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Title: Remediation of Metal Polluted Hotspot Areas through Enhanced Soil Washing —Evaluation of Leaching Methods

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Highlights:

- Acidic process waste water could leach $\geq 90\%$ 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.

1 **Remediation of Metal Polluted Hotspot Areas through Enhanced Soil**
2 **Washing –Evaluation of Leaching Methods Remediation of Metal**
3 **Contaminated Sites through Enhanced Soil Washing – Evaluation of**
4 **Leaching Methods**

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22 **Abstract**

23 Soil washing offers a permanent remediation alternative for metal **contaminated**

24 **polluted** sites. In addition, the washed out metals can be recovered from the

25 leachate and re-introduced into the social material cycle instead of landfilled. In

1 | this paper, soil, bark and bark-ash washing was tested ofn four different kinds-of
2 | metal contaminatedpolluted soil and bark samples from hotspots at former
3 | industrial sites. Sixusing-6- different leaching agents; HCl, NH₄Cl, lactic acid,
4 | EDDS and two acidic process waters from solid waste incineration-, is-were
5 | tested. discussed and evaluated. For the soil washing processes, the final pH in the
6 | leachate strongly influences the metal leachability. The results show that a pH<2
7 | is needed to achieve a high leaching yield, while <50 w% of most metals were
8 | leached when the pH was higher than 2 or below 10. The acidic process waste
9 | waters were generally the most efficient at leaching metals from all the samples
10 | studied, and as much as 90–100 w% of the Cu was released from some soil
11 | samples. Initial experiments show that from one of these un-purified leachates, Cu
12 | metal (>99% purity) could be recovered. After a single leaching step, the metal
13 | contents of the soil residues still exceed the maximum limits according to the
14 | Swedish guidelines. An additional washing step is needed to reduce the contents
15 | of easy soluble metal compounds in the soil residues. The overall results from this
16 | study show that soil and bark-ash washing followed by metal recovery is a
17 | promising on-site permanent alternative to remediate metal contaminatedpolluted
18 | soils and to utilize non-used metal resources. ~~However, more research is needed to~~
19 | ~~develop an efficient and solid treatment method; this is currently underway.~~
20

1 **1. Introduction**

2 More than 80,000 sites that may be ~~contaminated~~polluted due to earlier industrial
3 activities are known in Sweden, and about 2 million potentially

4 ~~contaminated~~polluted sites have been identified in Europe and in the United States
5 (Dermont et al. 2008a, SEPA 2009a). Metals are the main problem at about 50%

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6 of these sites. Contrary to many organic pollutants, metals cannot be destroyed
7 and are non-degradable. For this reason, metal ~~contaminated~~polluted soils must
8 always be treated and remediated to decrease the risks of pollution. Consequently,

9 the need for metal remediation technologies is enormous. The most commonly
10 used metal remediation method is to excavate, transfer and landfill the

11 ~~contaminated~~polluted soil and replace it with new, clean material (Dermont et al.
12 2008a, Shammass 2009). Techniques such as solidification/stabilization (S/S) are

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13 often applied prior to landfilling to decrease the potential leaching of metals
14 (Dermont et al. 2008a, Shammass 2009). However, this treatment does not reduce
15 the amounts of pollutants in the materials and metals may leach out in the longer
16 term. In addition, metals are removed from the material cycle, resulting in the loss
17 of valuable resources.

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18
19 An alternative to landfilling is soil washing. Soil washing is used commercially in
20 both Europe and the Unites States and can be carried out on site (Dermont et al.

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21 2008b). A recent example is the remediation of the Olympic Park site in London
22 in 2012, where more than 800,000m³ of soil ~~contaminated~~polluted with e.g. oil
23 and Pb was treated (Douglas 2009). Soil washing can be based on either physical

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24 separation, like magnetic fractionation or size separation, on chemical leaching, or
25 on a combination of both. Water is often used as leaching agent, but it is also

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

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7
8 Generally, the costs for soil washing are comparable with those for techniques
9 like S/S and electrokinetics and much lower than for vitrification (Shammas
10 2009). ~~Vitrification means that the soil matrix is transferred into a glassy material~~
11 ~~through heating, something which requires a lot of energy and is therefore~~
12 ~~associated with high costs.~~ Soil washing offers another important opportunity to
13 reduce the overall costs: through the potential recovery of the released metals. The
14 leachate generated from the enhanced soil washing is rich in pollutants and can
15 act as a source for metal recovery. This is not much studied and the washing
16 procedures currently applied focus on metal removal, as it ~~has~~ this far not ~~has~~
17 been economically favorable to recover metals from waste materials like
18 ~~contaminated-polluted~~ soils and ashes. However, there is one example of a
19 leaching based profitable metal recovery process from ~~municipal solid~~-waste
20 incineration (~~MSWI~~)-ash. In Switzerland, the world's first commercial full-scale
21 plant where high purity Zn (99.9%) is recovered from ~~MSWI-waste~~ fly ash has
22 recently been started up (Schlumberger and Bühler 2012, Schlumberger et al.
23 2007). In another study, based on laboratory experiments on the recovery of Cu
24 from ~~MSWI-waste~~ fly ash, it was shown that 90% of the Cu could be selectively
25 recovered and that this treatment could potentially be more profitable than the

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1 way in which ash is usually handled, i.e. landfilling (Karlfeldt Fedje et al. 2012,
2 Karlsson et al. 2010). In the study by Karlsson et al (2010), the Cu content in the
3 ash was about 0.8%, and earlier studies on sites used for wood preservation show
4 that Cu concentrations of 0.5% or higher are common (Dermont et al. 2008b,
5 Shamma 2009). As a comparison, the Cu content in a workable Swedish mine is
6 0.3% (Boliden AB 2011). The world stocks of metals like Cr, Cu and Zn are at or
7 near historically low levels and are predicted to last about 15, 40 and 20 years,
8 respectively (Stenzel et al. 2011). ~~Consequently, it is likely-plausible~~ that metal
9 prices will increase in the near future, as the virgin resources are finite and there is
10 a great demand for metals. ~~The world stocks of metals like Cr, Cu and Zn are at or~~
11 ~~near historically low levels and are predicted to last about 15, 40 and 20 years,~~
12 ~~respectively (Stenzel et al. 2011).~~

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13
14 In this lab-scale study, soil, bark and bark-ash washing with various leaching
15 agents is used for leaching of metals, and its potential as a method to remediate
16 highly metal ~~contaminated~~polluted soil and bark samples is tested. The metal
17 leaching properties and the solid residues of soil samples taken at different
18 ~~contaminated~~polluted sites with different pollution situations are studied using the
19 various leaching agents. The aim is to maximize the metal release, with particular
20 focus on Cu and Cr, and to produce a metal rich leachate from which valuable
21 metals can be recovered by e.g. electrolysis.

23 **2. Material and methods**

24 **2.1 Soil samples**

1 Soil samples with different characteristics and degree of contamination from two
2 sites- Långö in western Sweden and Österbybruk in eastern Sweden- were used in
3 this study. Both sites are strongly ~~contaminated~~polluted with metals. The first site
4 (Långö=A) was historically used for wood preservation, using CuSO₄ according to
5 the Boucherie method (Vougy 1856). Based on results from sampling and
6 chemical analyses in previous studies, representative samples of bark and soil
7 were collected from a hotspot with a high metal content; A1 is a bark sample from
8 the surface ~~level~~horizon (0–10 cm depth) and A2 is a soil sample from a depth of
9 50–100 cm. Both samples are mixtures of several sub-samples taken from the
10 bark and the soil, respectively.

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

17

18 2.1.1 Pre-treatment of the soil samples

19 All samples were dried at 80°C (100 %DS) until a constant weight was achieved.

20 The pure soil samples i.e. A2 and B1 were directly cooled down in desiccators
21 before being stored in air-tight containers until used, while ~~The bark in the A1~~
22 sample was cut into smaller pieces using an automatic mixer. ~~Part -of the bark was~~
23 thereafter stored until further analyses (A1), and part of the sample while the other
24 part of the sample was incinerated ~~at 860°C~~ for 10h to form an ash sample (A1a).
25 This incineration step was done in order to reduce the organic content of the bark

1 and to increase the potential Cu release. The incineration temperature used was
2 860°C and chosen to avoid vaporization of Cu compounds. All samples were
3 cooled down in desiccators before being stored in air-tight containers until used.

4 No pre-treatment using e.g. grain-size fractioning to generate highly polluted and
5 less polluted fractions of the soils was done due to too small sample volumes.
6
7

8 ***2.2 Leaching agents***

9 For the leaching experiments, four chemically different leaching agents known to
10 effectively leach metals from natural materials like soils were chosen for this
11 study; 0.01M HCl, 8M NH₄Cl adjusted to pH 10 to enhance amine complex
12 formation, 1M lactic acid, and 0.1M EDDS ((S,S)-Ethylenediamine-N,N-
13 disuccinic acid tri sodium salt) adjusted to pH 7 to especially enhance Cu and Pb
14 leaching. The leaching agents and their concentrations were chosen based on
15 literature research (Lo et al. 2011, Moon et al. 2012, Schöning and Brümmer
16 2008). In addition, two highly acidic process waste waters “a” and “n” (pH around
17 0) were used. These process waters came from two different places in the wet flue
18 gas cleaning processes after waste incineration and therefore contained metal ions
19 and high concentrations of chlorides. The concentrations of different ions in the
20 process waters vary naturally depending on e.g. the conditions during the
21 incineration process and the kind of waste used, but representative concentrations
22 of the most common ions are given in Table 1. Today these acidic waters are
23 purified through precipitation processes of the toxic metal ions and small
24 particles. Thereafter the metal sludge is landfilled, while the clean water is
25 released to the recipient.

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2 **2.3 Leaching experiments**

3 **2.3.1 Sequential extraction**

4 The modified three-step BCR method is proposed by the commission of the

5 European communities Bureau (BCR) as the European standard method for

6 sequential extraction schedules (Rauret 1999). In brief, the leaching steps are first;

7 acetic acid (exchangeable ions), second: hydroxyl ammonium chloride (reducible

8 fraction) and third; H₂O₂ + ammonium acetate (oxidizable fraction). ~~This method~~

9 was used to predict the mobility of As, Ba, Co, Cr, Cu, Mo, Ni, Pb, V and Zn in

10 the original samples. However, dueDue to toxicity the hydroxyl ammonium

11 chloride solution (NH₂OH·HCl) originally used in the second step was exchanged

12 for non-toxic ascorbic acid (0.2 M). It has been shown that ascorbic acid has the

13 same metal extraction efficiency as hydroxyl ammonium chloride, especially in

14 the case of Cu (Shuman 1982). This method was used to predict the mobility of

15 As, Ba, Co, Cr, Cu, Mo, Ni, Pb, V and Zn in the original samples. All experiments

16 were carried out in triplicates.

17

18 **2.3.2. Enhanced batch leaching**

19 In each experiment, 0.5 g soil was leached in airtight plastic containers using 5

20 mL of either of the chosen leaching agents (liquid-to-solid ratio (L/S) of 10). The

21 leaching time was set to 2 hours with continuous shaking at 140 rpm. After

22 leaching, the soil-liquid-mixture was centrifuged for 15 minutes at 3000G

23 (gravity). The supernatant was transferred to a new container and acidified before

24 being stored in a refrigerator until analyzed. The ash residue was washed for 5

25 minutes with continuous shaking using 5 mL ultrapure water (18.2 MΩ/cm²).

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

4 5 **2.4 Analytical methods**

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

16
17 The total element concentrations of all the solutions from the total digestion were
18 measured using ICP-MS (inductively coupled plasma mass spectrometry) (Al, As,
19 Ba, Pb, Ca, Cd, Co, Cu, Cr, Fe, K, Mg, Mn, Na, P, Ti, Hg, Mo, Ni, S, Sb, Sn, Sr,
20 V and Zn) or ICP-AES (inductively coupled plasma atomic emission
21 spectrometry) (Se and W). The soil leachates obtained from the leaching
22 experiments and the sequential extraction were analyzed for metals (Al, As, Ba,
23 Be, Pb, Cd, Co, Cu, Cr, Li, Mn, Mo, Ni, Se, Ag, Sr, Tl, U, V and Zn) using ICP-
24 MS. A Dionex ICS AS-DV ion chromatograph with ICS-900 columns for cation
25 and anion analyzes was used to analyze the K^+ , Mg^{2+} , Na^+ , NH_4^+ , Ca^{2+} , Cl^- , NO_2^- ,

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1 NO₃⁻, PO₄³⁻ and SO₄²⁻ concentrations in the acidic process waters, while the
2 amounts of Al, Pb and Zn were analyzed using ICP-MS ~~or ICP-AES~~.

3
4 The main crystalline compounds in the original samples, and in some of the
5 leached samples, were identified by qualitative X-ray powder diffractometry
6 (XRD) using a Siemens D5000 X-ray powder diffractometer with the
7 characteristic Cu radiation and a scintillation detector. Identification of
8 compounds was carried out using the JCPDS database (Joint Committee of
9 Powder Diffraction Standards 2006). The detection limit of this method is about 1
10 % by weight. The samples were dried and ground in an agate mortar before being
11 analyzed. The particle size distributions in the original dried samples were
12 measured using manual dry sieving with sieve size fractions of between 0.125 mm
13 and 1 mm. The pH was measured in the original samples (pH_(H₂O)) and at the start
14 and end of each leaching experiment using a Methrom SM 702 pH meter.

16 3. Results and discussion

17 3.1 Characterization of original samples

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

21

22 In the original samples from site A, i.e. A1 and A2, only Cu exceeds the Swedish
23 guidelines for ~~contaminated~~polluted soils, while at site B several metals exceed
24 the guidelines (Table 2). In an earlier study of site B, four times higher amounts of
25 Fe, Al and K, and 15 times higher amounts of Na, were detected at spot B1

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1 compared to the results in this study (Elander et al. 2010). This is due to
2 heterogeneities between sub-samples but the choice of digestion method is also
3 very important. In the previous study, the methods in ASTM 3682 and 3683 (total
4 digestion using bomb and melting) were used, while the SS 028311 (HNO₃ and
5 H₂O₂ leaching method) was used in this study. For the minor elements, like As,
6 Co and Cu, no significant differences could be seen, suggesting that these metals
7 are present in compounds soluble in strong acid solutions. Chromium and W are
8 exceptions, perhaps because they are incorporated together with Fe, Al, K and Na
9 in very low-soluble minerals and compounds. In sample A1, the total amounts of
10 minor elements are generally somewhat higher when using ASTM 3682 and 3683
11 than with acidic leaching (7M HNO₃), which was used in an previous study on
12 soils from the same spot (Kemakta Konsult AB 2012). However, for Cu the
13 content is about 2.5 times higher when bomb digestion is used than with acid
14 leaching, which shows that Cu is effectively adsorbed to the organic matter in the
15 bark, thus reducing the leachability.

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16
17 From 3 g of dry bark about 0.6 g of ash was obtained. Theoretically, if no Cu was
18 volatilized during incineration, the Cu content in the ash would be about 5 times
19 higher than in the original bark. However, according to the total content analyses,
20 Cu is enriched less than 3 times during incineration (Table 2). This means that the
21 chosen incineration temperature of 860°C is too high to optimize the enrichment
22 of Cu in the bottom ash. The reason for this is probably an uneven oxygen
23 distribution, resulting in a reducing atmosphere, which can increase metal
24 volatilization (Mojtahedi et al. 1987, Wikman et al. 2003). However, in a real
25 incineration process, the volatilized Cu would be caught in the flue gas cleaning

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1 system and captured in the fly ash. The enrichment factors for most other
2 elements were around 5, but for the soil matrix forming elements, such as Al, K,
3 Mg and Na, the enrichment factors were higher (Table 2). This shows that these
4 elements are present as low-volatile minerals in the original ~~soil~~sample as well as
5 in the ash, ~~which to some extent is shown in the XRD analyses (Table 3)~~. Barium
6 was enriched almost 8 times during incineration, causing the amount in the
7 resulting ash to exceed the Swedish guidelines for less sensitive land use (Table
8 2). This is not surprising, as a majority of the most common Ba compounds have
9 boiling and smelting points well above 850°C (Alberty et al. 2008).

10

11 Even though the Cu content in sample A1 and A2 were around 1% or higher, no
12 crystalline Cu compounds could be identified (Table 2 and 3). This suggests that
13 the Cu is present in amorphous forms, in very small crystals or as several different
14 Cu compounds. The first reason is the most likely in sample A1, as Cu effectively
15 sorbs to organic matter, ~~something which has been thoroughly discussed in the~~
16 ~~literature~~ (Bodek 1988, Kalmykova et al. 2008, Stumm and Morgan 1981).

17 However, when the bark was incinerated to ash the amorphous, i.e. the organic,
18 phase drastically decreased and Cu oxides were clearly identifiable (Table 3). The
19 presence of amorphous material was low both in A2 and in B1. Silica oxide, SiO₂,
20 was identified as a major compound in all samples but the presence of other
21 minerals varied between the samples, indicating different characteristics, which
22 will influence the metal leaching (Table 3).

23

24 An overview of tThe particle size distributions in the original samples are shown
25 in Figure 1. The bark (A1) contains pieces ~~larger than~~ ≥1mm, while the

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1 | corresponding ash (A1a) mainly consists of smaller particles. Sample A2 ~~hasis a~~
2 | ~~in an earlier investigation been classified as clayey soil~~ (Kemakta Konsult
3 | AB 2012) and was expected to contain a larger fraction of small particles. This
4 | could not be found, something which is probably due to clustering of the small
5 | clay particles into stable agglomerates during drying. An ocular inspection of the
6 | soil particles that remained after leaching confirmed this, as a majority of the
7 | particles were smaller than those in the original dried sample. A full size
8 | distribution analysis could unfortunately not be carried out, as the amount of soil
9 | residue was too small. ~~The dry sieving technique that was used in this study only~~
10 | ~~gives a brief overview of the particle size distribution. To get more accurate~~
11 | ~~results the use of a laser diffraction analyzer is recommended.~~

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13 | 3.2 Sequential extraction

14 | As a rule, about 50% or more of the studied metals are found in the residue
15 | fraction of all the samples, indicating low mobility during normal environmental
16 | circumstances (Figure 2). In the bark sample A1 (Figure 2a), $As > Co > Ni > Cu$
17 | are the metals released to the highest degree during the three-step leaching
18 | procedure, and all the metals were more easily released from the bark matrix than
19 | from the ash ~~from the combusted bark sample~~ A1a (Figure 2b). From the ash
20 | sample, $Mo > As > Cu > V$ were released to the highest percentage. ~~Copper is the~~
21 | ~~only metal released to a high percentage from the soil sample A2 (Figure 2c);~~
22 | ~~while several more metals were released from the sample from site B (Figure 2d);~~
23 | ~~$Co > Ni > As > Ba > Cu \approx Zn$. About 30% of the As, Co and Ni are found in the~~
24 | ~~2nd fraction, and can be released if the redox potential is changed towards a more~~
25 | ~~reducing environment.~~

1 |
2 | The metals are least mobile in sample A2 (Figure 2c). ~~However,~~ as much as
3 | 40% of the Cu is released in the first step of the leaching procedure, which shows
4 | that soil washing has a high potential as an efficient method for remediation and
5 | metal recovery. The reason for this may be that CuSO₄ from the wood
6 | preservation process has leached through the surface bark layer and into the
7 | underlying clay soil (50 -100cm). When water at high L/S ratio is added, as is the
8 | case during infiltration of rain water ~~in the soil at Långön~~ during storm events, the
9 | water soluble CuSO₄ may be released. In the bark (A1), the Cu is less mobile due
10 | to the high affinity between Cu and organic materials (Figure 2a) (Bodek 1988,
11 | Kalmykova et al. 2008, Stumm and Morgan 1981). When the bark is incinerated,
12 | the mobility is generally decreased due to the formation of less soluble metal
13 | compounds, such as CuO, identified in the XRD analysis (Figure 2b and Table 3).
14 | Additionally, encapsulation of the metals into the ash matrix further decreases the
15 | mobility.

16 |
17 | while ~~Several more~~ metals were released from the sample from site B (Figure
18 | 2d): Co > Ni > As > Ba > Cu ≈ Zn. About 30% of the As, Co and Ni are found in
19 | the 2nd fraction, and can be released if the redox potential is changed towards a
20 | more reducing environment.

22 | **3.2 Enhanced leaching**

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

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

1 (Karlfeldt and Steenari 2007). After leaching A1a, only the concentrations of Ba
2 were lower in the final leachates than in the original process waters as a
3 consequence of the stable and low-soluble Ba compounds formed during
4 incineration. In addition, if Ba is leached from the ash, formation of low soluble
5 BaSO₄ is likely to occur due to the presence of sulfates in the process waters
6 (Table 1).

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7
8 Ammonium nitrate, NH₄NO₃, has been used in many studies, both to leach and to
9 predict the bioavailability of metal contaminants in soils, and it has been shown to
10 be especially effective for Cu leaching from ash (Gryschko et al. 2005, Karlfeldt
11 Fedje et al. 2010, Pueyo et al. 2004, Schöning and Brümmer 2008). High Cl⁻
12 concentrations can promote metal release due to the formation of soluble metal-
13 chloride-complexes like CdCl_y^(2-y) and PbCl₃⁻. For this reason, it was expected that
14 NH₄Cl would also be effective for non-amine complex forming elements like Pb.
15 The results showed that about 70% of the Cu was leached from A1 and A2, while
16 only 6% was leached from the ash sample A1a (Table 4). This is consistent with
17 the results from the sequential extraction procedure where the Cu was shown to be
18 most mobile in A1 and A2, but transformed to less soluble CuO and/or
19 encapsulated in the ash, i.e. A1a (Figure 2). The same leaching tendencies for Cu
20 were also seen after the EDDS and lactic acid leaching; ≥50% of the Cu was
21 leached from A1 and A2, while <20% was leached from the other samples (Table
22 4). The leaching of Pb was generally <15% from all samples, irrespective of
23 whether NH₄Cl, EDDS or lactic acid was used.

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

12
13 The concentrations of Ag, Be, Cd, Se, Tl and U were also detected in the
14 leachates (<0.6 mg/kg) but for simplicity there are not included in Table 4.

15
16 Due to the combination of low fractional release and low total amounts of many
17 valuable metals in B1, the corresponding concentrations in the leachates are all
18 <0.25 g/L (Tables 2 and 4). Metal recovery from these leachates is therefore not
19 yet economically viable. However, when using the acidic process waters to leach
20 A1 and A1a, the concentrations of Cu in the corresponding leachates are around
21 1.5 and 6 g Cu/L, respectively. This is comparable with the concentrations in the
22 initial solutions from ores used for high purity Cu production by electrolysis (1-6
23 g/L) (Jenkins et al. 2002). To minimize the presence of impurities in the Cu
24 metal, solvent extraction is used in full-scale recovery systems prior to
25 electrolysis, to selectively extract Cu. In addition, the solvent extraction step

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1 increases the Cu concentration, which is necessary to operate an energy efficient
2 electrolysis. An interesting alternative, which would reduce the energy required
3 during electrolysis, is the use of microbial bio-electrochemical systems (BES). In
4 BES, microorganisms oxidize organic compounds present in e.g. waste-water,
5 thereby transforming the energy in the organic compounds into electrical energy.

6 ~~In several recent studies on diluted Cu solutions (~1g/L) the energy consumption~~
7 ~~was significantly lower with BES compared to traditional electrolysis (Modin and~~
8 ~~Karlfeldt Fedje 2012, Tao et al. 2011, Ter Heijne et al. 2010). At certain cathode~~
9 ~~potentials, electrical energy could even be extracted from the system together with~~
10 ~~the Cu metal (Modin and Karlfeldt Fedje 2012, Tao et al. 2011). By varying the~~
11 ~~cathode potential in the system it is not only possible to control the energy output~~
12 ~~but also which metal to recover. Modin and co-workers showed that high purity~~
13 ~~Cu (99.9%) could be recovered from a simulated ash leachate containing a~~
14 ~~mixture of Cu, Cd, Pb and Zn ions (1g/L) without energy input (Modin and~~
15 ~~Karlfeldt Fedje 2012). In addition, high purity Zn (>99.9%) could be recovered~~
16 ~~from the mixture, while the Cd and Pb metals needed further purification.~~ Initial
17 experiments to recover Cu using BES from the original process water ash
18 leachates used in this study have been performed with satisfying results. Copper
19 metal of at least 99% purity could be recovered from the ash process water
20 leachates, which contained a variety of metal ions (Table 4). This opens up for
21 simplification of the metal recovery process, as no purification step is needed
22 prior to electrolysis. In addition, the reduced energy consumption can make the
23 process profitable even though the Cu concentrations are lower than in
24 commercial electrolysis systems. More ~~experiments on how to reduce the energy~~

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

3 |
4 | The release of Cu from the A1a and A2 samples when using the acidic process
5 | waters varies between 90–100% (Table 4) and predictions indicate that there is as
6 | much as >30 tons of Cu present at the ~~contaminated~~polluted site A (Kemakta
7 | Konsult AB 2012). If on average 90% of this could be recovered from the
8 | leachates, the potential Cu metal value is about 170,000 Euro and if the
9 | incineration process is optimized to minimize the volatilization of Cu compounds,
10 | the corresponding potential value is almost 200,000 Euro. Even without taking
11 | into account the high environmental value of remediation of site A (~~Långö~~), this
12 | could motivate soil washing, ~~but further investigations into the quality and~~
13 | ~~function of the rest soil after metal recovery need to be carried out.~~

15 | **3.3 Characterization of leached soil samples**

16 | The major crystalline structure in the soil residues after leaching in the acidic
17 | process water “a” is more similar across the samples, than in the original samples
18 | (Table 3). The soil residues are dominated by silicates and oxides and no Cu
19 | compounds could be identified. Sample A1 still contained large amounts of
20 | amorphous material. However, no amorphous material was found after NH₄Cl
21 | leaching, probably because NH₄Cl hides the content of other phases (Table 3). In
22 | fact, leaching using NH₄Cl resulted in small (about 1%) or negative soil matrix
23 | dissolution (-41% for A1). For the other leaching agents, between 1 and 15w% of
24 | the solid samples was dissolved. The acidic leaching agents, i.e. the process
25 | waters and HCl, dissolved the highest fractions of A1, A1a and B1 (10-15 w%),

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1 while lactic acid showed the lowest weight losses (2-6 w%). Less than 6 w% of
2 sample A2 was dissolved irrespective of the leaching agent used, indicating a
3 stable soil matrix. In contrast, about 5 times more of sample A1a was dissolved
4 when the pH was decreased from 3.6 to ~0, i.e. when ~~HCl~~process water was used
5 instead of ~~process water~~HCl. ~~On the other hand,~~†The release of Cu and Zn from
6 A1a increased more than 20 times when the pH was decreased, confirming the
7 importance of metal encapsulation and that ash matrix dissolution is needed to
8 achieve efficient metal leaching.

9

10 Unfortunately, most of the metals which were present at concentrations above the
11 Swedish generic guideline values in the original soils are still above the guidelines
12 in the soil residues that remain after leaching (Table 5). This is due to the
13 dissolution of the soil matrixes, as well as to the adsorption of metal ions from the
14 process water in the case of Ba^{2+} , Zn^{2+} and Pb^{2+} , as discussed in section 3.2.
15 However, probably more important is the low leachability of some metals and the
16 fact that only one leaching step was used in these experiments. A qualitative
17 washing test using deionized water on the A sample residues remaining after
18 process water leaching clearly showed the release of blue Cu^{2+} ions, indicating a
19 higher metal release with an increased number of washing steps. However, it is
20 likely that even with the introduction of several leaching steps, some metals will
21 still exceed the Swedish guidelines (SEPA 2009b) due to their low leachability.

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22 On the other hand, the leaching is generally less than 50% for most metals when
23 pH is $2 \leq X \leq 10$ (Table 4) and therefore the potential release of these metals in a
24 natural environment is expected to be low, even though the total amounts exceed
25 the guidelines.

1

2 4. Conclusions

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

23

24 The results from this study show that soil washing followed by metal recovery is a
25 promising permanent alternative to remediate ~~contaminated~~polluted soils and to

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

14

15 **5. Acknowledgements**

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21

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14

15

1 **Remediation of Metal Polluted Hotspot Areas through Enhanced Soil**

2 **Washing –Evaluation of Leaching Methods**

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19 **Abstract**

20 Soil washing offers a permanent remediation alternative for metal polluted sites.

21 In addition, the washed out metals can be recovered from the leachate and re-

22 introduced into the social material cycle instead of landfilled. In this paper, soil,

23 bark and bark-ash washing was tested on four different metal polluted soil and

24 bark samples from hotspots at former industrial sites. Six different leaching

25 agents; HCl, NH₄Cl, lactic acid, EDDS and two acidic process waters from solid

1 waste incineration, were tested, discussed and evaluated. For the soil washing
2 processes, the final pH in the leachate strongly influences the metal leachability.
3 The results show that a pH<2 is needed to achieve a high leaching yield, while
4 <50 w% of most metals were leached when the pH was higher than 2 or below 10.
5 The acidic process waste waters were generally the most efficient at leaching
6 metals from all the samples studied, and as much as 90–100 w% of the Cu was
7 released from some samples. Initial experiments show that from one of these un-
8 purified leachates, Cu metal (>99% purity) could be recovered. After a single
9 leaching step, the metal contents of the soil residues still exceed the maximum
10 limits according to the Swedish guidelines. An additional washing step is needed
11 to reduce the contents of easy soluble metal compounds in the soil residues. The
12 overall results from this study show that soil and bark-ash washing followed by
13 metal recovery is a promising on-site permanent alternative to remediate metal
14 polluted soils and to utilize non-used metal resources.
15

1 **1. Introduction**

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

17

18 An alternative to landfilling is soil washing. Soil washing is used commercially in
19 both Europe and the Unites States and can be carried out on site (Dermont et al.
20 2008b). A recent example is the remediation of the Olympic Park site in London
21 in 2012, where more than 800,000m³ of soil polluted with e.g. oil and Pb was
22 treated (Douglas 2009). Soil washing can be based on either physical separation,
23 like magnetic fractionation or size separation, on chemical leaching, or on a
24 combination of both. Water is often used as leaching agent, but it is also common
25 practice to use stronger leaching agents like acids or complex forming ligands

1 such as EDTA (Bisone et al. 2012, Labanowski et al. 2008, Laporte-Saumure et
2 al. 2010, Moon et al. 2012, Moutsatsou et al. 2006, Tandy et al. 2004, Voglar and
3 Lestan 2013). The selection of leaching agent depends on e.g. the properties of the
4 contaminants at each specific site and on the remediation goal, i.e. the acceptable
5 levels of the pollutants in the soil after remediation.

6
7 Generally, the costs for soil washing are comparable with those for techniques
8 like S/S and electrokinetics and much lower than for vitrification (Shammas
9 2009). Soil washing offers another important opportunity to reduce the overall
10 costs: through the potential recovery of the released metals. The leachate
11 generated from the enhanced soil washing is rich in pollutants and can act as a
12 source for metal recovery. This is not much studied and the washing procedures
13 currently applied focus on metal removal, as it has this far not been economically
14 favorable to recover metals from waste materials like polluted soils and ashes.
15 However, there is one example of a leaching based profitable metal recovery
16 process from waste incineration ash. In Switzerland, the world's first commercial
17 full-scale plant where high purity Zn (99.9%) is recovered from waste fly ash has
18 recently been started up (Schlumberger and Bühler 2012, Schlumberger et al.
19 2007). In another study, based on laboratory experiments on the recovery of Cu
20 from waste fly ash, it was shown that 90% of the Cu could be selectively
21 recovered and that this treatment could potentially be more profitable than the
22 way in which ash is usually handled, i.e. landfilling (Karlfeldt Fedje et al. 2012,
23 Karlsson et al. 2010). In the study by Karlsson et al (2010), the Cu content in the
24 ash was about 0.8%, and earlier studies on sites used for wood preservation show
25 that Cu concentrations of 0.5% or higher are common (Dermont et al. 2008b,

1 Shammass 2009). As a comparison, the Cu content in a workable Swedish mine is
2 0.3% (Boliden AB 2011). The world stocks of metals like Cr, Cu and Zn are at or
3 near historically low levels and are predicted to last about 15, 40 and 20 years,
4 respectively (Stenzel et al. 2011). Consequently, it is plausible that metal prices
5 will increase in the near future, as the virgin resources are finite and there is a
6 great demand for metals.

7

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

16

17 **2. Material and methods**

18 ***2.1 Soil samples***

19 Soil samples with different characteristics and degree of contamination from two
20 sites- Långö in western Sweden and Österbybruk in eastern Sweden- were used in
21 this study. Both sites are strongly polluted with metals. The first site (Långö=A)
22 was historically used for wood preservation, using CuSO₄ according to the
23 Boucherie method (Vougy 1856). Based on results from sampling and chemical
24 analyses in previous studies, representative samples of bark and soil were
25 collected from a hotspot with a high metal content; A1 is a bark sample from the

1 surface horizon (0–10 cm depth) and A2 is a soil sample from a depth of 50–100
2 cm. Both samples are mixtures of several sub-samples taken from the bark and the
3 soil, respectively.

4

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

10

11 *2.1.1 Pre-treatment of the soil samples*

12 All samples were dried at 80°C (100 %DS) until a constant weight was achieved.

13 The pure soil samples i.e. A2 and B1 were directly cooled down in desiccators

14 before being stored in air-tight containers until used, while the bark sample was

15 cut into smaller pieces using an automatic mixer. Part of the bark was thereafter

16 stored until further analyses (A1), while the other part of the sample was

17 incinerated for 10h to form an ash sample (A1a). This incineration step was done

18 in order to reduce the organic content of the bark and to increase the potential Cu

19 release. The incineration temperature used was 860°C and chosen to avoid

20 vaporization of Cu compounds. All samples were cooled down in desiccators

21 before being stored in air-tight containers until used. No pre-treatment using e.g.

22 grain-size fractioning to generate highly polluted and less polluted fractions of the

23 soils was done due to too small sample volumes.

24

25

1 **2.2 Leaching agents**

2 For the leaching experiments, four chemically different leaching agents known to
3 effectively leach metals from natural materials like soils were chosen for this
4 study; 0.01M HCl, 8M NH₄Cl adjusted to pH 10 to enhance amine complex
5 formation, 1M lactic acid, and 0.1M EDDS ((S,S)-Ethylenediamine-N,N-
6 disuccinic acid tri sodium salt) adjusted to pH 7 to especially enhance Cu and Pb
7 leaching. The leaching agents and their concentrations were chosen based on
8 literature research (Lo et al. 2011, Moon et al. 2012, Schöning and Brümmer
9 2008). In addition, two highly acidic process waste waters “a” and “n” (pH around
10 0) were used. These process waters came from two different places in the wet flue
11 gas cleaning processes after waste incineration and therefore contained metal ions
12 and high concentrations of chlorides. The concentrations of different ions in the
13 process waters vary naturally depending on e.g. the conditions during the
14 incineration process and the kind of waste used, but representative concentrations
15 of the most common ions are given in Table 1. Today these acidic waters are
16 purified through precipitation processes of the toxic metal ions and small
17 particles. Thereafter the metal sludge is landfilled, while the clean water is
18 released to the recipient.

19

20 **2.3 Leaching experiments**

21 *2.3.1 Sequential extraction*

22 The modified three-step BCR method is proposed by the commission of the
23 European communities Bureau (BCR) as the European standard method for
24 sequential extraction schedules (Rauret 1999). In brief, the leaching steps are first;
25 acetic acid (exchangeable ions), second; hydroxyl ammonium chloride (reducible

1 fraction) and third; H_2O_2 + ammonium acetate (oxidizable fraction). Due to
2 toxicity the hydroxyl ammonium chloride solution ($NH_2OH \cdot HCl$) originally used
3 in the second step was exchanged for non-toxic ascorbic acid (0.2 M). It has been
4 shown that ascorbic acid has the same metal extraction efficiency as hydroxyl
5 ammonium chloride, especially in the case of Cu (Shuman 1982). This method
6 was used to predict the mobility of As, Ba, Co, Cr, Cu, Mo, Ni, Pb, V and Zn in
7 the original samples. All experiments were carried out in triplicates.

8

9 *2.3.2. Enhanced batch leaching*

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

20

21 *2.4 Analytical methods*

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

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

7
8 The total element concentrations of all the solutions from the total digestion were
9 measured using ICP-MS (inductively coupled plasma mass spectrometry) (Al, As,
10 Ba, Pb, Ca, Cd, Co, Cu, Cr, Fe, K, Mg, Mn, Na, P, Ti, Hg, Mo, Ni, S, Sb, Sn, Sr,
11 V and Zn) or ICP-AES (inductively coupled plasma atomic emission
12 spectrometry) (Se and W). The soil leachates obtained from the leaching
13 experiments and the sequential extraction were analyzed for metals (Al, As, Ba,
14 Be, Pb, Cd, Co, Cu, Cr, Li, Mn, Mo, Ni, Se, Ag, Sr, Tl, U, V and Zn) using ICP-
15 MS. A Dionex ICS AS-DV ion chromatograph with ICS-900 columns for cation
16 and anion analyzes was used to analyze the K^+ , Mg^{2+} , Na^+ , NH_4^+ , Ca^{2+} , Cl^- , NO_2^- ,
17 NO_3^- , PO_4^{3-} and SO_4^{2-} concentrations in the acidic process waters, while the
18 amounts of Al, Pb and Zn were analyzed using ICP-MS.

19
20 The main crystalline compounds in the original samples, and in some of the
21 leached samples, were identified by qualitative X-ray powder diffractometry
22 (XRD) using a Siemens D5000 X-ray powder diffractometer with the
23 characteristic Cu radiation and a scintillation detector. Identification of
24 compounds was carried out using the JCPDS database (Joint Committee of
25 Powder Diffraction Standards 2006). The detection limit of this method is about 1

1 % by weight. The samples were dried and ground in an agate mortar before being
2 analyzed. The particle size distributions in the original dried samples were
3 measured using manual dry sieving with sieve size fractions of between 0.125 mm
4 and 1 mm. The pH was measured in the original samples ($\text{pH}_{(\text{H}_2\text{O})}$) and at the start
5 and end of each leaching experiment using a Methrom SM 702 pH meter.

6

7 **3. Results and discussion**

8 *3.1 Characterization of original samples*

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

12

13 In the original samples from site A, i.e. A1 and A2, only Cu exceeds the Swedish
14 guidelines for polluted soils, while at site B several metals exceed the guidelines
15 (Table 2). In an earlier study of site B, four times higher amounts of Fe, Al and K,
16 and 15 times higher amounts of Na, were detected at spot B1 compared to the
17 results in this study (Elander et al. 2010). This is due to heterogeneities between
18 sub-samples but the choice of digestion method is also very important. In the
19 previous study, the methods in ASTM 3682 and 3683 (total digestion using bomb
20 and melting) were used, while the SS 028311 (HNO_3 and H_2O_2 leaching method)
21 was used in this study. For the minor elements, like As, Co and Cu, no significant
22 differences could be seen, suggesting that these metals are present in compounds
23 soluble in strong acid solutions. Chromium and W are exceptions, perhaps
24 because they are incorporated together with Fe, Al, K and Na in very low-soluble
25 minerals and compounds. In sample A1, the total amounts of minor elements are

1 generally somewhat higher when using ASTM 3682 and 3683 than with acidic
2 leaching (7M HNO₃), which was used in an previous study on soils from the same
3 spot (Kemakta Konsult AB 2012). However, for Cu the content is about 2.5 times
4 higher when bomb digestion is used than with acid leaching, which shows that Cu
5 is effectively adsorbed to the organic matter in the bark, thus reducing the
6 leachability.

7

8 From 3 g of dry bark about 0.6 g of ash was obtained. Theoretically, if no Cu was
9 volatilized during incineration, the Cu content in the ash would be about 5 times
10 higher than in the original bark. However, according to the total content analyses,
11 Cu is enriched less than 3 times during incineration (Table 2). This means that the
12 chosen incineration temperature of 860°C is too high to optimize the enrichment
13 of Cu in the bottom ash. The reason for this is probably an uneven oxygen
14 distribution, resulting in a reducing atmosphere, which can increase metal
15 volatilization (Mojtahedi et al. 1987, Wikman et al. 2003). However, in a real
16 incineration process, the volatilized Cu would be caught in the flue gas cleaning
17 system and captured in the fly ash. The enrichment factors for most other
18 elements were around 5, but for the soil matrix forming elements, such as Al, K,
19 Mg and Na, the enrichment factors were higher (Table 2). This shows that these
20 elements are present as low-volatile minerals in the original sample as well as in
21 the ash. Barium was enriched almost 8 times during incineration, causing the
22 amount in the resulting ash to exceed the Swedish guidelines for less sensitive
23 land use (Table 2). This is not surprising, as a majority of the most common Ba
24 compounds have boiling and smelting points well above 850°C (Alberty et al.
25 2008).

1
2 Even though the Cu content in sample A1 and A2 were around 1% or higher, no
3 crystalline Cu compounds could be identified (Table 2 and 3). This suggests that
4 the Cu is present in amorphous forms, in very small crystals or as several different
5 Cu compounds. The first reason is the most likely in sample A1, as Cu effectively
6 sorbs to organic matter (Bodek 1988, Kalmykova et al. 2008, Stumm and Morgan
7 1981). However, when the bark was incinerated to ash the amorphous, i.e. the
8 organic, phase drastically decreased and Cu oxides were clearly identifiable
9 (Table 3). The presence of amorphous material was low both in A2 and in B1.
10 Silica oxide, SiO₂, was identified as a major compound in all samples but the
11 presence of other minerals varied between the samples, indicating different
12 characteristics, which will influence the metal leaching (Table 3).

13

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

1 the particle size distribution. To get more accurate results the use of a laser
2 diffraction analyzer is recommended.

3 **3.2 Sequential extraction**

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

24

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

5

6 **3.2 Enhanced leaching**

7 As discussed in section 1, mineral acid solutions have been used to leach metals
8 from polluted soils (Moon et al. 2012, Moutsatsou et al. 2006). Usually, a stronger
9 acid solution releases more metals but on the other hand it also dissolves the soil
10 matrix itself (Kuo et al. 2006, Moutsatsou et al. 2006). Depending on the
11 properties of each unique soil, these effects will be more or less pronounced. For
12 instance, the presence and release of alkaline compounds like CaCO_3 or
13 (hydr)oxides dissolve the soil matrix and could cause a higher pH and decreased
14 metal leaching. When comparing the metal release achieved with the mineral
15 acidic solutions used in this study, i.e. process waters and HCl, it is obvious that a
16 0.01M HCl solution is too weak to neutralize the released alkaline compounds and
17 keep the pH constant (Table 4). It should be noted that even though the original
18 ash, i.e. A1a, is more alkaline than B1, pH 12.1 and 7.9, respectively, the alkaline
19 compounds are more easily released from the latter, resulting in a higher end pH
20 after HCl leaching (Table 4). In contrast, the pH levels of the acidic process water
21 leachates are barely affected by the release of alkaline compounds and these were
22 the leaching agents that released metals most effectively from all the samples
23 (Table 4). In samples A1, A2 and B2, the concentrations of Pb^{2+} and Zn^{2+} in the
24 original process waters (Table 1) are often comparable to, or even higher than, the
25 concentrations in the final leachates. This is mainly due to the low amounts of

1 these metals that are present in the original soil samples compared to the
2 concentrations in the original process waters (Tables 1 and 2). Other reasons for
3 this phenomenon are the presence of active sites in the soil matrix to which the
4 metal ions can adsorb, the particle sizes, and the speciation of the metals. The
5 importance of size distribution and the presence of active sites on Pb and Zn
6 leaching have been studied earlier by Karlfeldt and Steenari (2007). They found
7 that grinding of the solid material (fly ash) before leaching in some cases strongly
8 reduced the detected amounts of Pb^{2+} and Zn^{2+} in the leachate (Karlfeldt and
9 Steenari 2007). After leaching A1a, only the concentrations of Ba were lower in
10 the final leachates than in the original process waters as a consequence of the
11 stable and low-soluble Ba compounds formed during incineration. In addition, if
12 Ba is leached from the ash, formation of low soluble $BaSO_4$ is likely to occur due
13 to the presence of sulfates in the process waters (Table 1).

14

15 Ammonium nitrate, NH_4NO_3 , has been used in many studies, both to leach and to
16 predict the bioavailability of metal contaminants in soils, and it has been shown to
17 be especially effective for Cu leaching from ash (Gryschko et al. 2005, Karlfeldt
18 Fedje et al. 2010, Pueyo et al. 2004, Schöning and Brümmer 2008). High Cl^-
19 concentrations can promote metal release due to the formation of soluble metal-
20 chloride-complexes like $CdCl_y^{(2-y)}$ and $PbCl_3^-$. For this reason, it was expected that
21 NH_4Cl would also be effective for non-amine complex forming elements like Pb.
22 The results showed that about 70% of the Cu was leached from A1 and A2, while
23 only 6% was leached from the ash sample A1a (Table 4). This is consistent with
24 the results from the sequential extraction procedure where the Cu was shown to be
25 most mobile in A1 and A2, but transformed to less soluble CuO and/or

1 encapsulated in the ash, i.e. A1a (Figure 2). The same leaching tendencies for Cu
2 were also seen after the EDDS and lactic acid leaching; $\geq 50\%$ of the Cu was
3 leached from A1 and A2, while $< 20\%$ was leached from the other samples (Table
4 4). The leaching of Pb was generally $< 15\%$ from all samples, irrespective of
5 whether NH_4Cl , EDDS or lactic acid was used.

6
7 The overall leaching results suggest that the lower leaching from A1a compared to
8 A1 and A2 is due to encapsulation and formation of stable metal compounds
9 during the incineration. In the case of B1, the lower leaching is mainly due to the
10 metal speciation and incorporation of the metals in the soil matrix, caused by the
11 former industrial activities at the site. Therefore, it is not only important to gain a
12 deep knowledge about the soil matrixes and their contamination history prior to
13 soil washing, but also to remember that pre-treatment, such as grinding and
14 incineration before the washing, influence the leaching properties.

15
16 The concentrations of Ag, Be, Cd, Se, Tl and U were also detected in the
17 leachates ($< 0.6 \text{ mg/kg}$) but for simplicity there are not included in Table 4.

18
19 Due to the combination of low fractional release and low total amounts of many
20 valuable metals in B1, the corresponding concentrations in the leachates are all
21 $< 0.25 \text{ g/L}$ (Tables 2 and 4). Metal recovery from these leachates is therefore not
22 yet economically viable. However, when using the acidic process waters to leach
23 A1 and A1a, the concentrations of Cu in the corresponding leachates are around
24 1.5 and 6 g Cu/L, respectively. This is comparable with the concentrations in the
25 initial solutions from ores used for high purity Cu production by electrolysis (1-6

1 g/L) (Jenkins et al. 2002). To minimize the presence of impurities in the Cu
2 metal, solvent extraction is used in full-scale recovery systems prior to
3 electrolysis, to selectively extract Cu. In addition, the solvent extraction step
4 increases the Cu concentration, which is necessary to operate an energy efficient
5 electrolysis. An interesting alternative, which would reduce the energy required
6 during electrolysis, is the use of microbial bio-electrochemical systems (BES). In
7 BES, microorganisms oxidize organic compounds present in e.g. waste-water,
8 thereby transforming the energy in the organic compounds into electrical energy.
9 Initial experiments to recover Cu using BES from the original process water ash
10 leachates used in this study have been performed with satisfying results. Copper
11 metal of at least 99% purity could be recovered from the ash process water
12 leachates, which contained a variety of metal ions (Table 4). This opens up for
13 simplification of the metal recovery process, as no purification step is needed
14 prior to electrolysis. In addition, the reduced energy consumption can make the
15 process profitable even though the Cu concentrations are lower than in
16 commercial electrolysis systems. More research is in progress and will be
17 discussed and published in future articles.

18

19 The release of Cu from the A1a and A2 samples when using the acidic process
20 waters varies between 90–100% (Table 4) and predictions indicate that there is as
21 much as >30 tons of Cu present at the polluted site A (Kemakta Konsult AB
22 2012). If on average 90% of this could be recovered from the leachates, the
23 potential Cu metal value is about 170,000 Euro and if the incineration process is
24 optimized to minimize the volatilization of Cu compounds, the corresponding

1 potential value is almost 200,000 Euro. Even without taking into account the high
2 environmental value of remediation of site A, this could motivate soil washing.

3

4 ***3.3 Characterization of leached soil samples***

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

22

23 Unfortunately, most of the metals which were present at concentrations above the
24 Swedish generic guideline values in the original soils are still above the guidelines
25 in the soil residues that remain after leaching (Table 5). This is due to the

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

14

15 **4. Conclusions**

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

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

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

11

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

1 toxic organic compounds during the optimized soil washing process, something
2 which will be studied in further research.

3

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10

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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

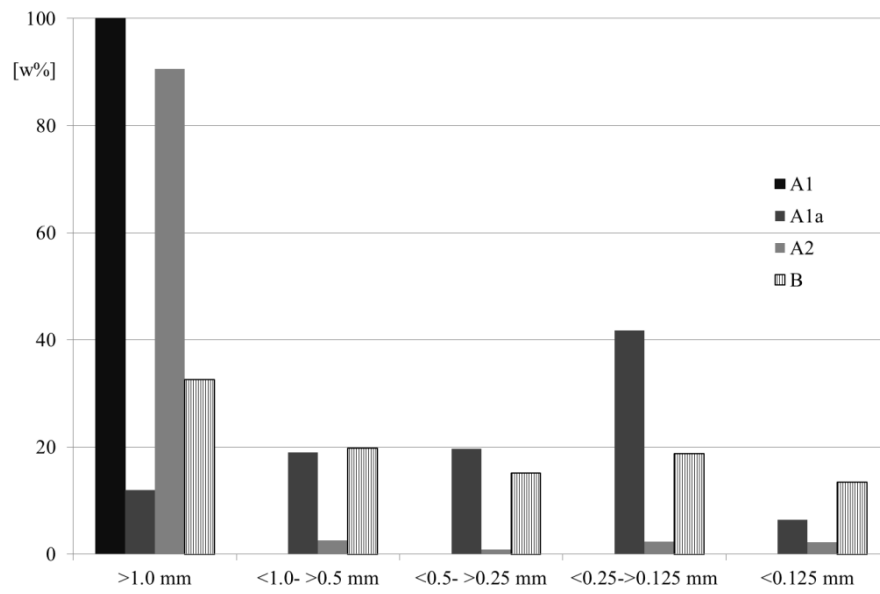
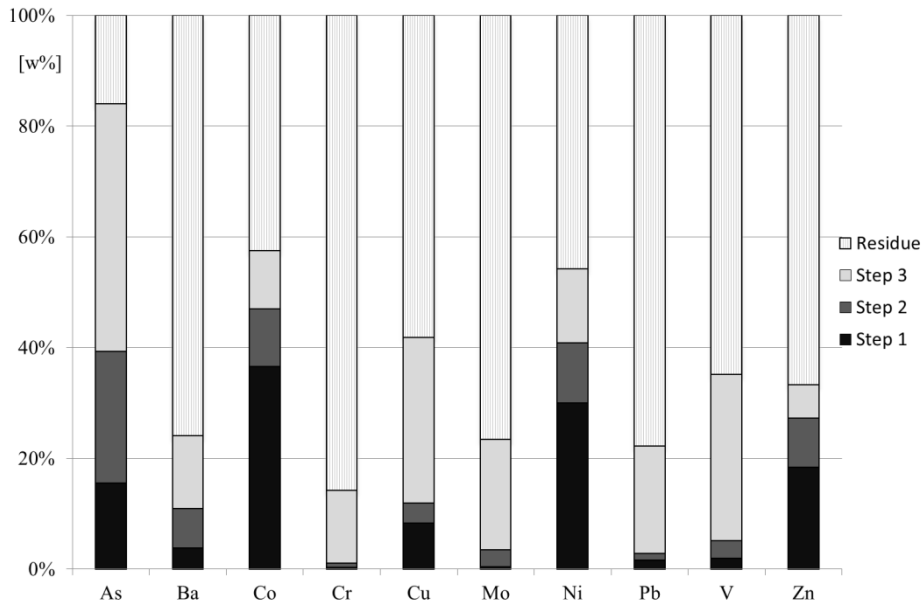
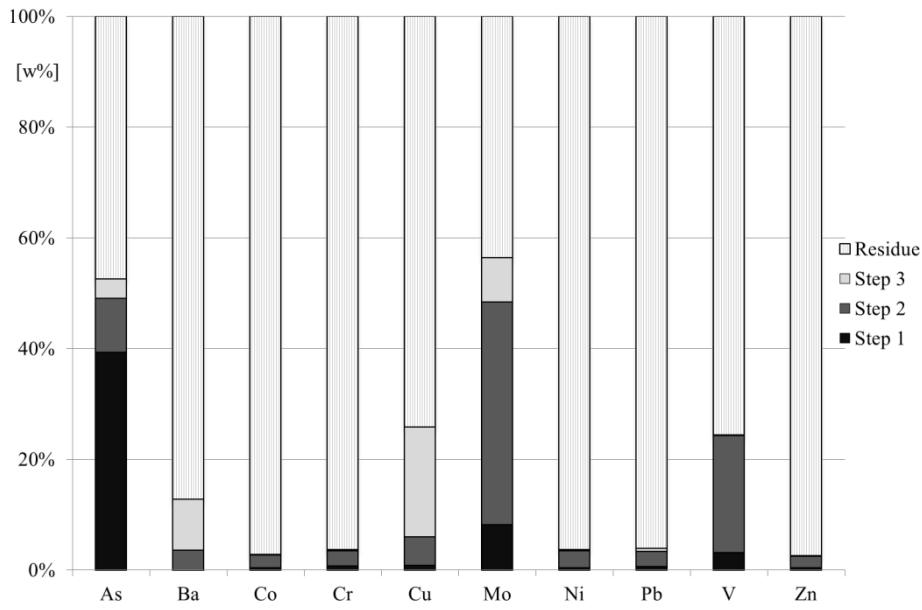


Figure 1. Particle size distribution profiles of the samples from the contaminated sites A1, A1a, A2 and B1 observed by dry sieving.

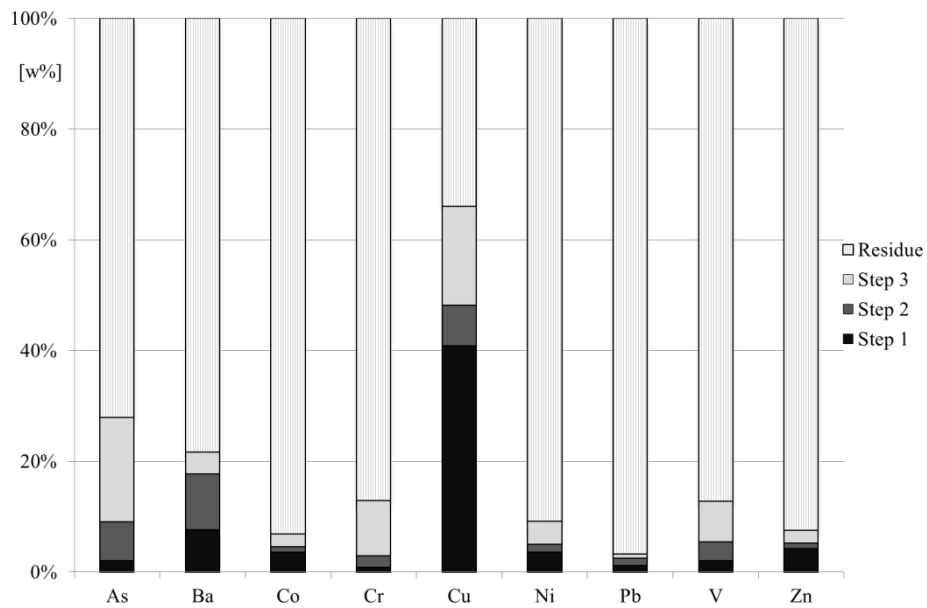
a)



b)



c)



d)

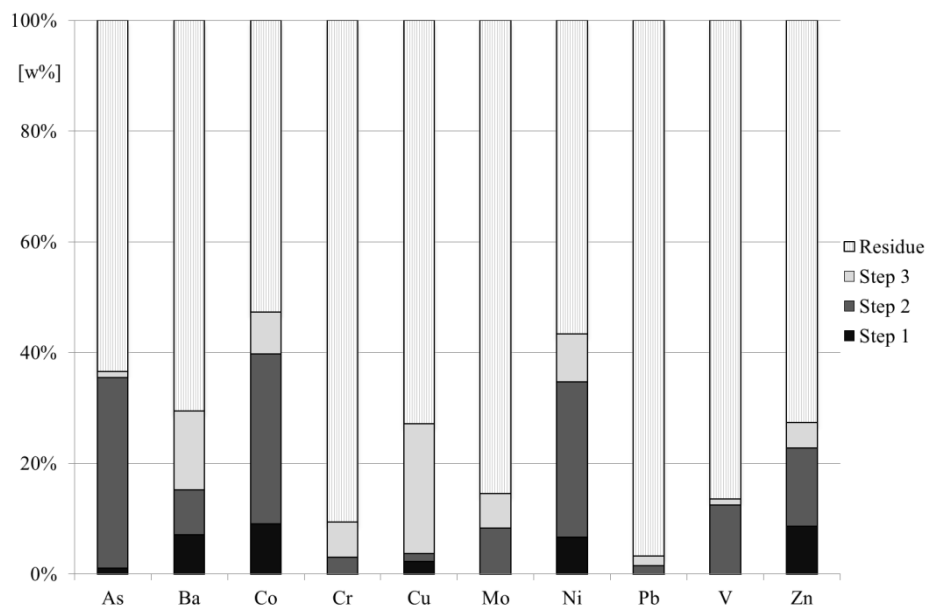


Figure 2. Sequential extraction distribution and release of As, Ba, Co, Cr, Cu, Mo, Ni, Pb, V

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 experiments¹.

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 Cu²⁺, K⁺, Mg²⁺, NO₂⁻, NO₃⁻ and PO₄³⁻ 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 use¹	Less sensitive land use¹
pH _(H₂O)	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	34⁴	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	<i>Major</i>	Minor	Trace	Trace
CaSiO ₃			Trace						
Fe _{2.45} Si _{10.55} O ₄								Minor	
KFeSi ₃ O ₈	Minor					Minor			
Mutinaite		Minor	Minor						
SiO ₂	<i>Major</i>	<i>Major</i>	Trace	<i>Major</i>	<i>Major</i>	<i>Major</i>	<i>Major</i>	<i>Major</i>	<i>Major</i>
Oxides									
Ca ₅ Al ₆ O ₁₄				Trace					
CaFe ₄ O ₇	Trace					Trace			
CuO				<i>Major</i>					
Cu ₄ O ₃				Minor					
Fe ₂ O ₃									Minor
MgFe ₂ O ₄									Minor
Others									
NaAl(SO ₄) ₂ *6H ₂ O								Trace	
NaCl			<i>Major</i>						
NH ₄ Cl			<i>Major</i>						

¹A = site Långön

²B = site Österbybruk

³Original

⁴Leached in process water ”a”

⁵Leached in NH₄Cl

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%] [±]														
Process water n														
A1	0.2	0.2	4646	3636	1616	8.08	7575	7272	<1.0	7676	<1.0	100+	4949	3535
									<1		<1	00		
A1a	0.2	0.2	4.04	100+	<1.0	2.02	4.04	8787	<1	2323	6161	5.05	4343	100+
				00	<1				+					00
A2	0.2	0.2	1616	<1.0	5.05	<1.0	4.04	9797	4.04	1515	2.2+	8.08	1717	<1.0
				<1		<1								<1
B1	0.2	0.2	2121	1010	<1.0	2222	6363	9393	1919	5555	5.05	9696	2323	5757
					<1									
Process water a														
A1	<0.1	<0.1	5050	5050	1010	5353	8282	9292	5.05	8383	<1.0	100+	5454	<1.0
											<1	00		<1
A1a	<0.1	<0.1	6.06	100+	<1.0	2.02	6.06	100+	3.03	2626	9393	6.06	4545	100+
				00	<1			00						00
A2	<0.1	<0.1	2121	<1.0	5.05	3939	1212	9191	1010	2626	--	1414	2020	<1.0
				<1										<1
B1	<0.1	0.1	2424	5252	2.02	2020	8282	1010	2020	4545	6.06	8585	2323	<1.0
														<1
HCl														
A1	2.0	3.6	<1.0	4.04	4.04	1.01	2828	2.02	<1.0	4747	<1.0	2828	<1.0	3131

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¹ Measurement uncertainties are 20-30%. -not measured

² -not measured

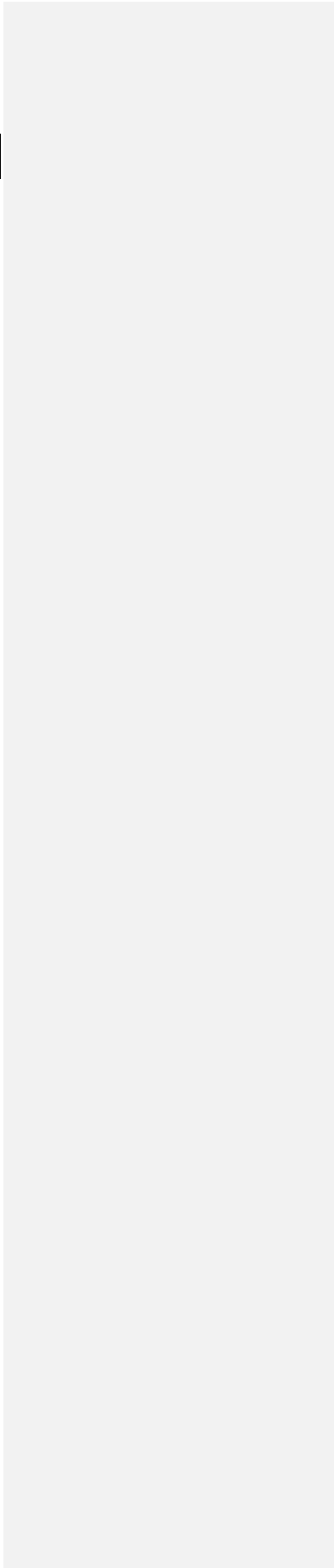


Table 4. Fractions of metals and soil matrix components released after 2 hours of leaching using various leaching agents. All amounts are given as w% released compared to the total amount in the original samples A1, A1a, A2 and B1. The pH values at the start and end of each leaching experiment are also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

Leaching agent	Start pH	End pH	Al	As	Ba	Pb	Co	Cu	Cr	Mn	Mo	Ni	V	Zn
[w%]¹														
<i>Process water n</i>														
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
<i>Process water a</i>														
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	<1.0	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
NH₄Cl														
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	840¹	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