Applied Geochemistry 170 (2024) 106063

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Challenges in geochemical modelling of metal(loid) solubility and binding mechanisms along a soil profile at a multi-contaminated site

Terese Uddh-Söderberg [a,*], Anna Augustsson [a], Dan B. Kleja [b,c], Jerker Jarsjö [d], Mats Fröberg [c,1], Mats Åström [a], Jon-Petter Gustafsson [b]

[a] Department of Biology and Environmental Science, Linnaeus University, Kalmar, Sweden
[b] Department of Soil and Environment, Swedish University of Agricultural Sciences, Box 7014, Uppsala, Sweden
[c] Swedish Geotechnical Institute, Olaus Magnus väg 35, Linköping, Sweden
[d] Department of Physical Geography, Stockholm University, Stockholm, Sweden

ARTICLE INFO

Keywords:
Lead
Cadmium
Arsenic
Antimony
pH-dependent solubility
Geochemical modelling

ABSTRACT

Recognising the need for robust models in predicting groundwater contamination risks from metal(loid)s in contaminated topsoil, this study focuses on the geochemical behaviour of As, Cd, Cu, Pb, Sb and Zn in one of Sweden's most heavily contaminated areas. Samples were collected from the waste zone and underlying subsoil down to 5 m and batch experiments were carried out to assess pH-dependent solubility. The results indicate that Cd, Cu, Pb and Zn are efficiently immobilized in the waste zone, while As(V) and Sb(V) are more easily leached. With the exception of Pb and Cu at high pH, the mobilized metals appear to be predominantly in a truly dissolved state, as confirmed by ultrafiltration at 10 kDa.

Speciation modelling using Visual MINTEQ did not suggest a significant role of precipitates such as Zn or Pb arsenates and phosphates, although their involvement could not be ruled out. To better understand sorption/desorption patterns, a multi-surface geochemical model was established, drawing on the Stockholm Humic and CD-MUSIC models for organic matter and Fe/Al (hydr)oxide sorption. However, when default parameters were used, the model consistently overestimated the solubility of Cd, Cu, Pb and Zn in both the waste zone and the uncontaminated subsoil. In contrast, As(V) solubility was generally underestimated, also when the reactive surface area of the Fe- and Al (hydr)oxides was decreased in the model. The model's performance was better for Sb(V), though not without imperfections. When the parameters for organic matter were adjusted such that 100% of the solid-phase organic matter was active with respect to ion binding, but only 25% of the dissolved organic matter, the model description improved considerably for Pb and Cu in the upper soil layers. The model revealed distinct differences in the adsorption behaviour of the metal cations, with Pb being sorbed mostly to Fe/Al (hydroxides), whereas a considerable part of Cu was sorbed to organic matter, particularly in the waste zone.

Possibly, the dissolution of easily weatherable metal-containing mineral phases may have contributed to the poor model performance for Cd, Zn and for Cu in the deeper soil layers, although other factors, such as a contribution of hydrous SiO_2 or Mn oxides to metal binding, could not be ruled out. Metal sorption to carbonate phases may also have been a contributing factor in the waste zone. Lastly, the reactivity of Fe- and Al (hydr) oxides may have been overestimated by oxalate extraction when default parameters for high-surface-area ferrihydrite were applied.

These findings provide valuable insights for environmental management and underscore the need for a more detailed characterization of metal(loid) sorption in contaminated soils, as well as the development of improved modelling strategies to enhance solubility predictions.

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* Corresponding author.
E-mail address: terese.uddh-soderberg@lnu.se (T. Uddh-Söderberg).

[1] Swedish environmental protection agency, Hammarby fabriksväg 19, Stockholm, Sweden (present address).

https://doi.org/10.1016/j.apgeochem.2024.106063
Received 12 December 2023; Received in revised form 6 May 2024; Accepted 3 June 2024

1. Introduction

Heavy metal contamination of soil stands as one of the major environmental and public health issues today. Most guideline values currently employed to assess soil contamination are expressed as total concentrations. These guidelines are derived from generic estimates of solubility and conservative principles concerning soil:solution partitioning. Thus, by assuming a high solubility they typically err on the side of caution. However, excessively conservative assessments may hinder the accurate prioritization of sites for remediation. Moreover, certain scenarios may lead to elevated metal concentrations in water recipients even with moderate metal concentrations in the soil, especially in cases where efficient sorbents like organic matter and Fe/Al (hydroxides) are present in low quantities. Augustsson et al. (2020), for example, compiled data for 200 severely metal-contaminated sites in Sweden and showed that the performance of a commonly used Swedish risk assessment model (similar to models used in other countries of the EU and North America) was no better than random chance when predicting the risk of exceeding regulatory limit concentrations in groundwater based on observed concentrations in soil. Consequently, it is imperative to accurately characterize and predict site-specific metal solubility for effective risk assessment and management, particularly regarding leaching into groundwater. This is additionally needed in order to assess plausible changes in metal solubility, as contaminated sites across the world are increasingly being subject to altered hydrogeochemical conditions caused by on-going climate change and land-use change (Augustsson et al., 2011; Wijngaard et al., 2017; Jarsjö et al., 2020).

Numerous geochemical factors are recognized to influence the sorption of free metal ions onto solid phases. Firsty, the equilibrium between solid and dissolved phases of a metal is affected by the amount adsorbed onto solid particles, such as organic matter, Fe-, Mn- and Al (hydr)oxides, and clay minerals (Groenenberg and Lofts, 2014; Sparks, 2003; McBride et al., 1997). Among these, the organic component typically exerts the most significant influence on common metal cations such as Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}(e.g., Gustafsson et al. (2003)). Secondly, the equilibrium is influenced by the binding to dissolved compounds and complexation with aqueous ligands, such as carbonate, phosphate, sulphate, nitrate and chloride. The metal(loid)s As and Sb, on the other hand, occur mainly as oxyanions in the environment. For arsenic, As(V) (arsenate, i.e. AsO_4^{3-} and its protonated forms) is expected to predominate, at least in unsaturated zones and for antimony, Sb(V) (antimonate, i.e. $Sb(OH)_6^-$) is the most common form. Both form surface complexes on Fe- and Al (hydr)oxides. For As(V), corner-sharing bidentate complexes form on both ferrihydrite and $Al(OH)_3$ (e.g. Waychunas et al. (1993), Arai et al. (2001), Haque et al. (2008) and Tiberg et al. (2020)), while Sb(V) forms both edge- and corner-sharing bidentate complexes on ferrihydrite and soil (hydr)oxides (Mitsunobu et al., 2010; Vithanage et al., 2013; Verbeeck et al., 2021). Under certain conditions (e.g. with time) Sb(V) can be incorporated into the Fe (hydr) oxide structure (Scheinost et al., 2006; Mitsunobu et al., 2010; Verbeeck et al., 2021). At high concentrations both As(V) and Sb(V) may also precipitate (e.g., Bajda (2010), Sjöstedt et al. (2022) and Johnson et al. (2005)). Additionally, the pH of the soil solution significantly impacts the solubility of metal(loid)s.

Several successful models have been developed to predict metal solubility from data on soil pH, soil organic matter and total metal concentrations (McBride et al., 1997; Sauvé et al., 2000; Degryse et al., 2009; Janssen et al., 1997). Nevertheless, natural soils contain a mixture of different sorbents and the partitioning between solid and soluble species is also influenced by the composition of pore water. To address this complexity in the assessment of metal(loid) solubility in contaminated soils, multi-surface models can be employed (Bonten et al., 2008; Groenenberg and Lofts, 2014). This approach is built on the principle of component additivity, where the final outcome results from a combination of mechanistically based models, each describing the sorption to a specific solid phase. For instance, various models are available for simulating binding to organic matter, including the NICA-Donnan model (Kinniburgh et al., 1999), the WHAM model (Tipping et al., 2011) and the SHM model (Gustafsson, 2001). Others, such as the CD-MUSIC model (Hiemstra and van Riemsdijk, 1996) and the 2-pK Diffuse Layer model (Dzombak and Morel, 1990), focus on sorption to Fe/Al/Mn (hydr)oxides. Meanwhile, ion-exchange equations, like the Gaines-Thomas equation, aim to describe sorption onto clay minerals (Voegelin et al., 2000). While there are several instances where multi-surface geochemical modelling has been applied to assess speciation and solubility of metal(loid)s in soils, most have primarily concentrated on either the surface horizons of natural soils (Weng et al., 2001; Bonten et al., 2008; Khai et al., 2008) or on the contaminated source zones in heavily polluted areas (Dijkstra et al., 2004; Sjöstedt et al., 2022). Nevertheless, subsoil horizons may be equally significant regarding the ongoing migration and leaching of metal pollutants into groundwater.

The objective of this study was to evaluate how the solubility of As, Cd, Cu, Pb, Sb and Zn changes with depth at a contaminated site, spanning from the contaminated source zone on the surface to the unsaturated subsoil and eventually into the saturated zone. To accomplish this, we examined a 5.3 m long intact soil core from a highly contaminated glassworks site in south-eastern Sweden, where As, Cd and Pb are the key pollutants and Cu, Sb and Zn are also elevated. We conducted batch experiments to assess the solubility of these target metal(loid)s while varying pH. Subsequently, we investigated to which extent the utilization of a multi-surface geochemical model could predict (replicate) the observed metal mobilization. To this end, we combined the Ferrihydrite CD-MUSIC model (Hiemstra and Zhao, 2016; Gustafsson and Antelo, 2022) with the Stockholm Humic Model (Gustafsson, 2001; Gustafsson and Kleja, 2005) to account for metal binding to (hydr)oxides and organic matter, respectively.

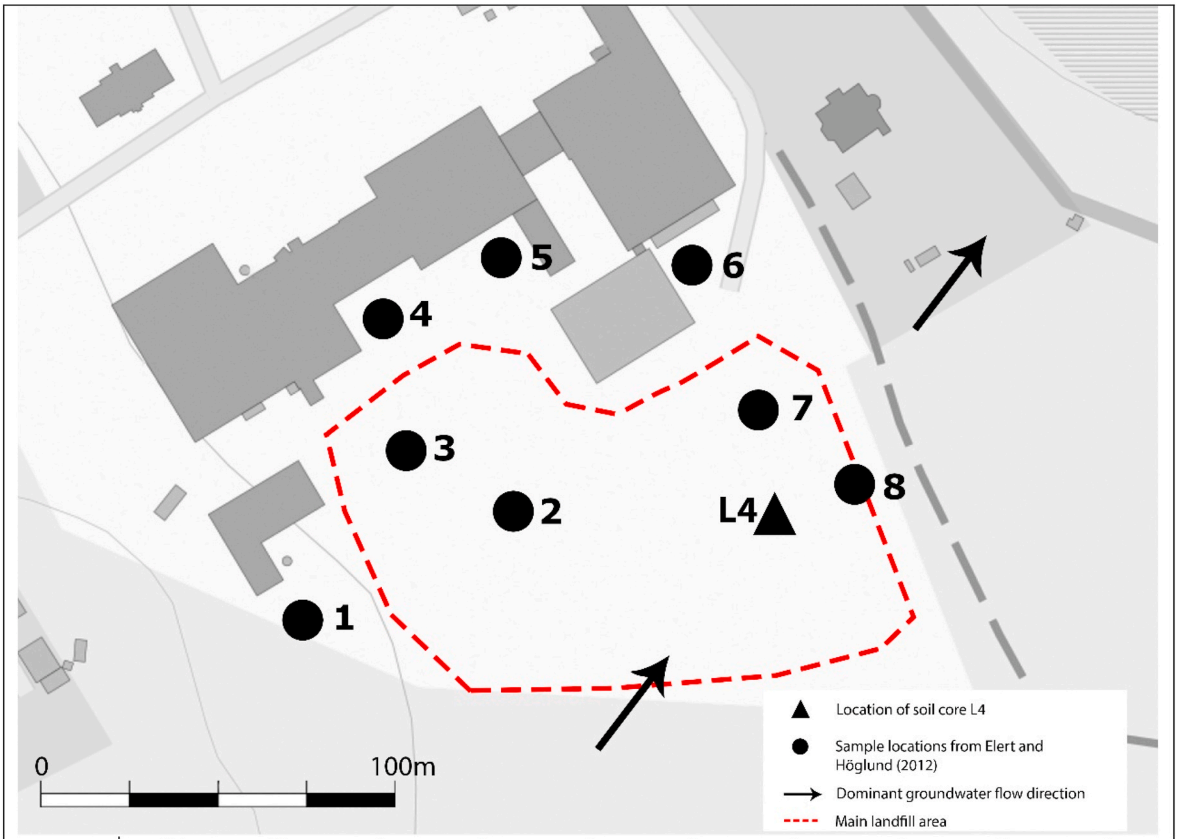
2. Material and methods

2.1. Study site and sampling

In the south-eastern part of Sweden, in the Swedish glass district, a long history of artistic and crystal glass production has resulted in extensive soil contamination. Among the most prevalent contaminants in the area are Pb and As. Investigations at 22 glassworks sites estimated their total amounts to be approximately 3100 and 420 tonnes, respectively (Höglund et al., 2007). One of the larger glassworks factories in this region is Pukeberg, located in Nybro municipality, where glass production commenced in 1871. An inventory conducted in 1970 found that around 450 tonnes of glass waste were annually deposited on the site's landfill (Elert and Höglund, 2012). However, local deposition of waste ceased in 1977 and the landfilled material was left untouched, without protective barriers to prevent the spread of contaminants. At the time of our investigations, the old landfill area was covered by soil and vegetation that had developed naturally over the past decades.

Previous soil sampling in various subareas at or near the primary landfill (locations 1–8 in Fig. 1) has shown average concentrations of As ranging from 3.5 to 400 mg/kg, average Cd concentrations ranging from 0.21 to 62 mg/kg and average Pb concentrations ranging from 28 to 2200 mg/kg (Fig. 1). Most concentrations of these three metals clearly exceed the guideline values set by the Swedish environmental protection agency (Swedish EPA, 2009): 10 mg/kg for As, 0.5 mg/kg for Cd and 50 mg/kg for Pb. For Cu, Sb and Zn, previously measured concentrations in the same subareas ranged from 6.5 to 65 mg/kg, <2.0–58 mg/kg and 45–420 mg/kg, respectively. While concentrations of these elements are also elevated, the elevation is considered relatively moderate compared to the guideline values (Fig. 1). Notably, the high concentrations of metal(loid)s in the waste zone have been observed to sharply decrease between the landfill and the underlying unsaturated natural soil zone, as demonstrated by Uddh Söderberg et al. (2019).

This study is based on a 5.3 m long, intact soil core from the landfill



	KM	L4	1	2	3	4	5	6	7	8
As	10	250	3.5	65	400	17	21	74	78	24
Cd	0.5	15	0.21	5.0	62	4.0	0.6	4.8	17	21
Cu	80	420	6.5	28	21	56	17	33	37	65
Pb	50	3400	28	610	1600	100	150	670	2200	350
Sb	12	60	<2.0	17	33	4.9	2.2	23	58	12
Zn	250	1000	45	340	290	93	65	260	420	360

Fig. 1. Map of Pukeberg glassworks landfill site. Mean concentrations of As, Cd, Cu, Pb, Sb and Zn (in mg kg^{-1}, expressed on a dry weight (dw) basis) are given for surface samples (0–1 m depth) from the soil core investigated in this study (L4) and from 8 previously sampled spots at and around the main landfill (Elert and Höglund, 2012). For comparison, the table below the figure also includes the Swedish EPA's generic guideline value for contaminated sites, derived for sensitive land use (KM) (Swedish EPA, 2009).

area. It is referred to as core L4 in the previous work by Uddh Söderberg et al. (2019), where further details about the sampling are provided. Before subjecting the core to various analyses, it was divided into four subsamples to facilitate a separate characterization of conditions in the following zones: i) the waste zone, characterized by a mix of natural soil and a substantial fraction of visible glass waste (0.9–1.8 m below the surface); ii) the upper unsaturated zone containing natural soil immediately beneath the waste zone, where visible glass waste is absent (1.8–2.3 m); iii) the lower unsaturated zone with natural soil (3.3–3.8 m); and iv) the saturated groundwater zone (5.0–5.3 m).

In addition to the solid material from the L4 core, soil pore water was collected from three locations within the landfill area (designated as locations L1, L2 and L5 in Uddh Söderberg et al. (2019)) over an 11-month period using tension lysimeters, with more detailed descriptions provided by Uddh Söderberg et al. (2019).

2.2. *Sample chemical and physical characterization*

Chemical analyses were conducted i) to characterize present-day solubility of As, Cd, Cu, Pb, Sb and Zn at the 4 investigated depths of the L4 soil core and ii) to generate the input data for modelling of these metal(loid)s' solubility and speciation.

2.2.1. *Analyses of landfill samples*

The pore water samples from the field lysimeters were filtered and thereafter analysed for dissolved Cl^- and SO_4^{2-} by ion chromatography (SS-EN ISO 10304-1).

The soil core subsamples were sieved to <2 mm (ISO 11464:2006) prior to further treatment and analyses and all analyses were performed on duplicates. The soil analyses included determination of pH (on fresh soil according to ISO 10390:2005), total organic and inorganic carbon (on dried material using a Carlo Erba CN analyzer (Flash1112 series) according to ISO 10694 and 13878) and multiple metal(loid)s. Pseudo-total metal concentrations were analysed after digestion with Aqua Regia ($1HNO_3$:3HCl). The geochemically active concentrations of all cationic metals except Al and Fe were analysed after soil extraction with 0.1 M HNO_3 (Gustafsson and Kleja, 2005) and the anion-forming As and Sb, together with Al and Fe, were analysed after extraction with 0.2 M oxalate/oxalic acid buffer at pH 3.0 (van Reeuwijk, 2002). These extraction procedures are described in more detail by Uddh Söderberg et al. (2019). For this follow up study, the geochemically available concentrations of the base cations Ca, Mg and K were also analysed following soil extraction with 0.1 M $BaCl_2$ (Gustafsson and Van Schaik, 2003).

Following all the above-mentioned soil extractions, samples were centrifuged at 2500 rpm for 20 min to separate coarse soil particles from the eluates and then filtered with 0.45 μm membrane filters. The clear solutions were acidified with 1% HNO_3 to keep dissolved metal ions in solution. All metals, irrespectively of the soil extraction applied, were determined with ICP-SFMS according to SS EN ISO 17294-1, 17294-2 and EPA-method 200.8.

2.2.2. pH-dependent batch experiment

A pH-dependent batch experiment was conducted on soils from the four different depth zones of the collected soil core in order to characterize the solubility of the six target contaminants (As, Cd, Cu, Pb, Sb and Zn) as a function of pH. The protocol used in this experiment followed the 'batch test for time dependent solubility of truly dissolved fractions' according to Löv et al. (2019). Here, 7.0 g of field-moist soil was mixed with 10 mM $NaNO_3$ to a final volume of 100 mL (generating a liquid-solid ratio (L/S) of 14, equal to L/S ~16 for dried samples) at 5 different pH values ranging from approximately 4 to 8. Due to the high buffering capacity in the glass waste zone, the lowest achievable pH for this zone was 6.0. Throughout the experiment, pH adjustments were made by adding HNO_3. Thereafter the samples were shaken for 5 days at room temperature, a duration shown to be appropriate for reaching equilibrium for Pb (Sjöstedt et al., 2018). After equilibration and centrifugation, the final pH values were measured (SS-EN ISO 10523:2012). The eluates were then filtered using two methods; membrane (0.45 μm) filtering and ultra-centrifuge filtering with10 kDa filters. The latter method removes particles larger than approximately 1 nm, i.e., colloids, thereby isolating only the species of the target elements that are either truly dissolved or bound to fractions smaller than colloids, such as certain dissolved organic compounds (DOC) (Garnier et al., 2011; Matura et al., 2010; Sjöstedt et al., 2018). It has previously been shown that batch experiments can lead to an increased presence of colloid-bound metals in the solution due to the release of fine particles during the shaking process (Bergendahl, 2005; Bergendahl and Grasso, 1998; Uddh Söderberg et al., 2019). Hence, the concentration of dissolved metal(loid)s may be overestimated in membrane-filtered samples and ultra-filtration may therefore be a better choice for a proper characterization of dissolved species. For Pb, some results suggest that the use of ultra-filtered concentrations improve the geochemical modelling for this element (Sjöstedt et al., 2018). Both the membrane-filtered and ultra-filtered eluates were analysed for the target contaminants (As, Cd, Cu, Pb, Sb and Zn), as well as dissolved organic carbon (DOC) and concentrations of Al, Fe, Si, Ca, K, Mg and PO_4^{3-}. Dissolved organic carbon was analysed with IR detection (SS-EN 1484) and phosphate was measured colourimetrically using a PerkinElmer UV/VIS spectrometer Lambda XLS+ (SS-EN ISO 6878:2005). Metal(loid)s were analysed with ICP-SFMS (SS EN ISO 17294-1, 17294-2 and EPA-method 200.8) after acidification with 1% HNO_3.

2.3. Geochemical modelling

Geochemical modelling was performed using a multi-surface model setup in Visual MINTEQ (VM), version 4.0 (Gustafsson, 2022). The chosen model considers speciation in the dissolved phase, sorption to Fe- and Al (hydr)oxides, binding to solid organic matter (SOM) and precipitation/dissolution of mineral phases. No calibration of the model was performed for the investigated samples. A summary of the model entries is provided in Table 1 and model parameterization values are detailed in Tables S1a–d of the supplementary material. The primary focus of the model output in this study is the solubility of the target metal(loid)s As, Cd, Cu, Pb, Sb and Zn at different depths of the investigated soil core and at various pH values.

The total concentrations of different metal(loid)s used as input to the model were derived from geochemically active concentrations rather than total concentrations since it is the geochemically active fraction that is expected to participate in reactions in the short and intermediate time perspective. Due to the oxic conditions at all analysed soil depths, as described by Uddh Söderberg et al. (2019), only oxidized species of As and Sb, i.e., As(V) and Sb(V), were used in the modelling. Before incorporation into the model, the geochemically active concentrations were adjusted to match the liquid-solid ratio (L/S) employed in the pH-dependent batch experiment. The dissolved concentrations of Fe (III), Al(III), Ca^{2+}, K^+, Mg^{2+}, PO_4^{-3} and Si (H_4SiO_4) in ultra-filtered solutions were fixed at their measured values in the model.

Table 1
Summary of model entries, with a summary of analytical procedure applied for their characterization.

Model entries	Characterization
1) Total concentration of the studied metal(loids); As(V), Cd(II), Cu(II), Pb (II), Sb(V), Zn(II) and other potentially competing metals; Ba(II), Co(III), Cr(III), Mn(II) and Ni (II) in soil.	Geochemically active concentrations, derived after soil extraction with HNO_3 (cations) and oxalate/oxalic acid buffer (anions; As(V), Sb(V)).
2a) Dissolved concentrations of Ca^{2+}, K^+, Mg^{2+}, Cl^-, SO_4^{2-}, PO_4^{3-} and Si (H_4SiO_4).	After batch leaching of soil with $NaNO_3$ at multiple pH values. Concentrations determined on 10 kDa ultra-filtrated solutions. Fixed in the model to calculate adsorbed amounts.
2b) Active concentration of DOM	Original model: Concentration of DOC determined in filtered (0.45 μm) solutions multiplied by a factor of 2. Revised model: DOC multiplied by a factor of 0.5.
3) Total concentration of Na^+ and NO_3^-	Set equal to the added concentrations in the pH dependent batch experiment
4) Dissolved concentrations of Fe^{3+} and Al^{3+}	Determined from concentrations in 10 kDa ultra-filtrated solutions derived for each pH value. If the system is supersaturated with respect to ferrihydrite and Al(OH)s (c.f. Table S6), the dissolved concentrations are set in equilibrium with these.
5a) Concentration of 'active' solid-phase HA and FA	Original model: Assumed to be 50% of the total organic C multiplied by a factor of 2. Revised model: Assumed to be 100% of the total organic C multiplied by a factor of 2.
5b) High affinity sites for Pb on solid-phase organic matter	Assumed to be 0.01% of the total organic C.
7) Concentration of inorganic sorbents, i.e. Al + Fe (hydr)oxides (assumed to behave as ferrihydrite)	Calculated from oxalate-extractable Fe and Al, using a surface area of 611 m^2 g^{-1} and parameters for ferrihydrite according to Gustafsson and Antelo (2022), but corrected for any Fe and Al dissolved in the batch experiment.

To model metal complexation to solid and dissolved organic matter (SOM and DOM), the Stockholm Humic Model (SHM) was employed (Gustafsson, 2001). The concentration of sites actively binding metals and protons to SOM and DOM was determined through measurements of total organic carbon (TOC) and dissolved organic carbon (DOC), respectively (Sjöstedt et al., 2018; Shi et al., 2013; Gustafsson et al., 2011). Active DOM was assumed to be 100% fulvic acid (FA) with a carbon content of 50% (Gustafsson et al. (2011); Table 1). Consistent with earlier applications of SHM, the fraction of active SOM was initially assumed to be 50% of the total SOM, which, in turn, was estimated to be twice the concentration of organic carbon (e.g., Gustafsson et al. (2003)). The active SOM was assumed to consist of equal proportions of humic acids (HA) and fulvic acids (FA) (Almås et al., 2007). Gustafsson et al. (2011) demonstrated that additional high-affinity sites for Pb are needed in the modelling to avoid underestimating the Pb binding by natural organic matter at low Pb concentrations. The concentration of these high-affinity sites was set to 0.01% of total organic C (Tiberg et al., 2018), assuming that the high-affinity sites reside on a solid-phase organic component. Relevant metal complexation parameters in the SHM are presented in Table S2 of the supplementary material. Because the standard settings for the SOM and DOM parameters provided relatively poor descriptions of metal sorption (c.f. Results and Discussion section), we also performed model simulations in which we used modified parameters as follows: the active SOM was assumed to be 100% of total SOM and that active DOM was assumed to consist of only 25% FA.

Sorption to Fe- and Al (hydr)oxides was modelled using the CD-MUSIC model, initially developed for goethite (Hiemstra and van Riemsdijk, 1996). Since suitable models for estimating sorption to Al (hydr)oxides are lacking, the CD-MUSIC model is commonly considered to encompass both Fe- and Al (hydr)oxides, assuming that all major Al/Fe (hydr)oxides have sorption mechanisms analogous to ferrihydrite (Dijkstra et al., 2004; Mendez et al., 2020). The CD-MUSIC model was applied according to the approach and parameters outlined by Gustafsson and Antelo (2022), who modelled arsenate and phosphate adsorption to ferrihydrite in the presence of Ca^{2+} and CO_3^{2-}. This model is similar to the model of Hiemstra and Zhao (2016), except that the division of bidentate sites into sites of low and high affinity is different. In this work, we extended the adsorption database with surface complexation reactions involving Al^{3+}, Cd^{2+}, Cu^{2+}, H_4SiO_4, Mg^{2+}, Pb^{2+}, $Sb(OH)_6^-$, SO_4^{2-} and Zn^{2+} using the same methodology as in Gustafsson and Antelo (2022), which took spectroscopic information into account when defining the surface complexes that form in the model. The datasets and assumptions used, along with the resulting surface complexation constants, are provided in Tables S3–S5 of the supplementary material. Sorption to crystalline (hydr)oxides and clay minerals were assumed to be of minor importance for sorption and their possible contribution was not considered in the modelling. Similarly, cation exchange onto permanently charged clay minerals was not considered. The clay content of the Pukeberg materials is around 3% (Sjöstedt et al., 2018) and preliminary model runs assuming the CEC of the clay to range between 0 and 0.2 molc kg^{-1} suggested cation exchange to clay to be of minor importance to the overall sorption of the metals considered.

Given the high concentrations of metals, especially in the waste zone, Visual MINTEQ was utilized to investigate possible equilibria with respect to some common phosphate and arsenate mineral phases, presented in Table S6 of the supplementary material. This table also shows the equilibria of $Al(OH)_3(s)$ and ferrihydrite, which were used to provide the upper limits of the solubility of Al^{3+} and Fe^{3+}, respectively.

3. Results and discussion

3.1. Soil properties

In the contaminated waste zone, the geochemically active concentrations (as evidenced by 0.1 M HNO_3 extraction for metal cations and by oxalate extraction for As and Sb) were practically the same as the pseudototal concentrations (determined after extraction with Aqua Regia), indicating that the metals in this zone were potentially soluble (Table 2). In the subsoil, however, metal(loid) concentrations were significantly lower and a smaller fraction was geochemically active. The $pH(H_2O)$ values were consistently high throughout the soil profile; 8.1 in the waste zone, then 7.6 and 7.2 in the upper and lower unsaturated zones, respectively and 7.5 in the saturated groundwater zone.

3.2. Solubility of metals

Fig. 2 displays the concentrations of As, Cd, Cu, Pb, Sb and Zn in equilibrated solutions following the batch leaching experiment as a function of pH. The corresponding data for the other parameters that were also analysed after the batch leaching test (DOC, Al, Ca, Fe, K, Mg, Si, PO_4) are provided in the supplementary information, Tables S1a–d. In the waste zone, where the pH was 8.1 under ambient conditions, the measured concentrations of As and Sb were higher than those of Pb, Cu, Zn and Cd. Additionally, the solid:liquid partitioning ratios, i.e., K_d values (defined as the ratio of the geochemically active metal concentration of the soil to the “truly dissolved” metal concentration), were much lower for As and Sb, corresponding to 230 and 620 L kg^{-1}, respectively, in contrast to the higher values for Cd, Cu, Pb and Zn of 26,000, 21,000, 85,000 and 42,000 L kg^{-1}, respectively. This discrepancy indicates that As and Sb exhibit a greater solubility and a higher potential for leaching than the other metals. This is also confirmed by data from the lower unsaturated zone. When compared to samples from the waste zone, the concentrations had decreased substantially for all elements, but significantly more for Pb (1200 times) than for the other prominent contaminant elements, i.e., As, Cd and Sb (30, 57 and 14 times, respectively). Thus, Pb was not only less soluble in the waste zone but also more efficiently immobilized below this zone. For Cu and Zn, the corresponding factors were lower (5.2 and 3.2 times, respectively), likely due to the lower level of contamination for these two elements (Fig. 1). Efficient retention of Pb in Pukeberg has been observed previously too (Augustsson et al., 2016b; Uddh Söderberg et al., 2019). According to Augustsson et al. (2016b), the efficient immobilization of Pb appears to be a generic feature of the glassworks sites in the region, resulting in dissolved Pb concentrations in analysed groundwater being below the WHO drinking water criteria (WHO, 2011). In contrast, the same study (Augustsson et al., 2016a) found that Sb and As frequently exceeded the WHO drinking water criteria in groundwater around the investigated glassworks sites. The exceptionally high Pb concentrations in the solid material of the waste zone of Pukeberg (Fig. 1) still resulted in relatively high aqueous concentrations in this material (Fig. 2), on average 0.25 μmol L^{-1} (0.051 mg L^{-1}). The study by Uddh Söderberg et al. (2019) suggested that the majority of the aqueous Pb was associated with DOC and inorganic complexes. Even so, as mentioned above, the K_d values for Pb^{2+} and for other metal cations were high, which was likely in part due to the low DOC values in this soil – all leachates from the batch experiment contained less than 3 mg L^{-1} DOC (Fig. S2). In contrast, the dissolved phase of both As and Sb was assessed to contain

Table 2
Soil chemical properties of the investigated soil profile, with concentrations of the contaminant metals presented as both pseudototal concentrations (tot) and geochemically active concentrations (act). The values for Fe and Al refer to oxalate-extractable concentrations (ox).

Depth (m)	Dry Weight	pH (H_2O)	Org C	As_{tot}	Cd_{tot}	Cu_{tot}	Pb_{tot}	Sb_{tot}	Zn_{tot}
	%		%	mg kg^{-1}					
0.9–1.8	74.4	8.1	2.4	180	11	140	4300	78	730
1.8–2.3	91.5	7.6	0.23	19	0.20	24	41	10	57
3.3–3.8	95.8	7.2	0.02	2.4	0.10	16	12	1.6	32
5.0–5.3	91.3	7.5	0.03	3.0	0.10	41	18	0.40	64

	DOC mg L^{-1}	Fe_{ox} mg kg^{-1}	Al_{ox}	As_{act} mg kg^{-1}	Cd_{act}	Cu_{act}	Pb_{act}	Sb_{act}	Zn_{act}
0.9–1.8	2.72	3200	1500	170	12	94	4300	72	710
1.8–2.3	2.34	1500	1900	19	0.15	8.3	21	12	10
3.3–3.8	1.30	430	280	1.9	0.018	3.2	3.0	1.5	2.9
5.0–5.3	1.27	1000	550	1.9	0.026	31	7.7	0.26	21

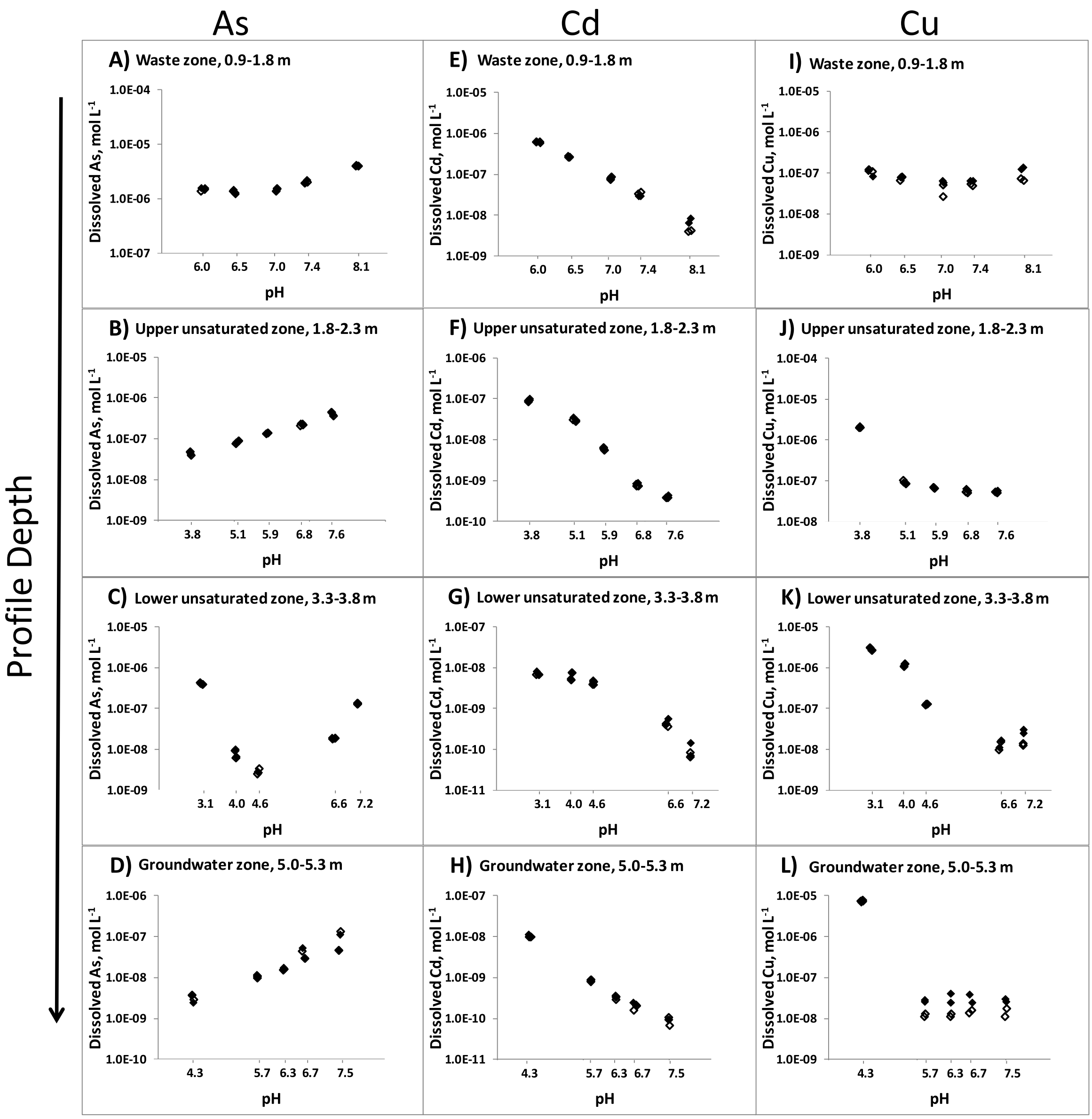


Fig. 2. The solubility of As, Cd, Cu, Pb, Sb and Zn (mol L^{-1}) at different pH values in duplicates: membrane-filtered concentrations (0.45 μm) are shown as solid symbols and ultra-filtered (<10 kDa) as open symbols. The pH values at the right-hand side of each subfigure represent ambient conditions.

100% free ions (Uddh Söderberg et al., 2019).

Furthermore, the batch experiment showed that dissolved Cd, Cu, Pb and Zn almost always increased when the pH value was lowered, as expected for cationic metals. This was observed for all soil depths (Fig. 2) despite differences in metal concentrations and properties of the solid materials, with the exception of Cu in the waste zone. The flat curve for Cu can be explained by its strong association with organic material (Fig. 5), together with the fact that the pH in the surface soil could not be lowered below 6.05. On the other hand, dissolved As generally decreased with decreasing pH, as expected when surface complexation to Fe- and Al (hydr)oxides governs As binding (e.g., Hiemstra and van Riemsdijk (1996)). In the sample from the lower unsaturated zone, a substantial increase of dissolved As occurred at pH 3.1, which is explained by substantial dissolution of the Al sorbent mineral under these conditions; dissolved Al at this pH was 0.7 mM. For Sb, the pH-dependent dissolution was less pronounced compared to As (Fig. 2).

When comparing ultra- and membrane-filtered samples, there was a marked difference for Cu and Pb at pH higher than ca 7 (Fig. 2), indicating a mobilization of colloidal-bound Cu and Pb at high pH. For As, Cd, Sb and Zn, the difference in concentrations between ultra-filtered and membrane-filtered samples was small.

3.3. Processes governing metal solubility as evidenced by Visual MINTEQ modelling

As the dissolved concentrations of some metal(loid)s, in particular As, Pb and Sb were very high in the waste zone, we used the 10 kDa ultrafiltration data from the batch experiment to investigate whether some commonly reported mineral phases that involve these metals (Table S6) could govern the dissolved concentrations. This was not assessed as relevant for the remaining metals, i.e., Cd, Cu and Zn. The saturation indices show that at the natural pH (8.1), the leaching test solution was undersaturated with respect to almost all ofthe investigated mineral phases (Fig. 3). The exception was chloropyromorphite for Pb,

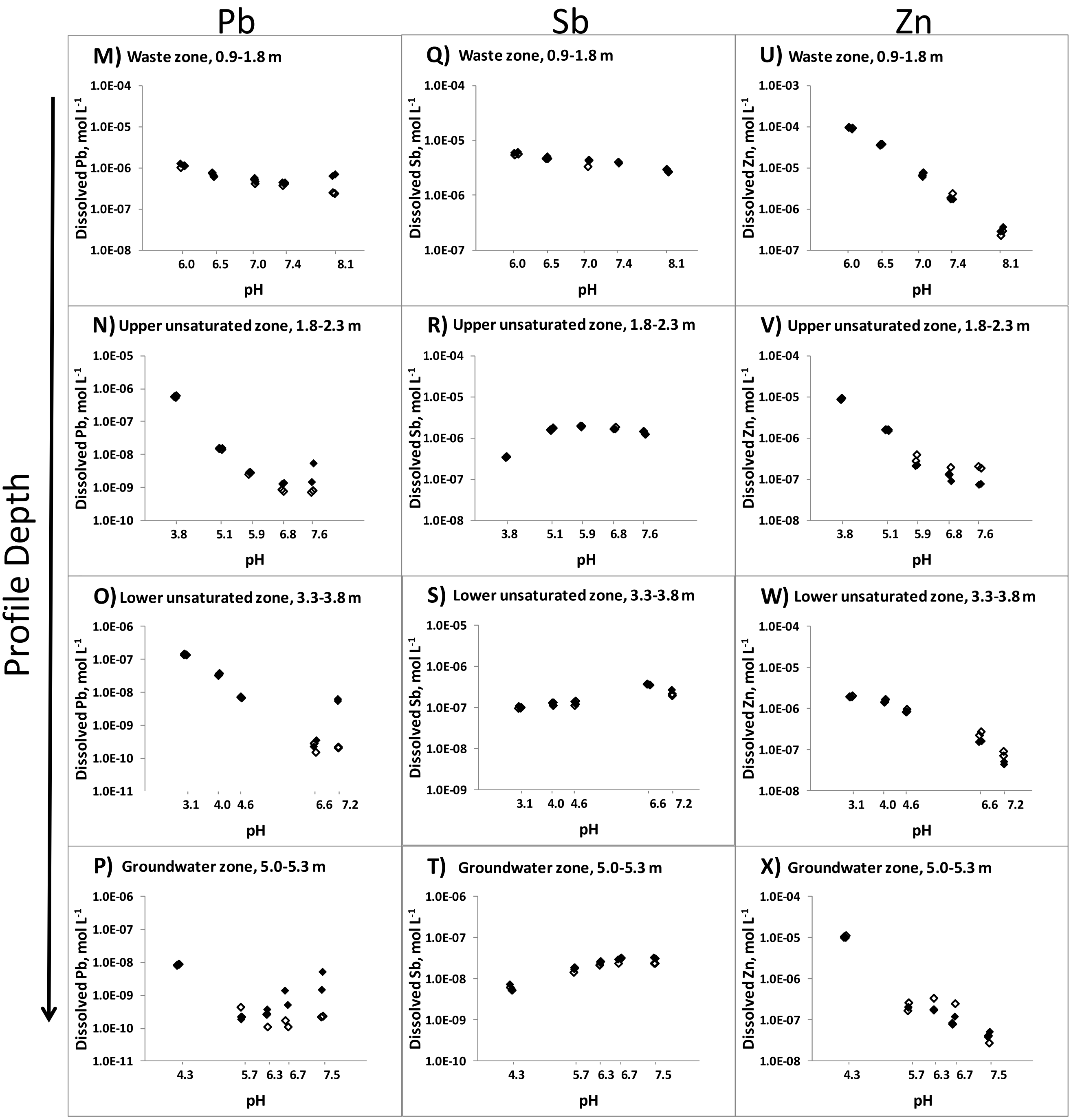


Fig. 2. (*continued*).

which was supersaturated. However, mimetite, Ca antimonate and koritnigite were all relatively close to saturation. All solutions were also undersaturated with respect to metal hydroxides (data not shown). For carbonates the saturation index could not be calculated as inorganic C was not determined. However, it seems possible that supersaturation with respect to some carbonate phases might have occurred in the waste zone, due to the presence of calcite in this layer. In the subsoil, there was no indication of carbonate mineral phases. Ca antimonates and koritnigite have been shown to govern the solubility of As(V), Pb(II) and Sb (V) in other contaminated soils (Johnson et al., 2005; Sjöstedt et al., 2022). After acid additions, the solutions even became supersaturated with respect to mimetite. Thus, it is possible that one or more of these phases may have been influential in determining the solubility of As, Pb and Sb in these experiments. However, direct evidence for a role of these mineral phases is lacking. The other investigated mineral phases, such as the barium arsenates, were more strongly undersaturated and are thus not likely to have played a significant role. In the deeper soil layers, the solutions were more strongly undersaturated with respect to all As(V), Pb(II) and Sb(V) minerals listed in Table S6 (data not shown) and are thus not likely to have affected the dissolved metal(loid) concentrations.

In the next step, we evaluated the results of the multi-surface geochemical model to investigate whether sorption to organic matter and Fe/Al (hydr)oxides could explain the results of the batch experiment. In the first attempt, we used default assumptions regarding sorbent inputs, i.e., assuming that 50% of the SOM is active based on TOC measurements, that all of the DOM was active with respect to metal

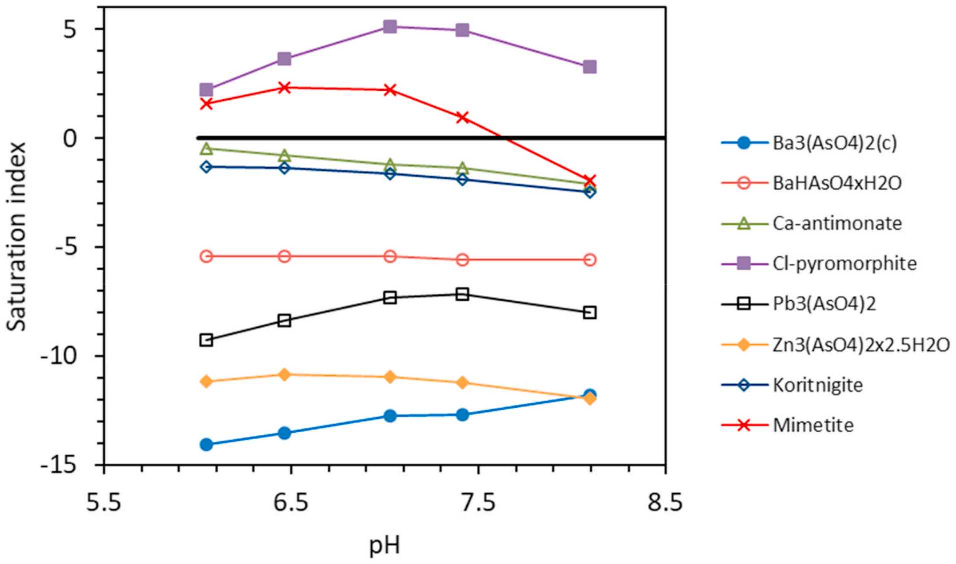


Fig. 3. The saturation index (SI) of selected mineral phases as a function of pH in the waste zone, as calculated by Visual MINTEQ. The natural pH of this zone is 8.1, represented by the set of data points on the right-hand side. The thick horizontal line is at saturation (SI = 0). The saturation index is defined as log (IAP/K_s), where IAP is the ion activity product and K_s is the solubility constant given in Table S6.

binding and that oxalate-extracted amounts of Al and Fe behave as high-surface area ferrihydrite (611 m^2 g^{-1}) in terms of metal(loid) binding. Fig. 4 shows how the measured concentrations of soluble As, Cd, Cu, Pb, Sb and Zn relate to modelled concentrations at the assessed range of pH values, with red solid lines representing the results with default model assumptions. Under these conditions, dissolved Pb was generally overestimated by the model and most clearly so in the waste zone where the metal concentrations are high and again in the saturated groundwater zone at the bottom. In the unsaturated zones, however, the modelled Pb solubility was in better agreement with the measured one, with only a relatively small overestimation. The results for Cu, Cd and Zn show the same trends as for Pb, i.e. the model overestimated Cu, Cd and Zn solubility in all zones, with the smallest deviations for the both unsaturated zones.

Also for Sb did the model, using default parameter settings, overestimate the solubility in the glass waste zone. In the other zones, there was a better agreement between the model and the observations, although the model underestimated Sb solubility at low pH and overestimated it at the highest (i.e. the natural) pH. For As, the solubility was underestimated by the model in all zones, however, in the lower unsaturated zone, the deviation was relatively small.

The standard SOM and DOM parameters, used in previous applications of SHM, imply a very high reactivity of DOM, i.e., 100% of the DOM is considered as metal-binding FA. However, previous applications of the NICA-Donnan model to soils suggest a lower DOM reactivity, i.e. in the range 15–40% (Fest et al., 2008). As the investigated systems contained very low DOM (3 mg L^{-1} DOC or lower, see Fig. S2), it can also be suspected that part of this DOM was non-humic in nature. For example, Lofts et al. (2001) found that predictions of dissolved Al were improved when the presence of a non-humic DOC fraction, inert with respect to metal binding, was accounted for. Moreover, the DOM of waste materials such as glass waste may have a different reactivity than the one of natural soils. Olsson et al. (2007), for example, showed a lower reactivity of DOM in municipal solid waste incinerator bottom ash, due to a larger proportion of hydrophilic DOM fractions. For our soils, when it was assumed that only 25% of the DOM was FA, the model fits improved significantly at the higher pH range. Moreover, increasing the reactivity of SOM to 100% of the SOM, further improved the fit, particularly at low pH. In combination, these modified parameters offered a much improved model description, in particular for Pb and for Cu, although the fits for Cu remained poor in the two deepest soil horizons. The modelled solubility after the adjustments made to characterize the organic material is depicted with dashed red lines in Fig. 4.

The modelled speciation for Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} in the system is shown in Fig. 5. The results for As and Sb are not shown here since these oxyanions are assumed not to bind to the organic matter component and thus they are distributed only over dissolved ions and the (hydr)oxide, which also is illustrated in Fig. S1 of the supplementary material. As the model fit for Cu^{2+}, Cd^{2+} and Zn^{2+} leaves much to be desired, the modelled speciation only gives an indication of the sorbent phases for the metal cations. In the waste zone, organic matter was important for the modelled metal binding, particularly for Cu^{2+} (Fig. 5), but for Pb^{2+}, adsorption to oxides was even more important. At greater depths, adsorption to Fe- and Al (hydr)oxides became increasingly important for all metal cations, which is explained by the relatively low soil organic C in these zones. Further, the extent of Fe- and Al (hydr) oxide binding increased with increasing pH. These results are consistent with other results from multi-surface geochemical modelling (Dijkstra et al., 2004; Khai et al., 2008).

In an attempt to improve the model fit for As, the active sites on the Fe- and Al (hydr)oxides were reduced from 100% to 50% and finally 25%. This can be interpreted as a decrease of the reactive surface area of the Fe- and Al (hydr)oxides, from 611 m^2 g^{-1} (the default value for ferrihydrite) to 305 and finally to 153 m^2 g^{-1}. These results are presented as yellow and violet lines in Fig. 4. Previously, a similar approach was made to adjust the model for other contaminated soils, with some success (Sjöstedt et al., 2018). Here, the reduction resulted in a clear improvement of the model fit for As. However, decreasing the number of sites of the Fe- and Al (hydr)oxides also results in a worse fit concerning dissolved Pb, which is explained by the fact that the Fe- and Al (hydr) oxides are important also for Pb^{2+} adsorption at this site. Similarly, the fits for Cd^{2+}, Cu^{2+} and Zn^{2+} were also deteriorated. For Sb, a decrease of the surface area of the Fe- and Al (hydr)oxides led to an improvement of the model fit for Sb at low pH, but at high pH the fit instead became poorer.

3.4. Possible reasons for the suboptimal model performance

There may be different reasons why the geochemical model, when using the default parameters, consistently underestimated the solubility of metal cations and at the same time overestimated the solubility of As (V). To start with, the much improved model performance for Cd^{2+},

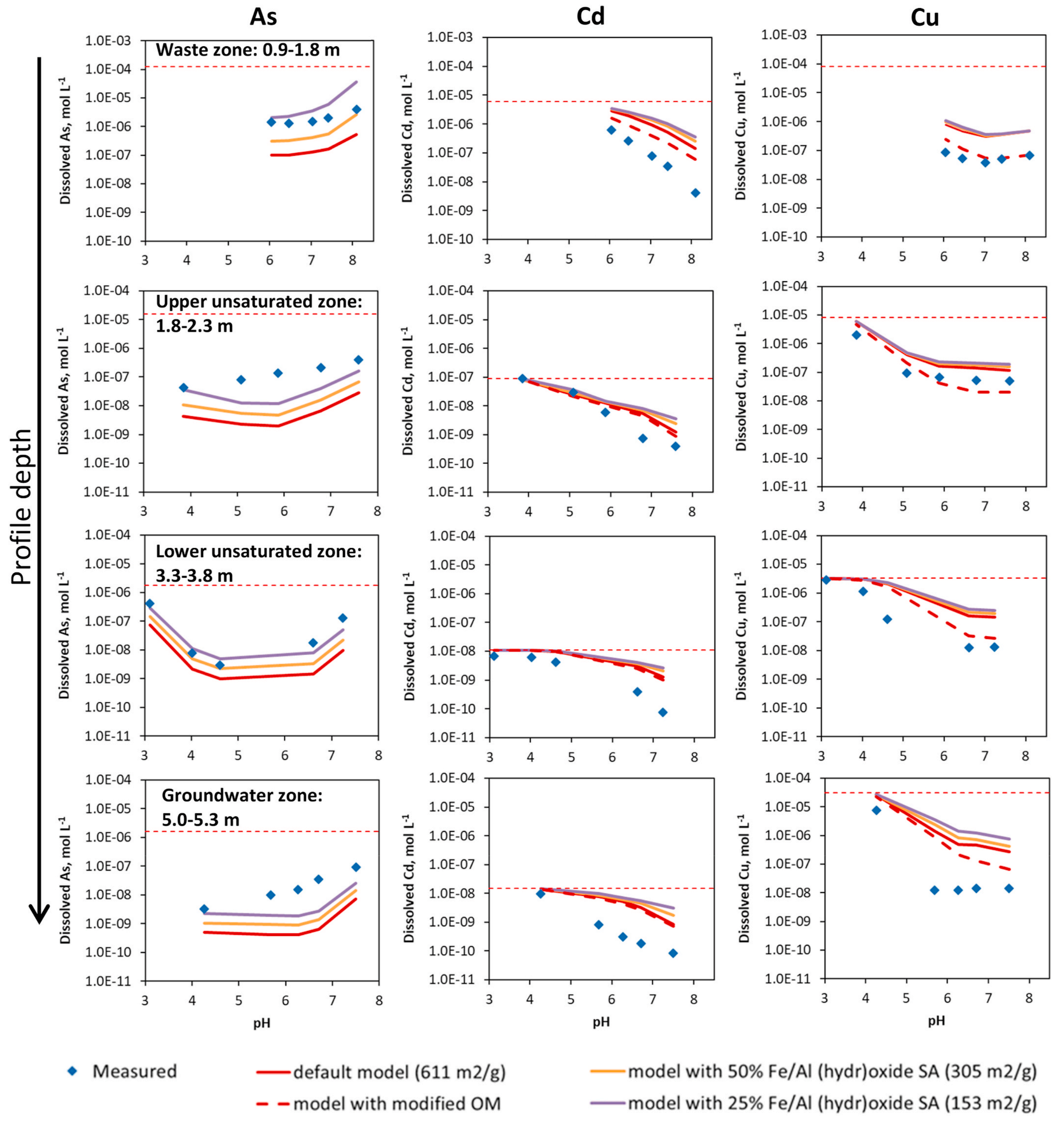


Fig. 4. Measured dissolved As, Cd, Cu, Pb, Sb and Zn concentrations (symbol, mol L^{-1}) compared to modelled dissolved metal concentrations (by Visual MINTEQ) at different pH in each zone (the waste zone, two depths of the unsaturated zone and the saturated groundwater zone). The solid lines represent different assumptions on the reactive surface area of the Fe- and Al (hydr)oxide sorbents (see text). The dashed red line is the model when the active SOM was assumed to be 100% of total SOM and the active DOM was assumed to consist of only 25% FA. The dotted line on top is the total geochemically active concentration.

Cu^{2+}, Pb^{2+} and Zn^{2+} when adjusting the parameters for organic matter suggests that the reactivity of DOM was rather low in the extracted solutions, indicating the presence of non-humic hydrophilic components, but also that the reactivity of the solid-phase organic matter was higher than expected. These results are in agreement with Sjöstedt et al. (2018), who studied the dissolution of Pb^{2+} from waste zone materials at the same site. Similar to us, they obtained the "best" model performance when the reactivity of the organic matter was set at 100%, together with a high surface area for the Fe- and Al (hydr)oxides. However, for Cd^{2+} and Zn^{2+}, and for Cu^{2+} in the two deepest soil layers, the effects of these model adjustments were insufficient in bridging the gap between model and observations (Fig. 4). For these reasons, other factors need also to be considered.

It may also be hypothesized that the dissolution of certain secondary

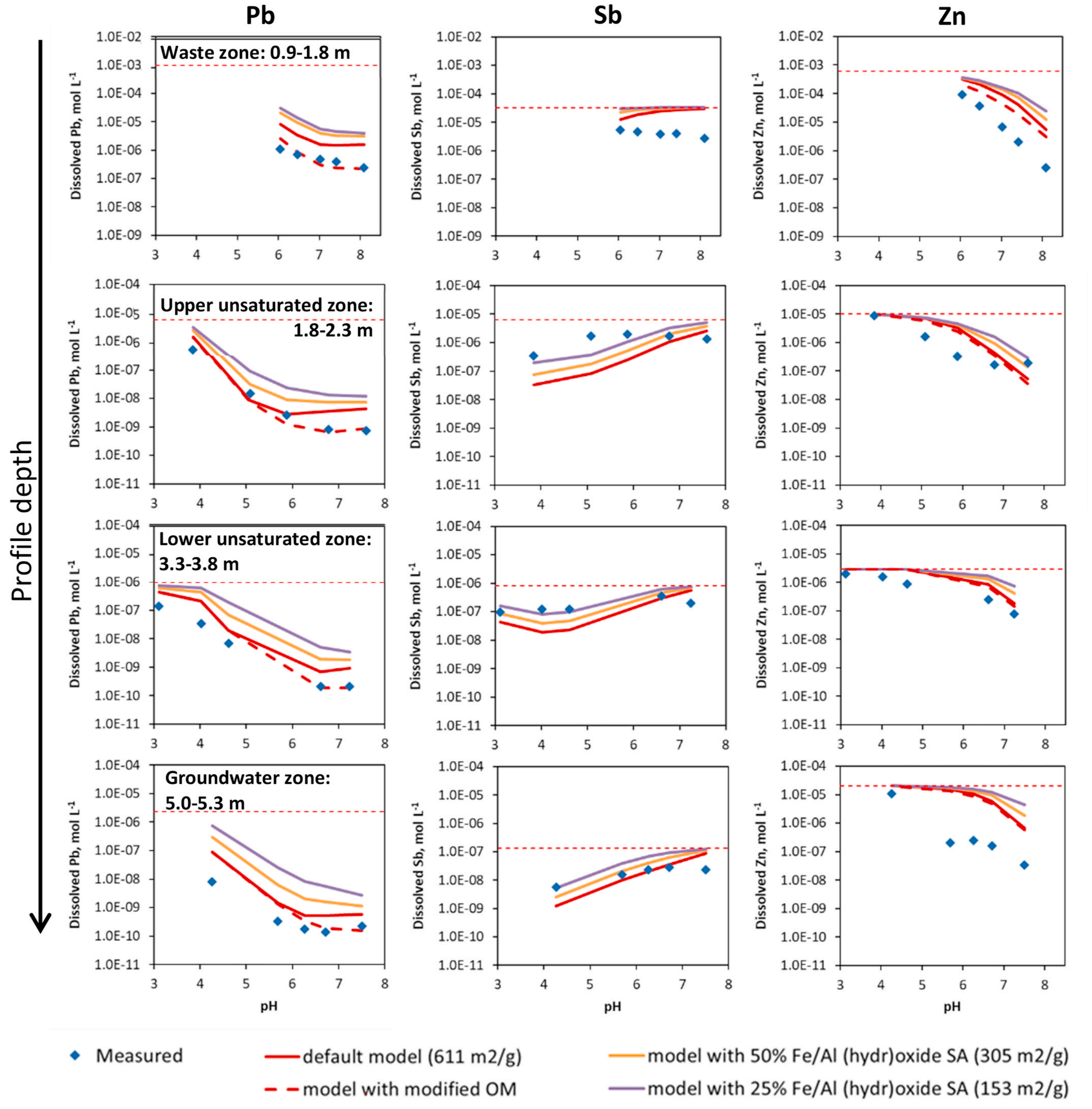


Fig. 4. (*continued*).

solid phases, e.g. mimetite and chloropyromorphite (Fig. 3), may have affected As and Pb solubility in the waste zone. This hypothesis is, however, difficult to reconcile with the EXAFS results of Sjöstedt et al. (2018), who ruled out a significant role of mimetite and chloropyromorphite in the waste zone.

An over- or underestimation of the modelled solubility will occur when the geochemically active concentration in the solid material, which is a key entry in the model, is either over- or underestimated. For example, the extraction with 0.1 M HNO_3 may release matrix-bound metal cations that, under normal pH conditions, would have been geochemically inactive. If the fraction of metal cations that are actually geochemically active under the conditions of the batch experiment is smaller than suggested by the 0.1 M HNO3 extraction, the actual solubility will be lower than the modelled value. For the Pukeberg material, Fig. 4 show that at low pH, all cations yielded concentrations in solution either at the same level as or close to those concentrations considered geochemically active (with the exception of Pb in the Waste Zone). This suggests that extraction with HNO3 was suitable for estimating the geochemically active concentration of cations in the solid material from this site. For this reason, the explanation of an erroneous characterization of the geochemical concentration appears rather unlikely as a major contributing factor to the model mis-fit of the cationic metals. However, for As, which was extracted with an oxalate/oxalic acid buffer, the concentrations in solution never reached the geochemically active concentration. This opens up the possibility that the geochemically active concentration of As in reality was higher than

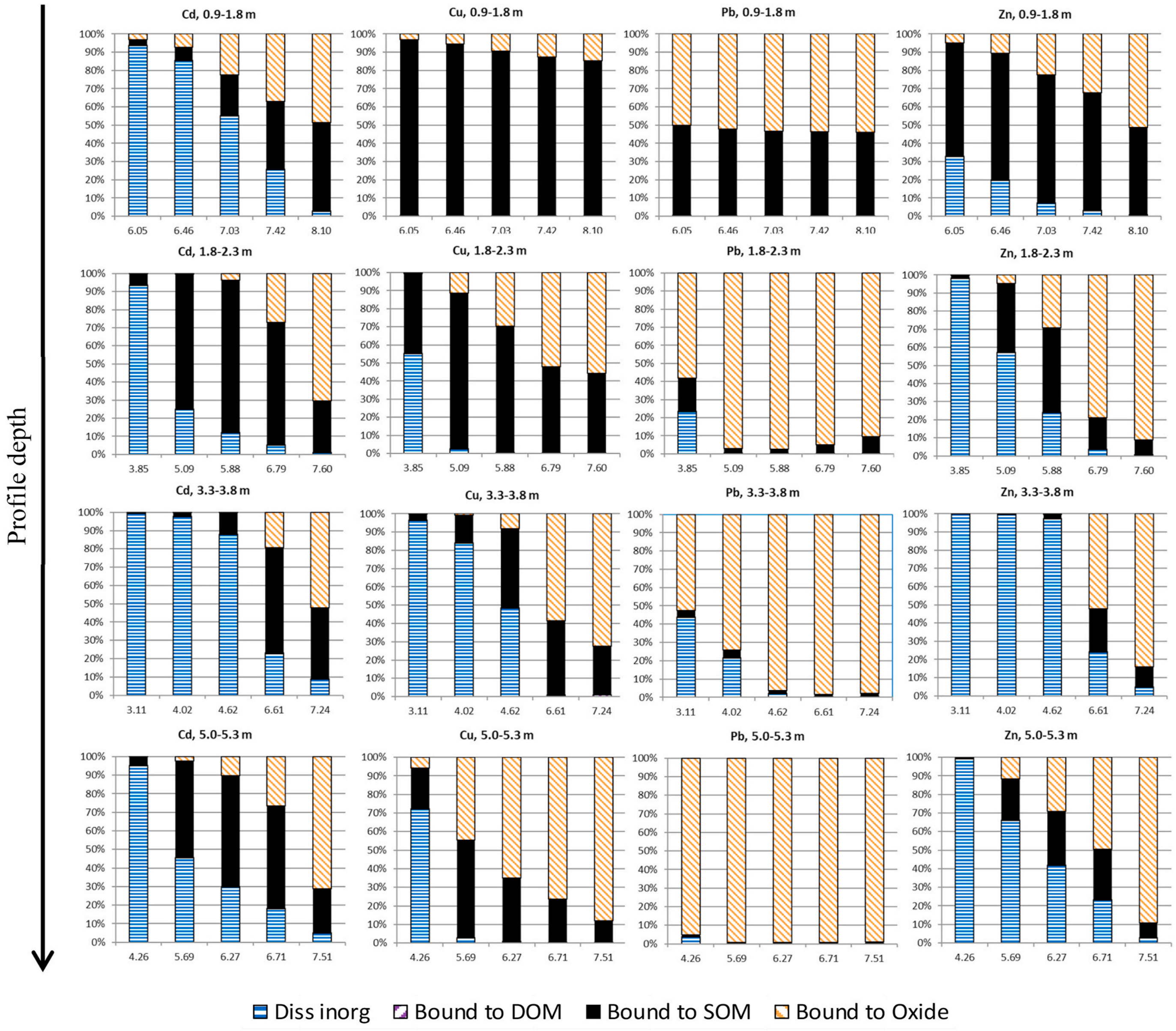


Fig. 5. Modelled distribution of Cd, Cu, Pb and Zn between dissolved inorganic species ("Diss inorg"), dissolved organic matter ("bound to DOM"), solid organic matter ("bound to SOM") and Fe- and Al (hydr)oxides ("bound to oxide") having a reactive surface area of 611 m^2 g^{-1}, when using modified SOM and DOM parameters (see text). The rightmost pH values of each subfigure represent the ambient pHs, while the lower values resulted from addition of HNO_3. The four rows represent the investigated soil depths, i.e., the waste zone, the upper unsaturated zone, the lower unsaturated zone and the saturated groundwater zone, respectively.

indicated by the soil extraction protocol.

In the waste zone, high Ca^{2+} concentrations, up to 11 mM, were observed after acid additions in the batch experiment (data not shown). This probably reflects the existence of reactive calcite in the waste (Uddh Söderberg et al., 2019). To an unknown extent, carbonate minerals may have caused increased sorption of metals such as Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}in the waste zone, either by direct precipitation, or by adsorption or incorporation into the calcite phase. Yet another possible reason for the suboptimal model performance is that other sorbents than those used in the model were responsible for the sorption of metal cations. In the waste zone, the alteration of silicate glass may lead to the formation of silanol groups and to secondary silicate phases with high surface area (e.g. amorphous silica (Gin et al., 2021)). SiO_2-type surfaces may be efficient in retaining metal cations, particularly at $pH > 6$ (Schindler et al., 1976; Reich et al., 2010). In this regard, it is of interest to note that the shapes and first-shell parameters of the Pb L_3-edge EXAFS spectrum of Sjöstedt et al. (2018) for the waste zone material are similar to the ones of Elzinga and Sparks (2002) and Farquhar et al. (1997) for Pb^{2+} adsorbed to quartz and silicate clays, respectively. On the other hand, the modelling work of Lofts and Tipping (1998) contradicts a significant role of SiO_2-type particle surfaces for soils. However, with the possible exception of the model of Lofts and Tipping (1998), there is no well-established surface complexation model for predicting metal sorption to silica and silicate clays. For example, the diffuse layer model approach by Reich et al. (2010) was unable to predict the large ionic strength dependent of Pb^{2+} adsorption onto quartz. Moreover, there is no known extraction or method that can directly estimate the site concentration of SiO_2-type groups in the soil. For these reasons, we did not try to extend the model with metal adsorption to SiO_2 to check this possibility. Another sorbent that may be of potential significance, particularly in the deeper soil zones, is manganese dioxide, MnO_2; however, in the current study no effort was made to determine the amount or reactivity of MnO_2 phases.

Most previous "multi-surface models" for soil, whether in contaminated or pristine settings, have been employed for the surface horizon of soils, i.e., the upper decimetres that have undergone long-term intense weathering and accumulation of appreciable amounts of organic matter and Fe/Al (hydr)oxides (MacDonald and Hendershot, 2006; Tipping et al., 2003; Khai et al., 2008; Sjöstedt et al., 2022). While there are examples where deeper soil horizons have been sampled and incorporated into such models (Bonten et al., 2008; Schröder et al., 2005; Weng et al., 2001), few have attempted to apply the same model approach to (i) contaminated waste material at the soil surface and (ii) deeper soil strata with low levels of organic C and (hydr)oxides. It is clear from our results that the transfer of the same multi-surface model approach to these environments was subject to significant problems. Although a role of SiO_2 and MnO_2 particle surfaces could not be ruled out, we hypothesize that a major reason behind the discrepancy between the model and observations, particularly for Cd and Zn, was that the soil samples contained easily weatherable Cu-, Cd- and Zn-containing phases that dissolved after the addition of acid in the batch experiment. Further, in the waste zone, metal sorption to carbonate minerals such as calcite may also have been of significance.

For As(V) and partly for Sb(V), oxalate-extracted Fe and Al did not seem to adequately represent Fe- and Al (hydr)oxides, at least not when a high default surface area of 611 $m^2\ g^{-1}$ was used. There are different possible explanations: first, other solutes such as DOM, which were not considered, may have competed successfully with As(V) (e.g., Gustafsson (2006)). However, as already mentioned, DOC was low in the profile and in the subsoil solid-phase organic matter was also low, suggesting a small or negligible influence of DOM. A second possibility is that oxalate may, to some extent, have dissolved Fe and Al not only from (hydr)oxide phases but also from silicate minerals. Thirdly, the Fe- and Al (hydr)oxides may have had a lower surface area. There is no evidence from the current study that supports any particular of the two latter hypotheses.

Thus, to improve geochemical modelling attempts for glass waste-affected surface soils, as well as subsoils, there is a need for detailed characterization of the adsorbed metal phases through spectroscopic and other methods. Further, the development of a consistent surface complexation model for silicate minerals may be important. Moreover, the reasons why the current, as well as other similar models, underestimate As(V) and Sb(V) solubilities when a high default surface area is used should be investigated.

4. Conclusion

This study explored the solubility and geochemical behaviour of several metal(loid)s in a waste zone and the subsoil environment, including both unsaturated zones and the saturated groundwater zone. The results showed that metal cations such as Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} are strongly retained in the waste zone, while oxyanions such as As(V) and Sb(V) are more easily leached. For Cu^{2+} and Pb^{2+}, colloids and organic matter complexes are important vectors for metal transport in the aqueous phase within the waste zone, while As(V), Cd^{2+}, Sb(V) and Zn^{2+} are present chiefly as inorganic ions.

For the metal cations, geochemical modelling suggested Pb^{2+} to be primarily sorbed to oxide minerals in the soil, while Cu^{2+} and Cd^{2+} were bound mostly to organic matter. However, findings suggest that metal(loid) solubility in both the waste zone and in the underlying subsoil is influenced by processes that are not yet understood in detail. Notably, the solubility of Cd and Zn appeared to be consistently overestimated by our geochemical model, also when all organic matter was assumed to be active with respect to metal binding, while As(V) solubility was underestimated. Several factors may contribute to these discrepancies.

First, the soil may have contained easily weatherable metal-containing phases that were easily dissolved after acid additions in the batch experiment. Second, the participation of sorbent minerals not considered in the geochemical model, e.g. silicate minerals and MnO_2, cannot be ruled out although there was no direct evidence for this. In the waste zone, the sorption of Cd, Cu, Pb and Zn to calcite may also have been of significance. Moreover, for As(V) and Sb(V), the model results suggest that the assumption that oxalate-extractable Fe and Al represents secondary Fe- and Al (hydr)oxides with a high surface area may not always be correct.

In summary, our results underscore the need for a comprehensive understanding of the adsorbent phases through detailed characterization, employing spectroscopic and other methods to understand processes at sites heavily contaminated with multiple metals. Furthermore, developing a consistent framework for modelling metal sorption to silicate minerals may be important for accurate predictions of metal solubility in glass waste and in subsoils.

CRediT authorship contribution statement

Terese Uddh-Söderberg: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Anna Augustsson:** Writing – original draft, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Dan B. Kleja:** Writing – review & editing, Methodology, Investigation, Funding acquisition, Conceptualization. **Jerker Jarsjö:** Writing – review & editing, Investigation, Funding acquisition, Conceptualization. **Mats Fröberg:** Writing – review & editing, Investigation, Funding acquisition. **Mats Åström:** Writing – review & editing, Investigation, Funding acquisition, Conceptualization. **Jon-Petter Gustafsson:** Writing – review & editing, Software, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author(s) used ChatGPT in order to improve readability and language of the work. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

Financial support for this study was provided by the Geological Survey of Sweden (grant number 36-1778/2014), the Faculty of Health and Life Sciences at Linnaeus University, Sweden and the Swedish Geotechnical Institute.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2024.106063.

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