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Metal contamination at a wood preservation site: characterisation and experimental studies on remediation

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Abstract

The aim of this investigation was to determine the occurrence of As, Cu, Cr and Zn in the soil at an abandoned wood preservation unit and to examine some possible extractants for the contaminants in the soil. The mean As content of the contaminated surface soils (0–10 cm) was 186 mg kg^{-1}, where as the mean concentrations of Cu, Cr and Zn in soils from the contaminated area were 26, 29 and 91 mg kg^{-1}, respectively. The elevated As content in the mineral soils is related to adsorption of inorganic As phases in the fine grained fractions, which are characterised by large surface area and high positive surface charge under the current acidic conditions. Cu and Cr were found to be rather mobile, which is reflected in their lower abundance in soils and significant accumulation in sediments in the drainage leaving the area. The fine fraction of the soil (<0.125 mm) has an average metal content increased by nearly 34% as compared to the <2-mm fraction conventionally used for the analysis and assessment of soil contamination. The <2-mm fraction constitutes approximately 65% of the total weight while the fine fraction (<0.125 mm) constitutes approximately 10%. These facts, taken together, are essential for the choice of remediation measures. Oxalate solutions have been tested as extractants for soil remediation. Dark acid oxalate extraction dissolves the amorphous Al- and Fe-oxides and hydroxides and mobilises the adsorbed inorganic As species. Oxalate also acts as a ligand for the cationic heavy metals, releasing them from exchangeable sites. With a three-step sequential leaching, up to 98–99% of the metals could be removed. At lower concentrations and higher pH, the leaching decreased to approximately 70%. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Wood preservation industries have been operating in Sweden since the middle of the 19th century to protect wood from bacterial, fungal and insect attack (Jacks and Bhattacharya, 1998). Chemicals such as copper sulfate, Boliden salt (BIS-salt)

mixed with zinc sulfate and chromated copper arsenate (CCA) have been used as common wood preservative for more than 50 years (Jacks and Bhattacharya 1998). However, pressure treatment with CCA has grown drastically over the past 20 years (Stephens et al., 1994) and has remained as the most preferred industrial method of wood preservation in Sweden. It has replaced the conventional use of pentachlorophenol (PCP) and

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Table 1
Some of the common water soluble As-based chemicals used for wood preservation in Sweden (Jacks and Bhattacharya, 1998)

Chemical	Year	Composition (%)		Percentage metal in pure form		
Boliden BIS	1936–1950	Zn(II) oxide (ZnO)	12.0%	Zn	9.8%	
+ZnSO$_4$		Chromium trioxide (CrO$_3$)	10.5%	Cr	5.5%	
		Diarsenic pentoxide (As$_2$O$_5$)	27.7%	As	18.1%	
		Sodium(I) oxide (Na$_2$O)	9.2%			
		Sulfur trioxide (SO$_3$)	28.5%			
Boliden S25	1951–1954	Zn(II) oxide (ZnO)	11.6%	Zn	9.3%	
		Copper(II) oxide (CuO)	3.9%	Cu	3.1%	
		Chromium trioxide (CrO$_3$)	23.0%	Cr	12.0%	
		Diarsenic pentoxide (As$_2$O$_5$)	36.0%	As	23.5%	
		Water (H$_2$O)	25.5%			
K33, CCA	1952–1990	Copper(II) oxide (CuO)	14.8%	Cu	11.8%	
type B		Chromium trioxide (CrO$_3$)	26.6%	Cr	13.8%	
		Diarsenic pentoxide (As$_2$O$_5$)	34.0%	As	22.2%	
		Water (H$_2$O)	24.6%			
Celcure/C33	1983–1990	Copper(II) sulfate (CuSO$_4$.5H$_2$O)	23.2%	Cu	8.2%	
(or equivalents)		Copper(II) oxide (CuO)	2.8%			
		Chromium trioxide (CrO$_3$)	40.0%	Cr	14.0%	
		Diarsenic pentoxide (As$_2$O$_5$)	22.7%	As	14.8%	
		Water (H$_2$O)	11.3%			

creosote, which are a complex and variable mixture produced from coal (Jacks and Bhattacharya, 1998). However, among the 130 wood preservation industries presently operating in Sweden, only three units are using creosote as a preservative, 24 units use artificial oils and the rest use different water soluble inorganic salts approved by the Nordic Council for Wood Preservation, based on arsenic, copper, chromium and zinc (Table 1).

The use of CCA and other As-based chemicals as wood preservatives in Sweden have caused widespread metal contamination in soils around the wood preservation sites due to raw material handling, spills, deposition of sludge and dripping from freshly impregnated wood or due to leaching from the piles of impregnated wood at these sites by rain water especially under low pH conditions (Lund and Fobian, 1991; Warner and Solomon, 1990; Andersen et al., 1996; Bhattacharya et al., 1996). Mechanisms of retention and mobility of metals in soils have been studied extensively by many authors (Adriano, 1986; Kabata-Pendias and Pendias, 2001), but studies pertaining to the behaviour of complex mixes of metal contaminants (As,

Cu, Cr, and Zn) in CCA contaminated soils under field conditions are few (Lund and Fobian, 1991; Bhattacharya et al., 1996; Stilwell and Gorny, 1997).

The site of a former wood preservation facility at Konsterud in Kristinehamn Community in central Sweden (Fig. 1) was selected as an object for the present investigations on metal contamination in the soils, where BIS-salt and CCA had been used extensively. Following the detection of As in an adjacent drinking water well, remediation of the site was considered by the local community. Hence, the purpose of this study was two-fold: (a) to ascertain the extent of metal contamination (As, Cu, Cr, and Zn) in the soil in the area; and (b) to develop techniques for the removal of contaminant metals in the vicinity of the impregnation facility.

2. CCA metals in soil environment and their removal

2.1. Chemistry of CCA metals in soils

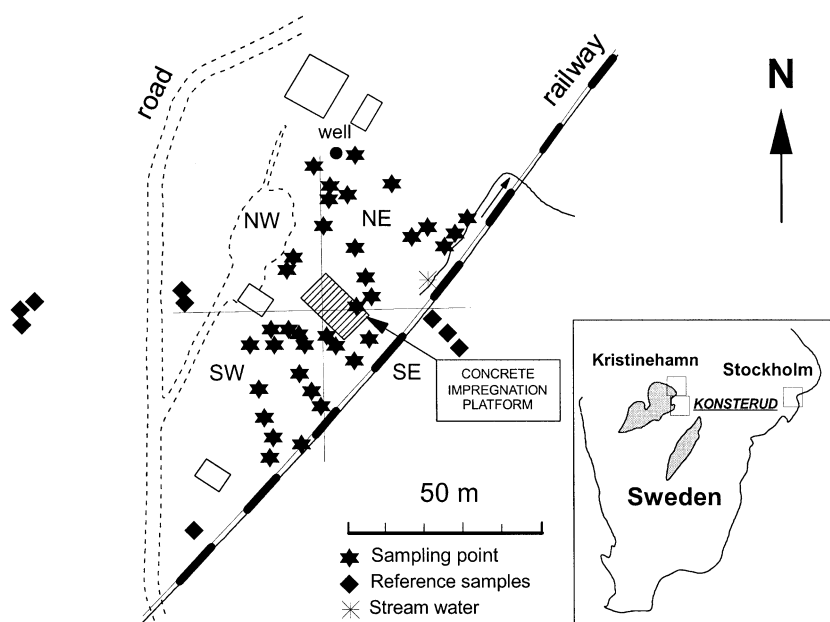The chemicals such as the mixture of Boliden (BIS) and zinc sulfate and CCA used for industrial

Fig. 1. Location map of the site of wood preservation at Konsterud, Kristinehamn Community, central Sweden along with the sampling plan.

wood preservation have contributed the toxic elements such as As, Cu, Cr and Zn in the soils environment. Bioavailability of these metals in contaminated soils may vary according to pH, redox conditions and the quantity of organic matter in the soils, and due to changes in the land use pattern. The mobility of the metals are generally controlled by precipitation, diffusion, volatilization and dissolution of unstable minerals (Kabata-Pendias and Pendias, 2001), besides other surface complexation processes. The sorption of anionic contaminants such as As differs significantly from those of cationic contaminants Cu, Cr and Zn depending on soil pH and redox conditions (Eh). The fate of CCA contaminants thus varies widely in soil environments.

Arsenic is widely distributed in soils and with average concentrations in the range of 1–40 mg kg^{-1}, with a mean value of approximately 5 mg kg^{-1} (Eckel and Langley, 1988; Yan Chu, 1994). In Swedish tills, (<0.06 mm), the As content ranges between <5 and 175 mg kg^{-1} with a median value of 8 mg kg^{-1} (Geological Survey of Sweden, personal communication, 1999). The background As concentration in soils is controlled by the lithology of the parent rocks (Yan Chu, 1994) and it is important to assess this in a given area prior to remediation. In view of the potential risk of bioaccumulation and toxicity of As (Bhumbla and Keefer, 1994; Bhattacharya et al., 1997, 2001), the geochemical behaviour of As in nature has generated much concern in environmental research in recent years.

Under the range of Eh and pH in soil compartments, As normally occurs in +III and +V oxidation states (Cullen and Reimer, 1989). As(III), $H_3AsO_3^0$ or $H_2AsO_3^-$ dominates under reducing conditions (pe+pH<8) which is more toxic and more mobile as compared to the As(V), $H_2AsO_4^-$ or $HAsO_4^{2-}$ forms, which are prevalent under oxidising conditions (pe+pH>8) (Sadiq et al., 1983; Masscheleyn et al., 1991).

An increased As content has been noted with increasing clay content of the contaminated soils (Galba and Polacek, 1973). Preferential sorption of As(V) on clay minerals like kaolinite, illite and montmorillonite occurs at pH 2–<8, while As(III) sorbs preferentially at pH 8–10 (Manning and Goldberg, 1997). The geochemical behaviour of As(V) and P are strikingly similar and are
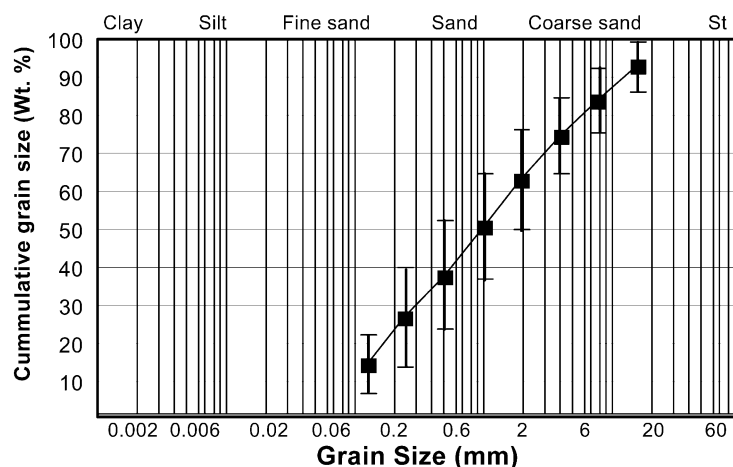
Fig. 2. Average grain size distribution in the contaminated soils from Konsterud ($n = 36$). The bars indicate the range of variation in the respective grain size fractions.

adsorbed on the oxides of Al, Fe and, under specific circumstances, even with Mn (Manning and Goldberg, 1996). Imogolite-type materials (ITM) and ferrihydrite occurring in the podzolic B-horizon are characterised by a large surface area and high positive surface charge in an acidic environment and account for the sorption of the bulk of As(V) (Gustafsson et al., 1995).

The solubility of Cu and Zn is governed by the pH and redox conditions and in the pH range of 5.4–6.5, Cu and Zn are distinctly more soluble under oxidising conditions than reducing conditions (Hermann and Neumann-Mahlkau, 1985). Cu is complexed by the organic ligands, especially by the carboxylic and phenolic groups (Tipping, 1993). As the solubility of organic matter increases with increasing pH, the dissociation of Cu–organic matter complexes can result in the leaching of Cu to groundwater. On the other hand, in the soil environments, Cr occurs in oxidation states Cr(III) and Cr(VI), which govern its mobility and toxicity (Bartlett and James, 1979). In Cr(III)-dominated systems, the prevalent species is $CrOH^{2+}$ at pH 2–6, $Cr(OH)_3^0$ at pH 6.5–11.5 and $Cr(OH)_4^-$ at pH > 11.5 (Sass and Rai, 1987). In the presence of Fe(III) in geological environments, the solubility of Cr(III) is ubiquitously controlled by the solid solution $(Cr,Fe)(OH)_3$ (Sass and Rai, 1987).

The adsorption of Cr(VI) increases with decreasing pH due to the protonation of surface hydroxyl groups on mineral solids (Rai et al., 1989), including the imogolite type materials (ITM) in the podzolic B-horizon (Lindberg et al., 1997).

2.2. Principles of remediation of contaminated soils

Soil remediation techniques depend on the concentration and physical state of the contaminants, the type of soil, grain size distribution, and content of organic matter. In recent years, traditional cleaning techniques, such as molecular and phase separation, chemical destruction, vapour extraction, electrokinetics and biodegradation are often practised (Saxen et al., 1999). All these techniques can be successfully applied if the physicochemical properties of pollutants and soil particles are well understood before selecting any methods (Rulkens et al., 1998; Adriano et al., 1998). However, mobilisation of the metals from the contaminated soils by soil-washing using suitable extractants has been envisaged as one of the potential methods for soil remediation (Bourg, 1983; Tessier et al., 1985).

Metals are mobilised through acidification, and the effects of pH on metal solubility have been

demonstrated by several investigations throughout the world (e.g. Smal, 1994; Bhattacharya et al., 1996; Kedziorek and Bourg, 1996). Geochemical processes that control solubility and the subsequent removal of heavy metals from the contaminated soils during chemical remediation could be attributed to desorption from the surface-reactive soil components, dissolution of the unstable mineral phases (i.e. carbonates and other metal-oxides) and the formation of soluble metal-complexes. Finer grain size fractions possess a greater surface area, and thereby adsorb the bulk of the heavy metals onto their surfaces. Since the fine grained fraction comprises, to a major extent, clay minerals, non-crystalline aluminosilicate phases (ITM) and amorphous Fe-oxides and hydroxides, it sorbs the anionic contaminants such as AsO_4^{2-} and AsO_3^{2-} as a function of pH (Gustafsson et al., 1995; Bhattacharya et al., 1996). In a similar way, the organic ligands also have the capacity to bind other cationic metal species. Moreover, the higher incidences of metals in the fine-grained fractions also reduce the volume of contaminated soils during remediation. In recent years, the soil washing technique has been successfully applied to remove heavy metals (such as Pb, Cd, Cr, Cu, Ni and Hg) from contaminated soils in the western world where the generation of hazardous wastes have been avoided (Fristad, 1995).

3. Material and methods

3.1. Field characteristics

The impregnation industry (area 5000 m^2) was established in approximately 1940 and was in operation until 1968. The facility was later destroyed by fire in 1974. The only remnant of the industry is a concrete platform on which the preservative chemical tank was placed. The area is presently fringed by forest to the north, a service road towards south and a meadow towards the south-east, separated from the contaminated area by an old railway embankment. The land is presently owned privately and used for residential purposes.

Podzolic sandy soil profiles with thin organic horizons are developed up to a depth of approximately 0.5–1.0 m, underlain by silty-clayey till and sediments resting on the basement rocks up to depths of 1–3 m. A thick grey clay layer at the bottom was exposed as a consequence of the removal of the concrete platform. The area has been repeatedly excavated which has caused considerable mixing of the contaminated soils. The pits in the area had been filled by organic materials, mainly wooden chips and saw dust. The groundwater levels in the observation wells indicate an eastward flow direction. A surface stream emerges east of the concrete platform with a north-easterly flow direction (Fig. 1).

3.2. Field investigations and sampling

In order to estimate and delineate the metal contamination in the area, 67 soil samples were collected in a 10-m^2 grid pattern from 38 points from the site (Fig. 1) during August, 1995. Sample representation from individual grids varied considerably due to hinders in the form of large boulders, roads and locally built cottages as well as other disturbances such as pre-excavations in certain parts. In general, 2–3 samples were taken from all possible undisturbed grids in the area. The soils were mainly collected by a sharp-edged auger from the top soil layer (0–0.1 m). Hand auger was used for the sampling of soil profiles at depths of 0.2–0.4, 0.4–0.5 and 1.7 m.

The area has been grouped into four sectors, in relation to the concrete impregnation platform (see Fig. 1) and site characteristics. The soils were relatively undisturbed towards the south-west, while the area towards east and south-east was highly disturbed due to excavations. The area towards north-east was filled with wooden chips and saw mill dust (WCH) with a maximum depth of approximately 1.7 m. Reference soil samples were collected from a meadow towards the south-east as well as from a few selected points away from the contaminated area to the west and south-west. The sediment samples (SST) were collected from a stream adjoining the railway embankment at the south-eastern end of the area. The water

sample collected from the stream was filtered through a 0.45-μm Sartorius online filter and acidified with 0.5 ml of concentrated HNO_3 for analysis.

3.3. Laboratory investigations

The laboratory investigations included the determination of soil moisture content, texture, loss on ignition (LOI) and soil chemical parameters such as pH and Eh. Soil pH was measured in a slurry with 1:2.5 soil/solution ratio, following the guidelines of the Nordic Council of Ministers (1988) using a Radiometer Copenhagen combination electrode (pHC2401-7). The soil redox potential (Eh) was measured using a platinum electrode (M241Pt) and a calomel reference electrode (REF401) submerged in the soil slurry in a enclosed cell on a Radiometer Copenhagen PHM 80 instrument. The pH and Eh values were noted after stabilisation of the electrodes. In general, a minimum of 15–20 min was allowed for the stabilisation of the Eh readings. At 20 °C and in saturated KCl, the standard potential of the calomel electrode was +244 mV (Appelo and Postma 1993) which was subtracted from the measured Eh values.

The analytical work involved determination of As, Cu, Cr and Zn in the <2-mm and <0.125-mm grain size fractions of the soils extractable by 7 M HNO_3 (referred hereafter as total metals). Two grams of contaminated soil samples were digested with 15 ml 7 M HNO_3 for 2.5 h on a temperature controlled sandbath at 70 °C for the first 30 min, and later at 100 °C for the next 2 h. After cooling, the samples were filtered through OOK filter paper and made to a volume of 50 ml (Andersson et al., 1991).

Sequential leaching batch experiments devised for soil washing were carried out using oxalic acid (OXA) with 0.4, 0.5 and 0.7 M concentrations and ammonium oxalate (AMOX) solution buffered with oxalic acid at pH 1.4, 2.5 and 4.0 with the objective of quantifying the removal of As, Cu, Cr and Zn from the contaminated soils. Oxalate was considered a suitable extracting agent for chemical remediation of the contaminated soils, because: (i) it forms a complex with positively charged heavy metals and is a strong reducing/

chelating agent for Fe- and Al-oxides and hydroxides (Tamm, 1932); and (ii) it is biodegradable and occurs naturally in soils (Fox and Comerford, 1990).

Fine grained fraction (<0.125 mm) of the mineral soil samples, Kc-32 (pH 5.6) and Kc-45 (pH 4.9) were tested for metal leaching. Five grams of air dried contaminated soil samples were extracted with the different solutions (1:50; solid/solution ratio) following horizontal shaking for a period of 5 min and filtered through OOK filter paper and the filtrate was further filtered using 0.45 μm online filters for analysis. The residual batches from the first leaching were further extracted twice and the filtrates were analysed for the metal contents. A Jobin Yvon (JY 24) sequential inductively coupled plasma (ICP) spectrophotometer was used for the analyses of metals in soil extracts and the water samples and the precision of analyses was ± 1 mg kg^{-1} for the analysed metals.

4. Analytical results

4.1. Grain size distribution and LOI

Average grain size distribution based on 36 analyses of the soils from the contaminated site at Konsterud (Fig. 2) indicates that the fraction <2 mm comprises 65% by weight. The fine grained fraction (<0.125 mm) constitutes on an average 10%. The content of organic matter was estimated by LOI and varied between 9 and 13%. The stream sediment, however, indicated high content of organic matter with LOI as high as 23%.

4.2. Soil chemical parameters

4.2.1. pH and redox potential (Eh)

The $pH(H_2O)$ ranges from 4.55 to 7.25 (av. 5.67 ± 1.08) in the mineral soils, indicating generally acidic conditions in the contaminated area (Table 2). The acidic character of the mineral soils is more pronounced in the north-eastern sector where pH values are the lowest. The organic fills (wooden chip) in this sector also indicated low pH in the range of 4.34–5.07 with an average of 4.71 ± 0.37. The pH of the reference soils (av.

Table 2

pH, redox potential (Eh in mV) and concentrations of As_{tot}, Zn_{tot}, Cu_{tot} and Cr_{tot} (mg kg^{-1}) in the average contaminated mineral soils, organic fills, stream sediments and reference soils from the wood preservation site at Konsterud, Central Sweden

Parameter	< 2 mm[a]	< 0.125 mm[a]
Average contaminated mineral soils ($n=54$)		
pH (H$_2$O)	4.55–7.25 (5.67, 5.49)	
Eh	$-134-+18$ (-61, -64)	
As_{tot}	10–1067 (186, 121)	45–1627 (282, 224)
Zn_{tot}	6-388 (91, 64)	9–724 (149, 112)
Cr_{tot}	3–153 (29, 18)	6–233 (51, 33)
Cu_{tot}	10–74 (26, 21)	12–289 (56, 43)
Organic fills (*wooden chips*) ($n=6$)[b]		
pH (H$_2$O)	4.34–5.07 (4.71, 4.73)	
Eh	$-70.5--18.7$ (-50.1, -61)	
As_{tot}	98–465 (237, 190)	255
Zn_{tot}	37–245 (125, 99)	112
Cr_{tot}	25–148 (83, 80)	89
Cu_{tot}	6–88 (42, 41)	106
Average stream sediments ($n=3$)		
pH (H$_2$O)	5.51–5.91 (5.67, 5.58)	
Eh	$-96.6--60.3$ (-73, -61)	
As_{tot}	103–1681 (632, 111)	3380–4460 (3972, 4077)
Zn_{tot}	179–6369 (2393, 631)	594–8158 (3330, 1239)
Cr_{tot}	23–2647 (1335, 1335)	34–5632 (2670, 2343)
Cu_{tot}	139–1772 (1092, 1366)	653–1881 (1465, 1862)
Average reference soils ($n=13$)		
pH (H$_2$O)	4.94–5.64 (5.23, 5,18)	
Eh	$-95.9--73.7$ (-85, -86)	
As_{tot}	34-260 (119, 109)	45–311 (185, 190)
Zn_{tot}	6–190 (59, 45)	9–208 (89, 71)
Cr_{tot}	4–37 (13, 7)	6–61 (22, 16)
Cu_{tot}	10–47 (25, 24)	14–86 (42, 38)

[a] Values given in parentheses: mean, median.
[b] $n=1$ for the analysed fraction < 0.125 mm.

5.23 ± 0.3) further supports the acidic character of the soils in the area.

The measured redox potential (Eh) of the contaminated soils varied between $+18$ and -134 mV with an average value of -61 mV (Table 2). The Eh–pH diagram presented in Fig. 3 depicts the stability fields of different inorganic contaminant metal species of As, Cu, Cr and Zn commonly occurring in the soil environment. The redox potential in the soil suspension suggests arsenic to be present in the reduced As(III) form (Fig. 3a) under the prevailing Eh-pH conditions in the soils at the contaminated site. Under the prevailing redox conditions in these soils Cu may be present in the reduced form, while Zn as Zn^{2+} species (Fig. 3b,d). A similar Eh–pH diagram for the different oxidation phases of Cr indicates the dominance of the trivalent state as $CrOH^{2+}$ or as uncharged $Cr(OH)_3^0$ species which is known to control the solubility of Cr under surface conditions (Fig. 3c).

4.2.2. Metal contaminants in the soils

The contaminant metals are found in the following order of abundance in the soils: $As > Zn > Cr > Cu$ (Table 2). The mean and median concentration of metals in the contaminated mineral soils, organic fills, stream sediments and the
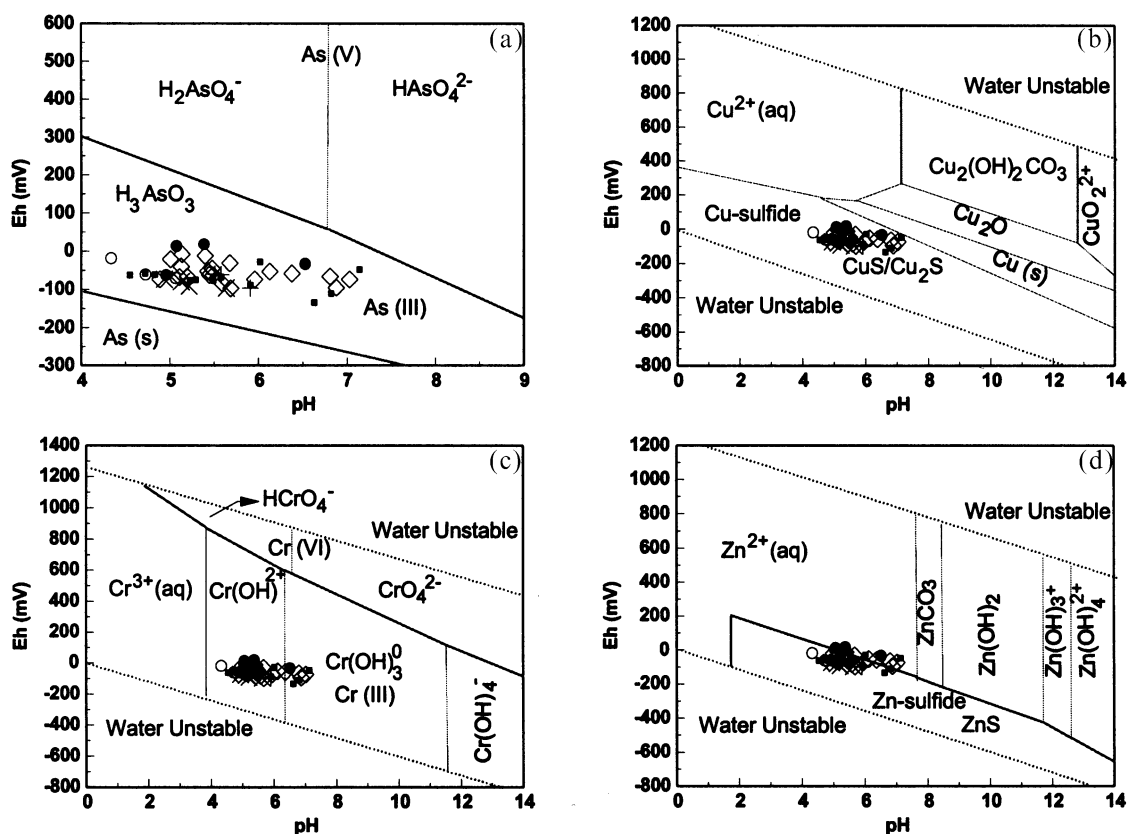
Fig. 3. Eh–pH diagram showing the stability fields (at 25 °C and 1 atm total pressure) for the different contaminant metal species occurring at the site of wood preservation. (a) As–H_2O–O_2 system, activity of As taken as 10^{-4} mol l^{-1} (after Masscheleyn et al., 1991); (b) Cu–H_2O–O_2–S–CO_2 system, $P_{CO_2} = 10^{-1}$ (after Garrels and Christ, 1965); (c) Cr–H_2O–O_2 system (after Rai et al., 1989); and (d) Zn–CO_2–S–H_2O system, activity of Zn taken as 10^{-5} mol l^{-1}, dissolved CO_2 and S species, 10^{-3} mol l^{-1} (from Hermann and Neumann-Mahlkau, 1985). Symbols: ■ NE sector (mineral soil); ○ NE sector (organic soil); ● SE sector; ◇ SW sector; × stream sediments; + reference soils.

reference soils in the two grain size <2 mm and <0.125 mm fractions are presented in Table 2. The fine grained (<0.125 mm) fraction, in general, reveals a higher metal concentration as compared to the coarser (<2 mm) fraction of the soils.

The mineral soils of the contaminated site revealed high concentration of total arsenic (As_{tot}) varying between 10 mg kg^{-1} and as high as 1067 mg kg^{-1} as compared to the total zinc ($Zn_{tot} = 6$–388 mg kg^{-1}), chromium ($Cr_{tot} = 3$–153 mg kg^{-1}) and copper ($Cu_{tot} = 10$–74 mg kg^{-1}). Such variations in the metal concentrations were also

reflected in the fine-grained (<0.125 mm) fractions of the soils where the metal concentrations were higher than the corresponding <2 mm fractions (Table 2).

A comparison between the mean and the median values for the analysed metals indicates considerable consistency in the nature of metal distribution in the area (Table 2). Analysis of WCH in the NE sector revealed higher As_{tot} and Cr_{tot} concentrations which is related to the retention of these metals in the treated wood. Analyses of the SST adjacent to the cemented platform with a high content of organic matter indicated accumulation

of the metals due to the formation of metal–organic complexes. The dissolved concentration of metal species of As, Zn and Cu in the stream water were quite appreciable and their respective concentrations were 238, 243, and 228 μg l^{-1}. The Cr concentration was, however, negligible ($<$ 10 μg l^{-1}).

4.2.3. Geochemical variations along two selected soil profiles

Variations in pH, Eh and metal abundances in the two grain size fractions in two selected soil profiles from the contaminated site are presented in Fig. 4. Variations in the pH were not conspicuous in the selected soil profiles but the measured redox potential (Eh) was more reducing in the NE sector as compared to the undisturbed soil profile at the SW sector (Fig. 4a,b). A decrease in the concentration of the analysed metals As, Cu, Cr and Zn was observed up to a depth of 30 cm. The metal contents increased in the Bs horizon at depths of 40–50 cm, because of the greater adsorption capacity of the spodic horizons in these soil profiles (see Section 5). The metal contents however, decreased at further depths.

4.2.4. Reference soil normalised plot

In order to assess the extent of metal contamination in the area, the average metal contents in both the soil fractions have been normalised to the reference soils and plotted on variation diagrams (Fig. 5a,b). Reference soils were collected from locations outside the compounds of the preservation site both towards west as well as the east of the railway track (Fig. 1). The mean As$_{tot}$ concentration (119 mg kg^{-1}) in the reference samples collected from several locations adjacent to the contaminated area was lower than the average mineral soil at the wood preservation site, but exceeded the level of As in average glacial till (Koljonen, 1992). The Zn$_{tot}$ content in the reference soils (59 mg kg^{-1}) was close to background level (Edén and Björklund, 1995), while Cu$_{tot}$ (25 mg kg^{-1}) and Cr$_{tot}$ (13 mg kg^{-1}) in the reference soils were comparable to the contaminated area as well as the analysed glacial tills (Geological Survey of Sweden, personal communication, 1999).

The reason for this is not clear, but aerosols from the process might have contributed in spreading the metal contaminants outside the industrial compound. Such aerosols may have been released while the pressure vessels were opened (ASS, 1989). Storage of the treated wood products as well as handling of the wastes like sawdust might also contribute to the metal contamination in the surroundings. Chromium in the preservative chemicals is generally reduced from Cr(VI) to Cr(III) in the presence of aromatic rings and carbonyl groups in lignin structures (Ostmeyer et al., 1988, 1989) and forms insoluble complexes leading to the fixation of As, Cu as well as Cr(VI) in the wood (Ryberg and Haugen, 1992). Moreover, As, Cu and Cr may leach in significant quantities prior to their complete fixation in the freshly impregnated wood.

Metal enrichment for the average contaminated soils at the site, however, follows the order Cr $>$ As $=$ Zn $>$ Cu. Both arsenic and zinc indicate similar enrichment factors in both the grain size fractions of the contaminated soils at the various sectors of the contaminated area. The wooden chip fills mixed with saw dust (WCH) in the area are possibly the remnants of the process wastes, and therefore, a high chromium content is ubiquitous. A significant metal enrichment could also be noted in the organic-rich bottom sediments of the stream (SST) which possibly serve as an effluent from the process platform.

4.3. Laboratory scale metal removal

4.3.1. Sequential leaching batch experiments

The sequential leaching batch studies on a laboratory scale indicated that the amount of leached metals As, Cu, Cr and Zn varied considerably with the concentration of OXA and pH of buffered AMOX solution. In general, the bulk of the contaminant metals were released during the first step of leaching and decreased in the following leachates. The extraction of metals also differed between the two selected soil samples having different pH values. The amount of the contaminant metals
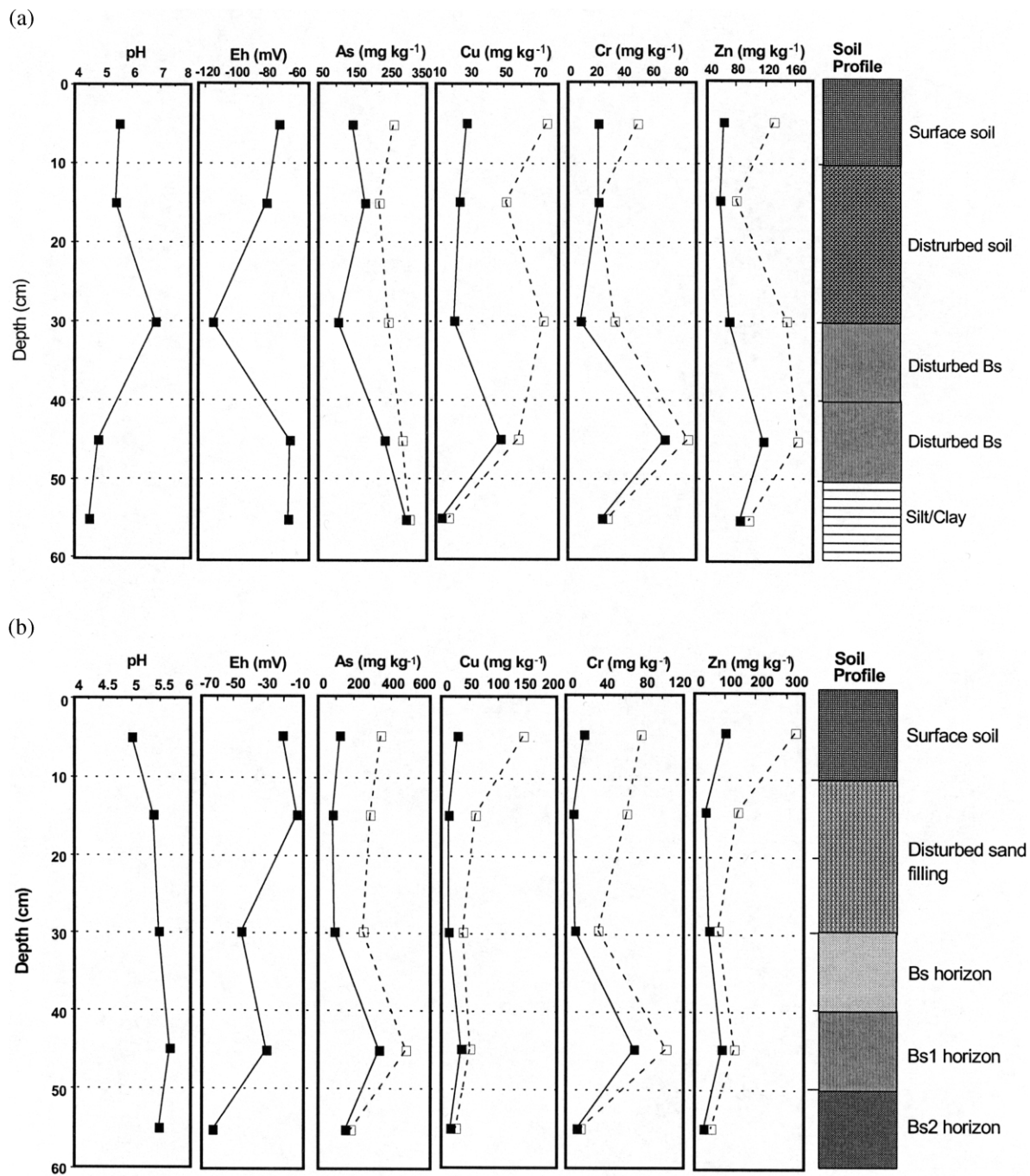
Fig. 4. Variation of pH and redox (Eh) along with the concentration of As, Cu, Cr and Zn (mg kg^{-1}) in <2 mm (■ solid line) and <0.125 mm (□ dashed line) at two selected soil profiles at (a) NE sector and (b) SW sector of the wood preservation site.
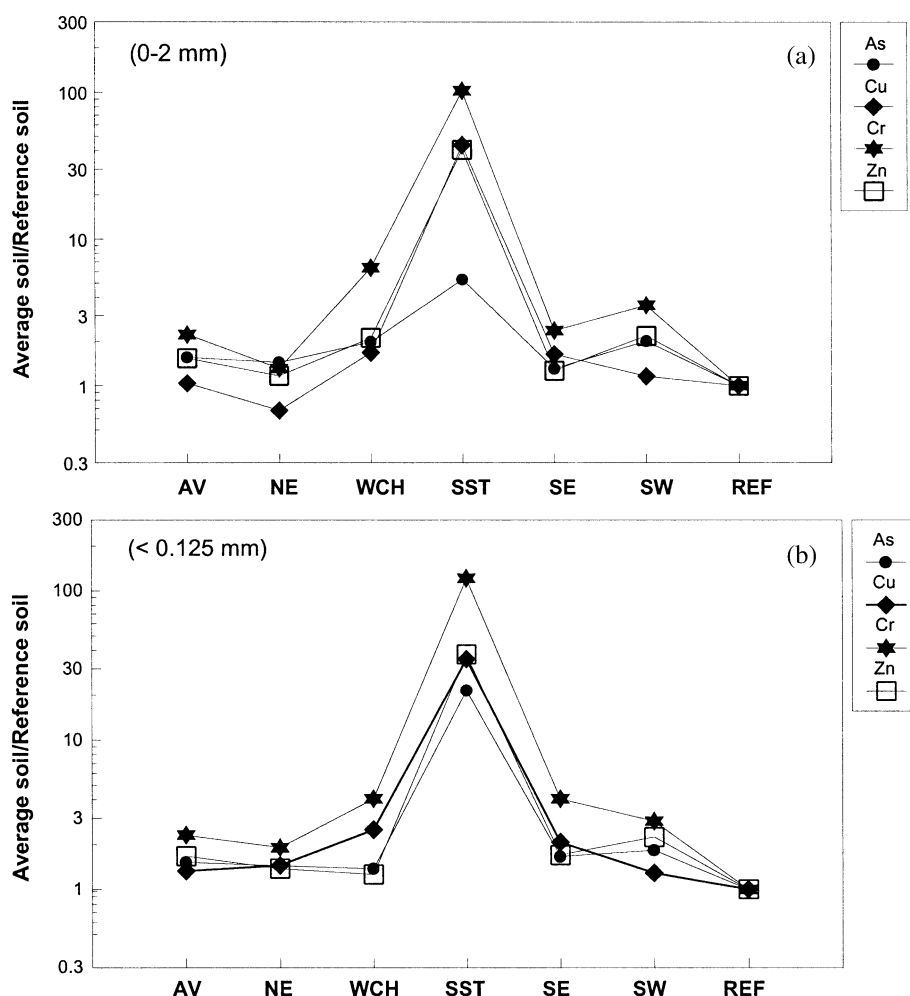
Fig. 5. Reference soil normalised plot of As_{tot}, Zn_{tot}, Cu_{tot} and Cr_{tot} concentration in (a) <2 mm and (b) <0.125 mm grain size fraction for the contaminated soil samples from the wood preservation site.

retained in the two soils after successive leaching stages are depicted in Fig. 6(a–d) and Fig. 7(a–d).

4.3.2. Quantification of effective removal of metal contaminants

Sequential leaching of the sample Kc-32 by OXA and AMOX buffered extracts indicated an effective removal of 93–99% of As (Fig. 6a). Nearly 69–78% of the As was soluble from the sample Kc-45 by OXA, while the solubility decreased further with increasing pH of AMOX for both the contaminated soil samples (Fig. 6a and Fig. 7a). A significant correlation was noted

between the amount of leached arsenic with pH of the oxalate medium during the batch experiments.

An effective removal of approximately 56–67% of Cu and Zn was achieved following the sequential leaching of Kc-32 in OXA and AMOX extraction media (Fig. 6b,d). Nearly 78–81% Cu and 62–66% Zn were leached from the reference soil Kc-45 following OXA extraction (Fig. 7b,d). The removal of Cr from Kc-32 was rather low (approx. 38–44%) in all the batch tests. An increased solubility of Cr was, however, shown by AMOX buffered at pH 1.4 and 2.5 (Fig. 6c). Nearly 98% of Cr was removed by 0.7 M OXA from the reference soil Kc-45 and the solubility decreased
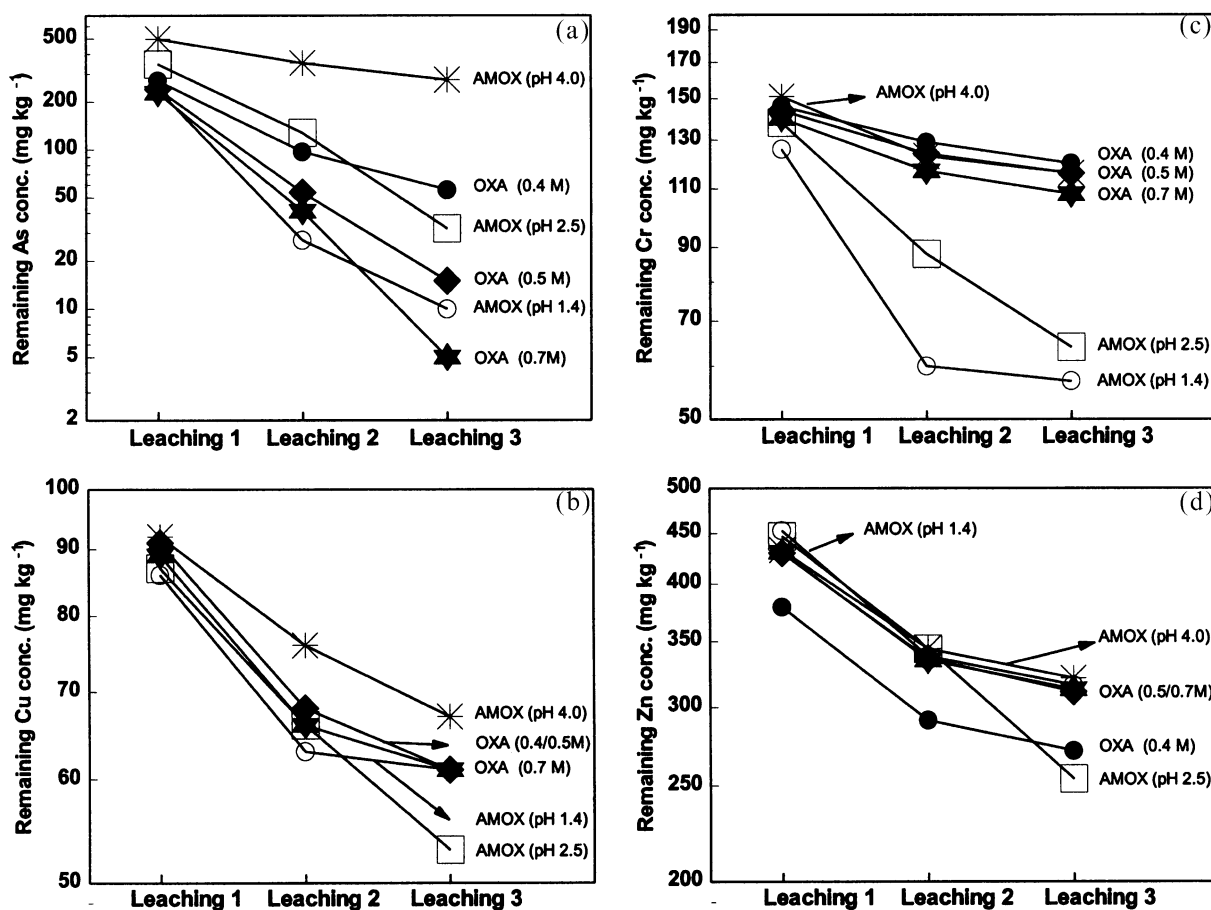
Fig. 6. Remaining metal concentrations in the <0.125-mm fraction of the Kc-32 soil sample, pH=4.9 after remediation. (a) As ($As_{tot}=261$ mg kg^{-1}); (b) Cu ($Cu_{tot}=157$ mg kg^{-1}); (c) Cr ($Cr_{tot}=193$ mg kg^{-1}); and (d) Zn ($Zn_{tot}=724$ mg kg^{-1}). Note logarithmic scale in the *y*-axis.

gradually through 87% to 72% with decreasing OXA concentrations (Fig. 6c and Fig. 7c).

4.3.3. Mechanisms of metal removal

The bulk of As in the soils was oxalate-extractable and related quantitatively to the oxalate-extractable fractions of Fe, Al and Si in the contaminated soils (Fig. 8). Arsenic solubility was found to be maximum at pH 0.9–1.4. A reducing agent such as oxalate, releases the oxyanionic inorganic As(V) adsorbed on the poorly ordered and non-crystalline secondary hydrous oxides of Fe and Al as well as the ITM materials common in these podsolic soils (Gustafsson et al., 1995). The presence of ITM in these soils has been confirmed by IR spectroscopic studies as well as the ratio of inorganic-Al to Si between 2.4 and 2.6 (Bhattacharya et al., 1996). The removal of Cu is related to the formation of Cu–oxalate complexes and related to association of Cu with the organic matter in the soils (Fig. 6b, Fig. 7b). Trivalent Cr coexisting with the Fe-oxyhydroxides in these soils may also be released due to reductive dissolution at low pH (Sass and Rai, 1987; see Fig. 3). Zn is often adsorbed to the surface reactive sites of Fe-oxyhydroxides (Kinniburgh and Jackson, 1982;
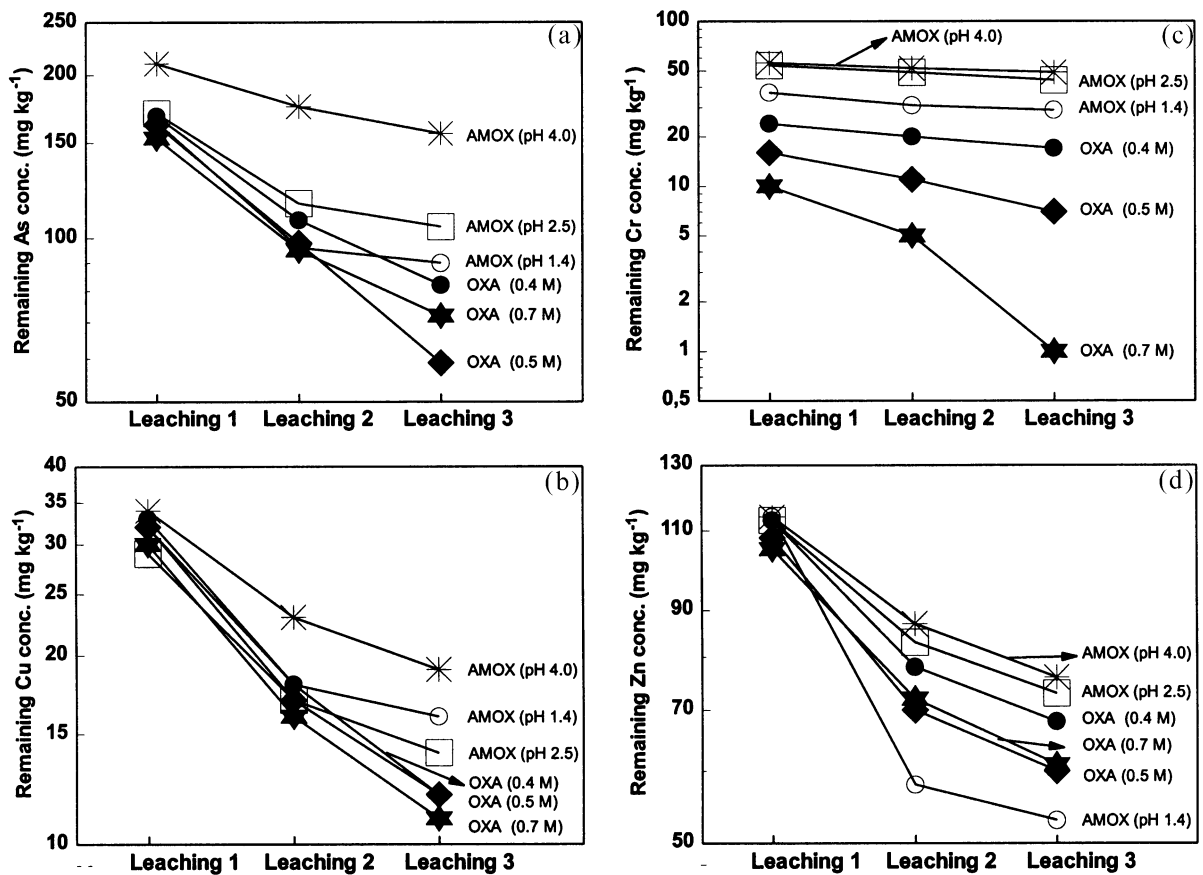
Fig. 7. Remaining metal concentrations in the <0.125-mm fraction of the Kc-45 soil sample, pH=4.9 after remediation. (a) As (As_{tot}=261 mg kg^{-1}); (b) Cu (Cu_{tot}=59 mg kg^{-1}); (c) Cr (Cr_{tot}=61 mg kg^{-1}); and (d) Zn (Zn_{tot}=177 mg kg^{-1}).

Sadiq, 1991) and may get slowly diffused along the hydrated layers of Fe-oxides leading to the formation of franklinite ($ZnFe_2O_4$).

5. Discussion and conclusions

5.1. Mobility and retention of contaminant metals

The analytical results reveal a large spread of the contaminant metals in the surface soils. The highest concentrations of the contaminant metals were found in the vicinity of the platform on which the chemical treatment was carried out. The distribution of the metals in the soil profiles (Fig. 4) were related to the pH and the redox conditions

of the soil horizons. Concentrations of the contaminant metals were accentuated in the Bs horizons (approx. 40–50 cm). In both the soil profiles, an increase in pH and concomitant decrease in soil Eh resulted in the mobilisation of As to a greater depth (see Fig. 4a,b). The trivalent As-species was the most mobile and sensitive to the changes in redox conditions. Within the redox interval 0 to −100 mV, inorganic As(V) species were adsorbed onto the surface of the amorphous and poorly crystalline Fe- and Al-phases at approximately pH 4.5–5 (Fig. 4a), and therefore, remain immobile (Guo et al., 1997). They can be readily mobilised due to desorption as well as reductive dissolution of the adsorbent phases due to the changes in soil
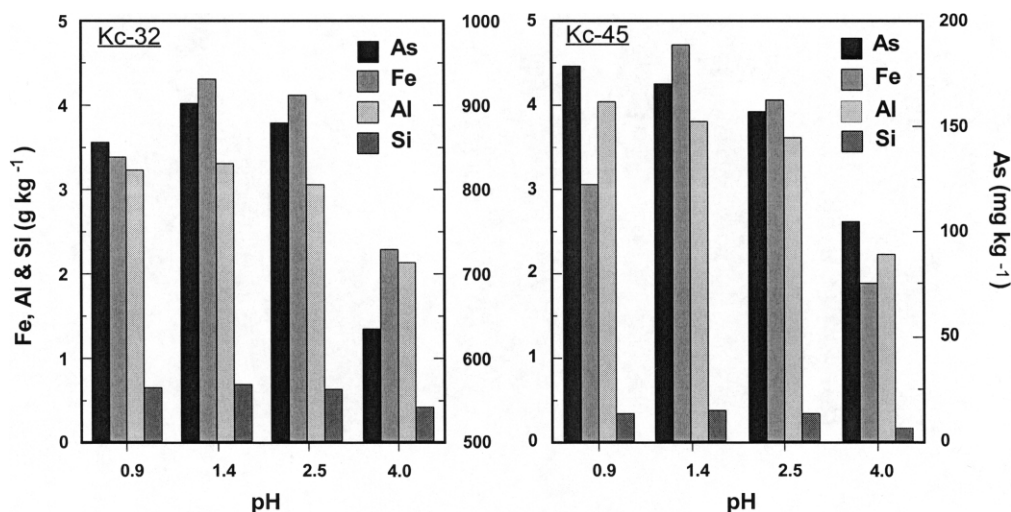
Fig. 8. Relationship between the oxalate leachable fractions of As, Fe, Al and Si in the contaminated soils with varying pH. Note separate scale for the As concentrations (see text for details).

redox and pH. It is, therefore, important to note that the As can be readily mobilised under reducing conditions within the Konsterud soils.

On the other hand, the acidic character of the soils has favoured the mobilisation of Cu, Cr and Zn which is manifested by their low abundance in the soils and consequent enrichment of these metals in the organic-rich stream sediments. The presence of contaminant metals As, Cu, Cr and Zn in the stream sediments further indicates their mobilisation from the soils from the contaminated area.

5.2. Effective remediation technique

According to the guidelines set up by the Swedish Environmental Protection Board (Naturvårdverket, 1997) and Swedish Institute for Environmental Medicine (Viktorin et al., 1990), soils at the industry-contaminated sites with metal contents above 15 mg kg^{-1} As, 100 mg kg^{-1} Cu, 120 mg kg^{-1} Cr(III), 5 mg kg^{-1} Cr(VI) and 400 mg kg^{-1} Zn need remediation for sensitive land use. The soil chemical data clearly indicates that the site of the former wood preservation facility is contaminated by As with concentrations nearly four-fold of the guideline values, while the concentrations of Zn, Cu and Cr were much lower.

The present study reveals that the selection of the fine fraction of the soils (i.e. <0.125 mm) is appropriate to handle the contaminated mass for remediation. Laboratory scale experiments using sequential leaching technique have revealed that as much as 98–99% of the principal contaminant As could be extracted from the soils by leaching with oxalic acid which is biodegradable. Leaching of As and other metals from the contaminated soils increased consistently with decrease in the pH of the extraction medium ($R^2 = 0.70$–0.95). The metals in the leachate could subsequently be separated using different ion exchange media or lime precipitation at a suitable pH favouring adsorption of both As and other cationic metal species.

6. Acronyms and abbreviations

AMOX	Ammonium oxalate
BIS-salt	Boliden-salt
CCA	Chromated copper arsenate
Eh	Redox potential
ICP	Inductively coupled plasma
ITM	Imogolite-type material
LOI	Loss on ignition
OXA	Oxalic acid
PCP	Pentachlorophenol
SST	Stream sediments
WCH	Wooden chips mixed with saw mill dust

Acknowledgments

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