

# METAL SPECIATION IN SOIL AT A CONTAMINATED GLASSWORKS SITE IN SOUTHEASTERN SWEDEN

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## ABSTRACT

Risk assessments of metal contaminated land are often based on total metal concentrations of the soil material, although it is well known that the potential for leaching is determined by the fractionation between labile metal forms and forms that are not to be assessed as geochemically active. In the present study, a 4-step sequential leaching procedure was applied to solid material from five subareas of a glass waste site in southeastern Sweden (including, for example, landfill areas and natural till material). The aim was to assess whether the major fraction of the total Cd and Pb content should be considered labile (easily mobilizable) or relatively stably sorbed, which is a question that is motivated by the fact that previous site-specific investigations have shown strongly elevated metal concentrations in soil, but very little impact on local groundwater. Although the total metal concentrations as well as the amount of visible glass particles differed between the subareas, the fractions extracted in the different steps of the sequential leach were similar for all areas. Only a minor part of the total content of both Cd and Pb was released in the final strong acid residual leach (9-19 %), which indicates that there has been a significant release of metal ions from the glass waste material in the past, followed by a transition to secondary phases. Of the two metals, Cd was assessed to be the most labile one. The first extraction, targeting the exchangeable and carbonate bound fraction, released 43-59 % of the total Cd content. So, although the relatively small effect seen on groundwater quality indicates an effective retention of these metal cations by the soil solid matrix, the relatively high fraction of potentially mobile forms highlights the need of further assessments of the stability in major retention mechanisms.

## KEYWORDS

Metals, cadmium, lead, contaminated sites, speciation, risk

## 1 INTRODUCTION

A critical aspect for assessing risks at contaminated sites is the understanding of how pollutants may be leached and transported from the primary source of pollution to various target objects (humans or natural environments). The higher the mobility of the critical pollutant, the greater is the risk for local residents (the pollutant may, for example, be more easily taken up by home-grown crops and have a higher oral bioavailability), and transport of mobile pollutants may threaten the quality of groundwater resources and downstream water recipients. This study focuses on cadmium (Cd) and lead (Pb) at the glasswork factory of

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Pukeberg, Nybro municipality, southeastern Sweden. This site is among some 1 200 sites in Sweden that have been classified to constitute a “very high risk” (risk class 1) according to the 4-degree scale applied in the Swedish EPA methodology for inventories of contaminated sites [1], thereby being in urgent need of remediation. However, the large number of contaminated sites as well as high remediation costs mean that decision makers have to prioritize when choosing which site is most critical to remediate and the extent of remediation measures. In this context, the need for prompt actions depends partly on whether the pollutants exist in easily leachable forms.

Cadmium and lead are two calcophile elements, for which the solubility/mobility after release from minerals or waste material (glass, for example) varies considerably with site-specific hydrology and geochemical conditions. Under oxidizing conditions, the solubility is controlled mainly by the pH value and availability of organic matter, iron/manganese oxyhydroxides, and clay minerals [2]. Even if there are established reactive transport models that can be used to estimate the metal leaching from the unsaturated zone [eg. 3], these models are associated with large uncertainties, and assessments of metal transport in practical risk assessments often assume that the metal concentration in pore water is in equilibrium with the solid phase and can be approximated by using a generic  $K_d$ -value [4, 5]. The solid phase metal content in these practical risk assessments is by tradition determined as a pseudo-total concentration after extraction with concentrated (or 7 M)  $\text{HNO}_3$  or Aqua Regia. However, the shortcomings of using total concentrations in routine risk assessments at contaminated sites, where metal mobility and bioavailability are crucial factors, are well known. For this reason there is a need to bridge the gap between how scientists and advisory/legislative agencies assess the risks of metal leaching from the unsaturated zone. To obtain a site-specific estimate of the “potentially mobile” fraction (or “labile” or “geochemically active” fraction), a variety of different single extractions have been proposed [eg. 6, 7]. As an alternative that may give additional information on which “sinks” that dominate for metals in the site-specific soil matrix, sequential extractions can be used [eg. 7-10]. These are based on dissolving a specific component and bringing into solution metals associated with the that particular component, but leaving other components and the metals associated with them intact.

### 1.1 Site description

The glasswork factory of Pukeberg is located in Nybro municipality in southeastern Sweden. The production started in 1871, and has since then been carried out with varying intensity in several buildings over the property. The main landfill covers an area of ca 15 000 m<sup>2</sup>, with a maximum depth of ca 2,5 m, and contains different types of glass waste. Previous consultant investigations and analyses of historical aerial photos have also revealed substantial glass waste depositions at other locations, mainly in a forested area just south of the glass factory buildings. Previous analyses of soil material from several sampling sites of the area (N=300) have shown maximum Pb och Cd concentrations of 8800 mg/kg dw and 140 mg/kg dw, respectively, and average concentrations of 220 mg/kg for Pb and 3,9 mg/kg for Cd [11].

These concentrations can be compared to the generic guidelines for contaminated soil in residential areas in Sweden [5], which are 50 mg/kg dw for Pb and 0.5 mg/kg for Cd. Hence, the pollution level of the soil is high. The maximum groundwater concentrations (N=27) measured at the site are however only 5.4 ug/L for Pb and 0.40 ug/L for Cd [11]. These concentrations are well below the drinking water criteria of both the Swedish National Food

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Agency, NFA (which have adopted a value of 10 ug/L for Pb and 5.0 ug/L for Cd; [12]), and of the World health organization (which recommends 10 ug/L for Pb and 3.0 ug/L for Cd; [13]).

## 2 METHOD

Soil samples were taken at 5 subareas of the glassworks site where previous investigations have found elevated metal concentrations [11]. These were:

- A) A spot with deposited glass waste found in the forested area south of the glass factory buildings.
- B) The main glass waste landfill.
- C) An area with natural till soil.
- D) An area of filling material (natural soil mixed with glass, porcelain, gravel etc).
- E) An area where sludge from the glass grinding process has been deposited.

From each subarea, 5 composite samples were taken from the upper 0,4 m, resulting in a total of 25 samples. Standard analyses of pH, water content and organic carbon were performed on the <2mm soil fraction, together with metal concentration analyses following sequential extractions of the same fraction. It is the results from the sequential extractions that are in focus in this paper. All extractions as well as the analyses were performed at Actlabs, Canada. Metal concentrations were determined with ICP-MS.

### *Trace metal sequential extractions*

In this study, the extraction scheme suggested by Hall et al. [8,14].

*The Exchangeable and carbonate bound fraction:* The first extraction uses 1.0 M sodium acetate at 21°C. This extraction brings into solution exchangeable metals that can be replaced by neutral salts (such as, for example, NaOAc). Buffering at pH 5 also dissolves carbonates, resulting in dissolution of metals that have been coprecipitated with these.

*The organic fraction:* The residue from the first leach is leached with 0.1 M sodium pyrophosphate at pH 10 and 21°C. Removing complexed or chelated metals from humic material requires a solution containing anions (for example pyrophosphate) that can form stronger metal chelates or complexes than those with the organic molecules. Performing the extraction at pH 10 minimizes the possible dissolution of iron (Fe) oxides, which may occur at lower pH.

*The fraction associated with Fe/Mn oxyhydroxides:* Residues from the pyrophosphate leach are leached in a 0.25 M hydroxylamine and nitric acid solution at 30°C. This treatment dissolves oxyhydroxides that may carry metals. Iron and manganese (Mn) oxides are the main hydroxides targeted in this step because of their high abundance and adsorption capacity compared to other oxyhydroxides (with, for example, aluminium (Al) and silicon (Si)). With 0.25M hydroxylamine, it is mainly the Mn oxides and amorphous Fe oxides that are dissolved, whereas crystalline Fe oxides require a stronger treatment.

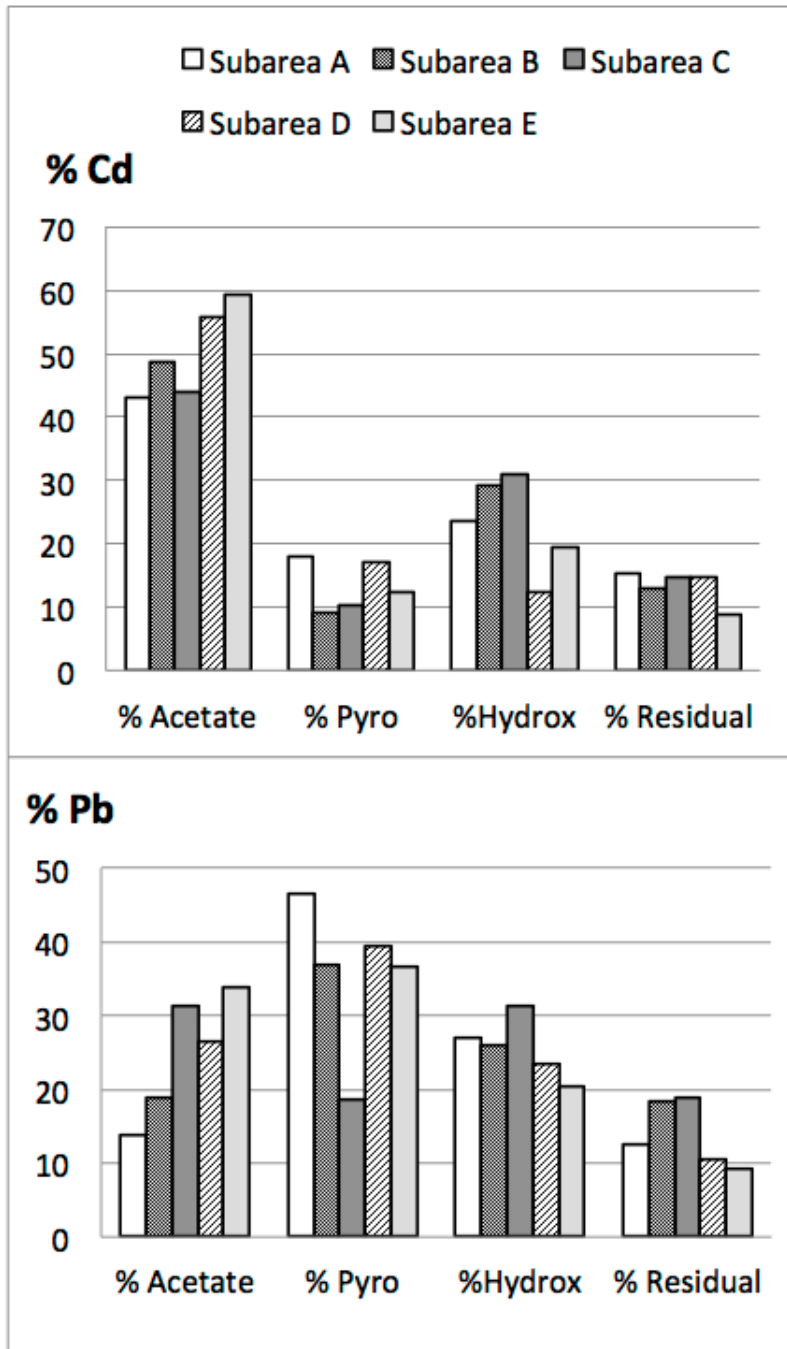
*The residual fraction:* In the final step of the sequence, the residue from the third extraction is leached at 260°C with a strong 4-acid attack (HCl-HF-HClO<sub>4</sub>-HNO<sub>3</sub>), which dissolves most of the minerals that have been left intact during the previous treatments.

### 3 RESULTS AND DISCUSSION

Fig. 1 shows the percentage of Cd and Pb released in the four extraction steps. These figures can be related to the total concentrations, which for Cd was on average 11 mg/kg dw in the five composite samples from subarea A, and the corresponding figures for areas B, C, D and E where 830 mg/kg, 9.6 mg/kg, 6.9 mg/kg and 0.3 mg/kg. Total Pb concentrations were on average 630 mg/kg, 1200 mg/kg, 1400 mg/kg, 290 mg/kg and 130 mg/kg for the same subareas.

Despite different total concentrations at the five subareas, the distribution between the four fractions was similar, which probably reflects a similar soil content of the sorbents attacked in the different extractions. Glass waste is often considered an inert material, although there are few studies that have addressed the leachability of metals from glass waste in natural environments. Had the sequential extractions focused on pure glass particles, one would therefore have assumed the major release of Cd and Pb to have occurred in the final extraction, targeting the residual fraction. However, the <2mm fraction of the upper 40 cm of the sampling spots gave “contaminated soil samples” rather than only “glass waste”, which means that the fractionation per se was determined primarily for secondarily sorbed phases. This can explain why only a small proportion (9-19 %) of the total Cd and Pb content was released in the final extraction. Other studies, which have applied sequential extractions to metal contaminated soils and sediments, have also found a low residual extractability for Cd and Pb [15, 16]. For Pukeberg it is, however, worth mentioning that the residual fraction was of about the same importance at subarea A and B as at the remaining three areas, although the first two represented landfills, and the < 2mm soil samples from these were containing a higher proportion of visible glass particles, while the residual fraction from the other subareas to a somewhat higher degree should have been composed of resistant primary minerals with a significantly lower Cd and Pb content.

That the major release occurred in the first three steps indicates that metals have been released from the primary source (the glass waste) in the past to a significant degree. These results are in accordance with a study of metal leaching from stained glass of different age, where it was found that Pb, as well as many other metals, may be severely leached [17]. Metals released mainly in step two and three of the extraction, such as Pb, are often assessed to be associated with organic complexes or chelates and to a high degree also with amorphous Fe and Mn oxides (Figure 1), although this interpretation indeed comes with some uncertainty as the extractions used are operationally based rather than truly restricted only to certain species. Metals bound to these solid phases are normally characterized by a low solubility, which limits their leachability to groundwater and uptake by plants [18]. A higher labile fraction was indicated for Cd, for which 43-59% were extracted in the first step of the sequence. A decrease in pH or an increase in the ion strength of the solution would have the potential to mobilize these metals. The higher fraction of Cd found in the first extraction compared to Pb is in accordance with the results from others [15, 19], and is explained by the well-known stronger tendency of Pb to be fixed by oxyhydroxide minerals and organic matter [2].



**Figure 1** Distribution of cadmium and lead between the four extractions of the sequential leach.

#### 4 CONCLUSION

Sequential extractions of the fine fraction (<2mm) of soil material from an old glassworks site revealed a relatively high fraction of potentially mobile forms of Cd and Pb in the upper, highly contaminated unsaturated zone, especially for Cd. However, as previous site investigations indicate negligible effects on groundwater quality, it nevertheless appears as if metal cations are efficiently sorbed by the soil solid material. The geochemical processes responsible for this sorption have to be further studied in order to assess the stability of the

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retention; in the short term such information is relevant when remediation options are evaluated, and in a longer time perspective it is relevant for assessing the risk of an increase in mobility following, for example, changes in land use or in climate.

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