried out in triplicates except for A1a, which was analyzed in duplicate.

The total element concentrations of all the solutions from the total digestion were measured using ICP-MS (inductively coupled plasma mass spectrometry) (Al, As, Ba, Pb, Ca, Cd, Co, Cu, Cr, Fe, K, Mg, Mn, Na, P, Ti, Hg, Mo, Ni, S, Sb, Sn, Sr, V and Zn) or ICP-AES (inductively coupled plasma atomic emission spectrometry) (Se and W). The soil leachates obtained from the leaching experiments and the sequential extraction were analyzed for metals (Al, As, Ba, Be, Pb, Cd, Co, Cu, Cr, Li, Mn, Mo, Ni, Se, Ag, Sr, Tl, U, V and Zn) using ICP-MS. A Dionex ICS AS-DV ion chromatograph with ICS-900 columns for cation and anion analyzes was used to analyze the K^+, Mg^{2+}, Na^+, NH_4^+, Ca^{2+}, Cl^-, NO_2^-,

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NO_3^-, PO_4^{3-} and SO_4^{2-} concentrations in the acidic process waters, while the amounts of Al, Pb and Zn were analyzed using ICP-MS~~ or ICP-AES~~.

The main crystalline compounds in the original samples, and in some of the leached samples, were identified by qualitative X-ray powder diffractometry (XRD) using a Siemens D5000 X-ray powder diffractometer with the characteristic Cu radiation and a scintillation detector. Identification of compounds was carried out using the JCPDS database (Joint Committee of Powder Diffraction Standards 2006). The detection limit of this method is about 1 % by weight. The samples were dried and ground in an agate mortar before being analyzed. The particle size distributions in the original dried samples were measured using manual dry sieving with sieve size fractions of between 0.125 mm and 1 mm. The pH was measured in the original samples ($pH_{(H_2O)}$) and at the start and end of each leaching experiment using a Methrom SM 702 pH meter.

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3. Results and discussion

3.1 Characterization of original samples

The total amounts of selected major and minor elements in the original samples are shown in Table 2. For comparison, the Swedish generic guideline values for sensitive and less sensitive land use are also given (SEPA 2009b).

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In the original samples from site A, i.e. A1 and A2, only Cu exceeds the Swedish guidelines for ~~contaminated~~polluted soils, while at site B several metals exceed the guidelines (Table 2). In an earlier study of site B, four times higher amounts of Fe, Al and K, and 15 times higher amounts of Na, were detected at spot B1 compared to the results in this study (Elander et al. 2010). This is due to heterogeneities between sub-samples but the choice of digestion method is also very important. In the previous study, the methods in ASTM 3682 and 3683 (total digestion using bomb and melting) were used, while the SS 028311 (HNO_3 and H_2O_2 leaching method) was used in this study. For the minor elements, like As, Co and Cu, no significant differences could be seen, suggesting that these metals are present in compounds soluble in strong acid solutions. Chromium and W are exceptions, perhaps because they are incorporated together with Fe, Al, K and Na in very low-soluble minerals and compounds. In sample A1, the total amounts of minor elements are generally somewhat higher when using ASTM 3682 and 3683 than with acidic leaching (7M HNO_3), which was used in an previous study on soils from the same spot (Kemakta Konsult AB 2012). However, for Cu the content is about 2.5 times higher when bomb digestion is used than with acid leaching, which shows that Cu is effectively adsorbed to the organic matter in the bark, thus reducing the leachability.

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From 3 g of dry bark about 0.6 g of ash was obtained. Theoretically, if no Cu was volatilized during incineration, the Cu content in the ash would be about 5 times higher than in the original bark. However, according to the total content analyses, Cu is enriched less than 3 times during incineration (Table 2). This means that the chosen incineration temperature of 860°C is too high to optimize the enrichment of Cu in the bottom ash. The reason for this is probably an uneven oxygen distribution, resulting in a reducing atmosphere, which can increase metal volatilization (Mojtahedi et al. 1987, Wikman et al. 2003). However, in a real incineration process, the volatilized Cu would be caught in the flue gas cleaning system and captured in the fly ash. The enrichment factors for most other elements were around 5, but for the soil matrix forming elements, such as Al, K, Mg and Na, the enrichment factors were higher (Table 2). This shows that these elements are present as low-volatile minerals in the original s~~oil~~ample as well as in the ash~~, which to some extent is shown in the XRD analyses (Table 3)~~. Barium was enriched almost 8 times during incineration, causing the amount in the resulting ash to exceed the Swedish guidelines for less sensitive land use (Table 2). This is not surprising, as a majority of the most common Ba compounds have boiling and smelting points well above 850°C (Alberty et al. 2008).

Even though the Cu content in sample A1 and A2 were around 1% or higher, no crystalline Cu compounds could be identified (Table 2 and 3). This suggests that the Cu is present in amorphous forms, in very small crystals or as several different Cu compounds. The first reason is the most likely in sample A1, as Cu effectively sorbs to organic matter~~, something which has been thoroughly discussed in the literature~~ (Bodek 1988, Kalmykova et al. 2008, Stumm and Morgan 1981). However, when the bark was incinerated to ash the amorphous, i.e. the organic, phase drastically decreased and Cu oxides were clearly identifiable (Table 3). The presence of amorphous material was low both in A2 and in B1. Silica oxide, SiO_2, was identified as a major compound in all samples but the presence of other minerals varied between the samples, indicating different characteristics, which will influence the metal leaching (Table 3).

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An overview of t~~T~~he particle size distributions in the original samples are shown in Figure 1. The bark (A1) contains pieces ~~larger than ~~>1mm, while the corresponding ash (A1a) mainly consists of smaller particles. Sample A2 has~~is a~~ in an earlier investigation been classified as ~~clay~~clayey -soil (Kemakta Konsult AB 2012) and was expected to contain a larger fraction of small particles. This could not be found, something which is probably due to clustering of the small clay particles into stable agglomerates during drying. An ocular inspection of the soil particles that remained after leaching confirmed this, as a majority of the particles were smaller than those in the original dried sample. A full size distribution analysis could unfortunately not be carried out, as the amount of soil residue was too small. The dry sieving technique that was used in this study only gives a brief overview of the particle size distribution. To get more accurate results the use of a laser diffraction analyzer is recommended.

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3.2 Sequential extraction

As a rule, about 50% or more of the studied metals are found in the residue fraction of all the samples, indicating low mobility during normal environmental circumstances (Figure 2). In the bark sample A1 (Figure 2a), As > Co > Ni > Cu are the metals released to the highest degree during the three-step leaching procedure, and all the metals were more easily released from the bark matrix than from the ash ~~from the combusted bark sample~~ A1a (Figure 2b). From the ash sample, Mo > As > Cu > V were released to the highest percentage. ~~Copper is the only metal released to a high percentage from the soil sample A2 (Figure 2c), while several more metals were released from the sample from site B (Figure 2d): Co > Ni > As > Ba > Cu ≈ Zn. About 30% of the As, Co and Ni are found in the 2nd fraction, and can be released if the redox potential is changed towards a more reducing environment.~~

The metals are least mobile in sample A2 (Figure 2c). ~~, h~~However, as much as 40% of the Cu is released in the first step of the leaching procedure, which shows that soil washing has a high potential as an efficient method for remediation and metal recovery. The reason for this may be that $CuSO_4$ from the wood preservation process has leached through the surface bark layer and into the underlying ~~clay~~ soil (50 -100cm). When water at high L/S ratio is added, as is the case during infiltration of rain water ~~in the soil at Långön~~ during storm events, the water soluble $CuSO_4$ may be released. In the bark (A1), the Cu is less mobile due to the high affinity between Cu and organic materials (Figure 2a) (Bodek 1988, Kalmykova et al. 2008, Stumm and Morgan 1981). When the bark is incinerated, the mobility is generally decreased due to the formation of less soluble metal compounds, such as CuO, identified in the XRD analysis (Figure 2b and Table 3). Additionally, encapsulation of the metals into the ash matrix further decreases the mobility.

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~~while s~~Several ~~more~~ metals were released from the sample from site B (Figure 2d): Co > Ni > As > Ba > Cu ≈ Zn. About 30% of the As, Co and Ni are found in the 2nd fraction, and can be released if the redox potential is changed towards a more reducing environment.

3.2 Enhanced leaching

As discussed in section 1, mineral acid solutions have been used to leach metals from ~~contaminated~~polluted soils (Moon et al. 2012, Moutsatsou et al. 2006). Usually, a stronger acid solution releases more metals but on the other hand it also

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dissolves the soil matrix itself (Kuo et al. 2006, Moutsatsou et al. 2006). Depending on the properties of each unique soil, these effects will be more or less pronounced. For instance, the presence and release of alkaline compounds like $CaCO_3$ or (hydr)oxides dissolve the soil matrix and could cause a higher pH and decreased metal leaching. When comparing the metal release achieved with the mineral acidic solutions used in this study, i.e. process waters and HCl, it is obvious that a 0.01M HCl solution is too weak to neutralize the released alkaline compounds and keep the pH constant ~~, see~~ (Table 4). It should be noted that even though the original ash, i.e. A1a, is more alkaline than B1, pH 12.1 and 7.9, respectively, the alkaline compounds are more easily released from the latter, resulting in a higher end pH after HCl leaching (Table 4). In contrast, the pH levels of the acidic process water leachates are barely affected by the release of alkaline compounds and these were the leaching agents that released metals most effectively from all the samples (Table 4). ~~As discussed in section 2.2, the process waters contain metal ions (Table 1).~~ In samples A1, A2 and B2, the concentrations of Pb^{2+} and Zn^{2+} in the original process waters (Table 1) are often comparable to, or even higher than, the concentrations in the final leachates. This is mainly due to the low amounts of these metals that are present in the original soil samples compared to the concentrations in the original process waters (Tables 1 and 2). Other reasons for this phenomenon are the presence of active sites in the soil matrix to which the metal ions can adsorb, the particle sizes, and the speciation of the metals. The importance of size distribution and the presence of active sites on Pb and Zn leaching have been studied earlier by Karlfeldt and Steenari (2007). They found that grinding of the solid material (fly ash) before leaching in some cases strongly reduced the detected amounts of Pb^{2+} and Zn^{2+} in the leachate

(Karlfeldt and Steenari 2007). After leaching A1a, only the concentrations of Ba were lower in the final leachates than in the original process waters as a consequence of the stable and low-soluble Ba compounds formed during incineration. In addition, if Ba is leached from the ash, formation of low soluble $BaSO_4$ is likely to occur due to the presence of sulfates in the process waters (Table 1).

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Ammonium nitrate, NH_4NO_3, has been used in many studies, both to leach and to predict the bioavailability of metal contaminants in soils, and it has been shown to be especially effective for Cu leaching from ash (Gryschko et al. 2005, Karlfeldt Fedje et al. 2010, Pueyo et al. 2004, Schöning and Brümmer 2008). High Cl^- concentrations can promote metal release due to the formation of soluble metal-chloride-complexes like $CdCl_y^{(2-y)}$ and $PbCl_3^-$. For this reason, it was expected that NH_4Cl would also be effective for non-amine complex forming elements like Pb. The results showed that about 70% of the Cu was leached from A1 and A2, while only 6% was leached from the ash sample A1a (Table 4). This is consistent with the results from the sequential extraction procedure where the Cu was shown to be most mobile in A1 and A2, but transformed to less soluble CuO and/or encapsulated in the ash, i.e. A1a (Figure 2). The same leaching tendencies for Cu were also seen after the EDDS and lactic acid leaching; ≥50% of the Cu was leached from A1 and A2, while <20% was leached from the other samples (Table 4). The leaching of Pb was generally <15% from all samples, irrespective of whether NH_4Cl, EDDS or lactic acid was used.

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The overall leaching results suggest that the lower leaching from A1a compared to A1 and A2 is due to encapsulation and formation of stable metal compounds during the incineration. In the case of B1, the lower leaching is mainly due to the metal speciation and incorporation of the metals in the soil matrix, caused by the former industrial activities at the site. Therefore, it is not only important to gain a deep knowledge about the soil matrixes and their contamination history prior to soil washing, but also to remember that pre-treatment, such as grinding and incineration before the washing, influence the leaching properties. ~~On the other hand, pre-treatment like incineration makes it possible to utilize the energy in the contaminated samples. This must be balanced against the potentially lower metal recovery efficiency.~~

The concentrations of Ag, Be, Cd, Se, Tl and U were also detected in the leachates (<0.6 mg/kg) but for simplicity there are not included in Table 4.

Due to the combination of low fractional release and low total amounts of many valuable metals in B1, the corresponding concentrations in the leachates are all <0.25 g/L (Tables 2 and 4). Metal recovery from these leachates is therefore not yet economically viable. However, when using the acidic process waters to leach A1 and A1a, the concentrations of Cu in the corresponding leachates are around 1.5 and 6 g Cu/L, respectively. This is comparable with the concentrations in the initial solutions from ores used for high purity Cu production by electrolysis (1-6 g/L) (Jenkins et al. 2002). To minimize the presence of impurities in the Cu metal, solvent extraction is used in full-scale recovery systems prior to electrolysis, to selectively extract Cu. In addition, the solvent extraction step

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increases the Cu concentration, which is necessary to operate an energy efficient electrolysis. An interesting alternative, which would reduce the energy required during electrolysis, is the use of microbial bio-electrochemical systems (BES). In BES, microorganisms oxidize organic compounds present in e.g. waste-water, thereby transforming the energy in the organic compounds into electrical energy. ~~In several recent studies on diluted Cu solutions (~1g/L) the energy consumption was significantly lower with BES compared to traditional electrolysis (Modin and Karlfeldt Fedje 2012, Tao et al. 2011, Ter Heijne et al. 2010). At certain cathode potentials, electrical energy could even be extracted from the system together with the Cu metal (Modin and Karlfeldt Fedje 2012, Tao et al. 2011). By varying the cathode potential in the system it is not only possible to control the energy output but also which metal to recover. Modin and co-workers showed that high purity Cu (99.9%) could be recovered from a simulated ash leachate containing a mixture of Cu, Cd, Pb and Zn ions (1g/L) without energy input (Modin and Karlfeldt Fedje 2012). In addition, high purity Zn (>99.9%) could be recovered from the mixture, while the Cd and Pb metals needed further purification.~~ Initial experiments to recover Cu using BES from the original process water ash leachates used in this study have been performed with satisfying results. Copper metal of at least 99% purity could be recovered from the ash process water leachates, which contained a variety of metal ions (Table 4). This opens up for simplification of the metal recovery process, as no purification step is needed prior to electrolysis. In addition, the reduced energy consumption can make the process profitable even though the Cu concentrations are lower than in commercial electrolysis systems. More ~~experiments on how to reduce the energy~~

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~~consumption and increase the pureness of the Cu and other metals~~research is ~~are~~ in progress and will be discussed and published in ~~a~~ future articles.

The release of Cu from the A1a and A2 samples when using the acidic process waters varies between 90–100% (Table 4) and predictions indicate that there is as much as >30 tons of Cu present at the ~~contaminated~~polluted site A (Kemakta Konsult AB 2012). If on average 90% of this could be recovered from the leachates, the potential Cu metal value is about 170,000 Euro and if the incineration process is optimized to minimize the volatilization of Cu compounds, the corresponding potential value is almost 200,000 Euro. Even without taking into account the high environmental value of remediation of site A~~ (Långö)~~, this could motivate soil washing~~, but further investigations into the quality and function of the rest soil after metal recovery need to be carried out~~.

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3.3 Characterization of leached soil samples

The major crystalline structure in the soil residues after leaching in the acidic process water “a” is more similar across the samples, than in the original samples (Table 3). The soil residues are dominated by silicates and oxides and no Cu compounds could be identified. Sample A1still contained large amounts of amorphous material. However, no amorphous material was found after NH_4Cl leaching, probably because NH_4Cl hides the content of other phases (Table 3). In fact, leaching using NH_4Cl resulted in small (about 1%) or negative soil matrix dissolution (-41% for A1). For the other leaching agents, between 1 and 15w% of the solid samples was dissolved. The acidic leaching agents, i.e. the process waters and HCl, dissolved the highest fractions of A1, A1a and B1 (10-15 w%), while lactic acid showed the lowest weight losses (2-6 w%). Less than 6 w% of sample A2 was dissolved irrespective of the leaching agent used, indicating a stable soil matrix. In contrast, about 5 times more of sample A1a was dissolved when the pH was decreased from 3.6 to ~0, i.e. when ~~HCl~~ process water was used instead of ~~process water~~HCl. ~~On the other hand, t~~The release of Cu and Zn from A1a increased more than 20 times when the pH was decreased, confirming the importance of metal encapsulation and that ash matrix dissolution is needed to achieve efficient metal leaching.

Unfortunately, most of the metals which were present at concentrations above the Swedish generic guideline values in the original soils are still above the guidelines in the soil residues that remain after leaching (Table 5). This is due to the dissolution of the soil matrixes, as well as to the adsorption of metal ions from the process water in the case of Ba^{2+}, Zn^{2+} and Pb^{2+}, as discussed in section 3.2. However, probably more important is the low leachability of some metals and the fact that only one leaching step was used in these experiments. A qualitative washing test using deionized water on the A sample residues remaining after process water leaching clearly showed the release of blue Cu^{2+} ions, indicating a higher metal release with an increased number of washing steps. However, it is likely that even with the introduction of several leaching steps, some metals will still exceed the Swedish guidelines (SEPA 2009b) due to their low leachability. On the other hand, the leaching is generally less than 50% for most metals when pH is $2 \leq X \geq 10$ (Table 4) and therefore the potential release of these metals in a natural environment is expected to be low, even though the total amounts exceed the guidelines.

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4. Conclusions

- When 2≤pH≥10 the release of metals is generally <50 w%, indicating a low metal leaching during normal environmental circumstances. However, for Cu a high total content (7600–2000 mg/kg DS at site A (Långö)) can lead to a significant environmental impact. From a metal recovery perspective, the pH value has to be lower than 2 to achieve effective leaching.
- The acidic process waste waters leached metals the most efficiently from all samples studied, i.e. bark (A1), bark ash (A1a) and soil (A2 and B1).
- Incineration of ~~contaminated~~polluted soils with a high organic content (sample A1) before washing generally reduced the metal leaching and is not suggested as a pre-treatment step before soil washing. However, the release of Cu was higher from the ash than from the original bark when the acidic process waters were used, indicating that in certain situations incineration can be a good pre-treatment alternative.
- Between 90 and 100 w% of the Cu was released from A1a and A2 and from the un-purified leachate Cu metal (>99% purity) could be generated by electrolysis, indicating that the potential for Cu metal recovery is high.
- After one leaching step the metal contents in the soil residues still exceed the Swedish guideline values. An additional washing step is likely to reduce the contents of easy soluble metal compounds in the soil residues.

The results from this study show that soil washing followed by metal recovery is a promising permanent alternative to remediate ~~contaminated~~polluted soils and to utilize non-used metal resources. However, more research is needed to develop an efficient and solid treatment method. Two urgent matters to investigate are how to optimize the leaching procedure to produce a satisfyingly clean and stable soil residue, and to carry out electrolysis experiments on how to reduce the energy consumption during electrolysis; both these are currently being studied. Pre-treatment of the soils using e.g. grain-sizing is another important issue to study as this effectively can reduce the soil amount needed to be washed and at the same time increase the metal content in the enriched fraction. Another important ~~issue~~question is that this study only looks at sites with metal contaminants, whereas in reality ~~contaminated~~polluted sites often contain not only metals or organic pollutants, but a mixture of both. For this reason, it is important to understand what happens to toxic organic compounds during the optimized soil washing process, something which will be studied in further research.

5. Acknowledgements

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Remediation of Metal Polluted Hotspot Areas through Enhanced Soil Washing ─Evaluation of Leaching Methods

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Abstract

Soil washing offers a permanent remediation alternative for metal polluted sites. In addition, the washed out metals can be recovered from the leachate and re-introduced into the social material cycle instead of landfilled. In this paper, soil, bark and bark-ash washing was tested on four different metal polluted soil and bark samples from hotspots at former industrial sites. Six different leaching agents; HCl, NH_4Cl, lactic acid, EDDS and two acidic process waters from solid waste incineration, were tested, discussed and evaluated. For the soil washing processes, the final pH in the leachate strongly influences the metal leachability. The results show that a $pH<2$ is needed to achieve a high leaching yield, while <50 w% of most metals were leached when the pH was higher than 2 or below 10. The acidic process waste waters were generally the most efficient at leaching metals from all the samples studied, and as much as 90–100 w% of the Cu was released from some samples. Initial experiments show that from one of these un-purified leachates, Cu metal (>99% purity) could be recovered. After a single leaching step, the metal contents of the soil residues still exceed the maximum limits according to the Swedish guidelines. An additional washing step is needed to reduce the contents of easy soluble metal compounds in the soil residues. The overall results from this study show that soil and bark-ash washing followed by metal recovery is a promising on-site permanent alternative to remediate metal polluted soils and to utilize non-used metal resources.

1. Introduction

More than 80,000 sites that may be polluted due to earlier industrial activities are known in Sweden, and about 2 million potentially polluted sites have been identified in Europe and in the United States (Dermont et al. 2008a, SEPA 2009a). Metals are the main problem at about 50% of these sites. Contrary to many organic pollutants, metals cannot be destroyed and are non-degradable. For this reason, metal polluted soils must always be treated and remediated to decrease the risks of pollution. Consequently, the need for metal remediation technologies is enormous. The most commonly used metal remediation method is to excavate, transfer and landfill the polluted soil and replace it with new, clean material (Dermont et al. 2008a, Shammas 2009). Techniques such as solidification/stabilization (S/S) are often applied prior to landfilling to decrease the potential leaching of metals (Dermont et al. 2008a, Shammas 2009). However, this treatment does not reduce the amounts of pollutants in the materials and metals may leach out in the longer term. In addition, metals are removed from the material cycle, resulting in the loss of valuable resources.

An alternative to landfilling is soil washing. Soil washing is used commercially in both Europe and the Unites States and can be carried out on site (Dermont et al. 2008b). A recent example is the remediation of the Olympic Park site in London in 2012, where more than 800,000m^3 of soil polluted with e.g. oil and Pb was treated (Douglas 2009). Soil washing can be based on either physical separation, like magnetic fractionation or size separation, on chemical leaching, or on a combination of both. Water is often used as leaching agent, but it is also common practice to use stronger leaching agents like acids or complex forming ligands such as EDTA (Bisone et al. 2012, Labanowski et al. 2008, Laporte-Saumure et al. 2010, Moon et al. 2012, Moutsatsou et al. 2006, Tandy et al. 2004, Voglar and Lestan 2013). The selection of leaching agent depends on e.g. the properties of the contaminants at each specific site and on the remediation goal, i.e. the acceptable levels of the pollutants in the soil after remediation.

Generally, the costs for soil washing are comparable with those for techniques like S/S and electrokinetics and much lower than for vitrification (Shammas 2009). Soil washing offers another important opportunity to reduce the overall costs: through the potential recovery of the released metals. The leachate generated from the enhanced soil washing is rich in pollutants and can act as a source for metal recovery. This is not much studied and the washing procedures currently applied focus on metal removal, as it has this far not been economically favorable to recover metals from waste materials like polluted soils and ashes. However, there is one example of a leaching based profitable metal recovery process from waste incineration ash. In Switzerland, the world´s first commercial full-scale plant where high purity Zn (99.9%) is recovered from waste fly ash has recently been started up (Schlumberger and Bühler 2012, Schlumberger et al. 2007). In another study, based on laboratory experiments on the recovery of Cu from waste fly ash, it was shown that 90% of the Cu could be selectively recovered and that this treatment could potentially be more profitable than the way in which ash is usually handled, i.e. landfilling (Karlfeldt Fedje et al. 2012, Karlsson et al. 2010). In the study by Karlsson et al (2010), the Cu content in the ash was about 0.8%, and earlier studies on sites used for wood preservation show that Cu concentrations of 0.5% or higher are common (Dermont et al. 2008b, Shammas 2009). As a comparison, the Cu content in a workable Swedish mine is 0.3% (Boliden AB 2011). The world stocks of metals like Cr, Cu and Zn are at or near historically low levels and are predicted to last about 15, 40 and 20 years, respectively (Stenzel et al. 2011). Consequently, it is plausible that metal prices will increase in the near future, as the virgin resources are finite and there is a great demand for metals.

In this lab-scale study, soil, bark and bark-ash washing with various leaching agents is used for leaching of metals, and its potential as a method to remediate highly metal polluted soil and bark samples is tested. The metal leaching properties and the solid residues of soil samples taken at different polluted sites with different pollution situations are studied using the various leaching agents. The aim is to maximize the metal release, with particular focus on Cu and Cr, and to produce a metal rich leachate from which valuable metals can be recovered by e.g. electrolysis.

2. Material and methods

2.1 Soil samples

Soil samples with different characteristics and degree of contamination from two sites- Långö in western Sweden and Österbybruk in eastern Sweden- were used in this study. Both sites are strongly polluted with metals. The first site (Långö=A) was historically used for wood preservation, using $CuSO_4$ according to the Boucherie method (Vougy 1856). Based on results from sampling and chemical analyses in previous studies, representative samples of bark and soil were collected from a hotspot with a high metal content; A1 is a bark sample from the surface horizon (0–10 cm depth) and A2 is a soil sample from a depth of 50–100 cm. Both samples are mixtures of several sub-samples taken from the bark and the soil, respectively.

The second site (Österbybruk=B) has been used within the iron and steel industry since the late 16th century. More recently, the area has also been used as e.g. a car breaker´s yard and for wood processing. Based on previous investigations on this site, a hotspot with high concentrations of several metals was chosen, and a representative surface horizon soil sample was collected, i.e. B1.

2.1.1 Pre-treatment of the soil samples

All samples were dried at 80°C (100 %DS) until a constant weight was achieved. The pure soil samples i.e. A2 and B1 were directly cooled down in desiccators before being stored in air-tight containers until used, while the bark sample was cut into smaller pieces using an automatic mixer. Part of the bark was thereafter stored until further analyses (A1), while the other part of the sample was incinerated for 10h to form an ash sample (A1a). This incineration step was done in order to reduce the organic content of the bark and to increase the potential Cu release. The incineration temperature used was 860°C and chosen to avoid vaporization of Cu compounds. All samples were cooled down in desiccators before being stored in air-tight containers until used. No pre-treatment using e.g. grain-size fractioning to generate highly polluted and less polluted fractions of the soils was done due to too small sample volumes.

2.2 Leaching agents

For the leaching experiments, four chemically different leaching agents known to effectively leach metals from natural materials like soils were chosen for this study; 0.01M HCl, 8M NH4Cl adjusted to pH 10 to enhance amine complex formation, 1M lactic acid, and 0.1M EDDS ((S,S)-Ethylenediamine-N,N-disuccinic acid tri sodium salt) adjusted to pH 7 to especially enhance Cu and Pb leaching. The leaching agents and their concentrations were chosen based on literature research (Lo et al. 2011, Moon et al. 2012, Schöning and Brümmer 2008). In addition, two highly acidic process waste waters “a” and “n” (pH around 0) were used. These process waters came from two different places in the wet flue gas cleaning processes after waste incineration and therefore contained metal ions and high concentrations of chlorides. The concentrations of different ions in the process waters vary naturally depending on e.g. the conditions during the incineration process and the kind of waste used, but representative concentrations of the most common ions are given in Table 1. Today these acidic waters are purified through precipitation processes of the toxic metal ions and small particles. Thereafter the metal sludge is landfilled, while the clean water is released to the recipient.

2.3 Leaching experiments

2.3.1 Sequential extraction

The modified three-step BCR method is proposed by the commission of the European communities Bureau (BCR) as the European standard method for sequential extraction schedules (Rauret 1999). In brief, the leaching steps are first; acetic acid (exchangeable ions), second; hydroxyl ammonium chloride (reducible fraction) and third; H_2O_2 + ammonium acetate (oxidizable fraction). Due to toxicity the hydroxyl ammonium chloride solution ($NH_2OH{\cdot}HCl$) originally used in the second step was exchanged for non-toxic ascorbic acid (0.2 M). It has been shown that ascorbic acid has the same metal extraction efficiency as hydroxyl ammonium chloride, especially in the case of Cu (Shuman 1982). This method was used to predict the mobility of As, Ba, Co, Cr, Cu, Mo, Ni, Pb, V and Zn in the original samples. All experiments were carried out in triplicates.

2.3.2. Enhanced batch leaching

In each experiment, 0.5 g soil was leached in airtight plastic containers using 5 mL of either of the chosen leaching agents (liquid-to-solid ratio (L/S) of 10). The leaching time was set to 2 hours with continuous shaking at 140 rpm. After leaching, the soil-liquid-mixture was centrifuged for 15 minutes at 3000G (gravity). The supernatant was transferred to a new container and acidified before being stored in a refrigerator until analyzed. The ash residue was washed for 5 minutes with continuous shaking using 5 mL ultrapure water (18.2 $M\Omega/cm^2$). Thereafter, the mixture was centrifuged for 15 minutes at 3000G and the ash residue was dried and stored in airtight containers until used. All leaching experiments were carried out in duplicates.

2.4 Analytical methods

In order to measure metal content in the original soil samples, two commonly used digestion methods were chosen, based on the sample characteristics. Due to its high organic content, sample A1 was completely dissolved following the procedure in ASTM D3683 (As, Cd, Co, Cu, Hg, Ni, Pb, S and Zn) and ASTM

D3682 (Al, Ca, Fe, K, Mg, Na, P, S, Si, Ti, Ba, Cr, Mn, Mo, Sb, Se, Sn, Sr and V). The methodology in the ASTM D3683 was also used to analyze the total metal content (Al, Sb, As, Ba, Pb, P, Fe, Cd, Ca, K, Cu, Cr, Hg, Mg, Mn, Mo, Na, Ni, Sr, S, Ti, V and Zn) in A1a, while A2 and B1 were digested using the standardized procedure SS 028311. All analyzes were carried out in triplicates except for A1a, which was analyzed in duplicate.

The total element concentrations of all the solutions from the total digestion were measured using ICP-MS (inductively coupled plasma mass spectrometry) (Al, As, Ba, Pb, Ca, Cd, Co, Cu, Cr, Fe, K, Mg, Mn, Na, P, Ti, Hg, Mo, Ni, S, Sb, Sn, Sr, V and Zn) or ICP-AES (inductively coupled plasma atomic emission spectrometry) (Se and W). The soil leachates obtained from the leaching experiments and the sequential extraction were analyzed for metals (Al, As, Ba, Be, Pb, Cd, Co, Cu, Cr, Li, Mn, Mo, Ni, Se, Ag, Sr, Tl, U, V and Zn) using ICP-MS. A Dionex ICS AS-DV ion chromatograph with ICS-900 columns for cation and anion analyzes was used to analyze the K^+, Mg^{2+}, Na^+, NH_4^+, $Ca^{2+,}$ Cl^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-} concentrations in the acidic process waters, while the amounts of Al, Pb and Zn were analyzed using ICP-MS.

The main crystalline compounds in the original samples, and in some of the leached samples, were identified by qualitative X-ray powder diffractometry (XRD) using a Siemens D5000 X-ray powder diffractometer with the characteristic Cu radiation and a scintillation detector. Identification of compounds was carried out using the JCPDS database (Joint Committee of Powder Diffraction Standards 2006). The detection limit of this method is about 1

% by weight. The samples were dried and ground in an agate mortar before being analyzed. The particle size distributions in the original dried samples were measured using manual dry sieving with sieve size fractions of between 0.125 mm and 1 mm. The pH was measured in the original samples (pH$_{(H_2O)}$) and at the start and end of each leaching experiment using a Methrom SM 702 pH meter.

3. Results and discussion

3.1 Characterization of original samples

The total amounts of selected major and minor elements in the original samples are shown in Table 2. For comparison, the Swedish generic guideline values for sensitive and less sensitive land use are also given (SEPA 2009b).

In the original samples from site A, i.e. A1 and A2, only Cu exceeds the Swedish guidelines for polluted soils, while at site B several metals exceed the guidelines (Table 2). In an earlier study of site B, four times higher amounts of Fe, Al and K, and 15 times higher amounts of Na, were detected at spot B1 compared to the results in this study (Elander et al. 2010). This is due to heterogeneities between sub-samples but the choice of digestion method is also very important. In the previous study, the methods in ASTM 3682 and 3683 (total digestion using bomb and melting) were used, while the SS 028311 (HNO_3 and H_2O_2 leaching method) was used in this study. For the minor elements, like As, Co and Cu, no significant differences could be seen, suggesting that these metals are present in compounds soluble in strong acid solutions. Chromium and W are exceptions, perhaps because they are incorporated together with Fe, Al, K and Na in very low-soluble minerals and compounds. In sample A1, the total amounts of minor elements are generally somewhat higher when using ASTM 3682 and 3683 than with acidic leaching (7M HNO_3), which was used in an previous study on soils from the same spot (Kemakta Konsult AB 2012). However, for Cu the content is about 2.5 times higher when bomb digestion is used than with acid leaching, which shows that Cu is effectively adsorbed to the organic matter in the bark, thus reducing the leachability.

From 3 g of dry bark about 0.6 g of ash was obtained. Theoretically, if no Cu was volatilized during incineration, the Cu content in the ash would be about 5 times higher than in the original bark. However, according to the total content analyses, Cu is enriched less than 3 times during incineration (Table 2). This means that the chosen incineration temperature of 860°C is too high to optimize the enrichment of Cu in the bottom ash. The reason for this is probably an uneven oxygen distribution, resulting in a reducing atmosphere, which can increase metal volatilization (Mojtahedi et al. 1987, Wikman et al. 2003). However, in a real incineration process, the volatilized Cu would be caught in the flue gas cleaning system and captured in the fly ash. The enrichment factors for most other elements were around 5, but for the soil matrix forming elements, such as Al, K, Mg and Na, the enrichment factors were higher (Table 2). This shows that these elements are present as low-volatile minerals in the original sample as well as in the ash. Barium was enriched almost 8 times during incineration, causing the amount in the resulting ash to exceed the Swedish guidelines for less sensitive land use (Table 2). This is not surprising, as a majority of the most common Ba compounds have boiling and smelting points well above 850°C (Alberty et al. 2008).

Even though the Cu content in sample A1 and A2 were around 1% or higher, no crystalline Cu compounds could be identified (Table 2 and 3). This suggests that the Cu is present in amorphous forms, in very small crystals or as several different Cu compounds. The first reason is the most likely in sample A1, as Cu effectively sorbs to organic matter (Bodek 1988, Kalmykova et al. 2008, Stumm and Morgan 1981). However, when the bark was incinerated to ash the amorphous, i.e. the organic, phase drastically decreased and Cu oxides were clearly identifiable (Table 3). The presence of amorphous material was low both in A2 and in B1. Silica oxide, SiO_2, was identified as a major compound in all samples but the presence of other minerals varied between the samples, indicating different characteristics, which will influence the metal leaching (Table 3).

An overview of the particle size distributions in the original samples are shown in Figure 1. The bark (A1) contains pieces >1mm, while the corresponding ash (A1a) mainly consists of smaller particles. Sample A2 has in an earlier investigation been classified as clayey soil (Kemakta Konsult AB 2012) and was expected to contain a larger fraction of small particles. This could not be found, something which is probably due to clustering of the small clay particles into stable agglomerates during drying. An ocular inspection of the soil particles that remained after leaching confirmed this, as a majority of the particles were smaller than those in the original dried sample. A full size distribution analysis could unfortunately not be carried out, as the amount of soil residue was too small. The dry sieving technique that was used in this study only gives a brief overview of the particle size distribution. To get more accurate results the use of a laser diffraction analyzer is recommended.

3.2 Sequential extraction

As a rule, about 50% or more of the studied metals are found in the residue fraction of all the samples, indicating low mobility during normal environmental circumstances (Figure 2). In the bark sample A1 (Figure 2a), As > Co > Ni > Cu are the metals released to the highest degree during the three-step leaching procedure, and all the metals were more easily released from the bark matrix than from the ash A1a (Figure 2b). From the ash sample, Mo > As > Cu > V were released to the highest percentage. The metals are least mobile in sample A2 (Figure 2c). However, as much as 40% of the Cu is released in the first step of the leaching procedure, which shows that soil washing has a high potential as an efficient method for remediation and metal recovery. The reason for this may be that $CuSO_4$ from the wood preservation process has leached through the surface bark layer and into the underlying soil (50 -100cm). When water at high L/S ratio is added, as is the case during infiltration of rain water during storm events, the water soluble $CuSO_4$ may be released. In the bark (A1), the Cu is less mobile due to the high affinity between Cu and organic materials (Figure 2a) (Bodek 1988, Kalmykova et al. 2008, Stumm and Morgan 1981). When the bark is incinerated, the mobility is generally decreased due to the formation of less soluble metal compounds, such as CuO, identified in the XRD analysis (Figure 2b and Table 3). Additionally, encapsulation of the metals into the ash matrix further decreases the mobility.

Several metals were released from the sample from site B (Figure 2d): Co > Ni > As > Ba > Cu ≈ Zn. About 30% of the As, Co and Ni are found in the 2nd fraction, and can be released if the redox potential is changed towards a more reducing environment.

3.2 Enhanced leaching

As discussed in section 1, mineral acid solutions have been used to leach metals from polluted soils (Moon et al. 2012, Moutsatsou et al. 2006). Usually, a stronger acid solution releases more metals but on the other hand it also dissolves the soil matrix itself (Kuo et al. 2006, Moutsatsou et al. 2006). Depending on the properties of each unique soil, these effects will be more or less pronounced. For instance, the presence and release of alkaline compounds like $CaCO_3$ or (hydr)oxides dissolve the soil matrix and could cause a higher pH and decreased metal leaching. When comparing the metal release achieved with the mineral acidic solutions used in this study, i.e. process waters and HCl, it is obvious that a 0.01M HCl solution is too weak to neutralize the released alkaline compounds and keep the pH constant (Table 4). It should be noted that even though the original ash, i.e. A1a, is more alkaline than B1, pH 12.1 and 7.9, respectively, the alkaline compounds are more easily released from the latter, resulting in a higher end pH after HCl leaching (Table 4). In contrast, the pH levels of the acidic process water leachates are barely affected by the release of alkaline compounds and these were the leaching agents that released metals most effectively from all the samples (Table 4). In samples A1, A2 and B2, the concentrations of Pb^{2+} and Zn^{2+} in the original process waters (Table 1) are often comparable to, or even higher than, the concentrations in the final leachates. This is mainly due to the low amounts of these metals that are present in the original soil samples compared to the concentrations in the original process waters (Tables 1 and 2). Other reasons for this phenomenon are the presence of active sites in the soil matrix to which the metal ions can adsorb, the particle sizes, and the speciation of the metals. The importance of size distribution and the presence of active sites on Pb and Zn leaching have been studied earlier by Karlfeldt and Steenari (2007). They found that grinding of the solid material (fly ash) before leaching in some cases strongly reduced the detected amounts of Pb^{2+} and Zn^{2+} in the leachate (Karlfeldt and Steenari 2007). After leaching A1a, only the concentrations of Ba were lower in the final leachates than in the original process waters as a consequence of the stable and low-soluble Ba compounds formed during incineration. In addition, if Ba is leached from the ash, formation of low soluble $BaSO_4$ is likely to occur due to the presence of sulfates in the process waters (Table 1).

Ammonium nitrate, NH_4NO_3, has been used in many studies, both to leach and to predict the bioavailability of metal contaminants in soils, and it has been shown to be especially effective for Cu leaching from ash (Gryschko et al. 2005, Karlfeldt Fedje et al. 2010, Pueyo et al. 2004, Schöning and Brümmer 2008). High Cl^- concentrations can promote metal release due to the formation of soluble metal-chloride-complexes like $CdCl_y^{(2-y)}$ and $PbCl_3^-$. For this reason, it was expected that NH_4Cl would also be effective for non-amine complex forming elements like Pb. The results showed that about 70% of the Cu was leached from A1 and A2, while only 6% was leached from the ash sample A1a (Table 4). This is consistent with the results from the sequential extraction procedure where the Cu was shown to be most mobile in A1 and A2, but transformed to less soluble CuO and/or encapsulated in the ash, i.e. A1a (Figure 2). The same leaching tendencies for Cu were also seen after the EDDS and lactic acid leaching; ≥50% of the Cu was leached from A1 and A2, while <20% was leached from the other samples (Table 4). The leaching of Pb was generally <15% from all samples, irrespective of whether NH_4Cl, EDDS or lactic acid was used.

The overall leaching results suggest that the lower leaching from A1a compared to A1 and A2 is due to encapsulation and formation of stable metal compounds during the incineration. In the case of B1, the lower leaching is mainly due to the metal speciation and incorporation of the metals in the soil matrix, caused by the former industrial activities at the site. Therefore, it is not only important to gain a deep knowledge about the soil matrixes and their contamination history prior to soil washing, but also to remember that pre-treatment, such as grinding and incineration before the washing, influence the leaching properties.

The concentrations of Ag, Be, Cd, Se, Tl and U were also detected in the leachates (<0.6 mg/kg) but for simplicity there are not included in Table 4.

Due to the combination of low fractional release and low total amounts of many valuable metals in B1, the corresponding concentrations in the leachates are all <0.25 g/L (Tables 2 and 4). Metal recovery from these leachates is therefore not yet economically viable. However, when using the acidic process waters to leach A1 and A1a, the concentrations of Cu in the corresponding leachates are around 1.5 and 6 g Cu/L, respectively. This is comparable with the concentrations in the initial solutions from ores used for high purity Cu production by electrolysis (1-6 g/L) (Jenkins et al. 2002). To minimize the presence of impurities in the Cu metal, solvent extraction is used in full-scale recovery systems prior to electrolysis, to selectively extract Cu. In addition, the solvent extraction step increases the Cu concentration, which is necessary to operate an energy efficient electrolysis. An interesting alternative, which would reduce the energy required during electrolysis, is the use of microbial bio-electrochemical systems (BES). In BES, microorganisms oxidize organic compounds present in e.g. waste-water, thereby transforming the energy in the organic compounds into electrical energy. Initial experiments to recover Cu using BES from the original process water ash leachates used in this study have been performed with satisfying results. Copper metal of at least 99% purity could be recovered from the ash process water leachates, which contained a variety of metal ions (Table 4). This opens up for simplification of the metal recovery process, as no purification step is needed prior to electrolysis. In addition, the reduced energy consumption can make the process profitable even though the Cu concentrations are lower than in commercial electrolysis systems. More research is in progress and will be discussed and published in future articles.

The release of Cu from the A1a and A2 samples when using the acidic process waters varies between 90–100% (Table 4) and predictions indicate that there is as much as >30 tons of Cu present at the polluted site A (Kemakta Konsult AB 2012). If on average 90% of this could be recovered from the leachates, the potential Cu metal value is about 170,000 Euro and if the incineration process is optimized to minimize the volatilization of Cu compounds, the corresponding potential value is almost 200,000 Euro. Even without taking into account the high environmental value of remediation of site A, this could motivate soil washing.

3.3 Characterization of leached soil samples

The major crystalline structure in the soil residues after leaching in the acidic process water "a" is more similar across the samples, than in the original samples (Table 3). The soil residues are dominated by silicates and oxides and no Cu compounds could be identified. Sample A1still contained large amounts of amorphous material. However, no amorphous material was found after NH_4Cl leaching, probably because NH_4Cl hides the content of other phases (Table 3). In fact, leaching using NH_4Cl resulted in small (about 1%) or negative soil matrix dissolution (-41% for A1). For the other leaching agents, between 1 and 15w% of the solid samples was dissolved. The acidic leaching agents, i.e. the process waters and HCl, dissolved the highest fractions of A1, A1a and B1 (10-15 w%), while lactic acid showed the lowest weight losses (2-6 w%). Less than 6 w% of sample A2 was dissolved irrespective of the leaching agent used, indicating a stable soil matrix. In contrast, about 5 times more of sample A1a was dissolved when the pH was decreased from 3.6 to ~0, i.e. when process water was used instead of HCl. The release of Cu and Zn from A1a increased more than 20 times when the pH was decreased, confirming the importance of metal encapsulation and that ash matrix dissolution is needed to achieve efficient metal leaching.

Unfortunately, most of the metals which were present at concentrations above the Swedish generic guideline values in the original soils are still above the guidelines in the soil residues that remain after leaching (Table 5). This is due to the dissolution of the soil matrixes, as well as to the adsorption of metal ions from the process water in the case of Ba^{2+}, Zn^{2+} and Pb^{2+}, as discussed in section 3.2. However, probably more important is the low leachability of some metals and the fact that only one leaching step was used in these experiments. A qualitative washing test using deionized water on the A sample residues remaining after process water leaching clearly showed the release of blue Cu^{2+} ions, indicating a higher metal release with an increased number of washing steps. However, it is likely that even with the introduction of several leaching steps, some metals will still exceed the Swedish guidelines (SEPA 2009b) due to their low leachability. On the other hand, the leaching is generally less than 50% for most metals when pH is $2 \leq X \geq 10$ (Table 4) and therefore the potential release of these metals in a natural environment is expected to be low, even though the total amounts exceed the guidelines.

4. Conclusions

- When $2 \leq pH \geq 10$ the release of metals is generally <50 w%, indicating a low metal leaching during normal environmental circumstances. However, for Cu a high total content (7600–2000 mg/kg DS at site A (Långö)) can lead to a significant environmental impact. From a metal recovery perspective, the pH value has to be lower than 2 to achieve effective leaching.
- The acidic process waste waters leached metals the most efficiently from all samples studied, i.e. bark (A1), bark ash (A1a) and soil (A2 and B1).
- Incineration of polluted soils with a high organic content (sample A1) before washing generally reduced the metal leaching and is not suggested

as a pre-treatment step before soil washing. However, the release of Cu was higher from the ash than from the original bark when the acidic process waters were used, indicating that in certain situations incineration can be a good pre-treatment alternative.

- Between 90 and 100 w% of the Cu was released from A1a and A2 and from the un-purified leachate Cu metal (>99% purity) could be generated by electrolysis, indicating that the potential for Cu metal recovery is high.
- After one leaching step the metal contents in the soil residues still exceed the Swedish guideline values. An additional washing step is likely to reduce the contents of easy soluble metal compounds in the soil residues.

The results from this study show that soil washing followed by metal recovery is a promising permanent alternative to remediate polluted soils and to utilize non-used metal resources. However, more research is needed to develop an efficient and solid treatment method. Two urgent matters to investigate are how to optimize the leaching procedure to produce a satisfyingly clean and stable soil residue, and to carry out electrolysis experiments on how to reduce the energy consumption during electrolysis; both these are currently being studied. Pre-treatment of the soils using e.g. grain-sizing is another important issue to study as this effectively can reduce the soil amount needed to be washed and at the same time increase the metal content in the enriched fraction. Another important question is that this study only looks at sites with metal contaminants, whereas in reality polluted sites often contain not only metals or organic pollutants, but a mixture of both. For this reason, it is important to understand what happens to toxic organic compounds during the optimized soil washing process, something which will be studied in further research.

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Figure captions

Figure 1. Particle size distribution profiles of the samples from the contaminated sites A1, A1a, A2 and B1 observed by dry sieving.

Figure 2. Sequential extraction distribution and release of As, Ba, Co, Cr, Cu, Mo, Ni, Pb, V and Zn in a) A1, b) A1a, c) A2 (not Mo) and d) B1. All values are given as w% (uncertainties 15-30%). Step 1; acid exchangeable fraction, Step 2; reducible fraction, Step 3; oxidizable fraction.

Figure 1

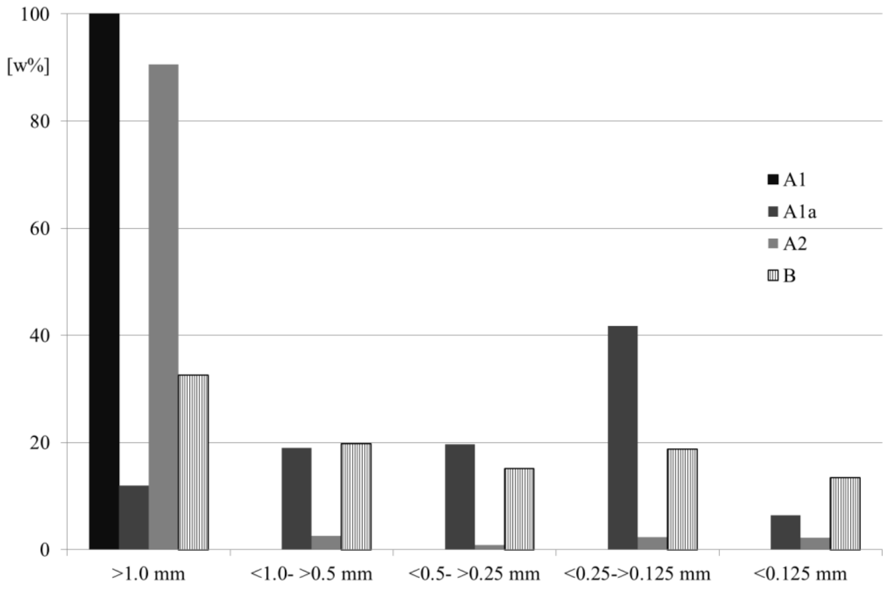
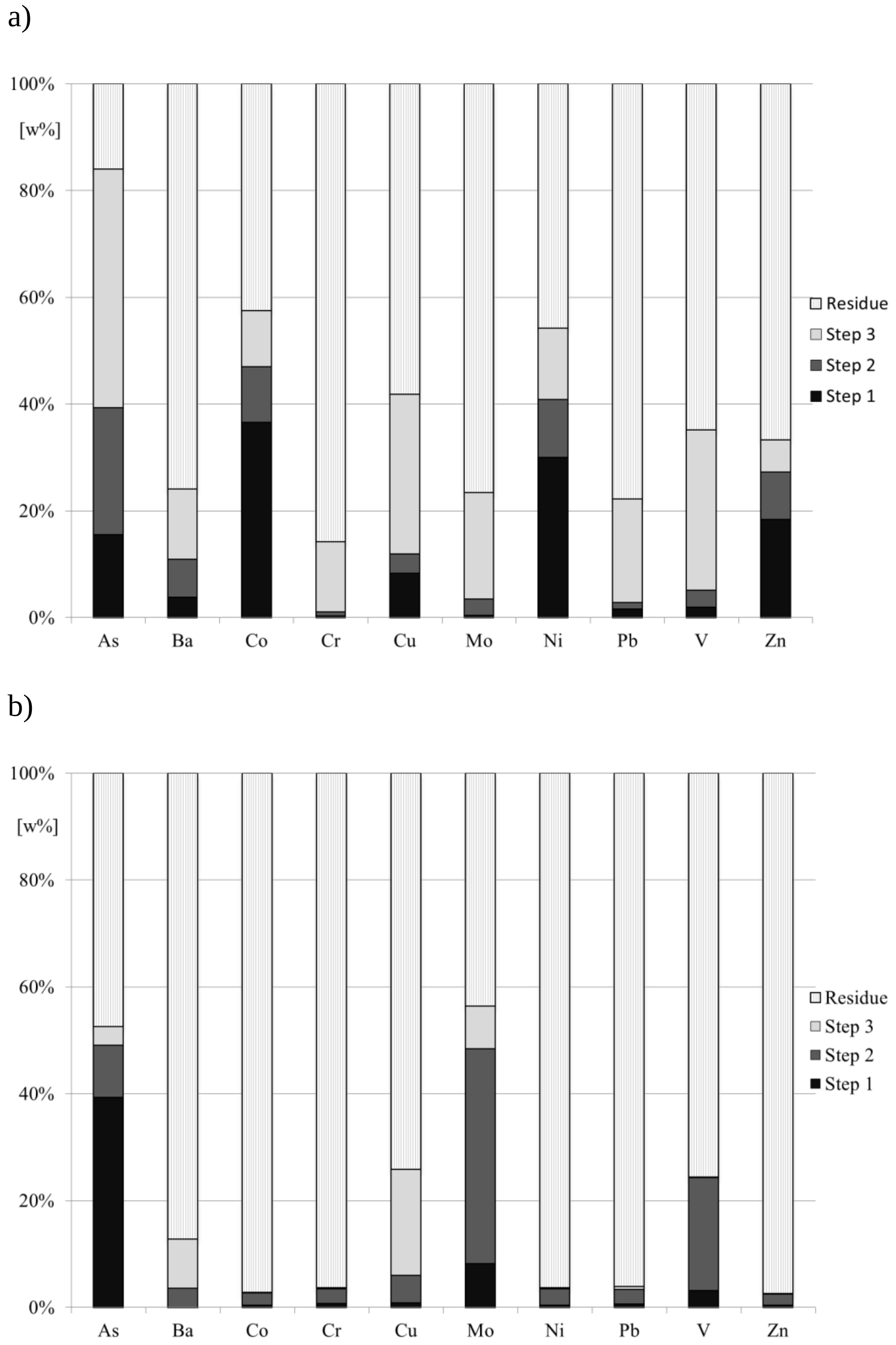


Figure 1. Particle size distribution profiles of the samples from the contaminated sites A1, A1a, A2 and B1 observed by dry sieving.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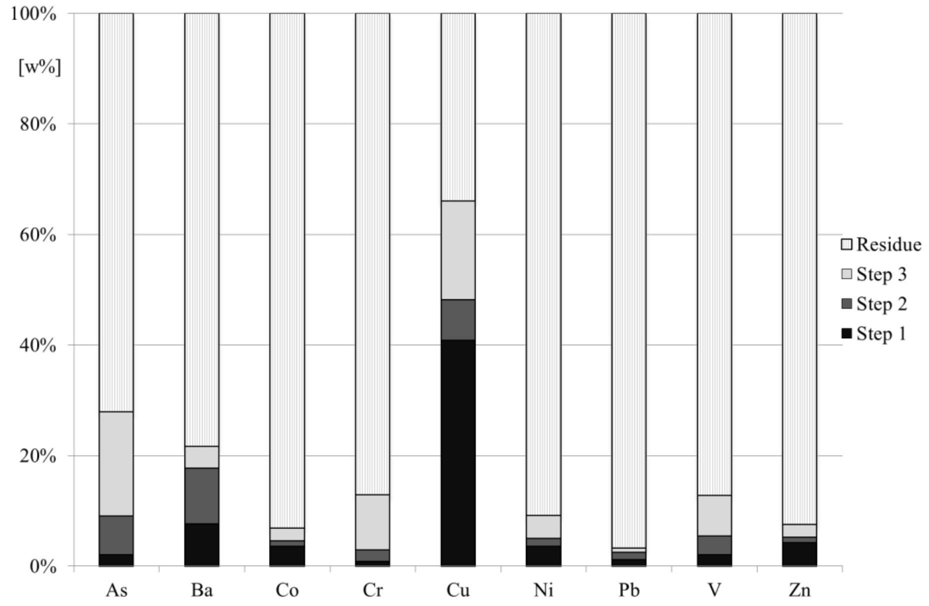

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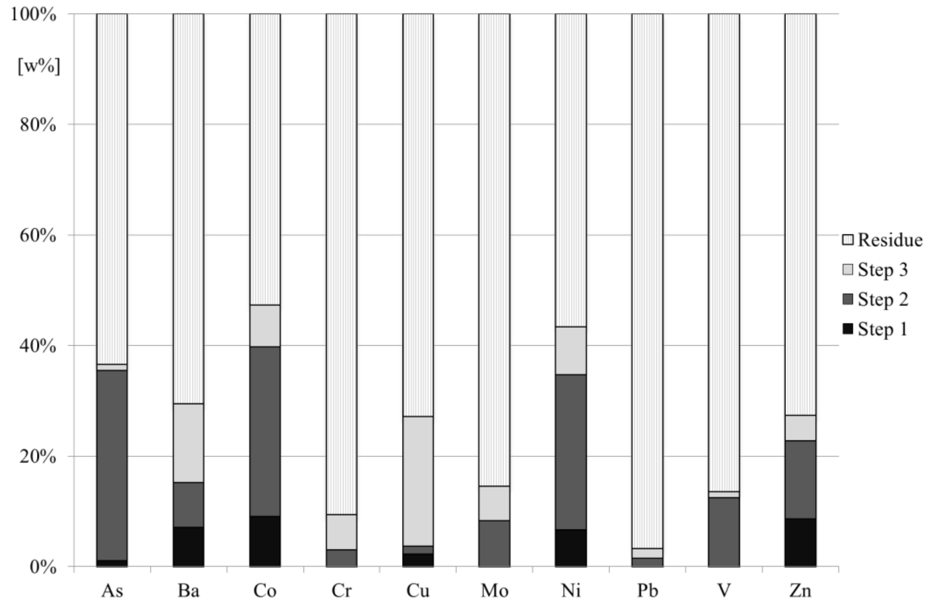

Figure 2. Sequential extraction distribution and release of As, Ba, Co, Cr, Cu, Mo, Ni, Pb, V and Zn in a) A1, b) A1a, c) A2 (not Mo) and d) B1. All values are given as w% (uncertainties 15-30%). Step 1; acid exchangeable fraction, Step 2; reducible fraction, Step 3; oxidizable fraction.

Table 1. Concentrations of major ions present in the acidic process waters “a” and “n” used for leaching experiments[1].

Process water	**Cl^-**	**SO_4^{2-}**	**Na^+**	**NH_4^+**	**Ca^{2+}**	**Pb^{2+}**	**Zn^{2+}**	**Al^{3+}**
[g/L][2]								
a	60	1.5	0.7	1.2	0.08	0.04	0.28	<0.01
n	53	1.0	0.5	1.8	2.2	0.03	0.15	0.07

[1] Cu^{2+}, K^+, Mg^{2+}, NO_2^-, NO_3^- and PO_4^{3-} were all detected in amounts <0.002g/L.

[2] Measurement uncertainties are 20-30%.

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Table 2. Average total amounts of selected major and minor elements in the original soil samples. All amounts are shown in mg/kg DS: uncertainties in the analyzes vary between 15-30%.

	A1 **(bark)**	**A1a** **(bark ash)**	**A2** **(Soil)**	**B1** **(Soil)**	**Sensitive land use**[1]	**Less sensitive land use**[1]
$pH_{(H_2O)}$	4.9	12.1	5.4	7.9		
DS, %	24	100	75	97		
Element [mg/kg DS]						
Si	42000	–[2]	–	–	*[3]	*
Al	4700	63000	18000	5700	*	*
Ca	6100	25500	2400	16000	*	*
Fe	5800	28000	12000	51000	*	*
K	520	23000	1600	1100	*	*
Mg	570	5500	2900	4600	*	*
Mn	120	590	170	1600	*	*
Na	<110	20000	120	200	*	*
P	670	2100	360	460	*	*
Ti	–	2700	–	5700	*	*
As	4	15	<3	***34***[4]	10	25
Ba	90	***700***	75	***1000***	200	300
Cd	0.4	1.0	<0.3	<0.2	0.5	15
Co	2	15	3	***1300***	15	35
Cr	15	30	10	***2100***	80	150
Cu	***20000***	***65000***	***7600***	100	80	200

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Hg	0.10	<0.05	–	–	0.25	2.5
Mo	2	4	–	***4000***	40	100
Ni	15	60	7.0	***960***	40	120
Pb	70	220	15	200	50	400
S	–	14000	1000	660	*	*
Sb	<1	<6	–	–	12	30
Se	1	–	<1	<1	*	*
Sn	2.0	–	<0.3	2	*	*
Sr	–	180	–	–	*	*
V	10	70	30	***1200***	100	200
W	–	–	–	560	*	*
Zn	140	400	40	180	250	500

[1] (SEPA 2009b)

[2] -not analyzed

[3] *no guideline values exist

[4] ***Italic style; above Swedish guidelines for less sensitive land use***

Table 3. Major crystalline compounds identified in the original and selected leached samples A1, A1a, A2 and B1 using XRD.

	A1[1] **bark**			**A1a** **bark ash**		**A2** **soil**		**B1[2]** **soil**	
Mineral	**Org[3]**	**$L_{”a”}$[4]**	**L_{NH4Cl}[5]**	**Org[3]**	**$L_{”a”}$[4]**	**Org[3]**	**$L_{”a”}$[4]**	**Org[3]**	**$L_{”a”}$[4]**
Silicates									
Albite		Minor			Minor		Minor		
Anorthite	Minor			Minor	Minor	***Major***	Minor	Trace	Trace
$CaSiO_3$			Trace						
$Fe_{2.45}Si_{0.55}O_4$								Minor	
$KFeSi_3O_8$	Minor					Minor			
Mutinaite		Minor	Minor						
SiO_2	***Major***	***Major***	Trace	***Major***	***Major***	***Major***	***Major***	***Major***	***Major***
Oxides									
$Ca_5Al_6O_{14}$				Trace					
$CaFe_4O_7$	Trace					Trace			
CuO				***Major***					
Cu_4O_3				Minor					
Fe_2O_3									Minor
$MgFe_2O_4$									Minor
Others									
$NaAl(SO_4)_2*6H_2O$								Trace	
NaCl			***Major***						
NH_4Cl			***Major***						

[1] A = site Långön
[2] B = site Österbybruk
[3] Original
[4] Leached in process water ”a”
[5] Leached in NH_4Cl

Table 4. Fractions of metals and soil matrix components released after 2 hours of leaching using various leaching agents. All amounts are given as w% released compared to the total amount in the original samples A1, A1a, A2 and B1. The pH values at the start and end of each leaching experiment are also included.

Leaching agent	**Start pH**	**End pH**	**Al**	**As**	**Ba**	**Pb**	**Co**	**Cu**	**Cr**	**Mn**	**Mo**	**Ni**	**V**	**Zn**
								[w%][1]						
Process water n														
A1	0.2	0.2	46~~46~~	36~~36~~	16~~16~~	8.0~~8~~	75~~75~~	72~~72~~	<1.0~~<1~~	76~~76~~	<1.0~~<1~~	100~~100~~	49~~49~~	35~~35~~
A1a	0.2	0.2	4.0~~4~~	100~~100~~	<1.0~~<1~~	2.0~~2~~	4.0~~4~~	87~~87~~	<1~~<1~~	23~~23~~	61~~61~~	5.0~~5~~	43~~43~~	100~~100~~
A2	0.2	0.2	16~~16~~	<1.0~~<1~~	5.0~~5~~	<1.0~~<1~~	4.0~~4~~	97~~97~~	4.0~~4~~	15~~15~~	–[2]~~–[1]~~	8.0~~8~~	17~~17~~	<1.0~~<1~~
B1	0.2	0.2	21~~21~~	10~~10~~	<1.0~~<1~~	22~~22~~	63~~63~~	93~~93~~	19~~19~~	55~~55~~	5.0~~5~~	96~~96~~	23~~23~~	57~~57~~
Process water a														
A1	<0.1	<0.1	50~~50~~	50~~50~~	10~~10~~	53~~53~~	82~~82~~	92~~92~~	5.0~~5~~	83~~83~~	<1.0~~<1~~	100~~100~~	54~~54~~	<1.0~~<1~~
A1a	<0.1	<0.1	6.0~~6~~	100~~100~~	<1.0~~<1~~	2.0~~2~~	6.0~~6~~	100~~100~~	3.0~~3~~	26~~26~~	93~~93~~	6.0~~6~~	45~~45~~	100~~100~~
A2	<0.1	<0.1	21~~21~~	<1.0~~<1~~	5.0~~5~~	39~~39~~	12~~12~~	91~~91~~	10~~10~~	26~~26~~	–~~–~~	14~~14~~	20~~20~~	<1.0~~<1~~
B1	<0.1	0.1	24~~24~~	52~~52~~	2.0~~2~~	20~~20~~	82~~82~~	10~~10~~	20~~20~~	45~~45~~	6.0~~6~~	85~~85~~	23~~23~~	<1.0~~<1~~
HCl														
A1	2.0	3.6	<1.0	4.0~~4~~	4.0~~4~~	1.0~~1~~	28~~28~~	2.0~~2~~	<1.0	47~~47~~	<1.0	28~~28~~	<1.0	31~~31~~

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			~~<1~~						~~<1~~		~~<1~~		~~<1~~	
A1a	2.0	3.6	<1.0 ~~<1~~	39~~39~~	<1.0 ~~<1~~	<1.0 ~~<1~~	1.0~~1~~	2.0~~2~~	<1.0 ~~<1~~	10~~10~~	19~~19~~	1.0~~1~~	6.0~~6~~	.05~~5~~
A2	2.0	3.9	<1.0 ~~<1~~	1.0~~1~~	1.0~~1~~	<10 ~~<1~~	40~~4~~	20~~20~~	1.0~~1~~	17~~17~~	–~~—~~	6.0~~6~~	<1~~<1~~	44~~44~~
B1	2.0	5.4	<1.0 ~~<1~~	<1.0 ~~<1~~	1.0~~1~~	<1.0 ~~<1~~	<1.0 ~~<1~~	<1~~<1~~	<1.0 ~~<1~~	<1.0 ~~<1~~	<1.0 ~~<1~~	<1.0 ~~<1~~	<1.0 ~~<1~~	6.0~~6~~
NH_4Cl														
A1	9.6	9.6	3.0~~3~~	21~~21~~	15~~15~~	5.0~~5~~	7.0~~7~~	67~~67~~	1.0~~1~~	56~~56~~	43~~43~~	100~~100~~	.04~~4~~	86~~86~~
A1a	9.6	9.6	<1.0 ~~<1~~	8.0~~8~~	3.0~~3~~	<1.0 ~~<1~~	<1.0 ~~<1~~	6.0~~6~~	1.0~~1~~	3.0~~3~~	100~~100~~	2.0~~2~~	8.0~~8~~	<1.0 ~~<1~~
A2	9.6	9.6	1.0~~1~~	4.0~~4~~	2.0~~2~~	1.0~~1~~	3.0~~3~~	79~~79~~	3.0~~3~~	13~~13~~	–~~—~~	23~~23~~	1.0~~1~~	7.0~~7~~
B1	9.6	9.6	<1.0 ~~<1~~	1.0~~1~~	5.0~~5~~	<1.0 ~~<1~~	4.0~~4~~	26~~26~~	<1.0 ~~<1~~	<1.0 ~~<1~~	1.0~~1~~	7.0~~7~~	<1.0 ~~<1~~	13~~13~~
Lactic acid														
A1	1.7	2.0	29~~29~~	41~~41~~	5.0~~5~~	9.0~~9~~	52~~52~~	48~~48~~	3.0~~3~~	67~~67~~	30~~30~~	66~~66~~	35~~35~~	52~~52~~
A1a	1.7	2.0	1.0~~1~~	81~~81~~	<1.0 ~~<1~~	4.0~~4~~	2.0~~2~~	18~~18~~	<1.0 ~~<1~~	15~~15~~	100~~100~~	2.0~~2~~	30~~30~~	1.0~~1~~
A2	1.7	1.9	14~~14~~	14~~14~~	2.0~~2~~	8.0~~8~~	7.0~~7~~	100~~100~~	6.0~~6~~	26~~26~~	–~~—~~	8.0~~8~~	14~~14~~	8.0~~8~~
B1	1.7	2.3	18~~18~~	14~~14~~	12~~12~~	6.0~~6~~	31~~31~~	18~~18~~	<1.0 ~~<1~~	30~~30~~	4.0~~4~~	22~~22~~	8.0~~8~~	31~~31~~
EDDS														
A1	7.0	6.7	9.0~~9~~	28~~28~~	2.0~~2~~	46~~46~~	70~~70~~	70~~70~~	2.0~~2~~	33~~33~~	12~~12~~	100~~100~~	25~~25~~	64~~64~~
A1a	7.0	5.4	<1.0 ~~<1~~	22~~22~~	2.0~~2~~	15~~15~~	<1.0 ~~<1~~	1.0~~1~~	<1.0 ~~<1~~	6.0~~6~~	97~~97~~	1.0~~1~~	23~~23~~	<1.0 ~~<1~~
A2	7.0	6.7	6.0~~6~~	9.0~~9~~	6.0~~6~~	16~~16~~	7.0~~7~~	99~~99~~	5.0~~5~~	28~~28~~	–~~—~~	9.0~~9~~	6.0~~6~~	36~~36~~
B1	7.0	7.0	<1.0	1.0~~1~~	3.0~~3~~	5.0~~5~~	3.0~~3~~	9.0~~9~~	<1.0	1.0~~1~~	<1.0	4.0~~4~~	1.0~~1~~	60~~6~~

			~~<1~~						~~<1~~		~~<1~~			

[1] Measurement uncertainties are 20-30%.~~–not measured~~

[2] –not measured

Table 4. Fractions of metals and soil matrix components released after 2 hours of leaching using various leaching agents. All amounts are given as w% released compared to the total amount in the original samples A1, A1a, A2 and B1. The pH values at the start and end of each leaching experiment are also included.

Leaching agent	**Start pH**	**End pH**	**Al**	**As**	**Ba**	**Pb**	**Co**	**Cu**	**Cr**	**Mn**	**Mo**	**Ni**	**V**	**Zn**
							[w%][1]							
Process water n														
A1	0.2	0.2	46	36	16	8.0	75	72	<1.0	76	<1.0	100	49	35
A1a	0.2	0.2	4.0	100	<1.0	2.0	4.0	87	<1	23	61	5.0	43	100
A2	0.2	0.2	16	<1.0	5.0	<1.0	4.0	97	4.0	15	–[2]	8.0	17	<1.0
B1	0.2	0.2	21	10	<1.0	22	63	93	19	55	5.0	96	23	57
Process water a														
A1	<0.1	<0.1	50	50	10	53	82	92	5.0	83	<1.0	100	54	<1.0
A1a	<0.1	<0.1	6.0	100	<1.0	2.0	6.0	100	3.0	26	93	6.0	45	100
A2	<0.1	<0.1	21	<1.0	5.0	39	12	91	10	26	–	14	20	<1.0
B1	<0.1	0.1	24	52	2.0	20	82	10	20	45	6.0	85	23	<1.0
HCl														
A1	2.0	3.6	<1.0	4.0	4.0	1.0	28	2.0	<1.0	47	<1.0	28	<1.0	31
A1a	2.0	3.6	<1.0	39	<1.0	<1.0	1.0	2.0	<1.0	10	19	1.0	6.0	.05
A2	2.0	3.9	<1.0	1.0	1.0	<10	40	20	1.0	17	–	6.0	<1	44
B1	2.0	5.4	<1.0	<1.0	1.0	<1.0	<1.0	<1	<1.0	<1.0	<1.0	<1.0	<1.0	6.0
NH_4Cl														
A1	9.6	9.6	3.0	21	15	5.0	7.0	67	1.0	56	43	100	.04	86
A1a	9.6	9.6	<1.0	8.0	3.0	<1.0	<1.0	6.0	1.0	3.0	100	2.0	8.0	<1.0
A2	9.6	9.6	1.0	4.0	2.0	1.0	3.0	79	3.0	13	–	23	1.0	7.0
B1	9.6	9.6	<1.0	1.0	5.0	<1.0	4.0	26	<1.0	<1.0	1.0	7.0	<1.0	13
Lactic acid														
A1	1.7	2.0	29	41	5.0	9.0	52	48	3.0	67	30	66	35	52

A1a	1.7	2.0	1.0	81	<1.0	4.0	2.0	18	<1.0	15	100	2.0	30	1.0
A2	1.7	1.9	14	14	2.0	8.0	7.0	100	6.0	26	–	8.0	14	8.0
B1	1.7	2.3	18	14	12	6.0	31	18	<1.0	30	4.0	22	8.0	31
EDDS														
A1	7.0	6.7	9.0	28	2.0	46	70	70	2.0	33	12	100	25	64
A1a	7.0	5.4	<1.0	22	2.0	15	<1.0	1.0	<1.0	6.0	97	1.0	23	<1.0
A2	7.0	6.7	6.0	9.0	6.0	16	7.0	99	5.0	28	–	9.0	6.0	36
B1	7.0	7.0	<1.0	1.0	3.0	5.0	3.0	9.0	<1.0	1.0	<1.0	4.0	1.0	60

[1] Measurement uncertainties are 20-30%.

[2] –not measured

Table 5. Calculated total amounts of selected metals present in the soil residues, which remain after leaching in process water “a” for samples A1, A1a, A2, and B1.

	A1	**A1a**	**A2**	**B1**
Element	**[mg/kg DS]**			
As	2.0	<1.0	3.0	15
Ba	80	***840***[1]	70	***1100***
Pb	30	250	8.0	180
Cd	<1.0	<1.0	<1.0	<1.0
Co	<1.0	15	3	***240***
Cu	***1700***	***340***	***700***	100
Cr	15	40	10	***1800***
Mo	3.0	<1.0	–[2]	***4100***
Ni	<1.0	70	6.0	***154***
V	5.0	50	25	***1000***
Zn	300	<1.0	300	***570***

[1] ***Italic style; Above Swedish guidelines for less sensitive land use***

[2] –not analyzed