UNIVERSITY OF WASHINGTON

Effects of pH and Redox Potentials on the Partition Coefficients Characterizing Heavy Metal Release from Oxy Site Soils

Report to Project Sponsors

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This document presents metal release data for Oxy site soils exposed to water chemistries characteristic for the site. The data are interpreted to calculate metal-specific partition coefficients and determine their sensitivity to soil provenance, pH and redox potentials of ambient water.

Contents

Executive Summary

This document discusses results of experiments carried out to ascertain partition coefficients needed for modeling of the fate and transport of heavy metals at the Oxy site. Major goals of the measurements were:

- To determine concentrations of representative heavy metals and other elements found in Oxy site soils;
- To determine effects of pH and redox potential of ambient water on the release of heavy metals from these soils;
- Based on the data of analyses for heavy metals and associated elements, to determine partition coefficients (K_d) that are necessary to model the behavior of heavy metals at the Oxy site.

In total, 27 Oxy site soils were used in the experiments. They were subjected to oxidative acidic digestions done to determine total concentrations of heavy metals (As, Cr, Cd, Cu, Ni, Pb, U, V, Zn) in the solid matrixes. Tl measurements were carried in some cases; these analyses showed that the concentrations of this element were typically too low.

A subset of ten Oxy soils was utilized in experiments concerned with determinations of soil/solution metal-specific partition coefficients at pHs varying from 8 to 14 and redox potentials representing mildly oxidizing to deeply reducing conditions. These coefficients are reported as their decimal logarithms, $\log K_d$ in the rest of the document.

$\log K_d$ values were calculated using metal concentrations determined in three reference conditions. These included i) metal concentrations obtained in complete soil digestions; ii) metal concentrations measured in exposures at pH 0 (this corresponds to a generally accepted condition of a nearly-complete metal mobilization from solid matrixes) and iii) metal concentrations released from the soil at pH 14 (this corresponds to an extreme case of highly alkaline areas of the plume).

Analyses performed for digested Oxy soils showed that concentrations of all heavy metals were strongly correlated with the concentration of iron which was the most important matrix component (after silicon) of the soils. The R^2 values characterizing these correlations were as high as 0.90. After iron, aluminum was the second most important metal component of the soils. Concentrations of the heavy metals in the Oxy site soils were as strongly correlated with aluminum levels as they were with iron.

Time profiles of metal release showed that at pH 0, concentrations of heavy metals increased throughout the entire exposure period but for contact times > 4 days metal release from the soils tended to plateau. Exposures at pH 14 showed comparable trends, except that for Cu. Concentrations of that metal behaved non-monotonically but for contact times > 4 days, they became stable.

Determinations of $\log K_d$ coefficients for pHs varying from 8 to 14 showed that in respect to their behavior in metal release experiments, the soils can be operationally separated into two groups. The first group (Group A) represents Oxy site soils originating from areas of the site that are not likely to have been affected by the high pH plumes. The second group (denoted as Group B) comprises soils originating from Oxy site areas that have been affected by high pH groundwater.

Interpretation of pH effects on the $\log K_d$ values for these soils was done based on two alternative hypotheses. First, the $\log K_d$ values were assumed to be randomly distributed. Accordingly, metal specific site- and pH-averaged $\log K_d$ constants were generated for the entire Oxy site. Alternatively, $\log K_d$ values were assumed to be intrinsically correlated with the pH, and such correlations were quantified either for the entire sets of the Oxy site soils or their two subgroups (operationally defined Group A and Group B).

Results obtained using the former approach showed that the $\log K_d$ values generated for the three alternative reference conditions exhibited a high degree of scatter and were not necessarily correlated between themselves. This suggested that in the absence of an explicit consideration of pH effects on the $\log K_d$ values, the use site- and pH-averaged $\log K_d$ values may have significant limitations.

An alternative approach to interpret the $\log K_d$ data involved calculating mean values of these constants for each pH separately. Analysis of the behavior of the site-averaged pH-specific $\log K_d$ values showed that for many elements, $\log K_d$ constants had a statistically strong linear correlation vs. pH (for some elements, relevant R^2 coefficients were close to 0.90 for all three reference conditions). Application of the same approach to two separate groups of Oxy site samples resulted in observations that were not dramatically different from those for the entire soil dataset.

Measurements of $\log K_d$ at varying redox potentials showed that for soils included in Group A, decreases of the redox potential were accompanied by decreases of the $\log K_d$ values. This was examined in more detail via generating correlations between $\log K_d$ values and redox potentials. This analysis showed that for Group A soils, $\log K_d$ values for practically all heavy metals decreased quasi linearly with the redox potential while the partition coefficients for Group B exhibited little or no changes in response to variation of the redox potential.

In sum, the data generated in this study support these conclusions:

1. Concentrations of all heavy metals (V, Cr, Ni, Cu, Zn, As, Cd, Pb and U) found in digestates of Oxy site soils are strongly correlated with the concentrations of major matrix components, notably Fe and Al. Physico-chemical aspects of these associations need to be explored in more detail. Still, the observed trends may indicate that the heavy metals occurring in the Oxy site soils may be dominated to their fractions sorbed on the surfaces and/or occluded in the bulk of iron oxyhydroxides, or mixed Al-Fe solid phases.
2. Examination of the sensitivity of $\log K_d$ values for changes of pH that was varied from 8 to 14 and those of the redox potential that was varied from ca. 0 to -500 mV showed that Oxy site soils can be separated into two major subgroups.
    a. The first group (denoted operationally as Group A) comprises soils for the Oxy site areas that do not appear to have been affected by high pH plumes and reducing conditions.
    b. The second group (denoted operationally as Group B) comprises soils from the areas deemed affected by high pH and reducing conditions.

3. $\log K_d$ values determined for Group A soils increase nearly linearly with the pH. This indicates that metal mobility decreases with pH for these soils.
4. In contrast with the results for Group A, $\log K_d$ values for Group B soils exhibit little sensitivity to pH variations.
5. The $\log K_d$ data for Group A and Group B could be combined to determine pH-specific $\log K_d$ constants for the entire set of the examined soils. This approach allowed generating reasonably strong linear functions correlating pH and metal-specific $\log K_d$ values.
    a. An alternative approach was to neglect effects of pH variations on the partition coefficients and average the $\log K_d$ values for the entire set of pH values and provenance of the Oxy site soils. While this approach may be simpler, its feasibility for fate and transport calculations remains to be determined in the context of the sensitivity of model predictions to uncertainties of $\log K_d$ values.
6. Variations of redox potential for Group A soils were accompanied by decreases of the $\log K_d$ constants that are nearly linearly correlated with the redox potential.
7. Metal release from Group B soils was largely unaffected by the presence of reducing agents. This observation confirms that redox (and pH) variations have relatively little importance for metal release in the areas of the Oxy site affected by high pH groundwater.

List of Tables

List of Figures

Goals of this study

This document presents results of experiments carried out to quantify soil/solution partition coefficients (K_d values) of heavy metals at the Oxy site. The ultimate use of these values is in calculations on the fate and transport of metals at the site. The major components of the analysis were:

- Determining the concentrations of selected heavy metals and other species that affect metal mobility in Oxy site soils;
- Determining the effects of pH and redox potential of the ambient water on the release of these metals from the soils;
- Based on these data, to determine the K_d values.

Provenance and selection of soil samples

Samples used in the analysis were selected in coordination with CRA, the Washington State Department of Ecology, the USEPA, and other project participants. These samples were selected from among soil cores extracted in Summer 2013 during the drilling of Borings A, B, F, G, H and Extraction Wells 7 and 9 (**Figure 1**). The latter two wells are located in the areas of the Oxy site that are deemed to have been exposed to high-pH plumes typical for this location.

The cores were collected with a sonic drilling rig equipped with a 4” stainless steel, 5’ long split core barrel. The cores were contained in a polyethylene tube, which upon retrieval was cut open longitudinally for field screening, soil sampling, and lithologic logging. Half of the core was kept and positioned on a plastic wrap. At the end of each day of field operations, the opened cores were covered with Visqueen plastic wraps and transferred to a trailer located on the Oxy site. Water samples were collected as the drilling progressed at each location either by bailer or peristaltic pump.

The field parameters were measured using the Horiba multi-parameter field meter equipped with a flow-through cell. Water from Extraction Well 7 was collected during the initial development of the well but its field parameters were not recorded at that time. Extraction Well 7 water was stored at the surface level on the Oxy site in a 300 gallon poly tote for ca. two weeks prior to being transferred into 5-gallon jugs and shipped to the UW. Work with this water was concerned with gelation phenomena which will be described in a separate document.

Composite soil samples for experiments carried out in UW were taken from the stored cores. The sub-sampling took place several days to several weeks after the drilling was completed. The composite samples were placed in glass jars and transported to UW in October 2013. During the entire period of activities carried out for the project, these samples were stored in the UW research laboratory in gas-tight glass jars, in dark at 4^oC. Aliquots of these soils were taken from the jars and processed as necessary.

In total, 27 Oxy site soil samples were used in the experiments. Their provenance and selected parameters characterizing the groundwater deemed to have been in contact with them are summarized in Table 1. The soil samples transferred to the UW laboratory were assigned sequential ID numbers listed in Table 1. As shown, soil samples from Boring A were assigned numbers S1 to S6. Boring B samples had ID number S7 to S10, and those from Boring F were S11 and S12. There was only one Boring G sample (S13) and three Boring H samples (S14 to S16). There were eight samples from Extraction Well 7 (S17 to S24) and three soil samples from Extraction Well 9 (S25 to S27). Locations of these wells are shown in **Figure 1**.

Digestions of Oxy site soils

Aliquots of all 27 samples listed in Table 1 were used in oxidative acidic digestions done to determine total concentrations of representative heavy metals (As, Cr, Cd, Cu, Ni, Tl, Pb, U, V, Zn) and, as needed, other elements (Al, Ba, Ca, Fe, Mg, Mn, and, in some cases, K, Sr, Si) in the solid matrixes. Because the version of EPA Method 3050B utilized in the digestions is not suitable for determinations of silica, Si concentrations found in the digestates were not considered representative of total silica content. Measurements of K and Sr concentrations in the digestates were only done during the initial phase of the experiments. They were then discontinued due the lack of need to take into account such data. Tl measurements were carried for digested samples and selected other experiments but the concentrations of this element were typically very low and discussed only very briefly in this report.

Experimental conditions and procedures used in the digestion experiments will be described in detail in a separate QA/QC document. Only a brief summary of relevant procedures is presented here. All digestions were carried out in duplicates using EPA Method 3050B. The procedure involved placing a weighed amount of homogenized soil (typically about 1.0 gram) in a mixture of 10 mL of concentrated high-purity nitric acid, 8 mL of deionized water, and 10 mL of 30% hydrogen peroxide. During reagent addition, the sample was heated just below its boiling point for four hours. After cooling, the sample was filtered through a Whatman 934-AH glass microfiber filter. The container was then rinsed with deionized water, the sample diluted with 1% nitric acid up to a 100 mL final volume. Concentrations of all elements present in the filtered digestates were determined by the method of inductively coupled plasma-mass spectroscopy (ICP-MS) per *Standard Method* 3125. Analyses were carried out with a PerkinElmer ELAN DRC-e ICP-MS instrument equipped with an AS 93 Plus autosampler (PerkinElmer Instruments, Shelton CT). Atomization was achieved with a MicroMist nebulizer with baffled cyclonic spray chamber (PerkinElmer Instruments, Shelton CT). Data processing and acquisition was carried out using ELAN instrument software (version 3.3).The following isotopes were normally targeted for analysis: ^{27}Al, ^{75}As, ^{138}Ba, ^{42}Ca, ^{111}Cd,

^{52}Cr, ^{56}Fe, ^{24}Mg, ^{55}Mn, ^{60}Ni, ^{31}P, ^{208}Pb, ^{123}Sb, ^{82}Se, ^{28}Si, ^{205}Tl, ^{238}U, ^{51}V, and ^{66}Zn. Some of these elements were excluded and other included where necessary.

Following ICP/MS determinations of the concentration of the heavy metals and matrix elements in the digested samples, liquid phase concentrations were converted to solid phase concentrations taking into account, where applicable, the dilution ratio. As a result of these conversion steps, the solids concentrations were expressed in mg_i/kg units, which are equivalent to μg_i/g units.

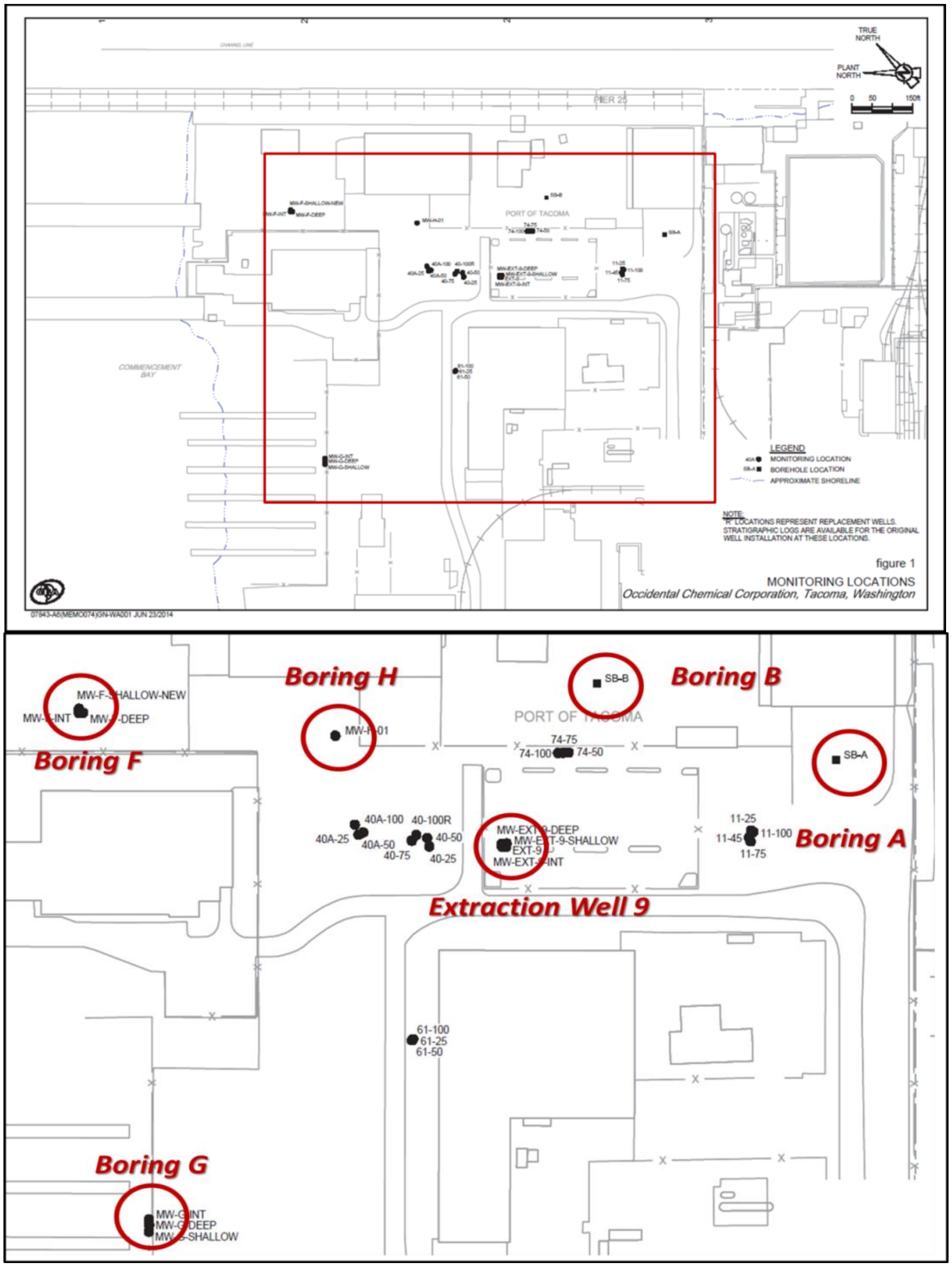

Figure 1 Location of Borings A, B, F, G, H and Extraction Well 9 on the Oxy site. Location of Extraction Well 7 is not shown.

Table 1 Oxy site soil samples used in digestion experiments.

UW Sample ID	Depth (feet bgs)	CRA WELL SCREEN INFORMATION	Temp (^{o}C)	Salinity (ppt)	Conductivity (mS/cm)	pH	DO (mg/L)	ORP (mV)	Tubidity (NTU)
Boring A									
S1	118-120	NO WELL at this location							
S2	122-124								
S3	134-36								
S4	140-42								
S5	144-146								
S6	150-52								
Boring B									
S7	112-114	NO WELL at this location							
S8	132-134								
S9	142-144								
S10	162-164								
Boring F									
S11	137-139	MW-F-INTERMEDI	32.4-31.6	46.8-46.4	68.6-67.9	7.4-7.2	2.0-1.0	-148/-147	698-511
S12	147-149	MW-F-DEEP	15.3	7.8	13.5	5.8	4	83	>1,000
Boring G									
S13	142-144	MW-G-SHALLOW	26.1-26.3	64.6-65.6	90.6-91.5	6.2-6.3	0.6-0.4	-14/-57	>1000-951
Boring H									
S14	132-134								
S15	152-154								
S16	162-164	MW-H-01	17.3	10.2	24.7	11.3	4.5	-72	>1,000
Extraction Well 7									
S17	90-92								
S18	98-100	83C4		4		11.1		0.175	0.004
S19	104-106								
S20	110-112								
S21	120-122								
S22	124-126								
S23	130-132	83C5		4		12.1		0.625	0.064
S24	134-136								
Extraction Well 9									
S25	132-134		25.2-28.2	>70	>100	7.4	1.6-0.7	-145/-147	597-313
S25	152-154	MW-EXT-9-INTERM	22.8	45	66.8	12.6	1.5	-319	>1,000
S27	162-164								

Experiments to determine pH-dependent site-specific K_d values.

A subset of the Oxy site soils (nine samples in total, **Table 2**) was utilized in experiments concerned with determinations of K_d partition coefficients at varying pHs. These experiments exposed selected soils to water containing an appropriate level of background ions (typically, 0.01 mol/L NaCl). All these tests were carried out in duplicates.

In tests representing extreme conditions, target pH values were 0 and 14. Reagents used to adjust solution pH to the target values were high purity HCl (or in limited cases HNO_3) or NaOH. Contact time was varied from 1 to 7 days. pH 0 experiments with alternative acidifying agents (HCl and HNO_3) were done for samples S18 and S23 only. Results of these exposures were practically identical.

Exposures representing more realistic groundwater conditions were carried out at pHs from 8 to 12. Given that experiments at pH 0 and 14 had demonstrated that metal release tends to plateau at a 7 day contact time, exposures with varying pHs utilized a 7 day contact time only. In these measurements (as well as those at pH 14 and 0) pH values were monitored and adjusted daily, and maintained nearly constant. Results of pH measurements in these experiments are presented in the tables compiled in the Appendix (Table A13 and Table A14).

As was the case with soil digestions, exposures of soils listed in **Table 2** utilized a 20 mg homogenized soil aliquot suspended in 200 mL of solution. The suspensions were placed in metal-free plastic containers which were gently shaken throughout 7-day exposure period. No effort to control dissolved oxygen was made in these experiments.

The soils examined in experiments with varying pHs (**Table 2**) included S7, S8, S10 (Boring B), S11 (Boring F), S18, S23 (Extraction Well 7), 25, 26, 27 (Extraction Well 9). Of the selected specimens, Samples S7, S8, S10 and 11 were deemed to represent soils originating from largely uncontaminated areas of the Oxy site. Samples S18 and S23 originate from Extraction Well 7 which is characterized by high pH values (reported pHs 11.1 and 12.6 for S18 and S23, respectively). These samples may have been also exposed to reducing conditions. However, the reported values of the redox potentials for these samples do not indicate, likely erroneously, the presence of deeply reducing conditions.

Samples S25, 26 and S27 originated from Extraction Well 9. pH values reported for these samples are variable (e.g., pH 7.4 for S25, and 12.6 for S25 and S26, respectively) while the reported values of the redox potential indicate the occurrence of deeply reducing conditions at this site.

Experiments concerned with effects of redox potential on K_d values.

Following the completion of measurements concerned with effects of pH on K_d values, additional experiments were carried to ascertain effects of variations of redox conditions. pH was kept constant at 10.0 in these experiments. This pH value was judged to be representative of large areas of the Oxy site, especially those in the fringes of the high pH, high silica groundwater plumes where the contaminated water comes into contact and mixes with ambient water that has circumneutral pH values.

Conditions used in the experiments with variable redox potentials were same as those used in the examination of pH effects on metal release, except that reducing reagents that scavenge the dissolved oxygen and interact with other oxidants, notably Fe(III) and Mn(IV) were added to the suspensions of Oxy site soils.

Reducing reagents applied to control the dissolved oxygen and the overall redox potential of the system were sodium sulfite, ascorbic acid and hydroxylamine. Their concentrations varied from 0 (no alteration of redox conditions) to 0.2 mol/L. Because many of these experiments utilized sulfite which could be oxidized to sulfate by dissolved oxygen and, potentially, by iron (III) and manganese (IV) minerals present in the soils, excess of sodium sulfate was added to the solutions. Na_2SO_4 *per se* does not affect redox properties of the system and is not expected to affect the release of most elements of interest to this study but it was added to compensate for potentially prominent matrix effects in ICP/MS measurements where concentrations of sodium and other background solution components may have a prominent effect of the analyses.

Measurements with varying concentrations of alternative redox-controlling agents showed that while the nature of the reductant (e.g., sulfite, ascorbic acid and hydroxylamine) had a marginal effect on metal release from Oxy site soils, metal release from some soils was sensitive to the redox potential of the system. Accordingly, the redox potential rather than the concentration and/or type of the reductant was considered as a master parameter.

Relevant metal release data presented in this document refer to the redox potential at which any specific set of measurements was carried out. In a majority of these experiments, hydroxylamine was used to control the redox potential. Hydroxylamine was chosen for that purpose due to its unlimited solubility, high reactivity in redox reactions of interest for environmental systems, lack of activity in complexation reactions that can affect metal release or adsorption and low possibility of affecting the results of ICP/MS analyses.

Redox potentials were measured a standard Pt redox electrode vs. a silver/silver chloride standard reference electrode. In the reported experiments, there had a range of ca. +50 mV to ca. -500 mV thus covering a range corresponding to both slightly oxidizing to highly reducing conditions similar to those reported for Oxy site soils (Table 1 and **Table 2**).

Samples used in the experiments to determine effects of redox potential variations included soils S7, S23 and S27. Soil S7 was from a site area which could have been exposed to somewhat reducing conditions but that soil was not deemed to have been affected by high pH plumes. In contrast, soils S23 and S27 were from the Oxy site area affected by high pH plumes and highly reducing conditions (albeit the results of field measurements of redox potentials for these soils are ambiguous, most likely due to experimental errors in measurements).

A limited set of experiments was carried out with soil SB-UW-82-31-33.5 extracted from the vicinity of Well 82 located within the high pH plume. This soil was extracted in July 2015 and kept anoxic at 4C in the UW laboratory until the commencement of the pertinent experiments. Full digestions and exposures at pH 0 and 14 were not performed for that soil and only metal concentrations released from soil SB-UW-82-31-33.5 at pH 10 and varying redox potentials were measured.

Table 2 Selected properties of the sub-set of soil samples used in exposures at varying pHs.

Sample ID	Depth, feet bgs (elev. NGVD)	Temp (^{o}C)	Salinity (ppt)	Conductivity (mS/cm)	pH	DO (mg/L)	ORP (mV)	Tubidity (NTU)
Boring B								
S7	112-114 (-100)	24.7-25.6	>70	>100	7.3-7.5	1.1-3.0	-161/-186	724-460
S8	132-134 (-120)	19.6-19.9	>70	>100	10.5-10.6	0.2-0.6	-418/-480	221-108
S10	162-164 (-150)	18.9	13.4	22.3	12	6.4	-225	877
Boring F								
S11	137-139 (-125)	32.4-31.6	46.8-46.4	68.6-67.9	7.4-7.2	2.0-1.0	-148/-147	698-511
Extraction Well 7								
S18	98-100		4 (?)		11.1		0.175 (?)	0.004 (?)
S23	130-132		4 (?)		12.1		0.625 (?)	0.064 (?)
Extraction Well 9								
S25	132-134 (-120)	25.2-28.2	>70	>100	7.4	1.6-0.7	-145/-147	597-313
S26	152-154 (-140)	22.8	45	66.8	12.6	1.5	-319	>1,000
S27	162-164 (-150)	18.9	7.2	12.5	11.7	4.3	39	>1,000

Calculations of K_d coefficients

In accord with applicable guidance documents (e.g., United States Environmental Protection Agency, Office of Air and Radiation. 1999. *Understanding Variation in Partition Coefficient K_d values.* Volume I: *The K_d Model, Methods of Measurement, and Application of Chemical Reaction Codes*; EPA 402-R-99-004A), K_d values were calculated as

$$K_{d,i} = \frac{A_i}{C_i} \tag{1}$$

In the above equation, C_i is the concentration of dissolved adsorbate released to solution at equilibrium (µg/ml or mg/L), and A_i is the concentration of the adsorbate remaining in the solid at equilibrium (µg/g or mg/kg).

It is to be noted the K_d definition and its use in the relevant calculations have several implied limitations. This is stated in the document referenced above (p. 2.16) "…*Describing the K_d in terms of this simple reaction assumes that A is in great excess with respect to C_i and that the activity of A_i is equal to 1. The K_d term is valid only for a particular adsorbent and applies only to those aqueous chemical conditions (e.g., adsorbate concentration,solution/electrolyte matrix, temperature) in which it was measured. Also inherent in the K_d term are the assumptions that the system is reversible and is independent of the adsorbate concentration in the aqueous phase*…"

Given these implicit assumptions and limitations associated with them, all K_d values calculated and discussed below should be seen as indicative of the behavior of the elements of interest in the Oxy site groundwater and its soils.

To ascertain important aspects of sorption or release of heavy metals from Oxy site soils, a wide range of experiments was conducted. These experiments aimed to determine A_i values at extreme conditions (e.g., total digestion, or in exposures at pH 0 or 14) and also when the pH of ambient water was within the range expected for the Oxy site groundwater and/or unaffected environments at the site. These experiments yielded site- and pH-specific C_i data.

Using these results, K_d values for the elements of interest were determined using three reference states. These included i) metal concentrations obtained in conditions of complete digestion (the latter condition is denoted as that resulting in “total” metal concentration (TOT); ii) metal concentrations measured in exposures at pH 0 (this corresponds to a generally accepted condition of a nearly-complete metal mobilization from solid matrixes) and iii) metal concentrations released from the soil at pH 14 (this corresponds to an extreme case of highly alkaline areas of the plume). Calculations to determine the respective K_d values were carried out as follows:

A. K_d values characterizing the mobilibity of adsorbates at pHs ranging from 8 to 12, assuming that the total mobilizeable metal equals the amount released from the solid phase at pH 14 and ambient temperature. The expressions for A_i and $K_{i.pH}^{pH14}$ for this choice are:

$$A_{i,pH}^{pH14} = A_{i,14} - \frac{V_L C_{i,pH}}{M_s} = \frac{V_L C_{i,pH14}}{M_s} - \frac{V_L C_{i,pH}}{M_s} \qquad (1)$$

$$K_{i.pH}^{pH14} = \frac{A_{i,pH}^{pH14}}{C_{i,pH}} = \frac{V_L C_{i,pH14} - V_L C_{i,pH}}{M_s C_{i,pH}} \qquad (2)$$

When the concentrations of metals released at pH<14 were higher than those observed at pH14, equation (2) could not be applied, so $K_{i.pH}^{pH14}$ values are not reported in those cases.

B. K_d values characterizing the mobility of adsorbates at pHs ranging from 8 to 14, assuming that the total mobilizable metal equals the amount released from the solid phase at pH 0 and ambient temperature. In this case, the expressions corresponding to Equations 6 and *7 are*:

$$A_{i,pH}^{pH0} = A_{i,0} - \frac{V_L C_{i,pH}}{M_s} = \frac{V_L C_{i,pH0}}{M_s} - \frac{V_L C_{i,pH}}{M_s} \qquad (3)$$

$$K_{i.pH}^{pH0} = \frac{A_{i,pH}^{pH0}}{C_{i,pH}} = \frac{V_L C_{i,pH0} - V_L C_{i,pH}}{M_s C_{i,pH}} \tag{4}$$

In the above equation, $C_{i,pH0}$ is the concentration of the metal released from the soil at pH 0.

<u>C. </u>*K_d values characterizing the mobility of elements at pHs ranging from 8 to 14, assuming that the mobilizable metal equals the amount released via oxidative acidic digestion of the solid*:

$$K_{i.pH}^{TOT} = \frac{A_{i,pH}^{TOT}}{C_{i,pH}} \tag{5}$$

In this expression, $A_{i,pH}^{TOT}$ is the concentration of the metal of interest that remains in the soil at the end of the exposure period at the pH of interest and that could subsequently be released by total digestion of the soil. For the calculations, this concentration was computed as the concentration of solid-phase metal actually released by total digestion of the original soil at pH 0 minus the concentration of solid-phase metal released during the exposure, i.e.:

$$A_{i,pH}^{TOT} = A_{i,0}^{TOT} - \frac{V_L C_{i,pH}}{M_s} \tag{6}$$

$$K_{i.pH}^{TOT} = \frac{A_{i,pH}^{TOT}}{C_{i,pH}} = \frac{M_s A_{i,0}^{TOT} - V_L C_{i,pH}}{M_s C_{i,pH}} \tag{7}$$

In these equations, M_S and V_L are the mass of exposed soil and solution volume (20 g and 200 mL, respectively, in the reported experiments), $A_{i,0}^{TOT}$ is the concentration of the metal of interest determined via the digestion of the soil, and $C_{i,pH}$ is the concentration of that metal in the aqueous phase at the given pH.

In general, slightly positive (zero to ca. 0.5) or negative $\log K_d$ values indicate that the concentration of a metal mobilized from the solid phase is comparable to or exceeds the concentration of that metal in the solid phase. This is in conflict with the implied assumption that the concentration of the metal of interest in the solid phase is always much higher than that in the liquid phase. For that reason negative $\log K_d$ values or those <ca. 0.5 should be considered as qualitatively indicative of a higher mobility of the metal of interest at actual exposure conditions compared with the respectively reference state (e.g., at pH 14) but caution should be exercised in their use for quantitative modeling of metal mobility.

Results of EPA Method 3050B digestions

This section provides a brief discussion of results obtained in digestions of the Oxy site soils using EPA method 3050B. Concentrations of representative heavy metals and matrix elements (except Si, C and S) determined in these experiments are compiled in **Table 3**. That table presents mean values calculated for two digestion experiments per sample, and applicable standard deviations.

Comparison of the mean values and standard deviations indicate that for most metals, the standard deviations were ca. 10% of the mean or less. The ratios of the standard deviations to the mean were higher for Cd and Tl. This was a result of a lower precision in determinations of these elements, as their levels in the solid matrixes were extremely low. Despite this limitation, the overall digestion data set was concluded to be highly robust.

The concentrations of any of the examined soil components varied from sample to sample, but their mean values and standard deviations calculated for the entire dataset of the soil specimens (**Table 4**) showed the presence of a consistent order in which the concentrations of the elements quantified in ICP/MS measurements decreased. This order is presented in **Figure 2** that compares the logarithms of the averaged metal concentrations in the solid phase. This figure demonstrates the sequence of concentration levels has the order Fe > Al > Mg > Ca >> Mn > V >> Zn ≈ Cr ≈ Cu ≈ Ba ≈ Ni >> As ≈ Pb >> U >> Cd >> Tl. This order is similar to that reported for the average concentrations of various elements in the Earth crust.

Given that iron was the dominant component of the soils and that heavy metals tend to interact strongly with iron oxyhydroxides that are likely to be present in the Oxy site soils, Fe concentrations in the digestates were compared with those of the heavy metals. This comparison indicated the heavy metal concentrations were strongly correlated with the concentration of iron (**Figure 3**). The R^2 values characterizing these correlations were as high as 0.90 for V, Cr and other elements except Cd and U (**Figure 4**). While Cd and U concentrations showed weaker correlations with the Fe levels, this may be a result of a comparatively lower analytical precision for these micropollutants.

After iron, aluminum was the second most important metal component of the soils (**Figure 4**) and concentrations of the heavy metals in the Oxy site soils were determined to be as strongly correlated with the levels of aluminum as they were with iron. This may be interpreted to indicate that the binding of heavy metals by the Oxy site soils is likely to involve both Fe and Al minerals, or their mixed solid phases.

The above interpretation is clearly simplistic and solid phases predominated by other elements, for instance Si and Mn (whose concentrations in the Oxy site soils were almost two orders of magnitude lower than those of Fe and Al) are likely to control the retention and release of heavy elements in the examined system. Still, given the strength of the observed correlations, the trends presented in **Figure 3** and **Figure 4** may give important insights into the nature of interactions governing the fate and transport of heavy elements in the Oxy site.

Table 3 Metal concentrations and standard deviations (determined in duplicate experiments) for 27 Oxy site soils digested using EPA method 3050B. All data in mg/kg units.

Element	S 1 (average)	S 1 (SD)	S 2 (average)	S 2 (SD)	S 3 (average)	S 3 (SD)	S 4 (average)	S 4 (SD)	S 5 (average)	S 5 (SD)	S 6 (average)	S 6 (SD)
V	24.7	0.7	25.1	0.9	25.9	0.9	26.0	0.2	27.0	0.1	28.7	0.2
Cr	9.8	0.1	10.3	0.2	10.9	0.1	11.6	0.9	11.9	0.9	11.9	1.0
Ni	4.1	0.1	4.8	0.2	5.0	0.8	5.0	0.7	5.2	0.8	5.3	1.0
Cu	7.4	0.4	8.4	0.4	9.7	0.7	10.6	0.8	10.8	0.2	12.5	0.3
Zn	9.8	1.7	9.8	4.6	9.7	4.1	10.1	3.6	11.3	2.1	11.7	4.5
As	0.73	0.03	0.75	0.05	0.81	0.07	0.82	0.16	0.84	0.03	0.97	0.18
Cd	0.31	0.03	0.30	0.07	0.27	0.05	0.30	0.01	0.40	0.03	0.41	0.07
Pb	0.82	0.03	0.85	0.05	0.90	0.08	0.97	0.03	1.05	0.00	1.11	0.09
U	0.94	0.00	1.01	0.01	0.88	0.01	1.00	0.02	1.03	0.02	1.00	0.00
Tl	0.023	0.032	0.031	0.015	0.036	0.018	0.029	0.019	0.039	0.021	0.023	0.023
Ba	7.8	0.2	7.8	0.2	7.9	0.5	8.1	0.8	8.3	0.3	9.6	0.2
Al	3614	52	3811	56	4100	82	4215	23	4431	60	4859	75
Fe	7707	372	8201	335	8576	246	8732	174	8854	216	9235	287
Mn	50.3	8.1	53.5	5.6	57.9	3.7	60.3	1.5	62.9	2.2	66.5	6.6
Mg	1643	45	1639	48	1784	48	1908	34	1989	46	2067	20
Ca	1231	7	1254	38	1439	37	1623	25	1694	41	1764	22

Element	S 7 (average)	S 7 (SD)	S 8 (average)	S 8 (SD)	S 9 (average)	S 9 (SD)	S 10 (average)	S 10 (SD)	S 11 (average)	S 11 (SD)	S 12 (average)	S 12 (SD)	S 13 (average)	S 13 (SD)
V	47.5	0.8	46.0	0.5	50.4	0.5	52.6	0.7	30.1	0.3	33.6	0.6	25.0	0.8
Cr	23.0	0.5	22.1	0.5	23.3	0.5	23.5	0.2	12.3	0.4	12.9	0.7	8.3	0.2
Ni	11.2	0.4	12.0	0.4	14.0	0.0	14.8	0.2	5.2	0.1	5.7	0.2	3.2	1.0
Cu	18.5	0.6	18.1	0.6	21.3	0.0	22.2	0.2	9.6	0.9	12.1	0.9	7.5	0.2
Zn	23.2	1.1	25.0	3.2	26.2	4.0	28.3	0.6	11.9	1.8	14.4	3.9	9.6	3.6
As	2.37	0.08	2.91	0.00	2.88	0.10	2.94	0.03	1.38	0.07	1.60	0.03	0.59	0.19
Cd	0.66	0.01	0.66	0.00	0.65	0.01	0.65	0.00	0.47	0.04	0.79	0.05	0.45	0.09
Pb	2.34	0.01	2.01	0.02	2.53	0.03	2.68	0.04	1.35	0.10	1.60	0.03	1.12	0.10
U	1.06	0.01	1.14	0.00	1.13	0.01	1.10	0.01	1.08	0.01	1.00	0.02	1.03	0.02
Tl	0.050	0.001	0.059	0.000	0.065	0.013	0.064	0.003	0.028	0.005	0.045	0.011	0.021	0.003
Ba	16.2	0.1	14.0	1.0	16.2	0.9	19.7	0.2	12.0	0.0	13.7	0.3	6.1	1.0
Al	11505	136	12043	203	13926	64	14146	185	5258	67	5678	51	3276	52
Fe	14301	349	15029	332	16500	10	17372	661	9932	143	10840	74	7657	240
Mn	101.4	2.5	109.0	4.0	110.5	1.9	110.2	1.1	61.5	8.7	67.4	0.4	44.5	7.7
Mg	3173	58	3209	49	3541	13	3793	23	1833	11	2011	35	1395	47
Ca	2232	60	2490	42	2674	16	2788	35	1476	22	1622	41	1465	39

Element	S 14 (average)	S 14 (SD)	S 15 (average)	S 15 (SD)	S 16 (average)	S 16 (SD)	S 17 (average)	S 17 (SD)	S 18 (average)	S 18 (SD)	S 19 (average)	S 19 (SD)	S 20 (average)	S 20 (SD)
V	35.1	0.6	27.7	0.6	27.8	0.2	28.2	1.0	25.6	1.0	26.6	0.8	29.8	0.7
Cr	12.2	0.3	12.1	0.2	12.2	0.6	9.6	0.1	9.8	2.0	11.2	1.0	12.8	0.2
Ni	6.0	0.4	6.2	0.1	6.4	0.0	4.2	0.6	4.2	0.2	4.4	0.1	5.0	0.1
Cu	11.6	0.1	12.0	1.0	13.3	0.2	8.9	0.4	8.9	1.8	9.2	0.9	11.1	0.5
Zn	13.4	0.4	13.1	4.4	13.0	2.5	11.1	0.6	11.0	2.0	11.5	4.1	12.4	1.5
As	1.79	0.03	1.80	0.12	1.72	0.08	1.22	0.19	1.39	0.04	1.40	0.05	1.50	0.07
Cd	0.45	0.07	0.50	0.04	0.40	0.03	0.39	0.05	0.45	0.00	0.41	0.09	0.50	0.04
Pb	1.50	0.01	1.40	0.03	1.34	0.03	1.09	0.07	1.38	0.00	1.39	0.06	1.40	0.08
U	1.00	0.00	1.09	0.00	0.91	0.03	0.99	0.03	1.00	0.07	1.01	0.03	1.02	0.00
Tl	0.024	0.001	0.035	0.014	0.034	0.025	0.029	0.019	0.036	0.002	0.022	0.033	0.030	0.017
Ba	12.6	0.7	11.1	0.0	7.7	0.9	10.0	0.9	7.3	0.0	7.9	1.1	11.1	0.3
Al	7248	50	6999	44	4238	62	4728	16	3869	223	3983	41	5997	81
Fe	10795	110	10692	370	10016	142	8887	184	8935	1440	9806	305	10091	294
Mn	73.0	2.0	73.0	0.6	74.7	1.1	60.0	0.4	70.1	2.0	72.2	2.8	73.0	0.2
Mg	2220	34	2242	8	2235	24	1912	14	1925	44	1966	29	2015	45
Ca	2177	17	2011	44	1893	37	1667	31	1722	21	1811	29	1988	14

Element	S 21 (average)	S 21 (SD)	S 22 (average)	S 22 (SD)	S 23 (average)	S 23 (SD)	S 24 (average)	S 24 (SD)	S 25 (average)	S 25 (SD)	S 26 (average)	S 26 (SD)	S 27 (average)	S 27 (SD)
V	29.7	0.6	31.8	0.7	38.2	0.7	39.6	0.9	25.1	0.3	29.2	1.8	35.0	1.1
Cr	12.6	0.6	16.2	0.5	19.7	0.2	17.9	0.5	9.7	0.8	13.9	0.2	15.0	1.0
Ni	5.6	0.0	6.7	0.0	9.6	0.3	10.2	0.1	4.9	0.9	7.7	0.3	14.0	0.0
Cu	13.7	0.6	13.8	0.5	14.0	0.3	14.3	0.2	8.9	0.7	9.3	0.3	12.0	0.0
Zn	14.2	0.9	16.5	2.6	20.2	0.5	22.0	1.5	13.3	4.6	15.2	0.7	17.0	1.0
As	1.69	0.19	1.81	0.04	2.06	0.04	2.27	0.13	0.80	0.03	1.15	0.03	2.04	0.00
Cd	0.55	0.09	0.59	0.07	0.63	0.00	0.71	0.02	0.50	0.05	0.59	0.00	0.67	0.00
Pb	1.59	0.07	1.65	0.09	2.15	0.04	2.21	0.04	1.29	0.05	1.61	0.02	2.04	0.87
U	0.97	0.01	1.01	0.03	1.00	0.01	1.01	0.02	0.61	0.03	0.90	0.01	1.05	0.09
Tl	0.055	0.018	0.038	0.011	0.041	0.001	0.044	0.019	0.022	0.002	0.019	0.000	0.035	0.002
Ba	17.7	0.4	19.9	0.4	20.1	4.0	22.8	0.4	7.0	0.5	7.7	0.0	10.0	1.0
Al	7972	22	9003	76	11431	196	11726	0	4044	68	5707	112	8760	209
Fe	10863	398	11538	320	12226	107	12442	218	7046	177	8849	100	9045	33
Mn	73.1	8.6	79.4	1.6	89.5	2.3	93.0	8.3	57.2	5.4	64.1	1.3	77.0	2.0
Mg	2340	10	2370	18	2480	25	2613	36	1566	45	1733	41	1934	50
Ca	2214	27	2216	6	2225	26	2244	33	1310	31	1609	39	1802	29

Table 4 Average metal concentrations and their standard deviations for the set of 27 Oxy site soils digested using EPA method 3050B.

Element	Average concentration, mg/kg	SD, mg/kg	SD/Aver, %	log of average concentration, mg/kg
Fe	10525	2644	25%	4.02
Al	6910	3427	50%	3.84
Mg	2205	598	27%	3.34
Ca	1876	418	22%	3.27
Mn	73.5	18.1	25%	1.87
V	32.3	8.2	26%	1.51
Zn	15.0	5.5	37%	1.18
Cr	14.0	4.6	33%	1.14
Cu	12.2	3.9	32%	1.09
Ba	11.9	4.8	41%	1.07
Ni	7.1	3.4	48%	0.85
As	1.6	0.7	44%	0.19
Pb	1.5	0.5	34%	0.19
U	1.00	0.10	10%	0.00
Cd	0.51	0.14	28%	-0.30
Tl	0.04	0.01	37%	-1.44

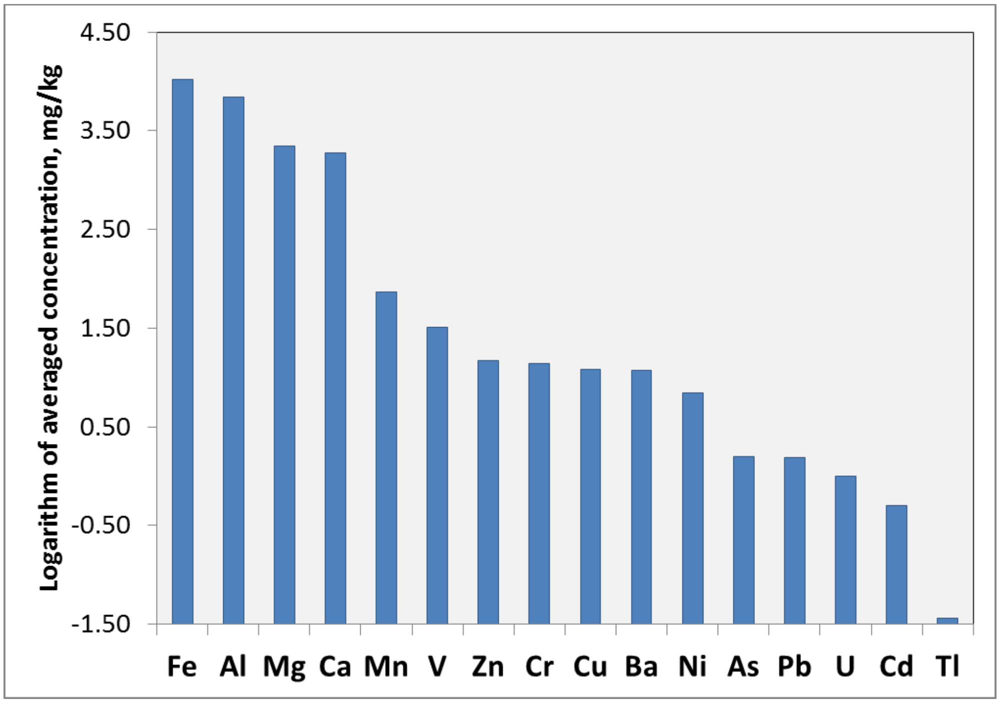

Figure 2 Logarithms of metal concentrations averaged across 27 samples of Oxy site soils. Results of digestion using EPA method 3050B.

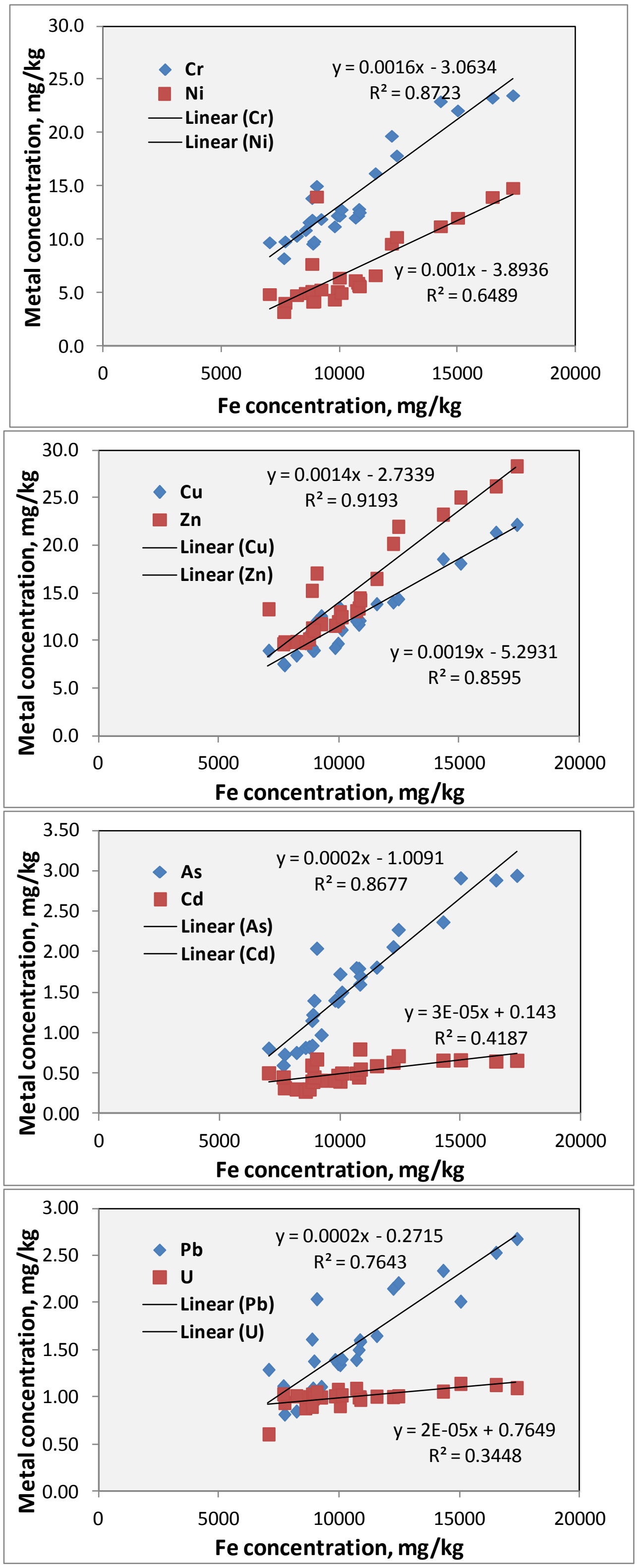

Figure 3 Correlations between concentrations of selected heavy metals and iron in aquifer samples digested using EPA method 3050B. Data for 27 aquifer samples listed in Table 1.

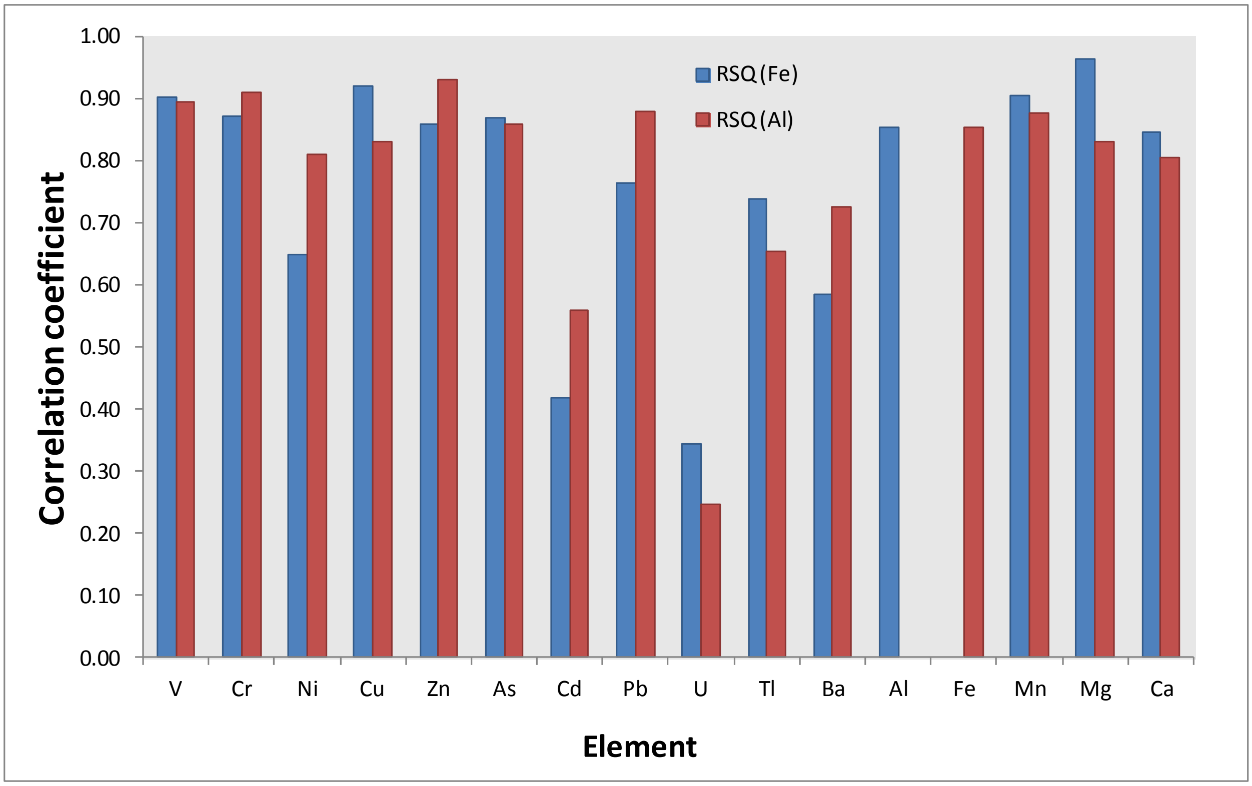

Figure 4 R^2 values for correlations between concentrations of various metals vs. concentrations of iron or aluminum in aquifer samples digested using EPA method 3050B.

Soil exposures at pH 0 and pH 14: metal concentrations released at varying contact times

Time profiles of metal release were examined for a subset of the Oxy site soils (S7, S10, S18 and S27) exposed at pH 0 and pH 14. These soils originated from both (assumedly) largely unaffected areas of the Oxy site and those that are thought to have been exposed to high-pH, high salinity groundwater plumes.

Results of measurements metal release from samples S7, S10, S18 and S27 at pH 0 are presented in Figure 5, Figure 7, Figure 9 and Figure 11, respectively. Results of metal release measurements at pH 14 for the same samples are shown in Figure 6, Figure 8, Figure 10 and Figure 12, respectively.

Trends seen in these figures can be summarized as follows. At pH 0, concentrations of heavy metals tended to increase throughout the entire exposure time but for contact times > 4 days incremental increases of metal concentrations tended to be relatively less prominent. This was evident in the data for samples S7 (Figure 5) and S10 (Figure

7). For sample S18, concentrations of some metals, for instance Cu, As and U tended to stabilize after a 4 day contact time (Figure 9) while the concentration of other elements such as Zn and V continued to increase. For sample S27, the concentrations of some metals, for instance Cu, Zn, Ni and Cr exhibited incremental increases for contact time > 4 days while the concentrations of Pb, As, Cd and U tended to plateau in these conditions.

Data for metal release at pH 14 showed comparable trends, with one notable exception observed for Cu. Measurements of copper release at pH 14 showed that highest concentrations of this element were consistently observed at short contact times following which Cu concentrations decreased several-fold (Figure 6, Figure 8, Figure 10 and Figure 12). For contact times > 4 days, Cu concentrations tended to become stable. The reason for the non-monotonic behavior of Cu at pH 14 is unclear but it is likely to be caused by the formation of soluble tri- and tetrahydroxo complexes of Cu(II) in the initial phase of exposure and their ensuing slow disproportionation to form tenorite at longer contact times.

For the heavy elements other than Cu, metal release at pH 14 tended to plateau at contact times > 4 days. Accordingly, it was decided that all further exposures would be carried out using a constant 7 day contact time (as also discussed in the preceding sections of the report). This decision is in accord with recommendations made in prior literature (e.g., USEPA, 1999. *Understanding Variation in Partition Coefficient K_d values.* Volume I: *The K_d Model, Methods of Measurement, and Application of Chemical Reaction Codes*).

Results of calculations of K_d values for a set of soil samples listed in **Table 2** using data obtained for a constant 7 day contact time but varying pHs are discussed separately for each soil sample.

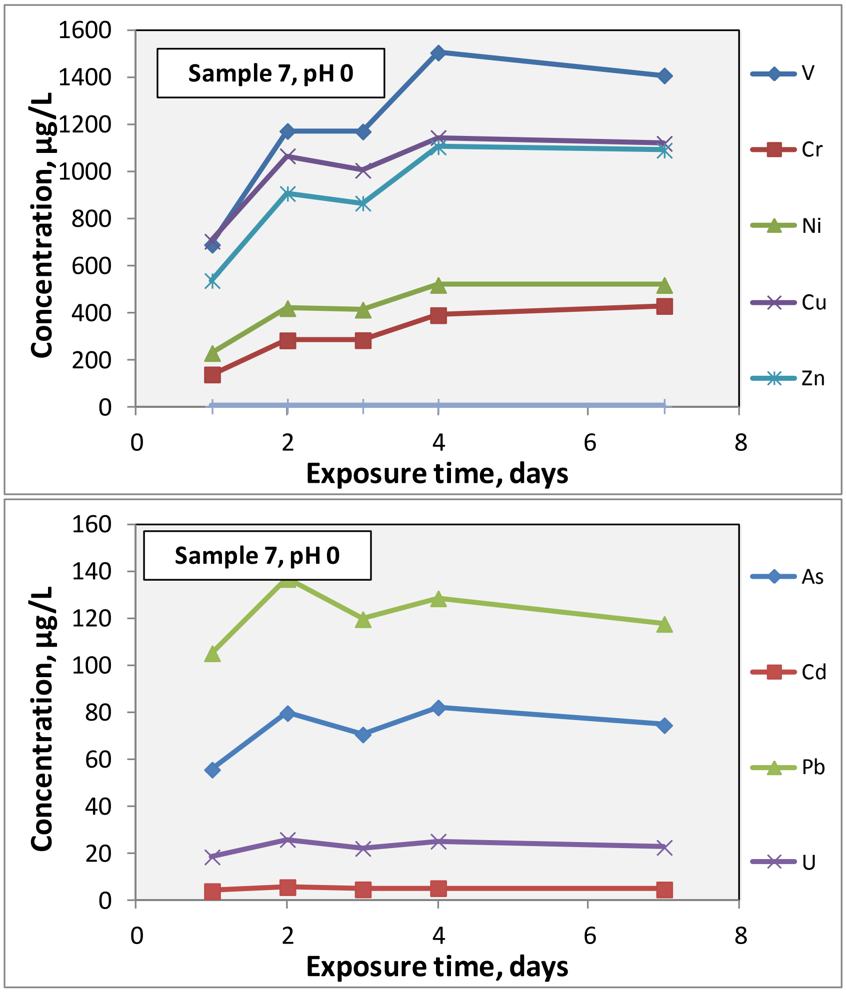

Figure 5 Time profiles of metal release for Sample 7 exposed at pH 0.

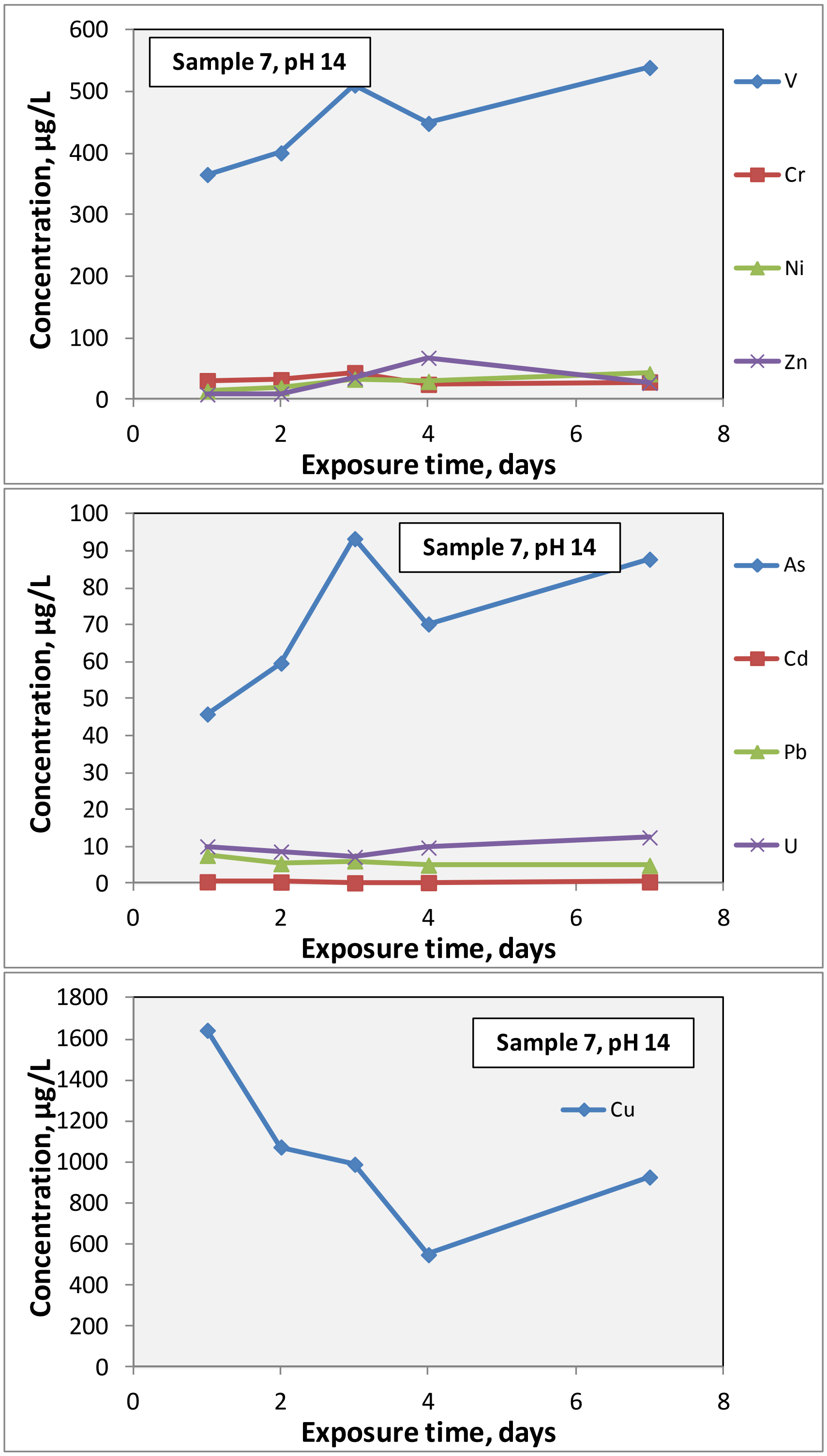

Figure 6 Time profiles of metal release for Sample 7 exposed at pH 14.

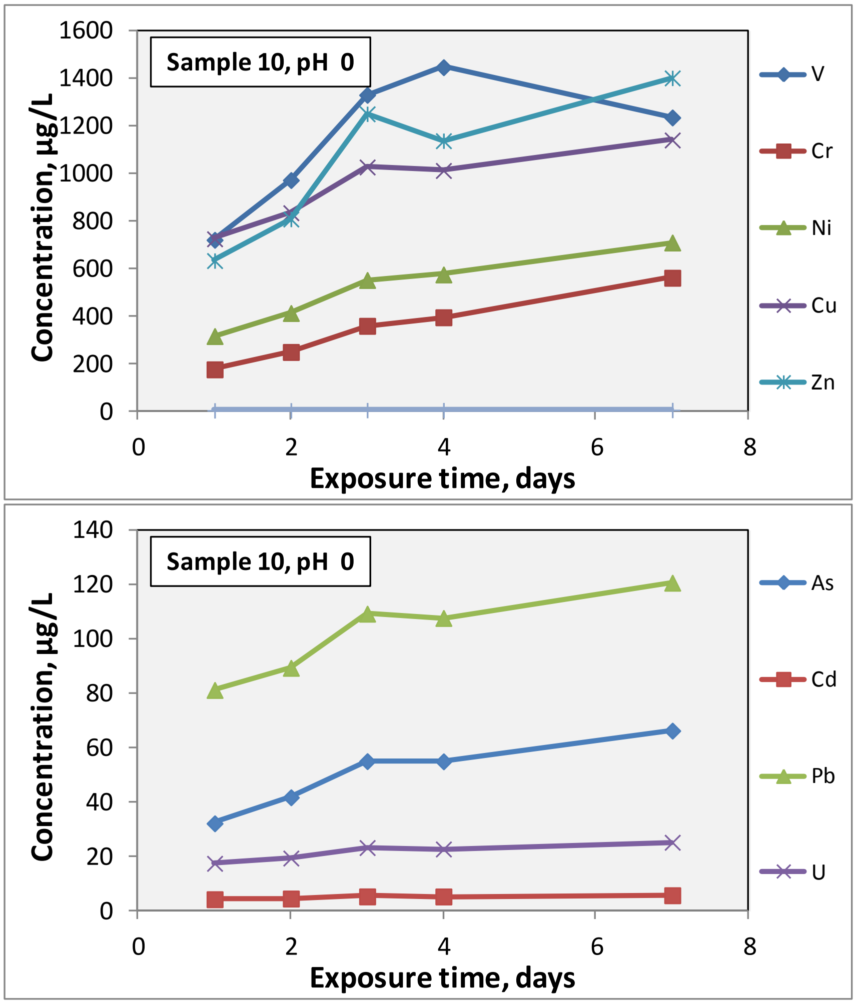

Figure 7 Time profiles of metal release for Sample 10 exposed at pH 0.

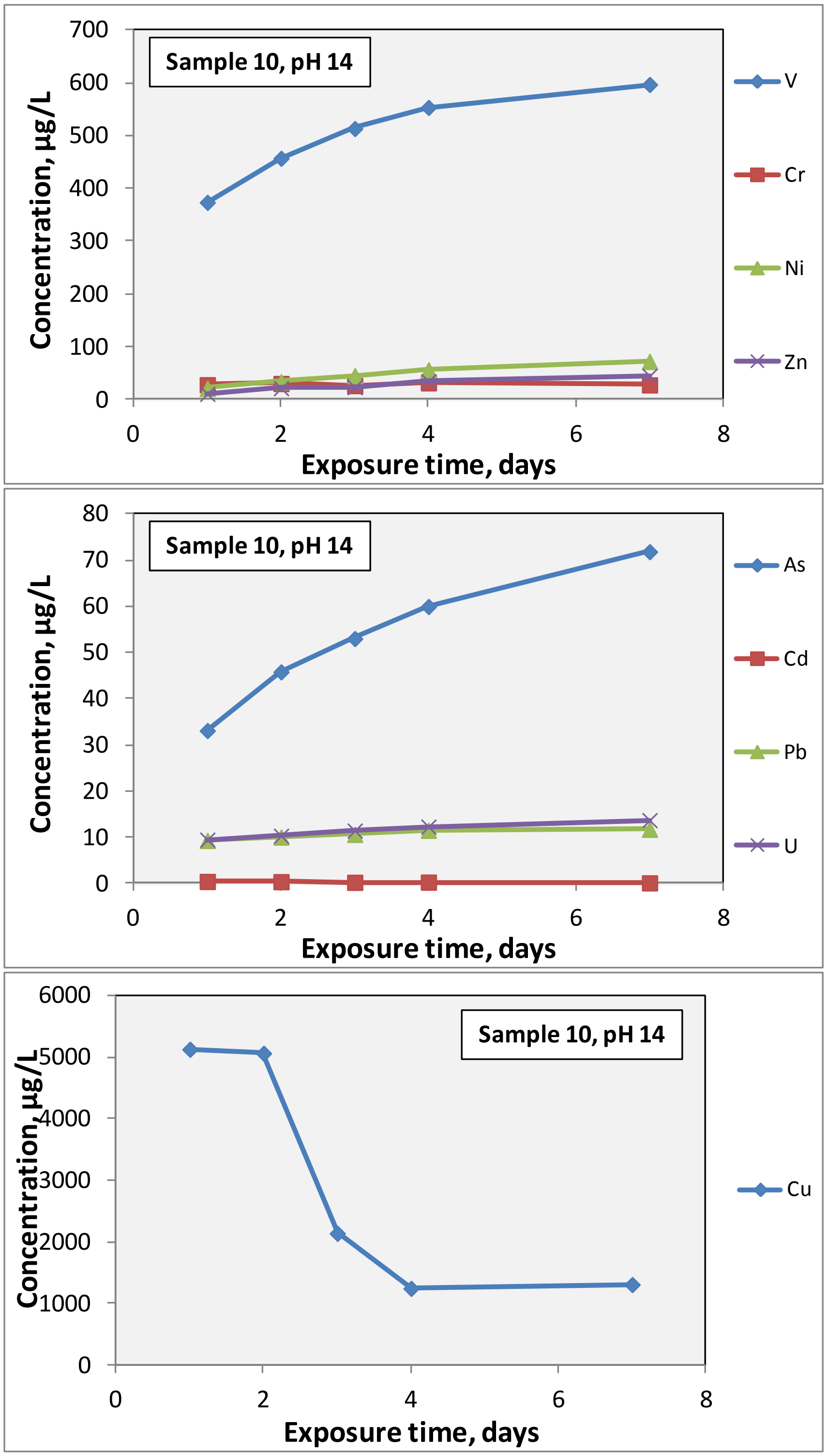

Figure 8 Time profiles of metal release for Sample 10 exposed at pH 14.

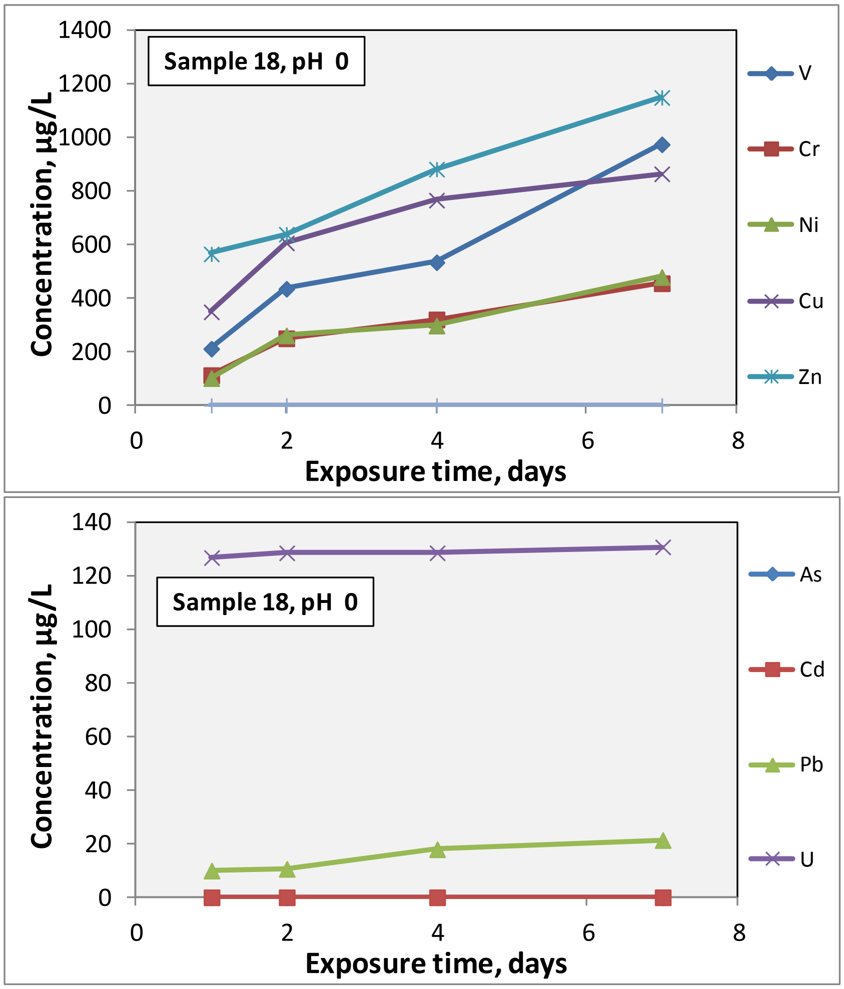

Figure 9 Time profiles of metal release for Sample 18 exposed at pH 0.

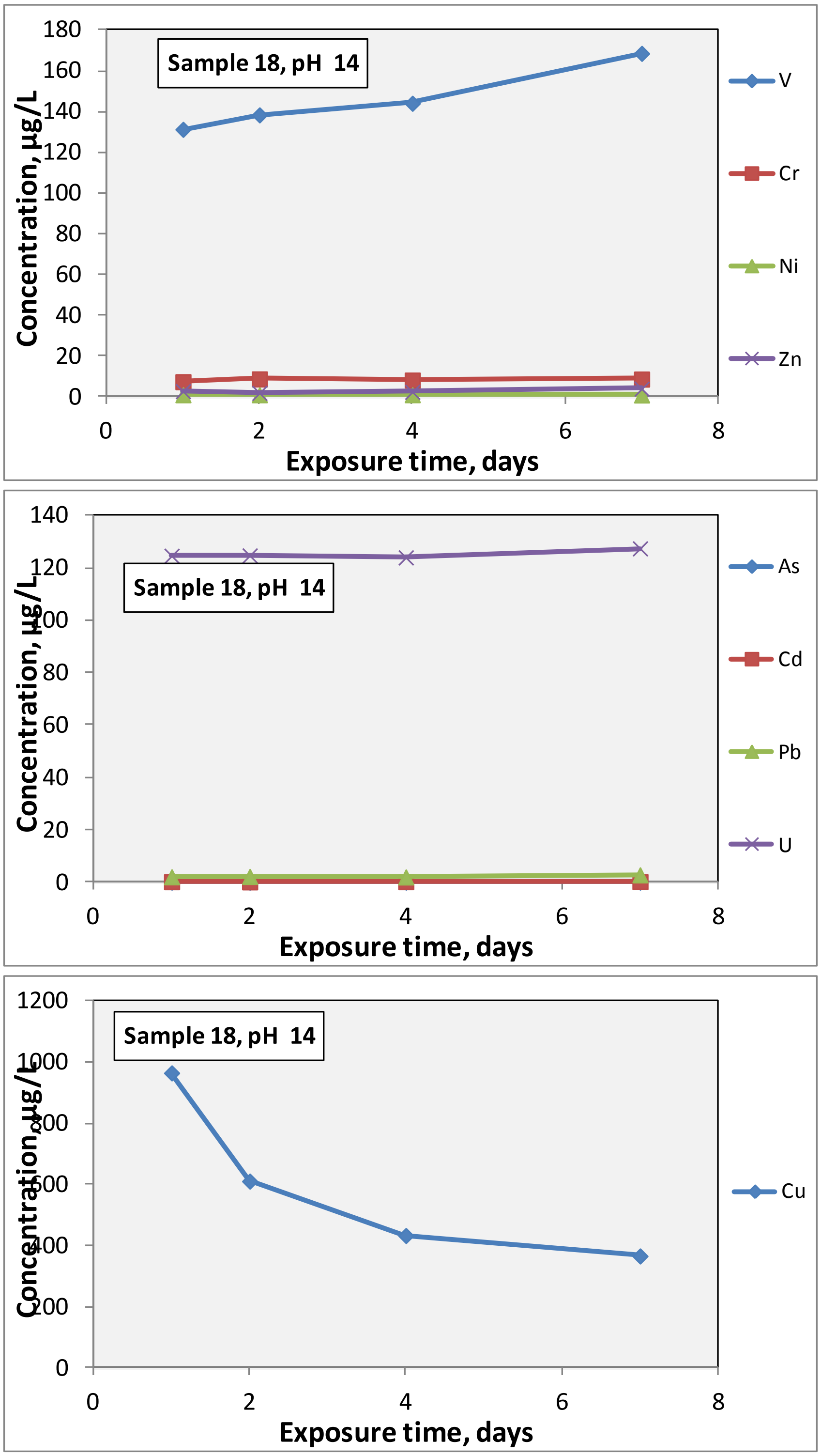

Figure 10 Time profiles of metal release for Sample 18 exposed at pH 14.

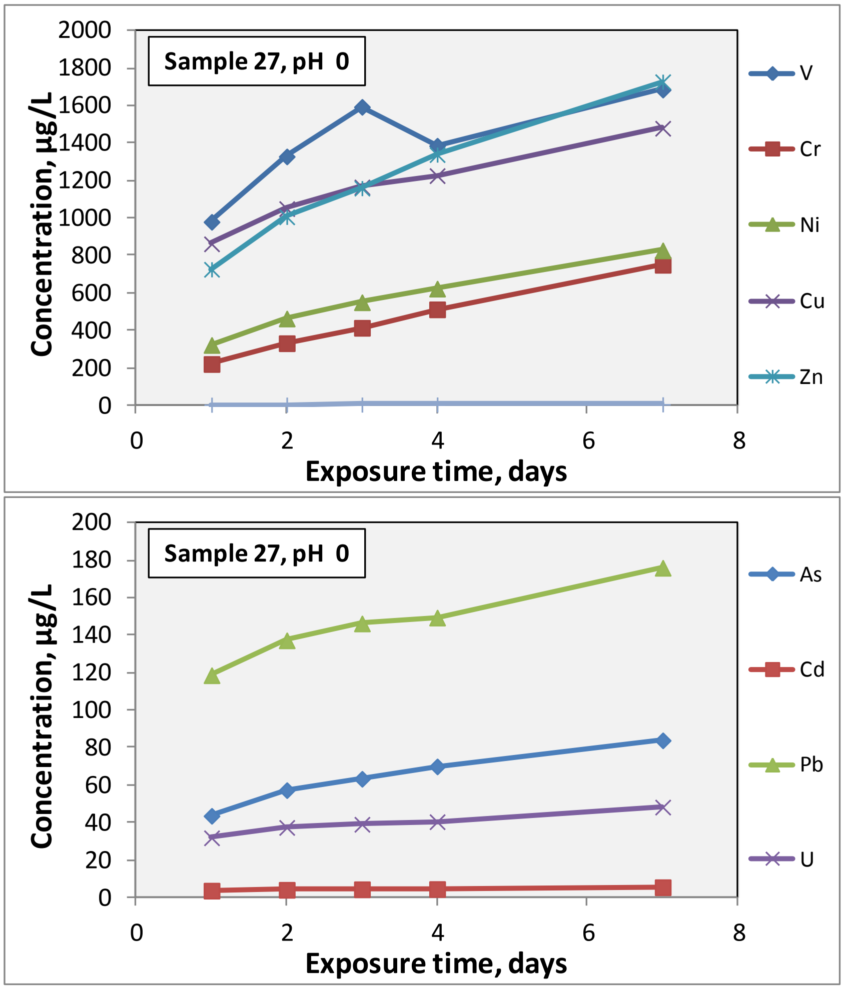

Figure 11 Time profiles of metal release for Sample 27 exposed at pH 0.

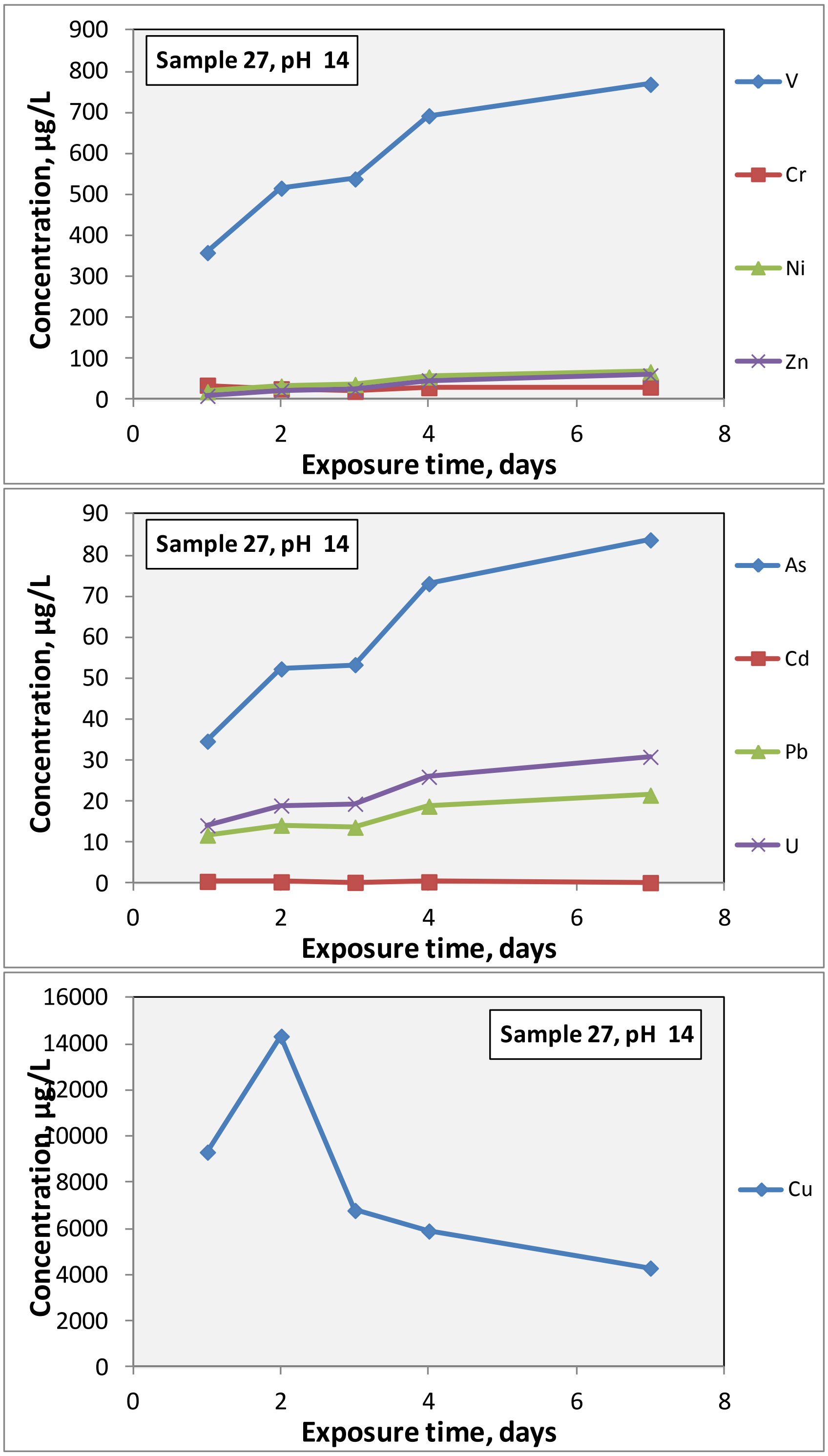

Figure 12 Time profiles of metal release for Sample 27 exposed at pH 14.

K_d values for Oxy soil samples

In this section, the K_d values for various metals interacting with the Oxy site soils listed in **Table 2** are presented and discussed briefly. As explained previously, K_d values for each metal and soil combination were calculated based on three estimates for the amount of metal available in the unaltered soil, namely (A) the amount released at pH 14; (B) the amount released at pH 0; and (C) the amount released by complete digestion of the soil. The respective K_d values were calculated using equations (7), (4) and (2), respectively.

The log K_d values at each pH investigated are shown in Figure 13 through Figure 21, and average log K_d values across the whole pH range for each metal/soil pair are presented in Table 5. The data vary, of course, from one soil sample to the next. Nevertheless, broad trends can be discerned, and the soils can be identified as falling into two distinct groups based on those trends. Specifically, the trends of K_d vs. pH for Group 1 (soil samples 7, 8, 10, 11, and 25) are all similar to one another, and different from those for Group 2 (samples 18, 23, 26, and 27), for which the trends are also similar to one another. These trends are discussed next.

K_d values for V, Cr, Ni, Cu, and As decreased significantly with increasing pH when exposed to soils in Group 1 (Figure 13, Figure 14, Figure 15, Figure 16, and Figure 19, respectively), and the decline in K_d was evident regardless of which approach was used to quantify the amount of metal available in the original soil solids.

The decline between the two end-members (pH 8 and 12) was typically larger for V, Cu, and As than for the other metals. K_d values for Zn and Cd also appeared to decline with increasing pH in these tests, but the declines were generally small and therefore not as reliable. K_d values for Pb and U, on the other hand were unaffected by pH in the range investigated.

Log K_d values for Group 2 soils differed from those for Group 1 in several ways. First, the concentrations for Cr, Ni, Zn, As, Cd and Pb that dissolved from these soils at the pHs of interest were consistently greater than at pH 14, causing K_d to be negative and log K_d to be undefined when the metal release at pH 14 was chosen as the baseline for estimating the total available metal in the soil. Similarly, although the concentration of U released at the pHs of interest was slightly less than at pH 14, the difference in the two values was very small, so the corresponding K_d was close to zero and log K_d was negative. Thus, reliable K_d values for the pH 14 baseline could be determined only for V and Cu. For both of these metals, log K_d decreased with increasing pH, but the absolute magnitude of K_d and its sensitivity to pH varied significantly from sample to sample.

When the available metal in the soil was based on either the pH 0 extraction or total digestion of Group 2 soils, increasing pH tended to increase the log K_d values for Cr, Ni, and Zn and to have either no effect on or increase log K_d for Cd. Note that this trend is opposite that for the Group 1 soils.

Copper behaved differently from the other metals when exposed to Group 2 soils; its log K_d decreased with increasing pH, as had occurred with Group 1 soils Log K_d values for V, As and Pb were insensitive to pH for Group 2 soils.

Table 5 Average and standard deviation (SD) of log K_d values for various soil samples over the pH range from 8 to 14.

S7	$\log K_i^{pH\,14}$		$\log K_i^{pH\,0}$		$\log K_i^{TOT}$	
	Avg	SD	Avg	SD	Avg	SD
V	1.5	1.0	2.1	0.8	2.7	0.7
Cr	1.8	0.3	3.1	0.2	3.8	0.2
Ni	1.8	0.3	3.0	0.2	3.3	0.2
Cu	2.3	0.9	2.4	0.9	2.7	0.8
Zn	1.4	0.1	3.1	0.1	3.4	0.1
As	1.9	1.3	1.7	1.4	2.5	1.1
Cd	3.0	0.2	4.0	0.2	5.2	0.2
Pb	-	-	1.9	0.0	2.2	0.0
U	-	-	0.5	0.1	1.7	0.0

S8	$\log K_i^{pH\,14}$		$\log K_i^{pH\,0}$		$\log K_i^{TOT}$	
	Avg	SD	Avg	SD	Avg	SD
V	1.2	0.9	1.9	0.6	2.5	0.6
Cr	1.8	0.3	2.8	0.2	3.6	0.2
Ni	1.5	0.5	2.8	0.3	3.1	0.3
Cu	2.1	1.0	2.0	1.1	2.3	0.9
Zn	1.6	0.2	2.9	0.1	3.4	0.1
As	1.6	1.3	1.5	1.4	2.3	1.0
Cd	1.1	0.7	3.8	0.5	5.1	0.5
Pb	-	-	1.7	0.0	2.1	0.0
U	-	-	0.8	0.0	1.9	0.0

S10	$\log K_i^{pH\,14}$		$\log K_i^{pH\,0}$		$\log K_i^{TOT}$	
	Avg	**SD**	**Avg**	**SD**	**Avg**	**SD**
V	1.5	1.1	2.0	1.0	2.7	0.9
Cr	2.1	0.7	3.4	0.6	4.1	0.6
Ni	2.8	0.5	3.8	0.4	4.1	0.4
Cu	2.6	0.9	2.5	0.9	2.8	0.9
Zn	2.8	1.0	4.3	1.0	4.6	1.0
As	1.6	1.0	1.6	1.1	2.4	0.8
Cd	0.3	0.7	2.6	0.4	3.7	0.4
Pb	-	-	1.9	0.0	2.3	0.0
U	-	-	0.7	0.0	1.7	0.0

S11	$\log K_i^{pH\,14}$		$\log K_i^{pH\,0}$		$\log K_i^{TOT}$	
	Avg	**SD**	**Avg**	**SD**	**Avg**	**SD**
V	1.8	1.4	2.7	1.1	3.1	1.1
Cr	1.7	1.6	3.4	1.1	3.8	1.1
Ni	2.4	0.6	3.6	0.5	3.6	0.5
Cu	4.6	1.1	2.7	1.2	2.8	1.2
Zn	1.3	0.1	3.6	0.8	3.8	0.8
As	1.5	1.3	2.0	0.9	2.5	0.8
Cd	0.8	0.7	3.1	0.3	4.0	0.3
Pb	0.7	0.2	1.8	0.1	1.9	0.1
U	0.2	0.3	0.9	0.1	1.7	0.0

S18	$\log K_i^{pH\,14}$		$\log K_i^{pH\,0}$		$\log K_i^{TOT}$	
	Avg	**SD**	**Avg**	**SD**	**Avg**	**SD**
V	0.1	0.4	1.8	0.1	2.2	0.1
Cr	-	-	2.3	0.5	2.7	0.5
Ni	-	-	3.1	1.0	3.0	1.0
Cu	1.6	0.5	2.0	0.4	2.0	0.4
Zn	-	-	2.5	0.7	2.5	0.7
As	-	-	-	-	2.3	0.3
Cd	-	-	-	-	3.0	0.2
Pb	-	-	-	-	1.6	0.0
U	-	0.3	-	0.2	-	-

S23	$\log K_i^{pH\,14}$		$\log K_i^{pH\,0}$		$\log K_i^{TOT}$	
	Avg	**SD**	**Avg**	**SD**	**Avg**	**SD**
V	0.5	0.1	1.5	0.1	2.1	0.1
Cr	-	-	1.8	0.3	2.4	0.2
Ni	-	-	2.3	0.2	2.5	0.2
Cu	0.9	0.1	1.2	0.1	1.4	0.0
Zn	-	-	3.6	0.6	3.9	0.6
As	-	-	-	-	1.2	0.1
Cd	-	-	-	-	2.9	0.0
Pb	-	-	0.1	0.0	1.8	0.0
U	-	-	-	0.7	-	-

S25	$\log K_i^{pH\,14}$		$\log K_i^{pH\,0}$		$\log K_i^{TOT}$	
	Avg	**SD**	**Avg**	**SD**	**Avg**	**SD**
V	1.3	2.0	2.3	1.4	2.7	1.4
Cr	1.8	1.0	3.1	0.7	3.4	0.7
Ni	2.2	0.2	3.8	0.1	3.6	0.1
Cu	3.5	0.4	2.2	0.5	2.1	0.5
Zn	2.0	0.7	3.4	0.6	3.5	0.6
As	2.2	0.4	2.5	0.7	2.3	0.8
Cd	0.8	0.5	1.8	0.2	2.7	0.2
Pb	0.5	0.2	2.0	0.0	1.9	0.0
U	0.1	0.2	0.5	0.1	1.4	0.0

S26	$\log K_i^{pH\,14}$		$\log K_i^{pH\,0}$		$\log K_i^{TOT}$	
	Avg	**SD**	**Avg**	**SD**	**Avg**	**SD**
V	0.9	0.0	2.1	0.0	2.7	0.0
Cr	-	-	1.8	0.1	2.5	0.1
Ni	-	-	1.9	0.1	2.2	0.1
Cu	1.1	0.3	-	-	0.4	0.4
Zn	-	-	1.9	0.1	2.3	0.1
As	-	0.4	-	-	1.5	0.1
Cd	-	-	0.7	0.3	3.1	0.1
Pb	-	-	0.8	0.0	1.7	0.0
U	-	-	0.3	0.0	2.0	0.0

S27	$\log K_i^{pH\,14}$		$\log K_i^{pH\,0}$		$\log K_i^{TOT}$	
	Avg	**SD**	**Avg**	**SD**	**Avg**	**SD**
V	1.5	1.4	1.9	0.9	2.3	0.9
Cr	-	-	2.2	0.1	2.6	0.1
Ni	-	-	1.9	0.1	2.2	0.1
Cu	1.5	1.1	2.7	-	2.6	-
Zn	-	-	1.5	0.6	1.4	0.6
As	-	0.2	-	0.2	1.2	0.0
Cd	-	-	1.1	0.3	2.5	0.2
Pb	-	-	1.7	0.0	1.8	0.0
U	-	0.1	0.8	0.0	1.4	0.0

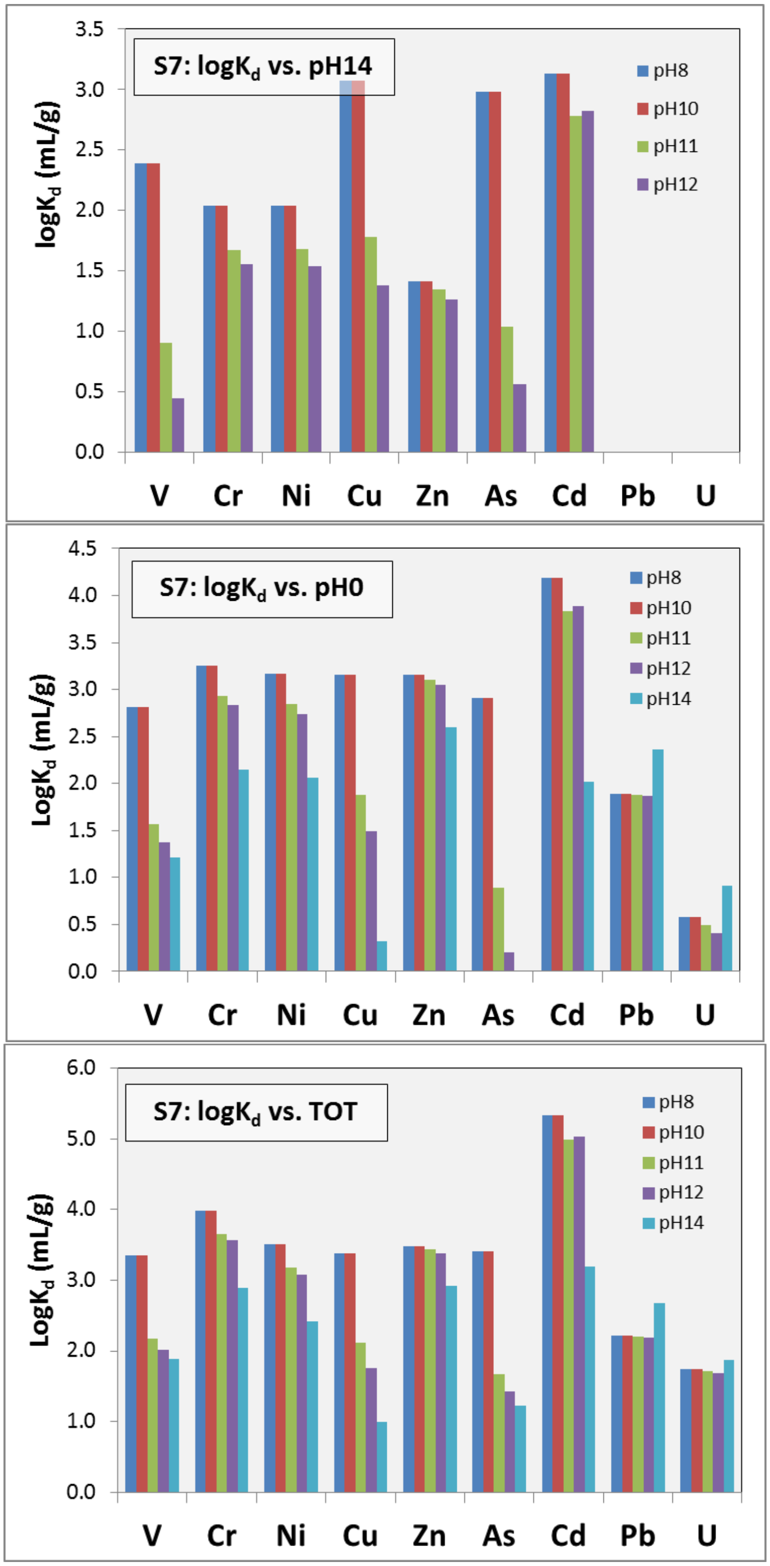

Figure 13 pH-dependent K_d values determined for Sample 7.

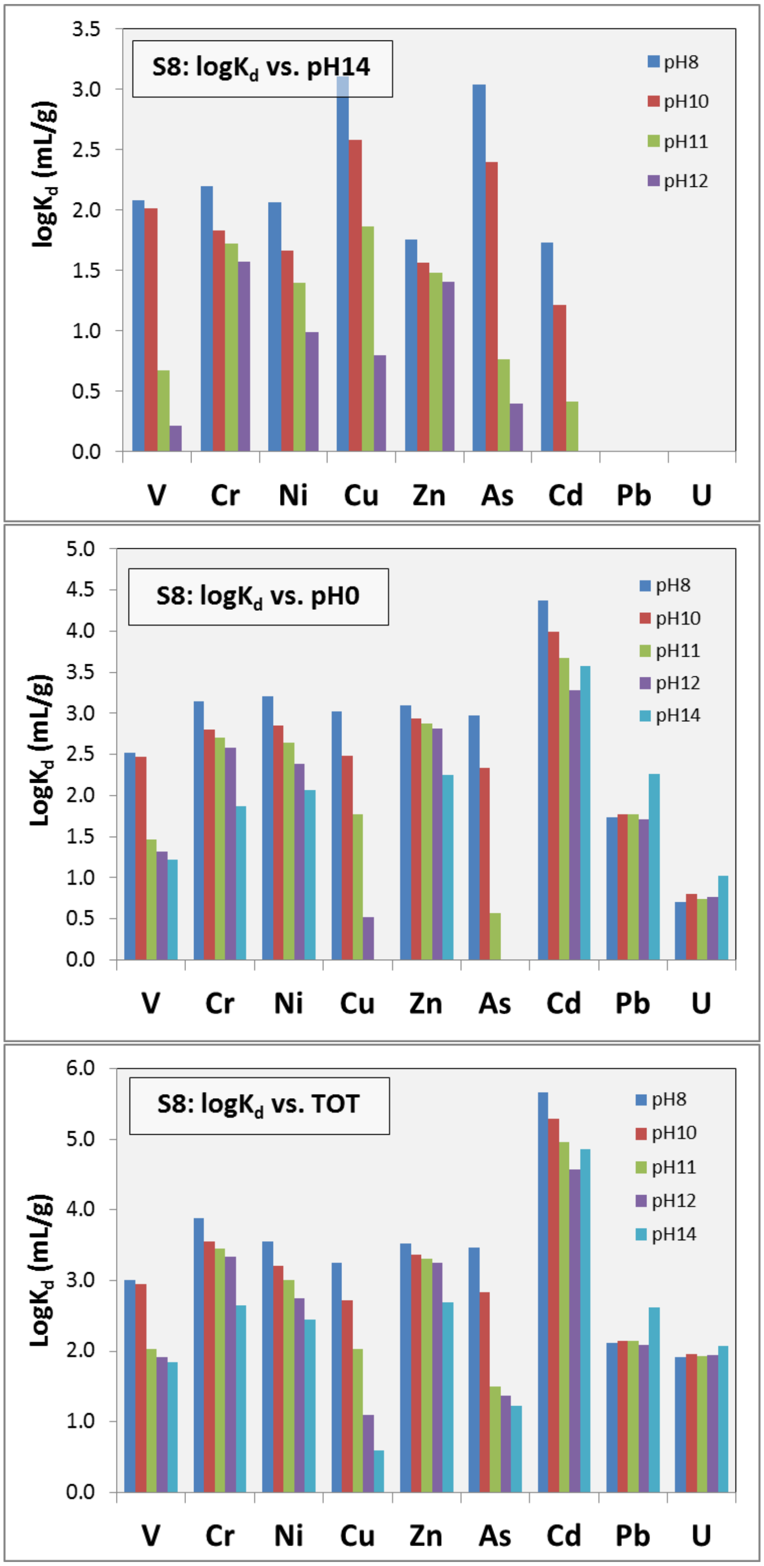

Figure 14 pH-dependent K$_d$ values determined for Sample 8.

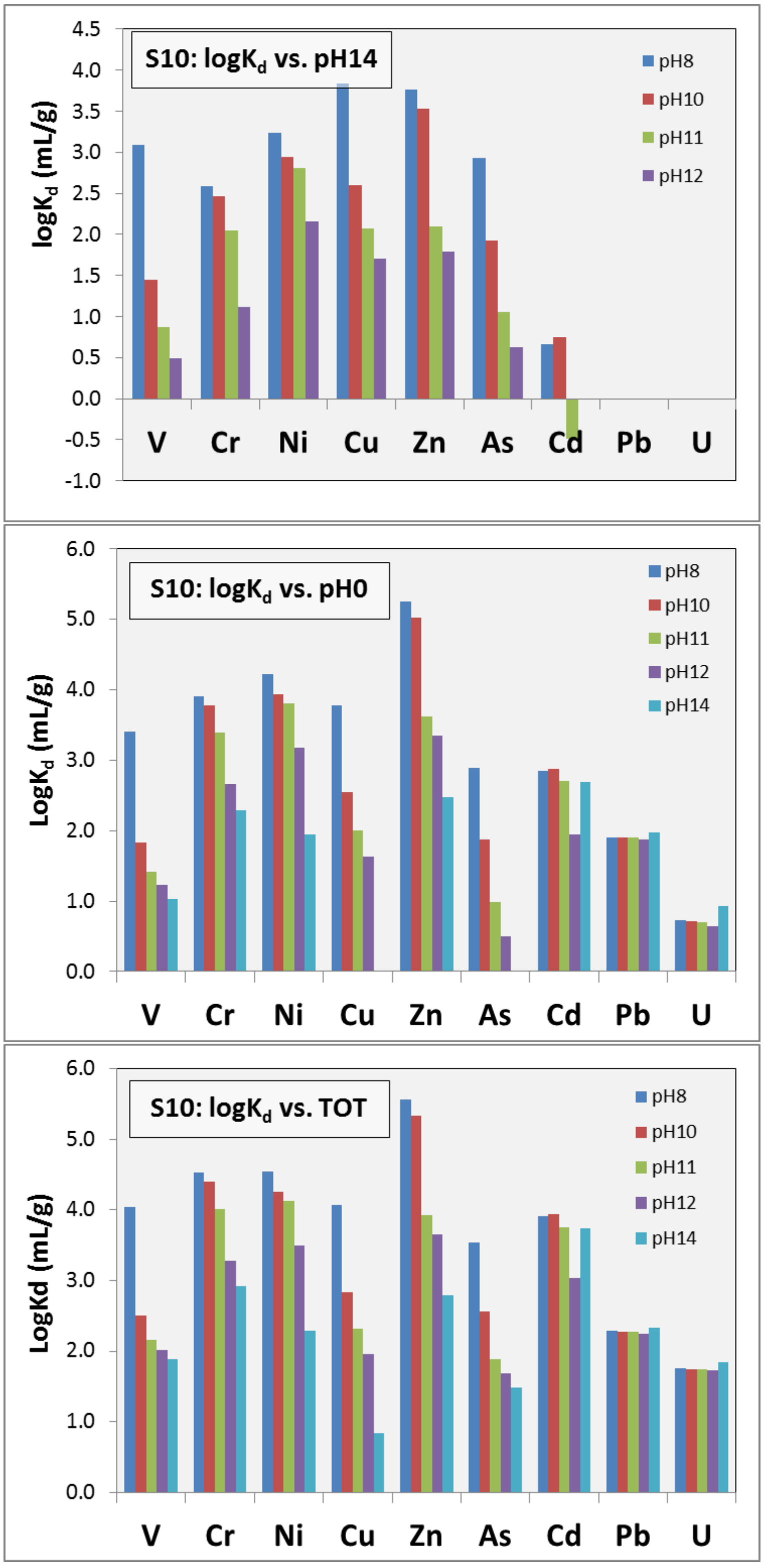

Figure 15 pH-dependent K_d values determined for Sample 10.

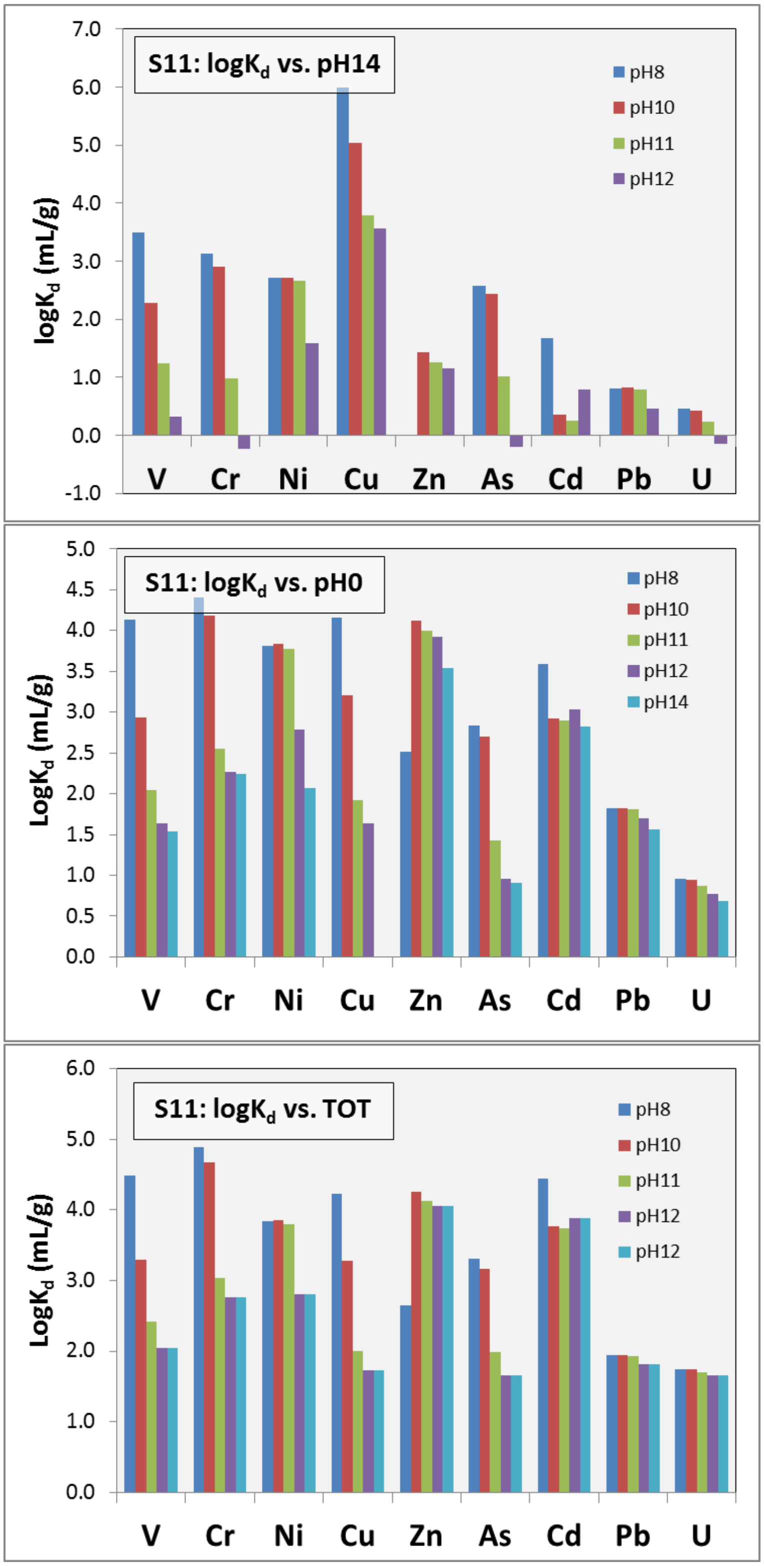

Figure 16 pH-dependent K_d values determined for Sample 11.

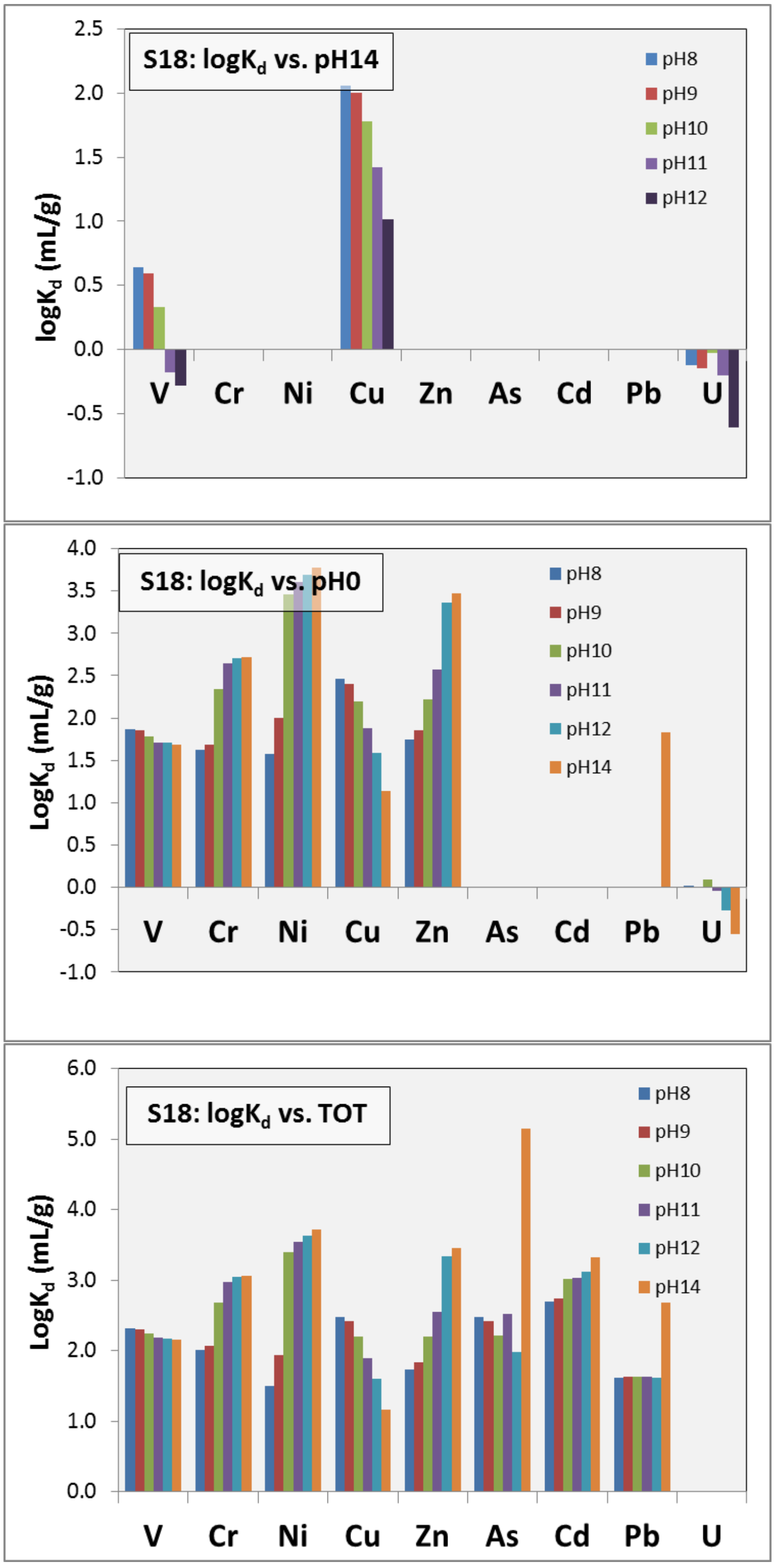

Figure 17 pH-dependent K$_d$ values determined for Sample 18.

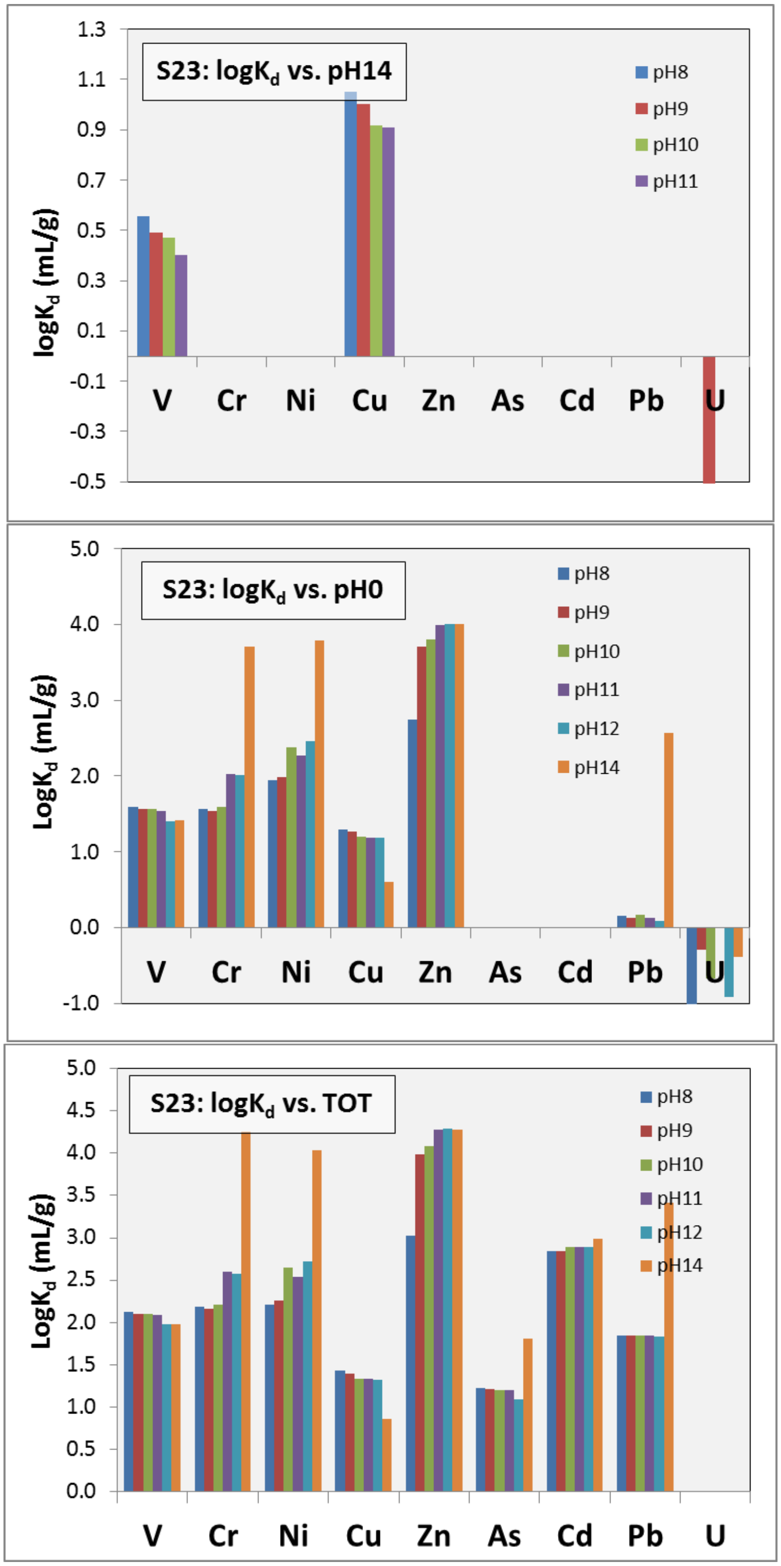

Figure 18 pH-dependent K$_d$ values determined for Sample 23.

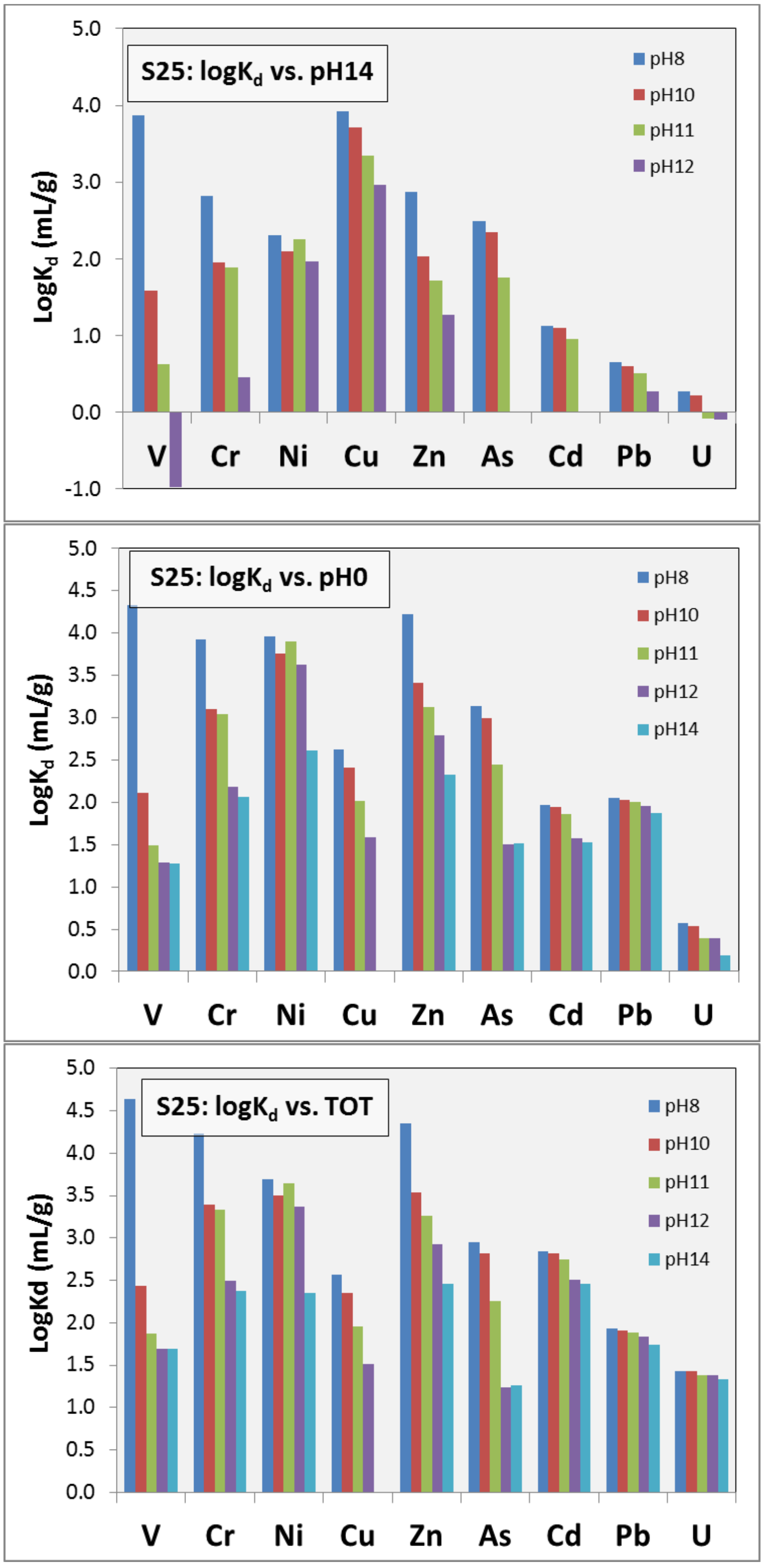

Figure 19 pH-dependent K$_d$ values determined for Sample 25.

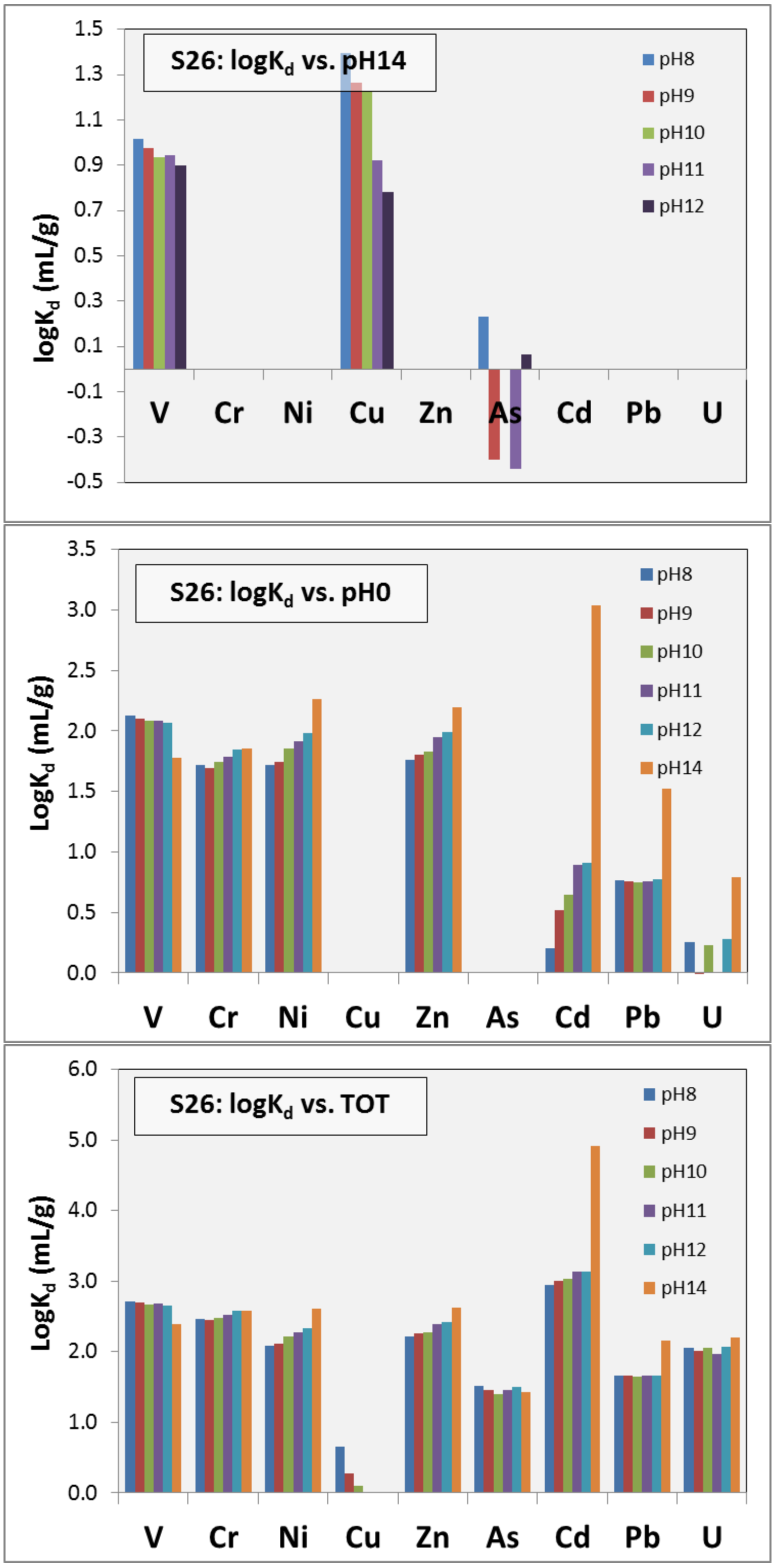

Figure 20 pH-dependent K$_d$ values determined for Sample 26.

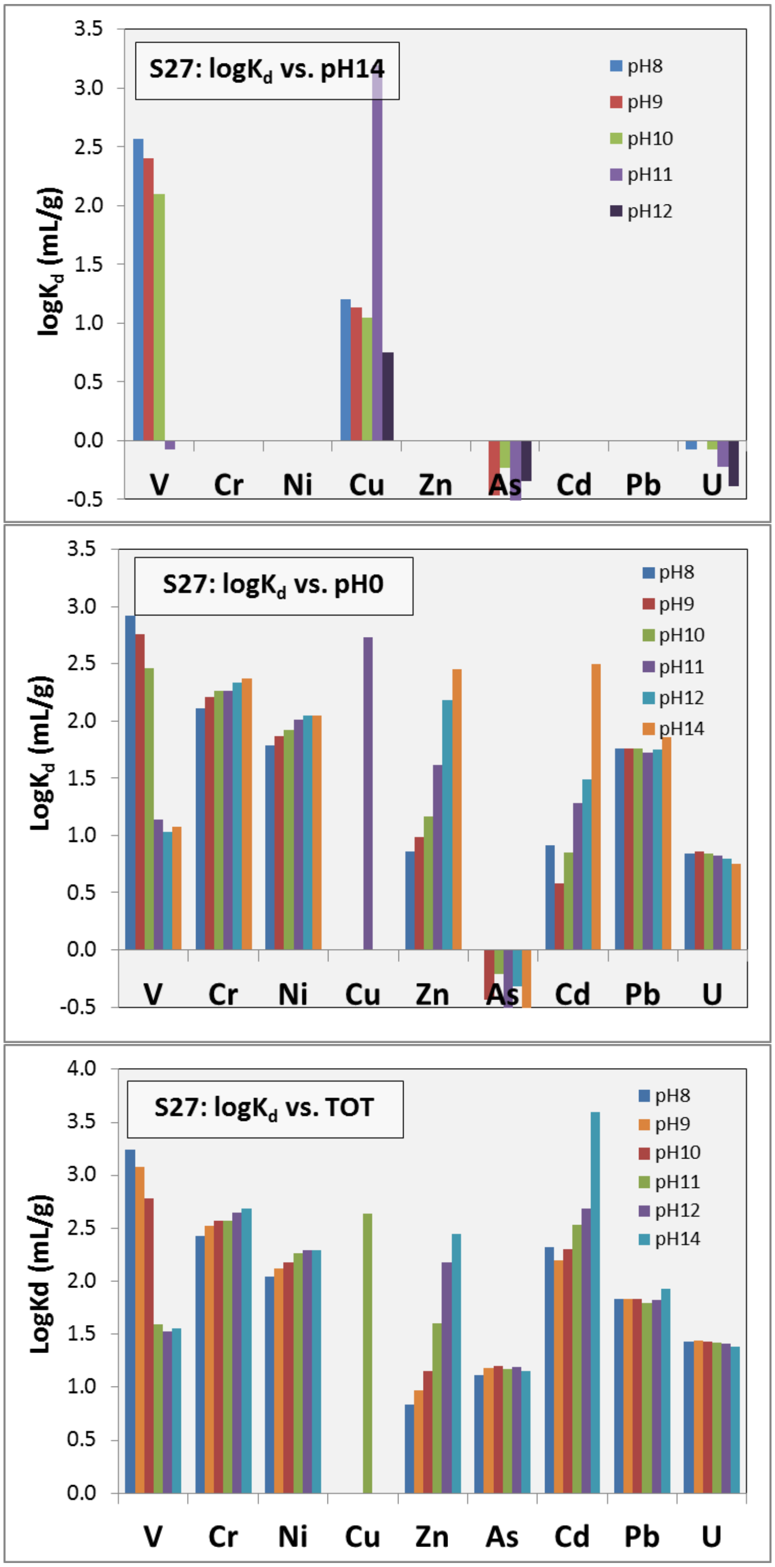

Figure 21 pH-dependent K_d values determined for Sample 27.

General comparison of $\log K_d$ values determined for Oxy site soil samples

To examine in more detail the commonalities and differences in the trends observed for the examined soils, $\log K_d$ values determined using the three reference conditions and different soil specimens are compared side by side in Figure 22 to Figure 30. Each of these figures represents a set of $\log K_d$ values determined for V (Figure 22), Cr (Figure 23), Ni (Figure 24), Cu (Figure 25), Zn (Figure 26), As (Figure 27), Cd (Figure 28), Pb (Figure 29) and U (Figure 30).

These figures demonstrate that for some elements, notably V, Cu and As, increases of pH of ambient water are accompanied by consistent decreases of the $\log K_d$ values in nearly all examined cases. In contrast, for Cr, Ni, Zn and Cd, this trend is present for some samples (S7, S8, S10, S11 and S25) but it is opposite for others (S18, S23, S26 and S27). For Pb and U, the data are less complete but the available results indicate the presence of relatively minor effects of pH variations.

Further examination of the trends mentioned above shows that the soils used in the experiments can be operationally separated into two groups. The first group (Group A) that includes samples S7, S8, S10, S11 and S25 is deemed to be representative of the Oxy site soils originating from areas that are not likely to have been affected by the high pH plumes characteristic for the site. The second group (samples S18, S23, S26 and S27, Group B) comprises soils originating for Oxy site areas that have been affected by high pH groundwater.

The suggested grouping of soils S7, S8, S10, S11 and S25 is conditional as the pH of the groundwater in contact with soil samples S8 and S10 is reported to be 10.6 and 12, respectively (**Table 2**). Despite the relatively high reported pH values, the trends observed for samples S8 and S10 are clearly different from those for the soils that originate from Extraction Wells 7 and 9. Given the close similarity between the properties of soils S8 and S10 and those of soils S7, S11 and S25, it may be assumed that that either the groundwater in contact with soils S8 and S10 did not have as high pH as that reported in **Table 2**, or the duration of such contact was not long enough so as to make their properties similar to those of soils from Extraction Well 7 and 9.

Alternative approaches to interpreting effects of pH and soil provenance on $\log K_d$ values

To determine the utility of the obtained $\log K_d$ values for the modeling of the fate and transport of heavy metals in the Oxy site aquifer, we compared on a systematic basis the logK_d values obtained using the alternative reference states, pHs of ambient water and soil provenance (e.g., using the two groups of soils, as suggested in the preceding section of the report). The point of such comparison was to determine whether use of the three alternative reference conditions results in dramatically different estimates of heavy metal release at pHs typical for the Oxy site, or these data can be combined to form a reasonably unified view on the metal mobility.

Such comparisons can be done using two alternative hypotheses. First, given the presence of diverse trends in the observed effects of pH on the logK_d values for the examined soils, the logK_d values can be assumed to be randomly distributed. Accordingly, they can be averaged over the entire dataset and mean logK_d constants so obtained could be used for fate and transport modeling for the Oxy site.

Alternatively, effects of pH on the logK_d values may be assumed to be intrinsically correlated with the pH, and such correlations should be explicitly quantified either for the entire sets of the Oxy site soils or its subgroups. Results of applications of both approaches to interpreting logK_d values are briefly discussed below.

Mean logK_d constants calculated for the entire range of soil samples and pH values

Calculations of the logK_d values over the entire range of pHs show that for V, Cu, Zn and Cd, the logK_d means determined for the pH 14 reference state change considerably from one soil to another (**Figure 31**). For Cr, Ni and As, such variations are less pronounced, while the data for Pb and U are absent or incomplete for this reference state.

Calculations of mean logK_d values determined vs the pH 0 reference condition produce less scatter (**Figure 32**). Still, the differences of the results for different soils remain pronounced for all elements, especially Cu, Zn, Cd and Pb. Calculations of pH-averaged logK_d values for total metal concentrations determined via soil digestions result in less differences between the data for different sites (**Figure 33**), except in the important cases of Cu, Zn and As.

Further processing of the pH-averaged logK_d values to calculate their means across the nine soils samples yield three data sets corresponding to the alternative reference conditions (**Figure 34** and **Table 6**). For some metals, notably Cu and As, such averaging produces comparable logK_d values but for the other metals the logK_d values obtained alternative reference conditions data are consistently different. The standard deviations calculated for the data reported in **Table 6** range from ca. 25% to >50% of the mean thus necessitating examination of effects of the uncertainty of the $\log K_d$ values on the modeling of the fate and transport of heavy metals in the Oxy site.

Another complication in the interpretation of the averaged $\log K_d$ values relates to an incomplete clarity of how results of the $\log K_d$ measurements carried out using the three alternative reference conditions can be compared and whether they confirm or contradict to each other. For instance, $\log K_d$ values obtained using metal concentrations measured in exposures at pH 0 and in total digestions are reasonably well correlated for the practically entire dataset of measurements at varying ambient pHs (R^2 0.86, **Figure 35**).

In contrast, comparison of the $\log K_d$ data obtained for either of the two latter reference conditions with, on the other hand, those generated using the pH 14 reference state does not indicate the presence of an unambiguously discernible trend (Figure 36). This suggests that in the absence of explicit consideration of pH effects on the $\log K_d$ values, their interpretation and use for practically important calculations may not be insufficient clear.

pH-specific $\log K_d$ values for Oxy site soils

An alternative approach to interpret the reported $\log K_d$ data involves calculating mean values of these constants for each specific pH separately. This can be done either for the entire set of Oxy site groups, or separately for the subgroups of Oxy site soils either unaffected by the high pH groundwater plumes or originating from within that area, respectively.

Results of applications of this approach for the entire set of the examined Oxy site soils are compiled in **Table 7**, **Table 8** and **Table 9**. They present site-averaged $\log K_d$ values calculated vs. the total digestion, pH 0 and pH 14 reference conditions, respectively. Same data are presented graphically in **Figure 37** and **Figure 38**. **Figure 37** shows effects of pH on the site-averaged $\log K_d$ values for V, Cr, Ni, Cu and Zn while **Figure 38** presents similar results for As, Cd, Pb and U.

These results establish that the site-averaged $\log K_d$ values for Cu and V determined vs. the total digestion reference decrease monotonically with the pH. There is also a minor decrease of the site-averaged $\log K_d$ values for Ni and Cr but the site-averaged $\log K_d$ value for Zn is practically constant.

These observations hold true for the site-averaged $\log K_d$ values calculated vs. the pH 0 reference condition although for Cr the decrease of the $\log K_d$ values with the pH is more evident. Finally, the site-averaged logK_d values determined vs. the pH 14 reference exhibit a strong and consistent decrease for all elements shown in **Figure 37**.

Similar data for As, Cd, Pb and U presented in **Figure 38** demonstrate that effects of pH on the site-averaged logK_d values for these metals were either absent or less prominent. However, the results for the pH 14 reference state show a more consistent decrease vs. pH.

Further examination of the observed trends shows that for many elements, the site-averaged logK_d values exhibit a statistically strong linear correlation vs. pH. Parameters of the applicable linear correlations are compiled in **Table 10**, **Table 11** and **Table 12**. These tables present, respectively, R^2 coefficients, slopes of the linear functions that fit the experimental logK_d vs. pH data for different elements and the logK_d constants projected to pH 7.0 using the linear best-fit functions.

Same data sets are presented for visual examination in **Figure 39**, **Figure 40** and **Figure 41**. **Figure 39** demonstrates that the correlations coefficients for the site-averaged logK_d values for V, Cr and Cu were close to 0.90 for all three reference conditions. The R^2 coefficients were also reasonably high but less consistent for Ni, Zn, As and Pb. For Cd and U, the R^2 coefficients were lower than those for the other elements.

Examination of the best-fit linear functions shown in **Figure 40** demonstrate that the use of alternative reference states results in generally different slopes of the applicable linear correlations although the data for Cu converge well.

On the other hand, calculations of estimated site-averaged logK_d coefficients for pH 7.0 using the three alternative reference conditions results in generally comparable results for V, Cr, Ni, Cu, Zn and As (**Figure 41**). For Cd, Pb and U the estimates are less convergent, which is not surprising given the weakness of the applicable linear correlations for these elements.

Application of the same approach to two separate groups of Oxy site samples (Group A and Group B) results in conclusions that are similar to those presented above for the entire soil dataset. Relevant results are presented in the Appendix in **Figure A52** and **Figure A53** for soils deemed unaffected by the high pH plumes while **Figure A54** and **Figure A55** show effects of pH on the site-averaged logK_d data for the soils from Extraction Wells 7 and 9. Results of statistical examination of these results are presented in **Table A24** to Table A29.

Further discussion of the data presented in these figures tables goes beyond the scope of this report. Suffice it to mention here that statistical analysis of the logK_d data for the two groups of Oxy site samples may provide some benefits but it does not seem to improve the clarity and, possibly, ease of implementation of the generated pH-specific site-averaged logK_d coefficients in the modeling of the fate and transport of heavy elements at the Oxy site. This recommendation may be however reevaluated based on results of applications of the reported logK_d values to the modeling of the fate and transport of the heavy metals at the Oxy site.

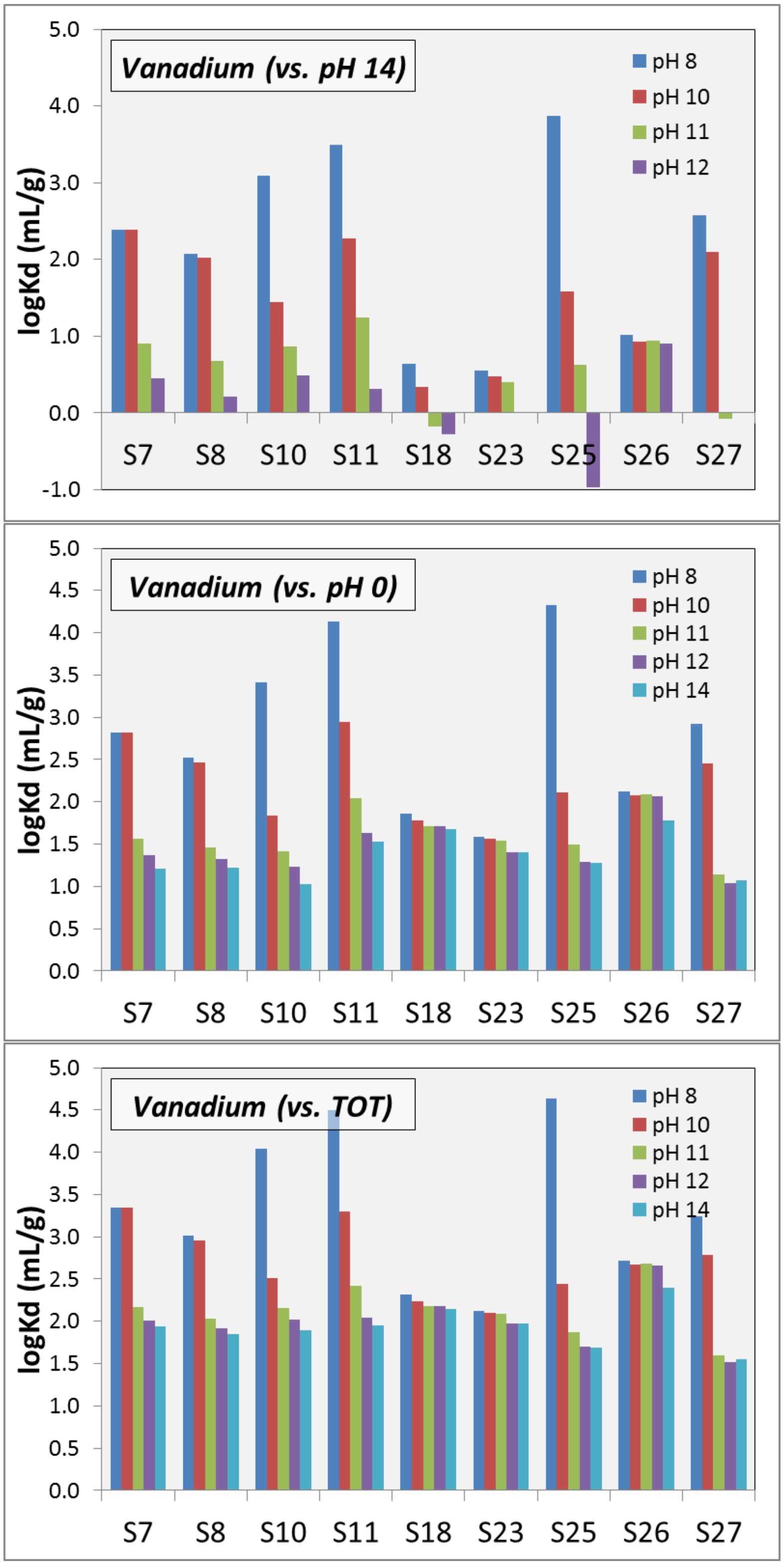

Figure 22 Effects of pH on logK$_d$ coefficients for vanadium determined in exposures at pH 14, pH 0 and in total digestions of the Oxy site soils.

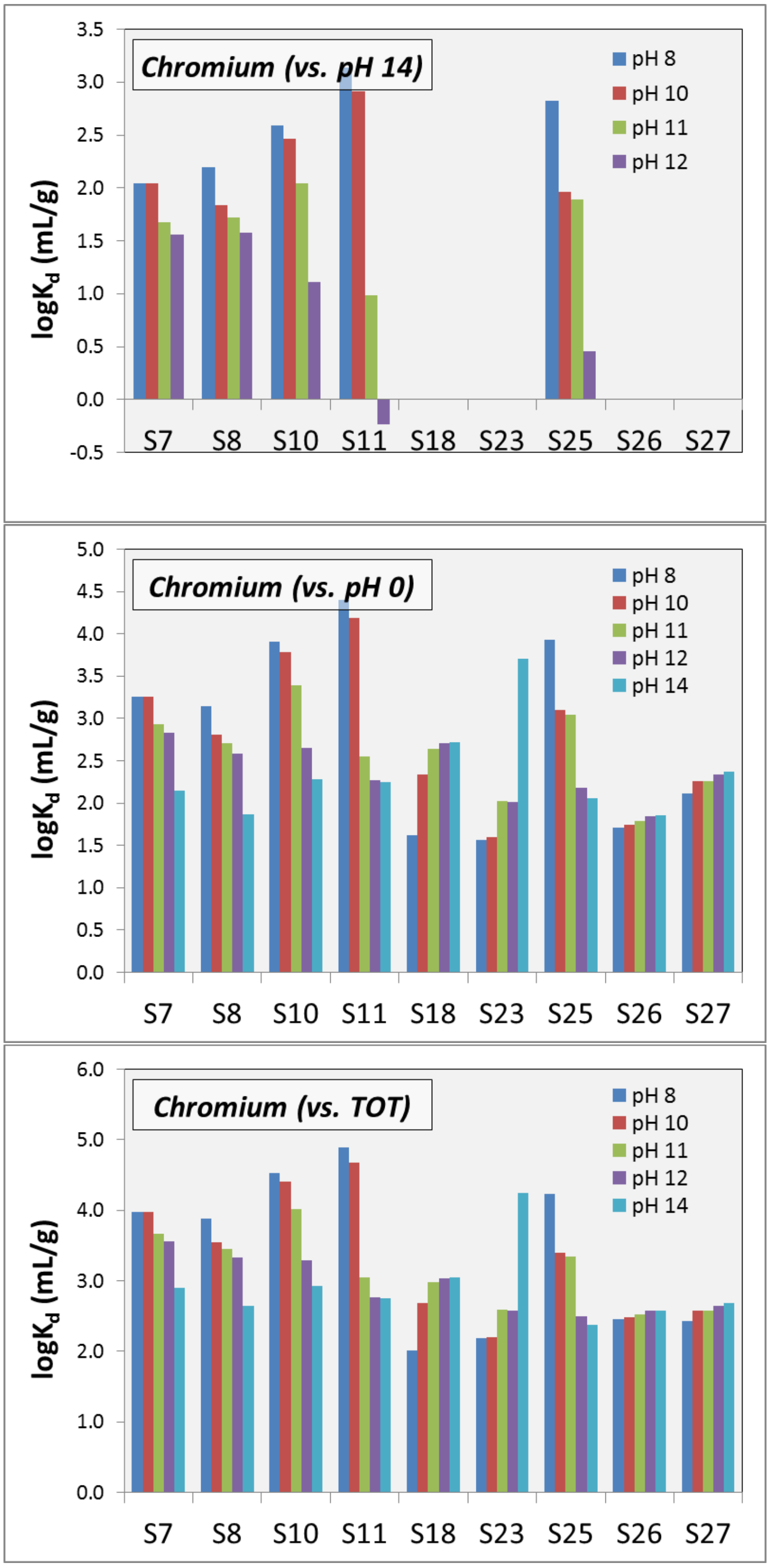

Figure 23 Effects of pH on logK$_d$ coefficients for chromium determined in exposures at pH 14, pH 0 and in total digestions of the Oxy site soils.

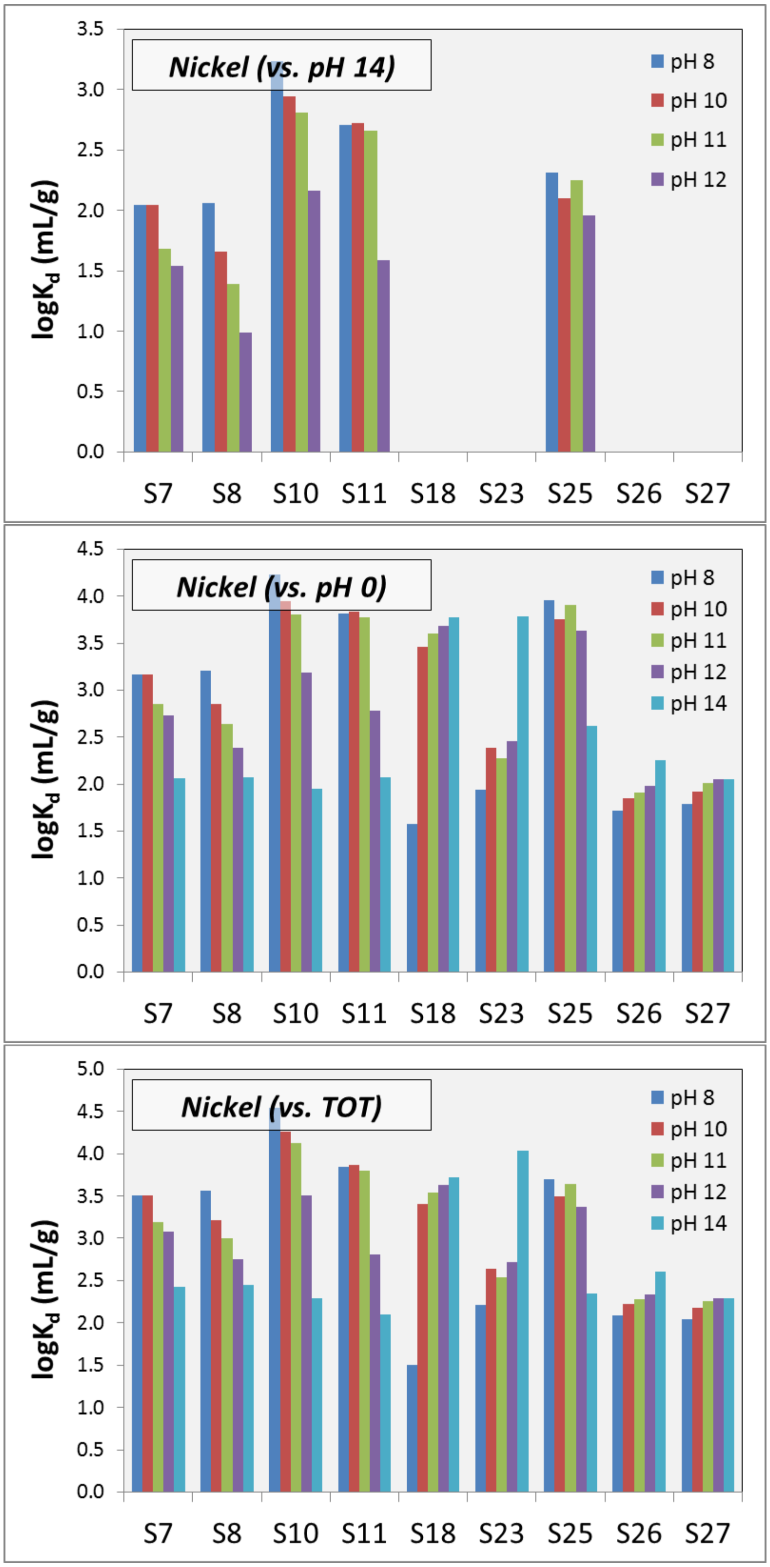

Figure 24 Effects of pH on logK$_d$ coefficients for nickel determined in exposures at pH 14, pH 0 and in total digestions of the Oxy site soils.

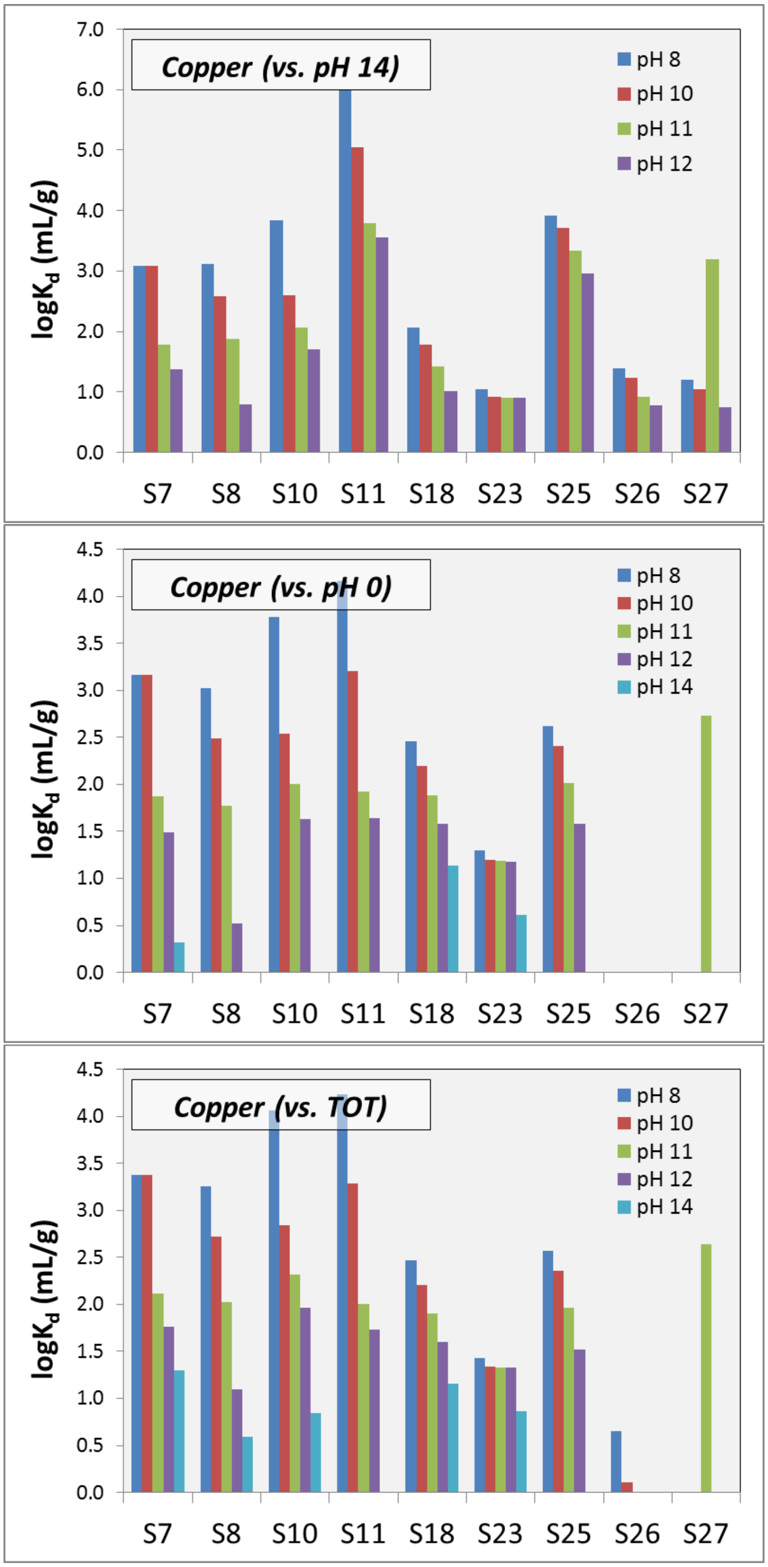

Figure 25 Effects of pH on logK$_d$ coefficients for copper determined in exposures at pH 14, pH 0 and in total digestions of the Oxy site soils.

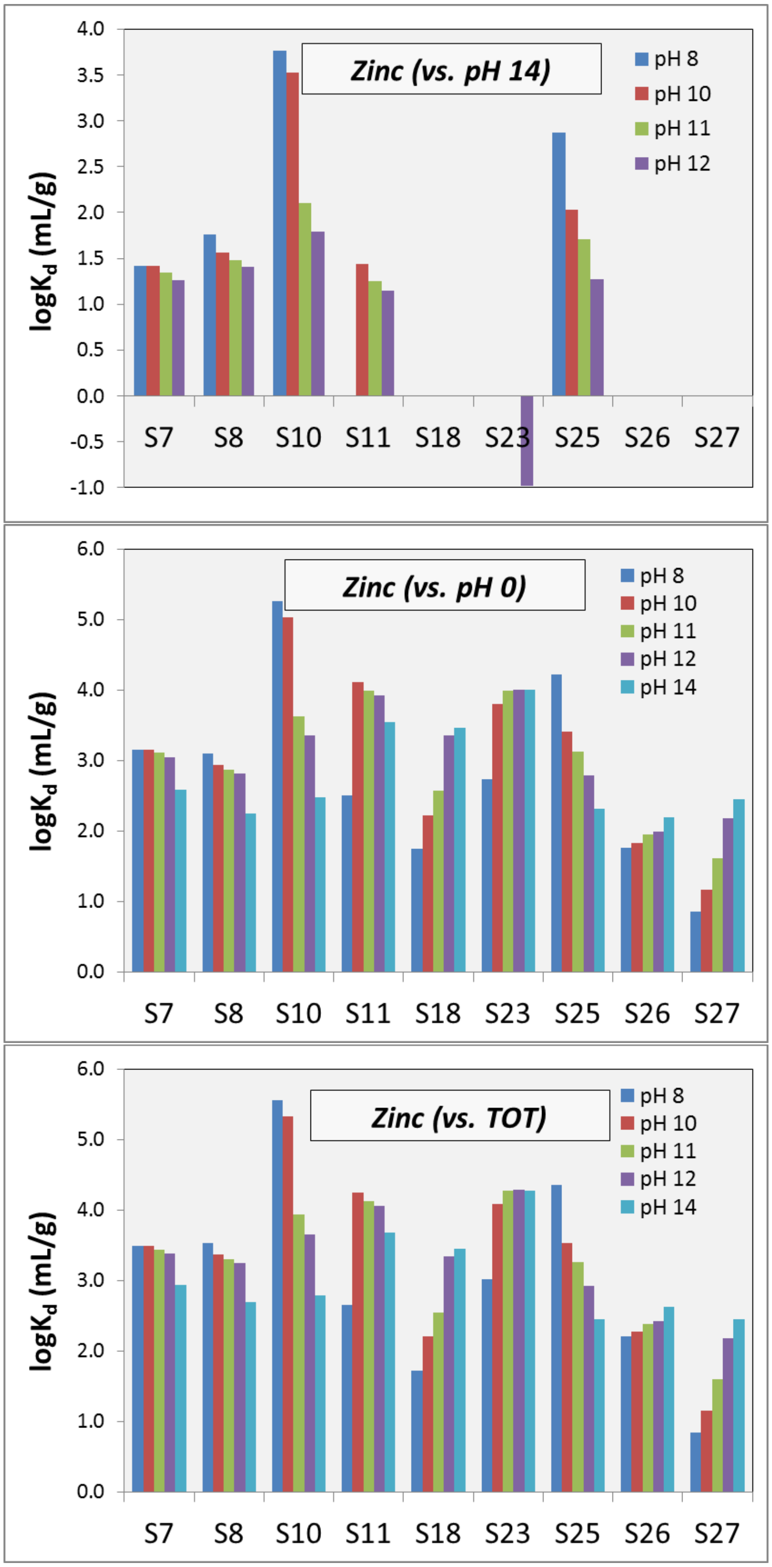

Figure 26 Effects of pH on $\log K_d$ coefficients for zinc determined in exposures at pH 14, pH 0 and in total digestions of the Oxy site soils.

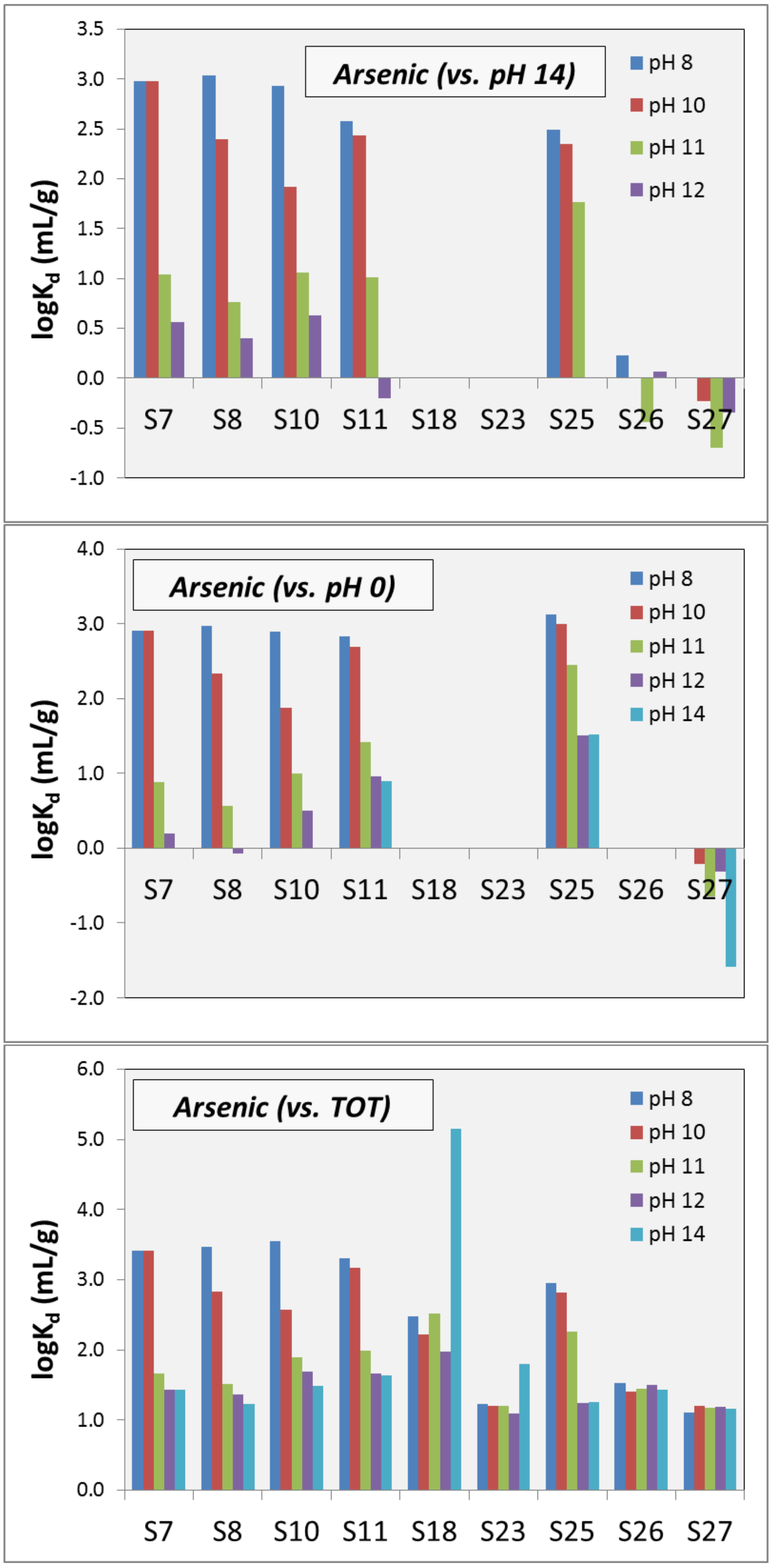

Figure 27 Effects of pH on logK$_d$ coefficients for arsenic determined in exposures at pH 14, pH 0 and in total digestions of the Oxy site soils.

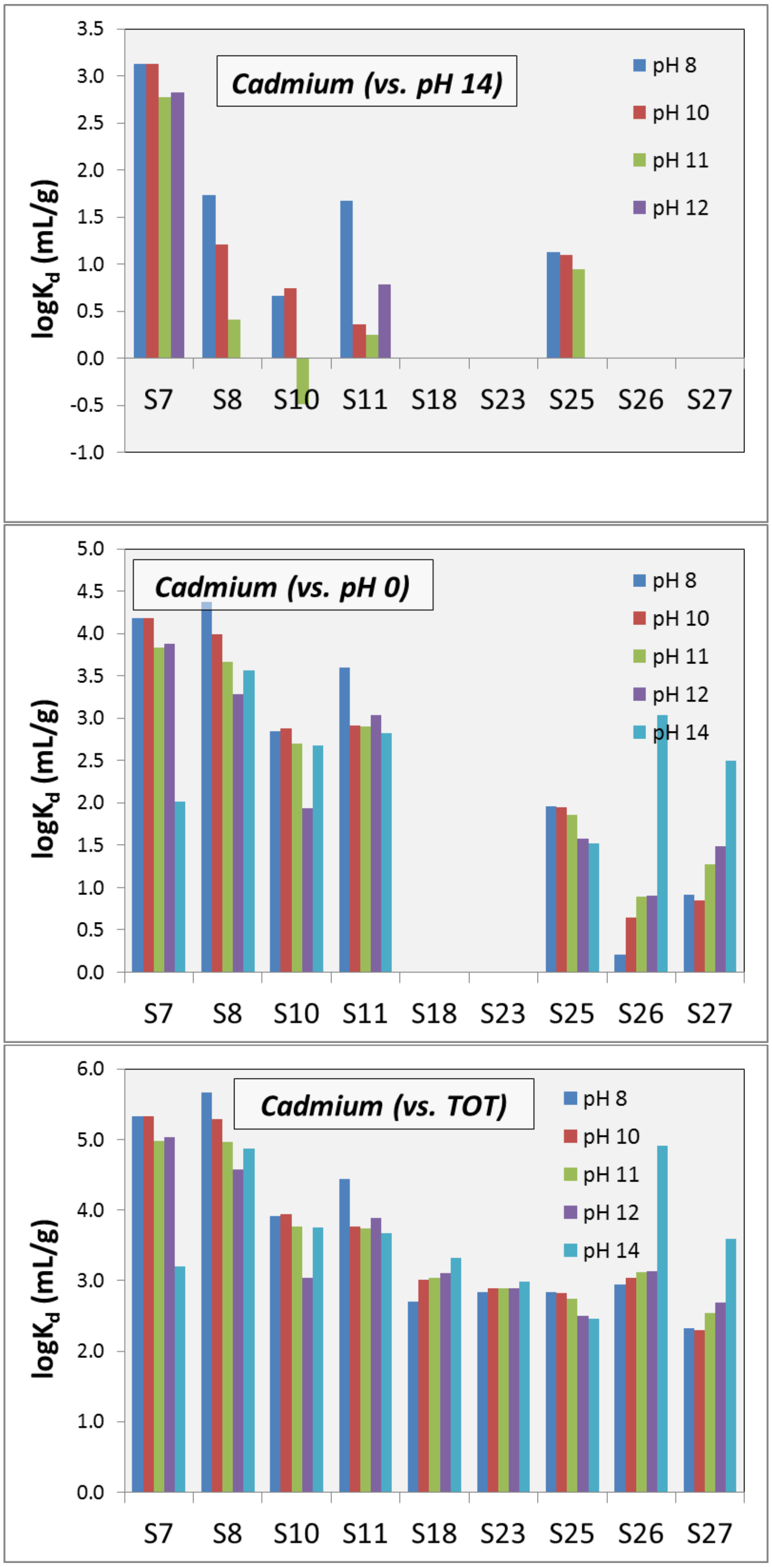

Figure 28 Effects of pH on $\log K_d$ coefficients for <u>cadmium</u> determined in exposures at pH 14, pH 0 and in total digestions of the Oxy site soils.

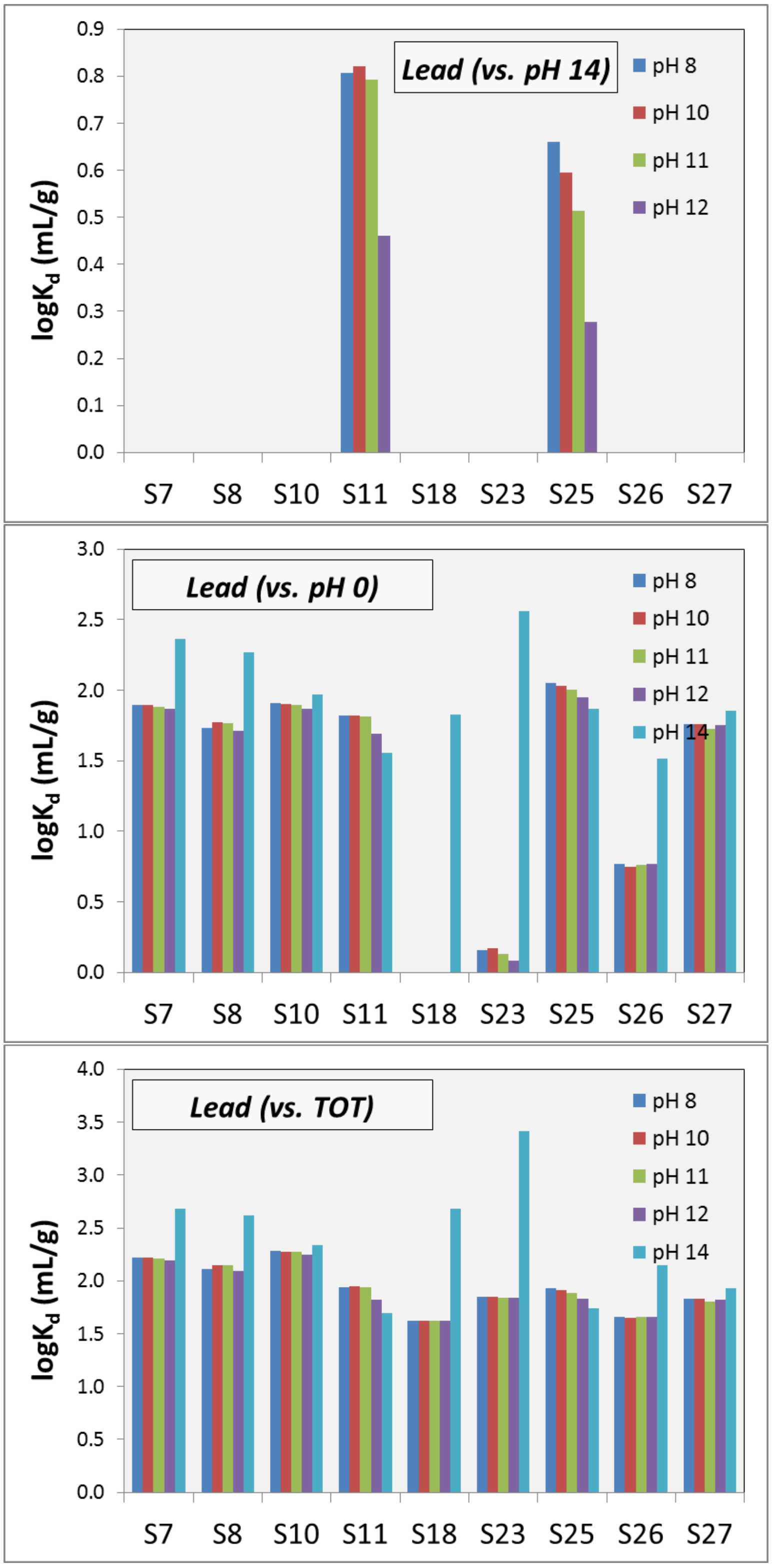

Figure 29 Effects of pH on logK$_d$ coefficients for lead determined in exposures at pH 14, pH 0 and in total digestions of the Oxy site soils.

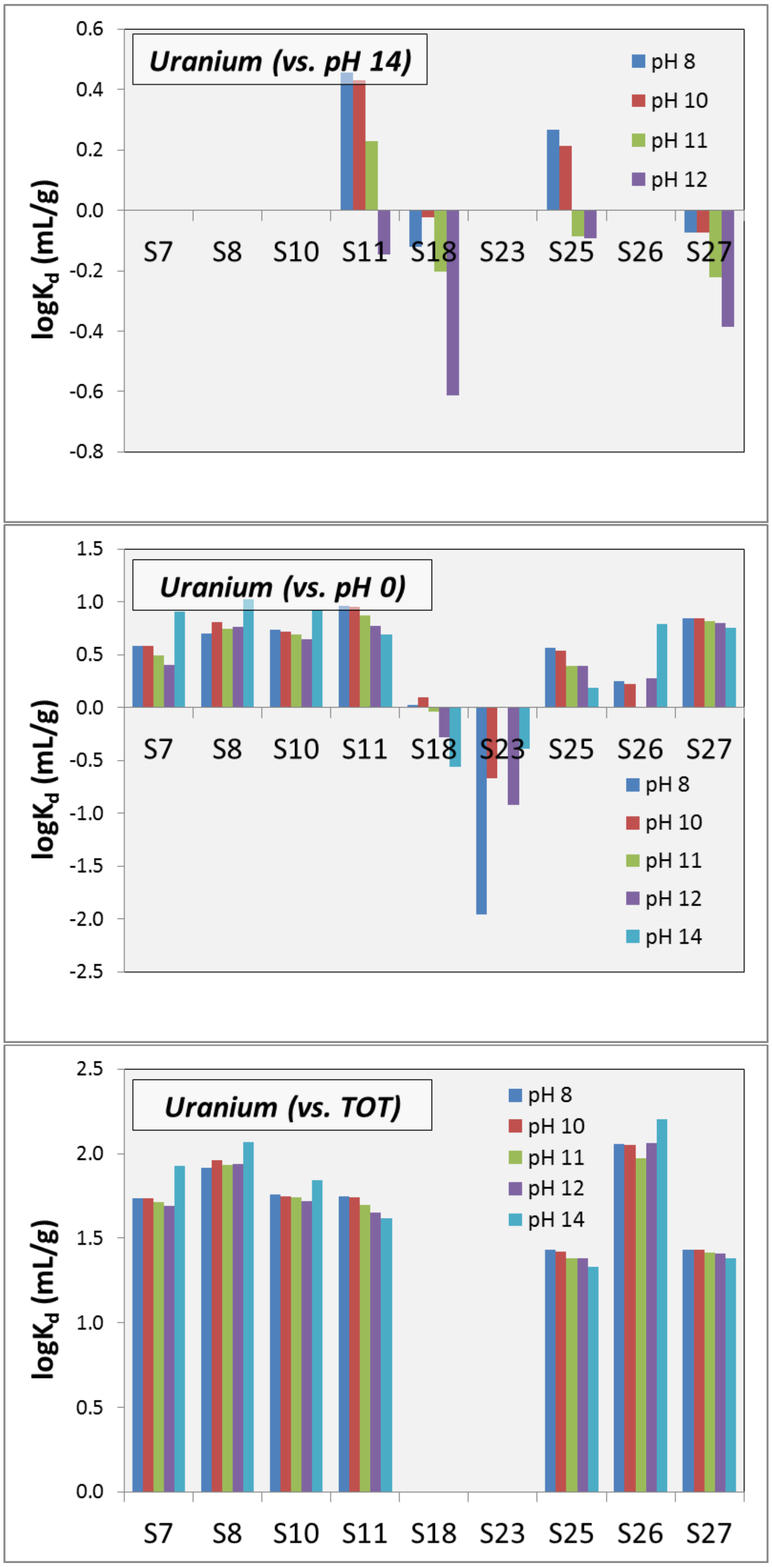

Figure 30 Effects of pH on logK_d coefficients for uranium determined in exposures at pH 14, pH 0 and in total digestions of the Oxy site soils.

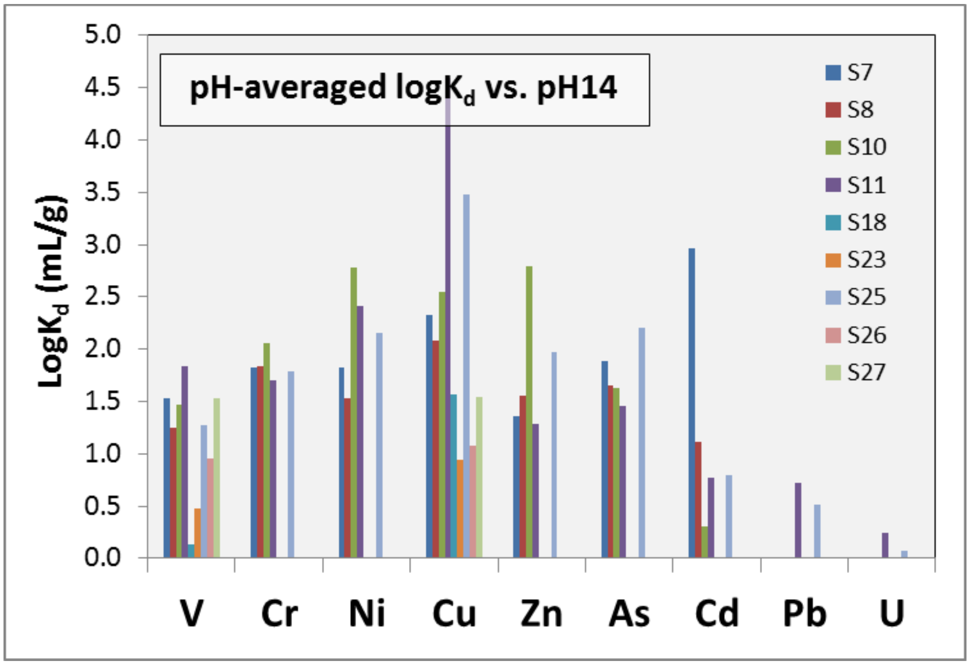

Figure 31 Comparison of pH-averaged logK$_d$ values calculated using metal concentrations measured in an 8 to 12 pH range vs. metal concentrations released at pH 14.

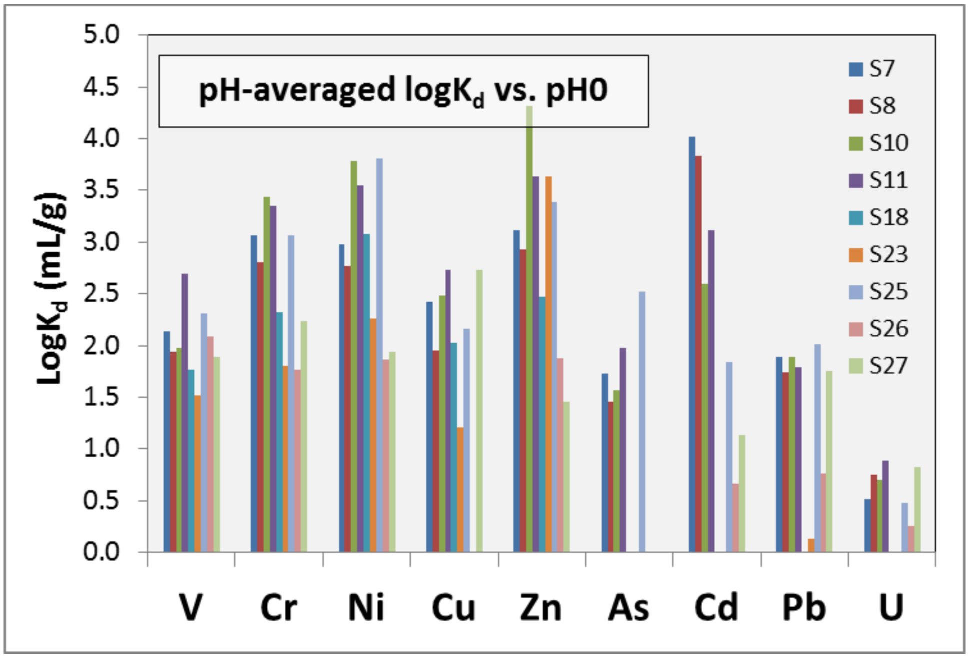

Figure 32 Comparison of pH-averaged logK$_d$ values calculated using metal concentrations measured in an 8 to 14 pH range vs. metal concentrations released at pH 0.

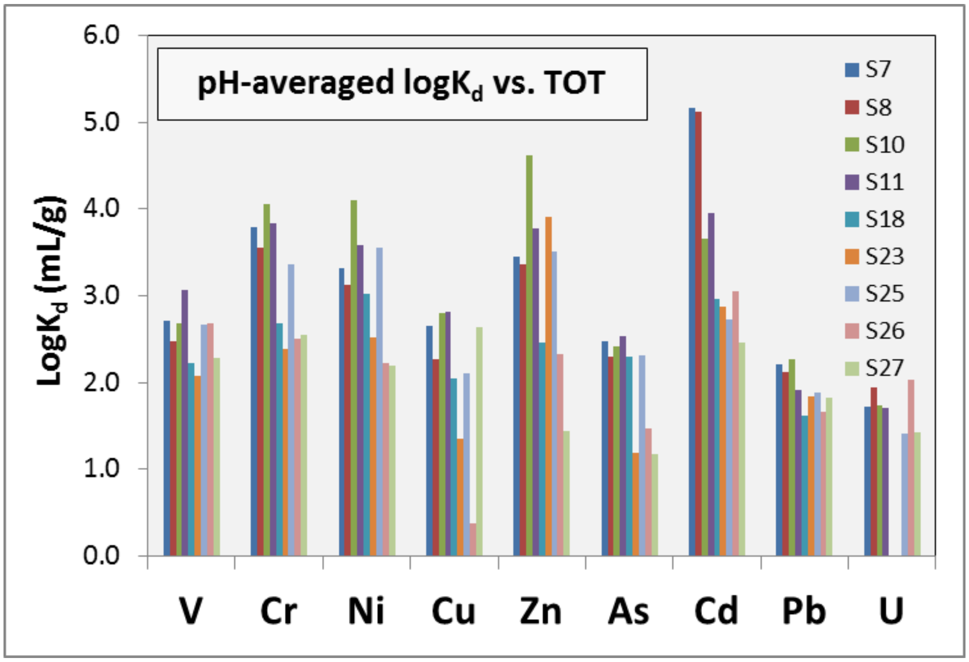

Figure 33 Comparison of pH-averaged logK$_d$ values calculated using metal concentrations measured in an 8 to 14 pH range vs. metal concentrations in the solid phase determined via total digestions of the Oxy site samples using EPA method 3050B.

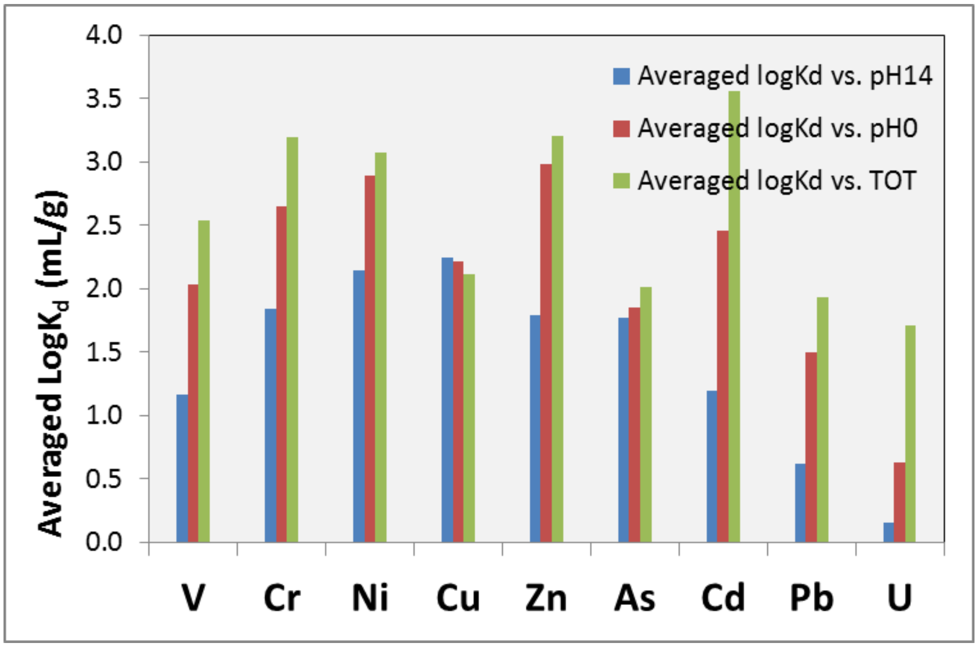

Figure 34 Comparison of pH-, site-averaged logK$_d$ values calculated using three alternative reference states.

Table 6 pH- and site-averaged $\log K_d$ values calculated using three alternative reference conditions.

Element	Average (vs. pH14)	Average (vs. pH0)	Average (vs. TOT)	SD (vs. pH14)	SD (vs. pH0)	SD (vs. TOT)
V	1.2	2.0	2.5	0.6	0.3	0.3
Cr	1.8	2.7	3.2	0.1	0.6	0.7
Ni	2.1	2.9	3.1	0.5	0.7	0.7
Cu	2.2	2.2	2.1	1.2	0.5	0.8
Zn	1.8	3.0	3.2	0.6	0.9	1.0
As	1.8	1.8	2.0	0.3	0.4	0.6
Cd	1.2	2.5	3.6	1.0	1.3	1.0
Pb	0.6	1.5	1.9	0.1	0.7	0.2
U	0.2	0.6	1.7	0.1	0.2	0.2

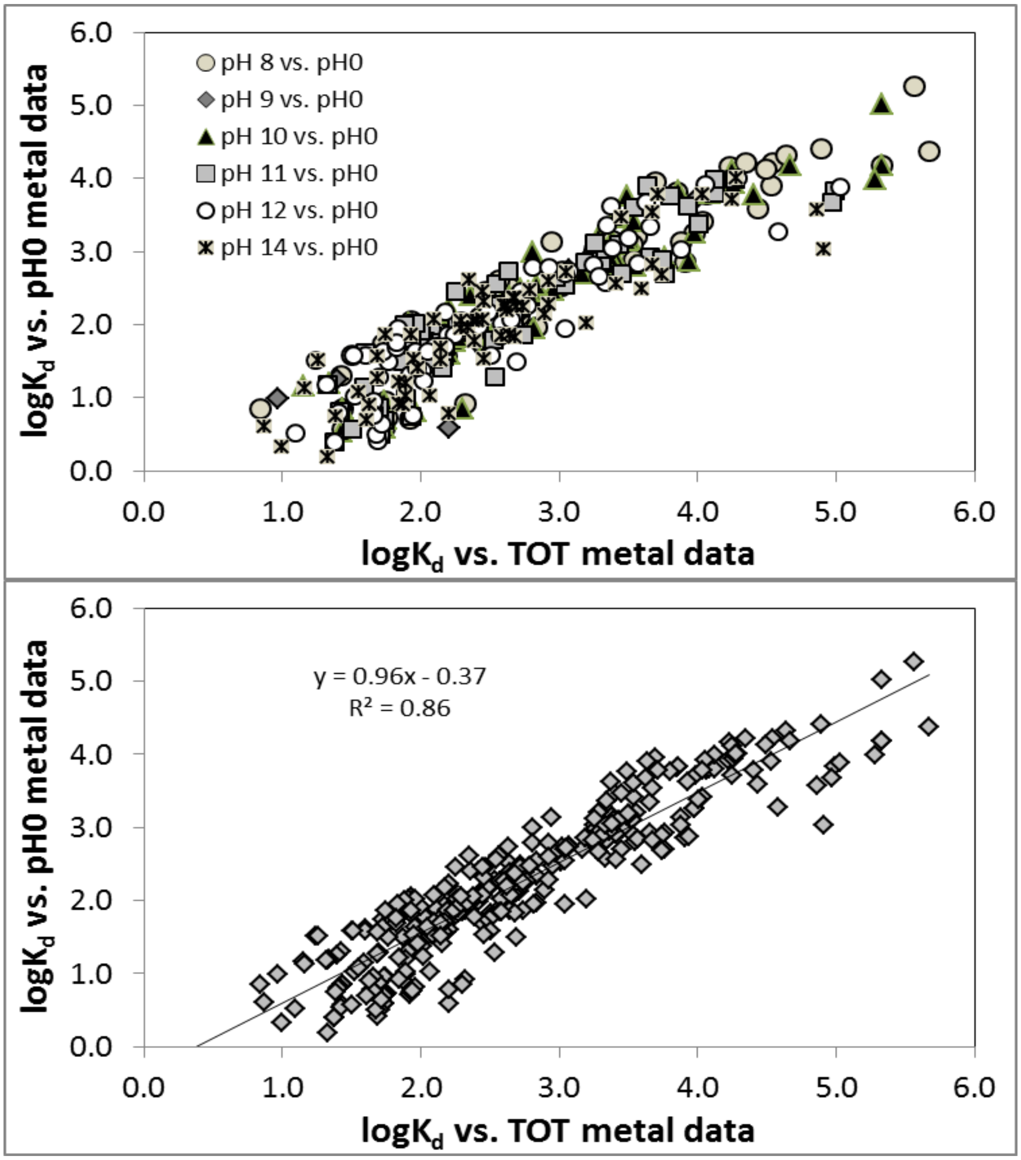

Figure 35 Correlation between logarithms of $K_{i.pH}^{pH0}$ and $K_{i.pH}^{TOT}$ values determined using metal release data for an 8 to 14 pH range (several outliers for Cd and U are excluded).

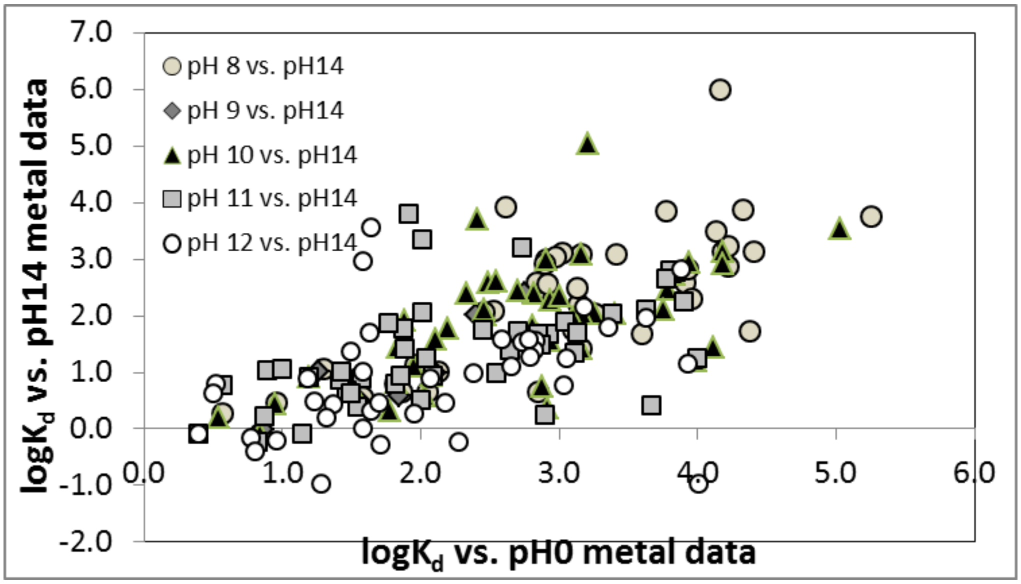

Figure 36 Relationships between logarithms of $K_{i.pH}^{pH14}$ and $K_{i.pH}^{pH0}$ values determined using metal release data for an 8 to 12 pH range.

Table 7 Mean values of pH-specific logK$_d$ calculated for nine Oxy site soils using total metal concentrations in digested soils.

Element	8	10	11	12	14
V	3.33	2.71	2.13	2.00	1.93
Cr	3.40	3.33	3.13	2.92	2.91
Ni	3.00	3.20	3.15	2.94	2.69
Cu	2.76	2.28	2.04	1.57	0.89
Zn	3.04	3.30	3.21	3.28	3.04
As	2.56	2.31	1.74	1.46	1.82
Cd	3.67	3.60	3.53	3.43	3.64
Pb	1.94	1.94	1.93	1.90	2.36
U	1.73	1.73	1.69	1.69	1.76

Table 8 Mean values of pH-specific logK$_d$ calculated for nine Oxy site soils using pH 0 metal release data.

Element	8	10	11	12	14
V	2.86	2.23	1.61	1.45	1.36
Cr	2.85	2.78	2.59	2.38	2.36
Ni	2.82	3.02	2.97	2.77	2.51
Cu	2.93	2.46	1.92	1.37	0.69
Zn	2.82	3.07	2.98	3.05	2.81

As	2.95	2.10	0.95	0.46	1.21
Cd	2.58	2.49	2.45	2.30	2.59
Pb	1.51	1.51	1.50	1.46	1.98
U	0.58	0.60	0.57	0.47	0.75

Table 9 Mean values of pH-specific logK_d calculated for nine Oxy site soils using pH 14 metal release data.

Element	8	10	11	12
V	2.19	1.51	0.60	0.16
Cr	2.56	2.24	1.66	0.89
Ni	2.47	2.29	2.16	1.65
Cu	2.85	2.44	2.15	1.54
Zn	2.45	2.00	1.58	0.98
As	2.37	1.98	0.64	0.18
Cd	1.67	1.31	0.78	1.21
Pb	0.73	0.71	0.65	0.37
U	0.13	0.14	-0.07	-0.31

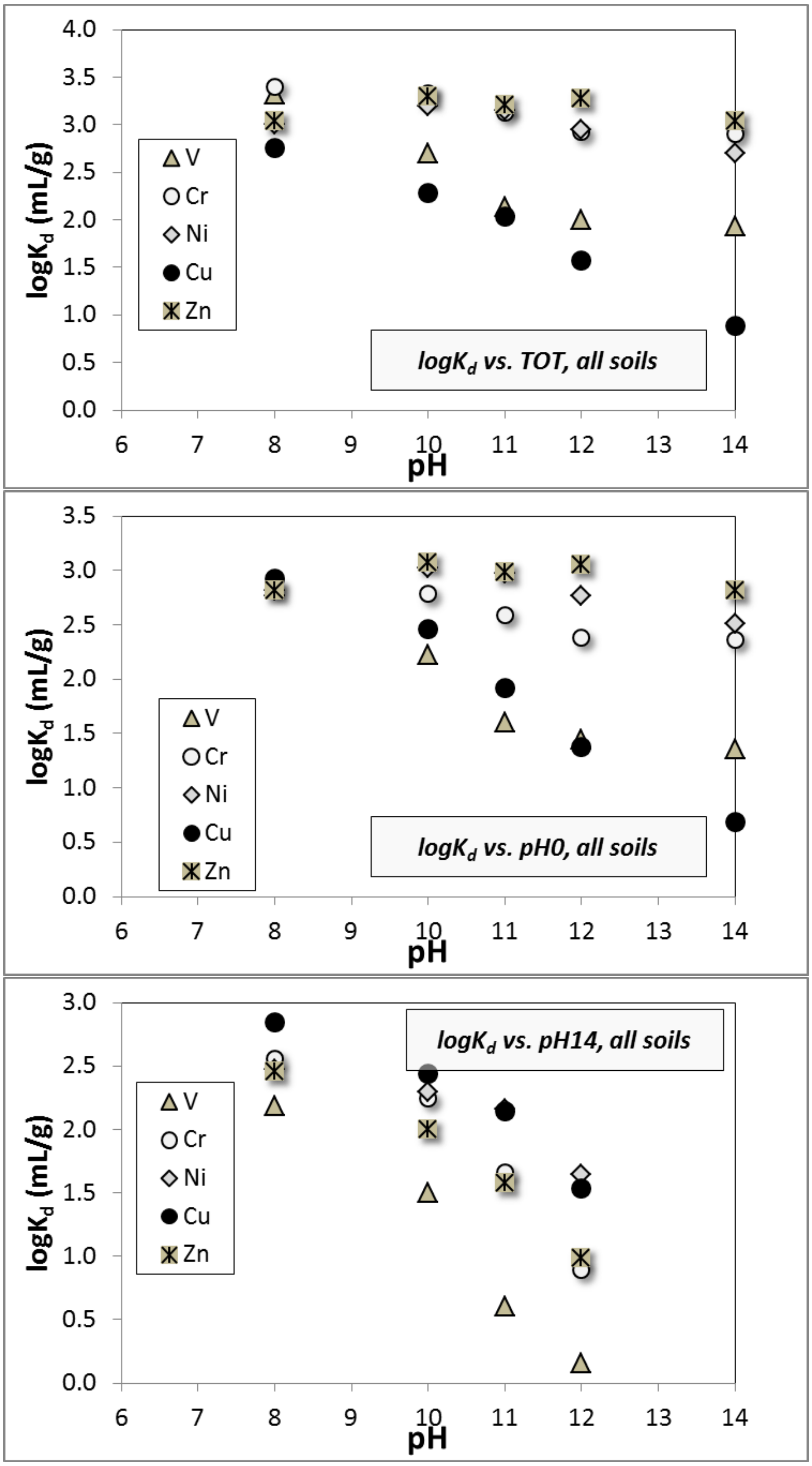

Figure 37 Effects of pH on sample-averaged pH-specific logK_d values for V, Cr. Ni. Cu and Zn for the entire set of all Oxy site soils used in the experiments and three different reference states.

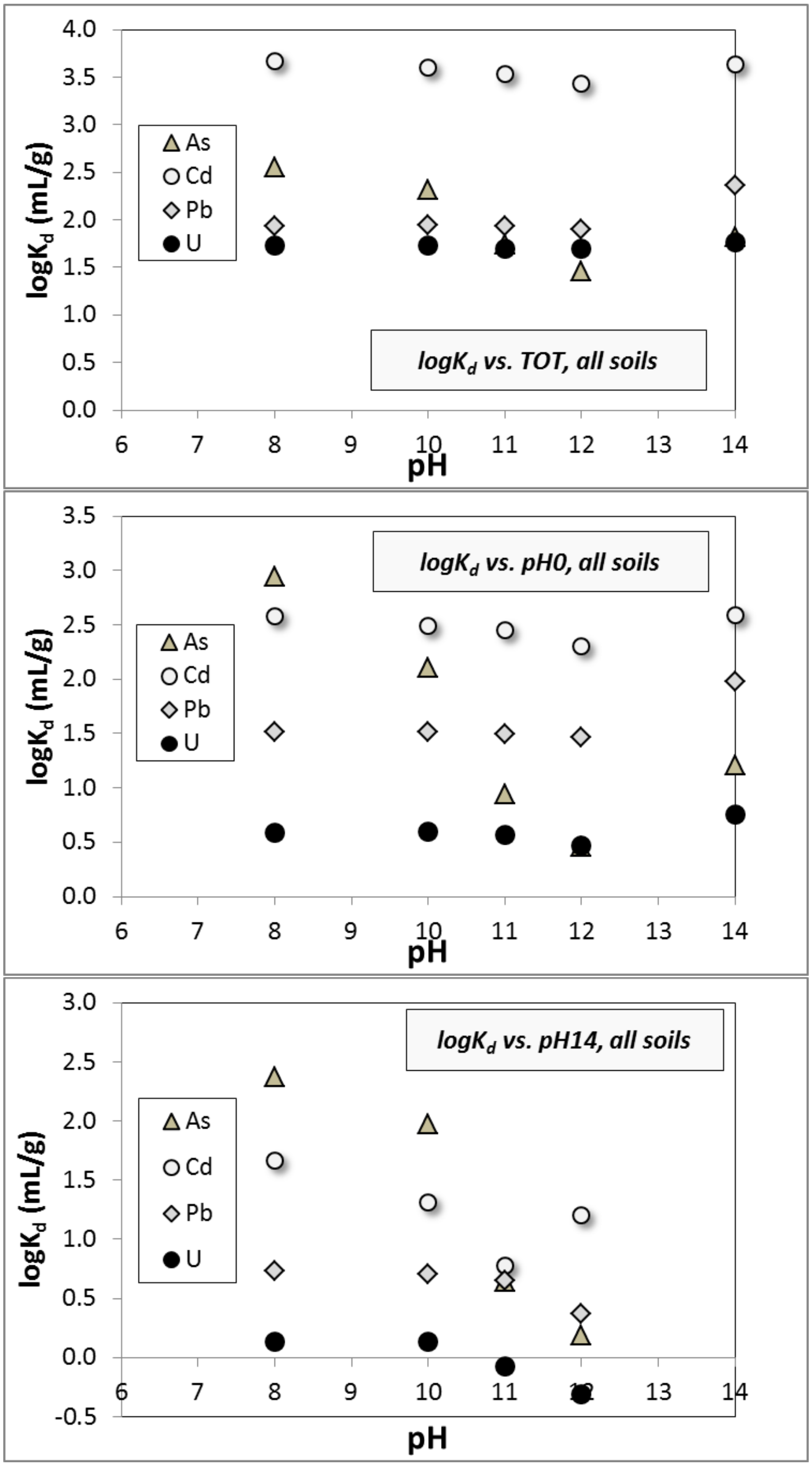

Figure 38 Effects of pH on sample-averaged pH-specific $\log K_d$ values for As, Cd. Pb and U for the entire set of all Oxy site soils used in the experiments and three different reference states.

Table 10 R^2 coefficients of linear correlations between pH of ambient water and mean values of pH-specific $\log K_d$ calculated for nine Oxy site soils using alternative reference states.

Element	vs. TOT	vs. pH0	vs. pH14
V	0.96	0.87	0.96
Cr	0.88	0.87	0.88
Ni	0.81	0.43	0.81
Cu	0.93	0.98	0.93
Zn	0.95	0.00	0.95
As	0.88	0.60	0.88
Cd	0.55	0.02	0.55
Pb	0.65	0.49	0.65
U	0.73	0.19	0.73

Table 11 Slopes of linear correlations between pH of ambient water and mean values of pH-specific $\log K_d$ calculated for nine Oxy site soils using alternative reference states.

Element	vs. TOT	vs. pH0	vs. pH14
V	-0.245	-0.264	-0.523
Cr	-0.094	-0.094	-0.401
Ni	-0.059	-0.059	-0.186
Cu	-0.315	-0.390	-0.311
Zn	-0.002	-0.002	-0.356
As	-0.153	-0.343	-0.575
Cd	-0.012	-0.008	-0.158
Pb	0.061	0.067	-0.079
U	0.003	0.020	-0.106

Table 12 Estimates of pH 7.0 $\log K_d$ values made based on the linear correlations between ambient water pH and mean pH-specific $\log K_d$ values for nine Oxy site soils.

Element	vs. TOT	vs. pH0	vs. pH14
V	3.4	3.0	2.8
Cr	3.5	3.0	3.1
Ni	3.2	3.1	2.7
Cu	3.2	3.4	3.3
Zn	3.2	3.0	2.9
As	2.6	2.9	3.2
Cd	3.6	2.5	1.8
Pb	1.8	1.3	0.9

U	1.7	0.5	0.3

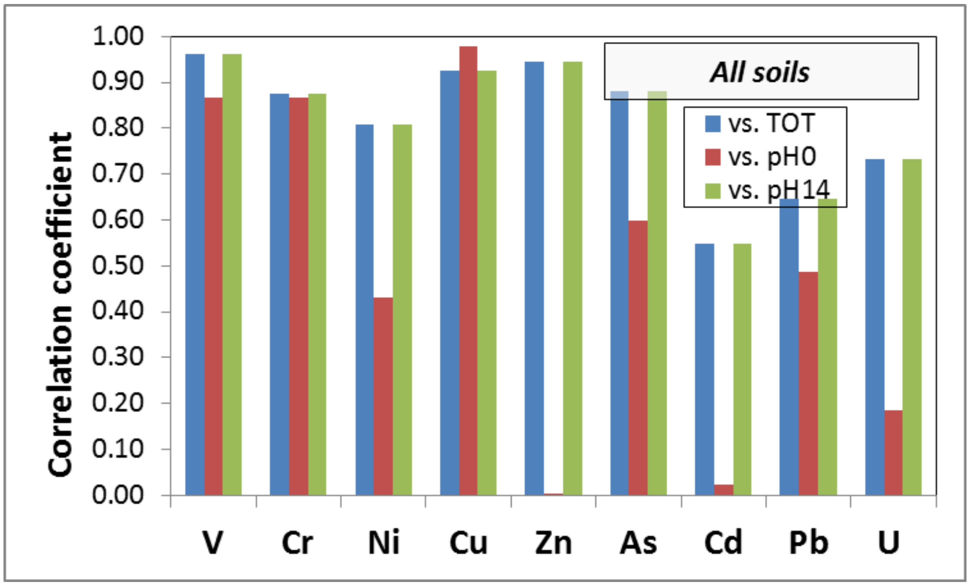

Figure 39 Comparison of R^2 coefficients for linear correlations between pH and site-averaged mean $\log K_d$ values for nine Oxy site soils.

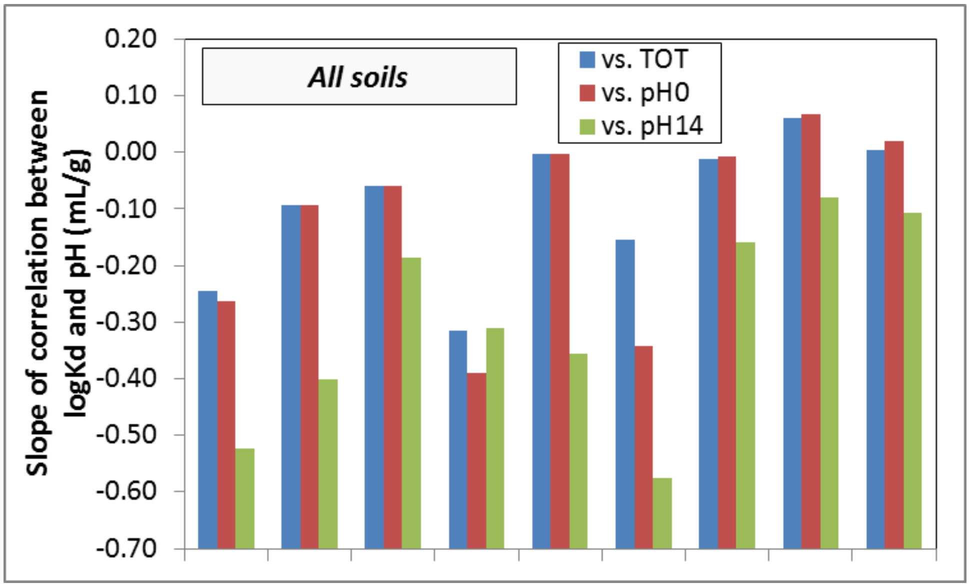

Figure 40 Comparison of slopes of linear correlations between pH and site-averaged mean $\log K_d$ values for nine Oxy site soils.

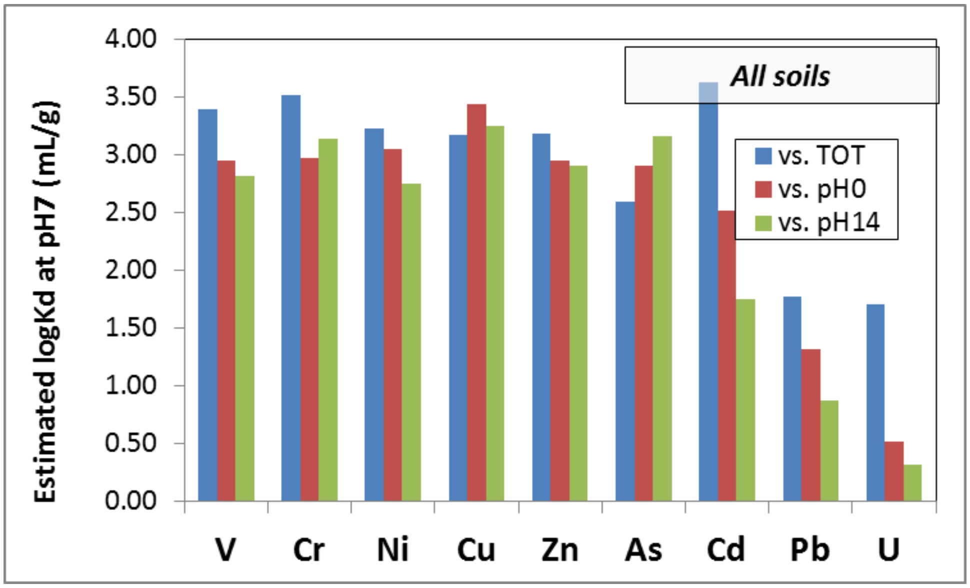

Figure 41 Comparison of estimates of LogK$_d$ values at pH 7.0 made based on the linear correlations between ambient water pH and mean pH-specific logK$_d$ values for nine Oxy site soils.

Effects of redox potential on logK$_d$ values for Oxy site soils

Effects of variations of redox potential on logK$_d$ values determined for the Oxy site soils are presented in **Figure 42**, **Figure 43** and **Figure 44** for soil samples S7, S23 and S27, respectively. As discussed in the preceding sections of the report, effects of pH variations on metal release from sample S7 and similar soils (S8, S10, S11, S25) were determined to be different from those from soils originating from Oxy site areas that have been affected by high pH plumes. Soils S23 and S27 are representative of such conditions.

Data for soil S7 (**Figure 42**) demonstrate that in the experiments carried out using varying hydroxylamine concentrations, decreases of the redox potential from + 4 mV to -233 mV were accompanied by some decreases of the logK$_d$ values determined vs. all three reference conditions (soil exposures at pH 14, pH 0 and oxidative digestion). This is indicative of an increased metal mobility at decreased redox potentials. The result is in agreement with the notion that heavy metals in Oxy site soils are likely to be bound by iron minerals and/or mixed iron/aluminum solid phases that may become unstable in highly reducing conditions.

In contrast with the trends seen for soil S7, data for soils S23 and S27 show only relatively minor decreases of logK$_d$ values occur as the redox potential decrease from slightly negative values (ca. -40 mV) for those > -350 mV in which case deep reduction of the soils is expected (**Figure 43** and **Figure 44**).

The difference between the effects of redox potential on metal release from the latter type of soils (S23 and S27) originating from the site areas affected by the high pH and potentially highly reducing plumes and, on the other hand, the soils that originate from outside of this area is similar to that seen for effects of pH on $\log K_d$ coefficients determined for these two types of Oxy site soils.

The issue of absence or presence of pronounced enough effects of redox conditions on the $\log K_d$ coefficients for the Oxy site soils can be examined in more detail via comparing the $\log K_d$ value vs. redox potentials for the experiments that combine the data obtained in soil exposures in the presence of varying amounts of hydroxylamine, ascorbic acid and sulfite. These results are shown in **Figure 45**, **Figure 46** and **Figure 47** for $\log K_d$ coefficients determined for soil S7 using the three reference conditions (pH14, pH 0 and oxidative digestion) while similar data for soil S23 are shown in **Figure 48**, **Figure 49** and **Figure 50**.

The data presented in **Figure 45**, **Figure 46** and **Figure 47** demonstrate that in the case of soil S7, $\log K_d$ values for practically all heavy metals tend to decrease nearly linearly as function of the redox potential of the system. Given that soil S7 originates from the area of the Oxy site that is likely to have been exposed to moderately oxidizing conditions, relatively prominent effects of redox potential on the metal release from that soil are not necessarily surprising.

In contrast, the $\log K_d$ values determined for sample S23 tended to be nearly stable when the redox potential was changed from ca. 0 to ca. -300 mV (**Figure 48**, **Figure 49** and **Figure 50**), except that some changes observed for Cd, Cu and some other metals. These latter effects may be an artifact associated either with very low concentrations of Cd in the examined soils, or effects of complexation between the redox-active agents and Cu (and other metals such as Zn and Pb). If present, metal-organic ligand complexation will strongly affect metal release and it is likely to have taken place in the presence of very high concentrations of sulfite and ascorbic acid (0.2 mol/L) that were used to drive the redox potential to below ca. - 350 mV. Despite these deviations from the general trend, effects of variations of the redox potential on the $\log K_d$ values for soil S23 from the high-pH area of the Oxy site were clearly much less prominent compared with those for soil S7.

The conclusion that variations of redox potential are not likely to affect $\log K_d$ values for Oxy site soils exposed to high pH and reducing conditions was confirmed by the data generated for soil sample SB-UW-82-31-33.5. That soil was extracted from the vicinity of Well 82 located at the origin of the high pH plume. Experiments with soil SB-UW-82-

31-33.5 were carried at pH 10 in the presence of varying hydroxylamine concentrations that altered the redox potential from 0 to -300 mV. These experiments showed that metal release from soil SB-UW-82-31-33.5 was not sensitive to the redox potential (**Figure 51**).

In sum, the data presented above support a conclusion that variations of redox potential are not likely to significantly affect metal release from Oxy soils that have been exposed to anoxic conditions and other conditions typical for the site (e.g., high pH groundwater). However, in the case of Oxy site soils present in the subsurface zone under oxic conditions or those soils that in the future may be exposed to a significant amount of ingress of dissolved oxygen, redox potential variations are likely to have a more prominent effect on metal release.

Conclusions

1. Concentrations of all heavy metals (V, Cr, Ni, Cu, Zn, As, Cd, Pb and U) found in digestates of Oxy site soils are correlated with the concentrations of major matrix elements, notably Fe and Al. While the physico-chemical aspects of these associations need to be explored in more detail, the observed trends may indicate that the heavy metals are likely to be sorbed on the surfaces of, and/or occluded in the bulk of minerals formed by iron oxyhydroxides, or mixed Al-Fe solid phases.

2. Examination of effects of pH that was varied from 8 to 14 and changes of the redox potential that was varied from ca. 0 to ca. -500 mV show that Oxy site soils can be operationally separated into two major groups. The first group (denoted as Group A) comprises soils for the Oxy site areas that do not appear to have been affected by high pH plumes and reducing conditions. The second group (denoted as Group B) comprises soils from the areas deemed affected by high pH and reducing conditions.

    a. LogK_d values determined for Group A soils tend to increase nearly linearly with the pH when it is varied in a 8 to 14 range. This indicates that metal mobility decreases with pH for these soils.

    b. In contrast with the results for Group A, logK_d values for Group B soils tend to exhibit little sensitivity to pH variations.

3. The data for Group A and Group B soils can be combined to determine pH-specific logK_d constants for the entire set of the examined soils. This approach allows generating reasonably strong linear functions correlating pH

and metal-specific logK_d values. Calculations employing these linear correlations can yield logK_d values for any particular pH. The logarithms of the partition coefficients calculated for circumneutral pHs using applicable logK_d vs. pH correlations are comparable for all three alternative reference conditions (soil exposures at pH 14, pH 0 and their oxidative digestions).

4. An alternative suggestion was to neglect effects of pH variations and use metal-specific logK_d values obtained via averaging of the partition coefficients for the entire set of pH and Oxy site soils of different provenance. While this approach may be simpler, its feasibility needs to be determined in the context of the sensitivity of model predictions to uncertainties of logK_d values. Such uncertainty is much higher for the averaged logK_d values deemed to be independent of pH and soil provenance.

5. Variations of redox potential for Group A soils are accompanied by decreases of the logK_d constants that are nearly linearly correlated with the redox potential. This is indicative of increased metal release from Group A soils when they interact with oxygen-free water.

6. In contrast with the sensitivity of Group A soils to variations of redox potential, metal release from Group B soils was largely unaffected by the presence of reducing agent. Even less sensitivity to the variations of redox potential was observed from a soil extracted practically contemporaneously with logK_d measurements from a location close to the origin of the high pH plume located in the Oxy site. This observation confirms the conclusion that redox (and pH) variations are of relatively little importance for metal release in the areas of the most affected areas of the suite.

Suggestions for future research

Future efforts need to address the behavior of elements other than those examined in detail in this study (V, Cr, Ni, Cu, Zn, As, Cd, Pb and U), notably mercury and possibly in more detail thallium whose release and mobility were not ascertained in the reported experiments. This was because measurements of Hg concentrations and speciation require using analytical instrumentation other than the conventional ICP/MS equipment used in our experiments while the Tl concentrations observed for the examined set of Oxy site soils were typically too low to be considered of environmental significance. Yet, given the history of the site and large volumes of effluent that were generated in the chloralkali process that uses Hg electrodes, separate examination of Hg mobility and speciation may be critical for determining the environmental status of the Oxy site.

It is also highly important to use in further experiments Oxy site soil samples extracted from areas that are likely to or known to be contaminated with heavy elements. Such samples were not available for the present study, and equilibria pertinent to metal release and transport from them may differences from those reported in this document.

Another important goal is to examine the performance of applicable numerical fate and transport models that would implement the partition coefficients generated in this study. Determination of the sensitivity of such models to uncertainties of $\log K_d$ constants and examination of pros and contras of using either site- and pH-averaged partition coefficients or explicitly taking into account effects of pH and, where applicable, redox potential on $\log K_d$ values is critical for the success of numerical modeling of the fate and transport of heavy metals at the Oxy site.

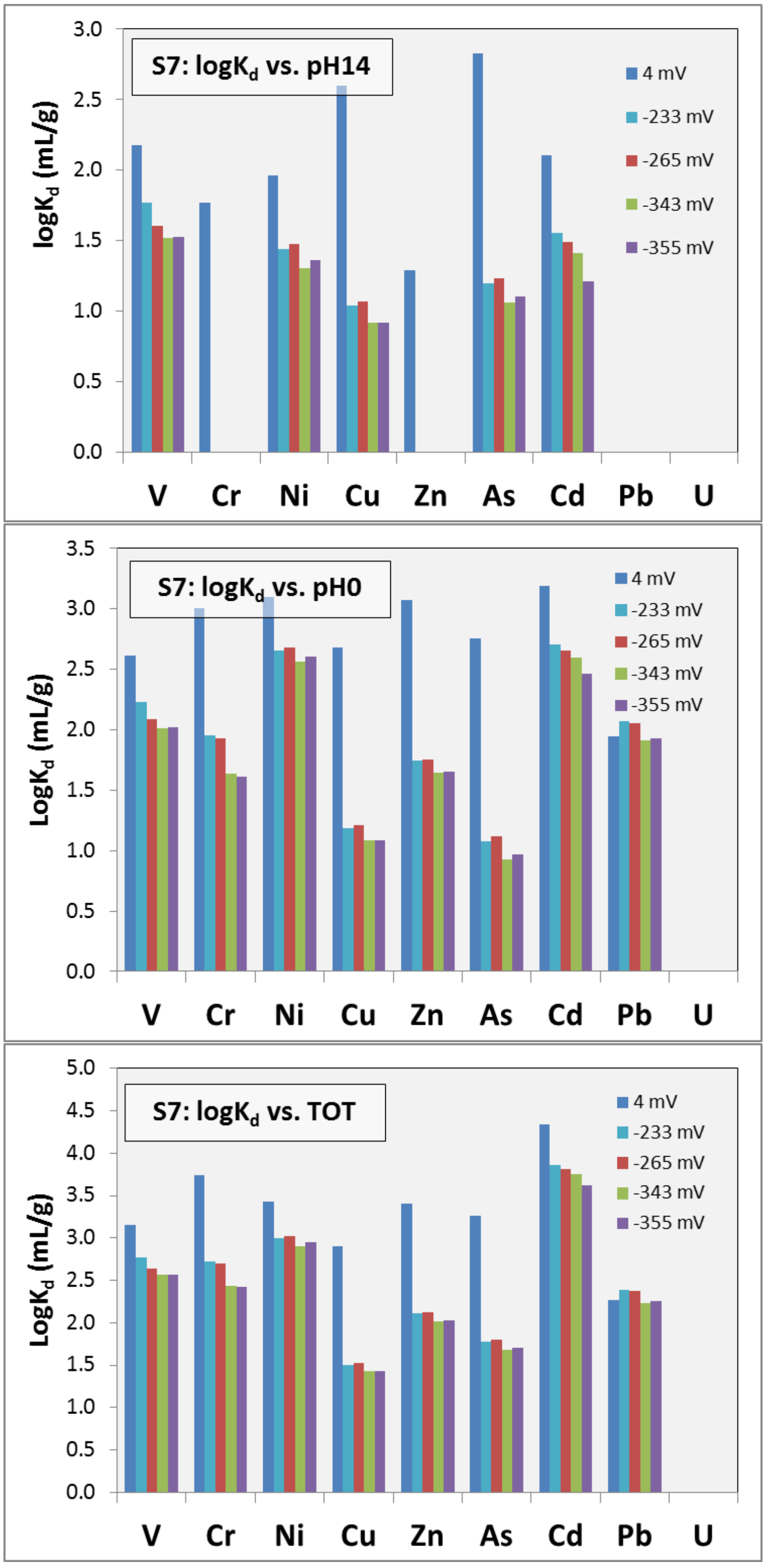

Figure 42 Effects of redox potential on logK$_d$ coefficients for soil sample S7. Exposures at pH 10, Kd determination vs. reference conditions at pH 14, pH 0 and in total digestions of Oxy site soils.

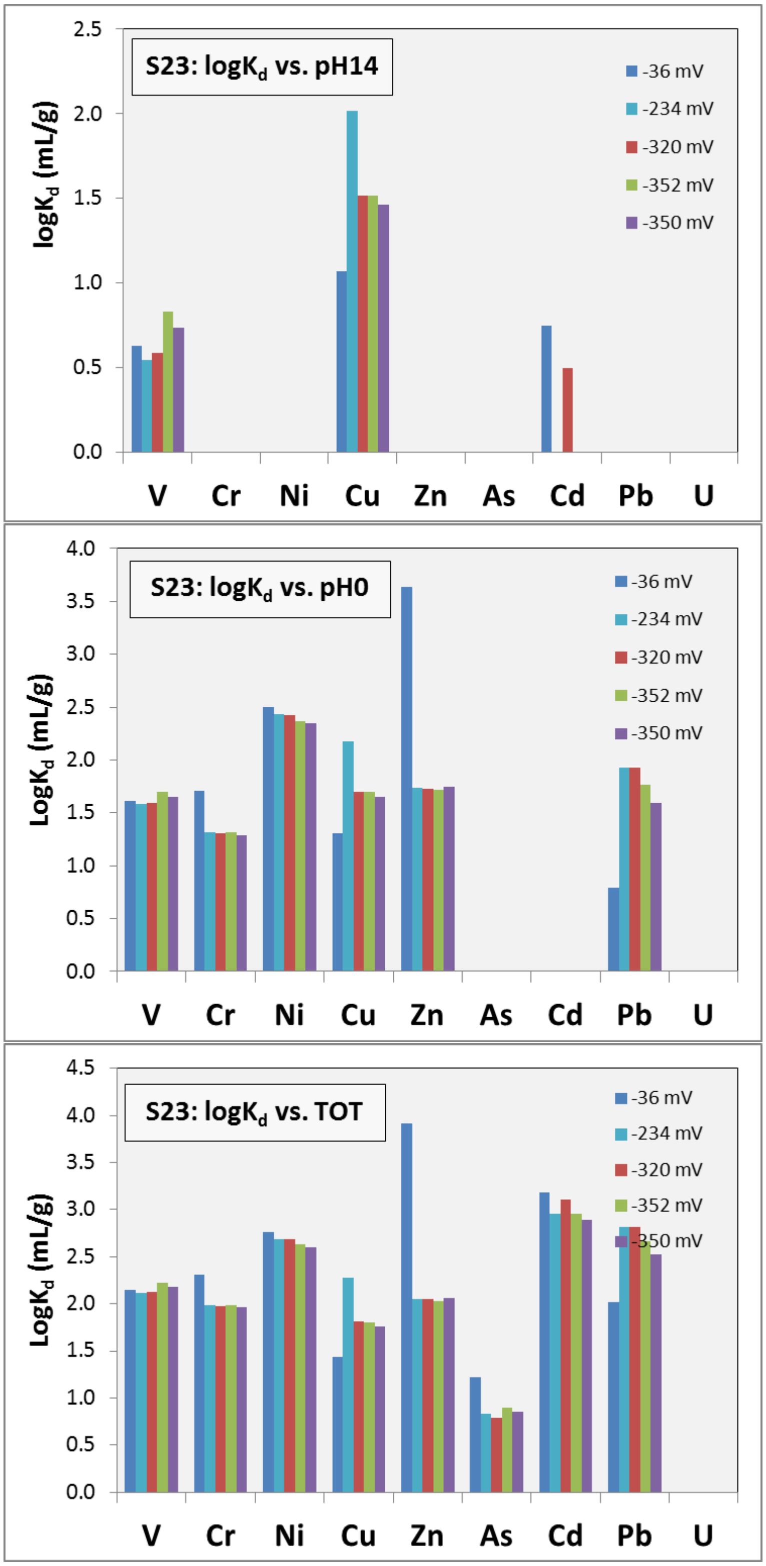

Figure 43 Effects of redox potential on logK$_d$ coefficients for soil sample S23. Exposures at pH 10, Kd determination vs. reference conditions at pH 14, pH 0 and in total digestions of Oxy site soils.

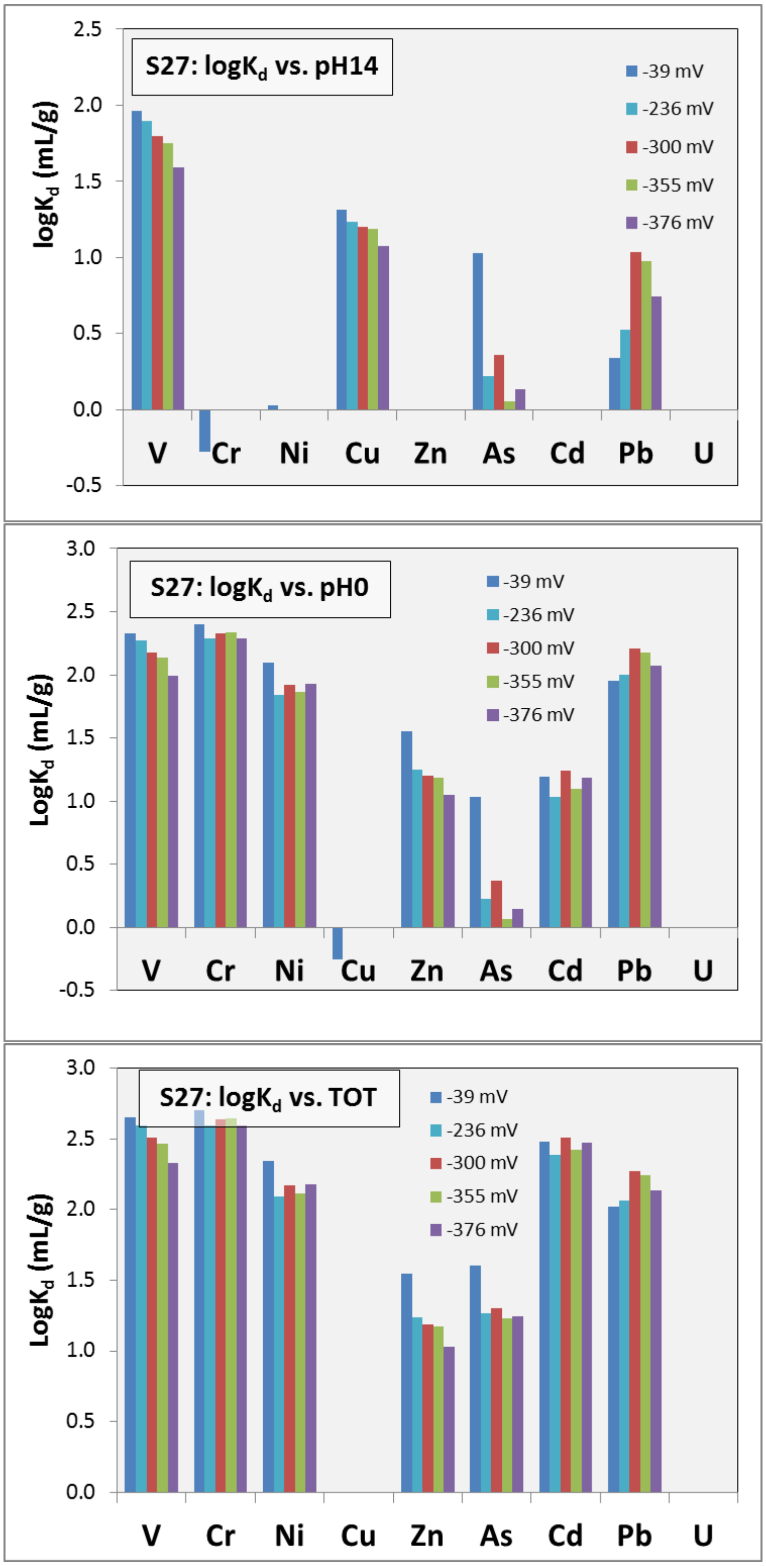

Figure 44 Effects of redox potential on logK$_d$ coefficients for soil sample S27. Exposures at pH 10, Kd determination vs. reference conditions at pH 14, pH 0 and in total digestions of Oxy site soils.

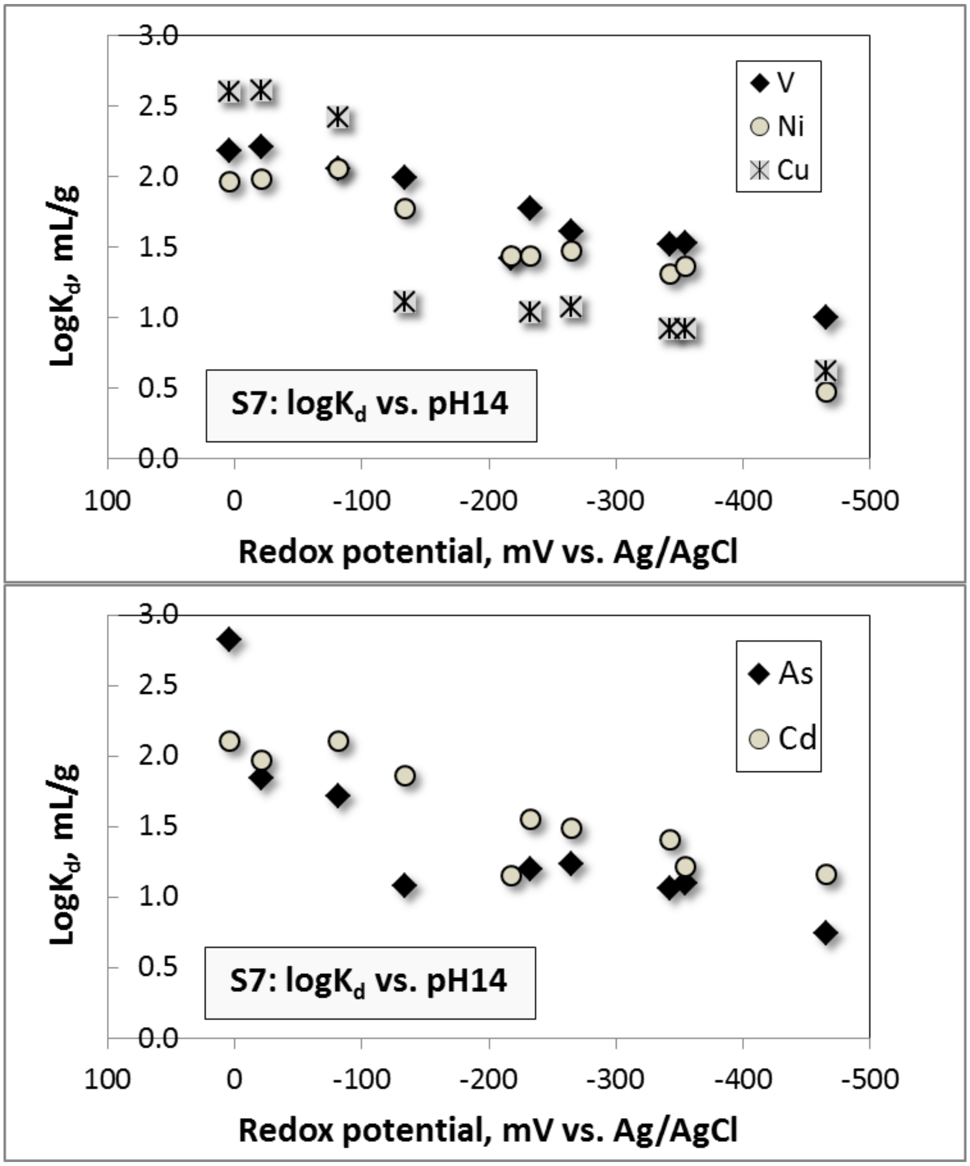

Figure 45 Effects of redox potential on logK$_d$ coefficients determined for soil S7 vs. pH 14 reference condition. pH10, exposure time 7 days.

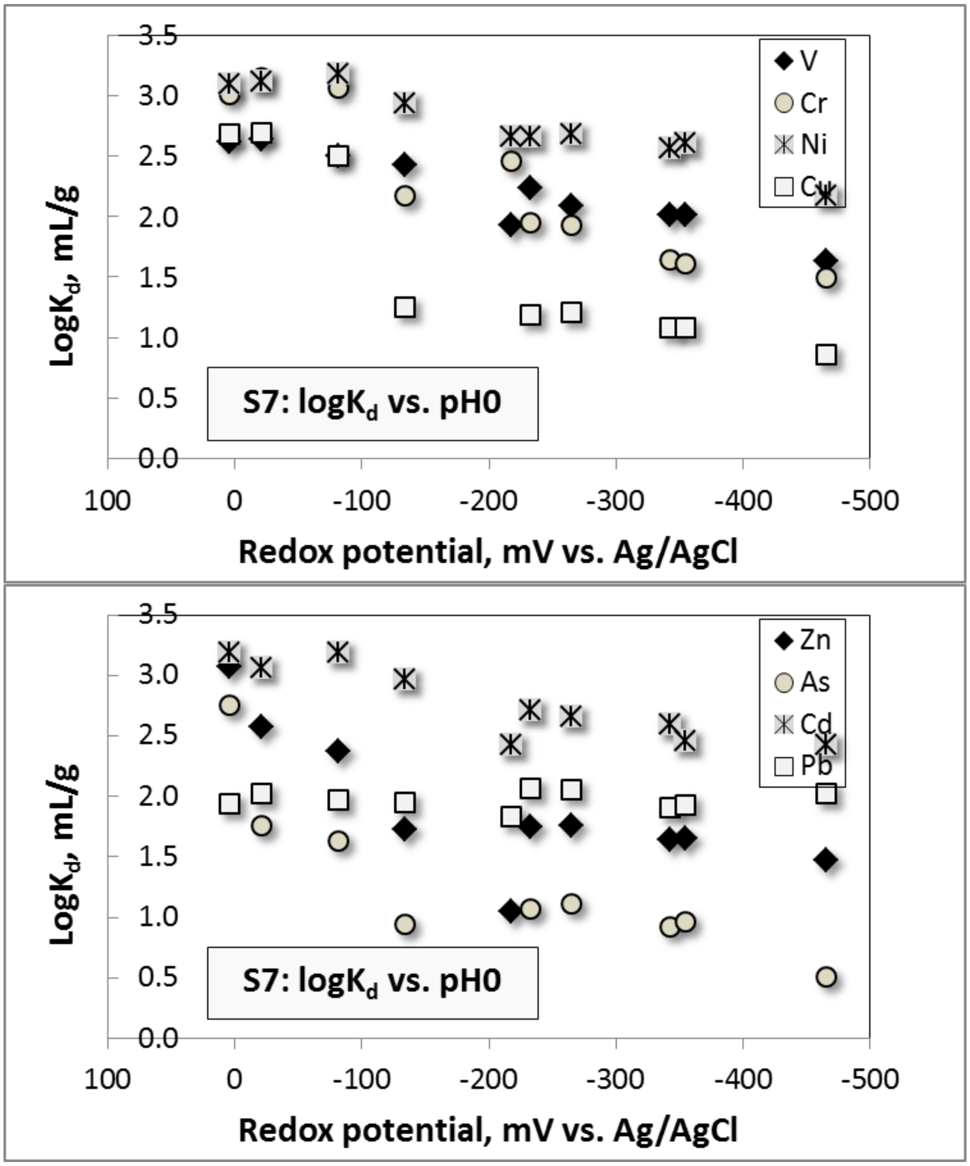

Figure 46 Effects of redox potential on logK$_d$ coefficients determined for soil S7 vs. pH 0 reference condition. pH10, exposure time 7 days.

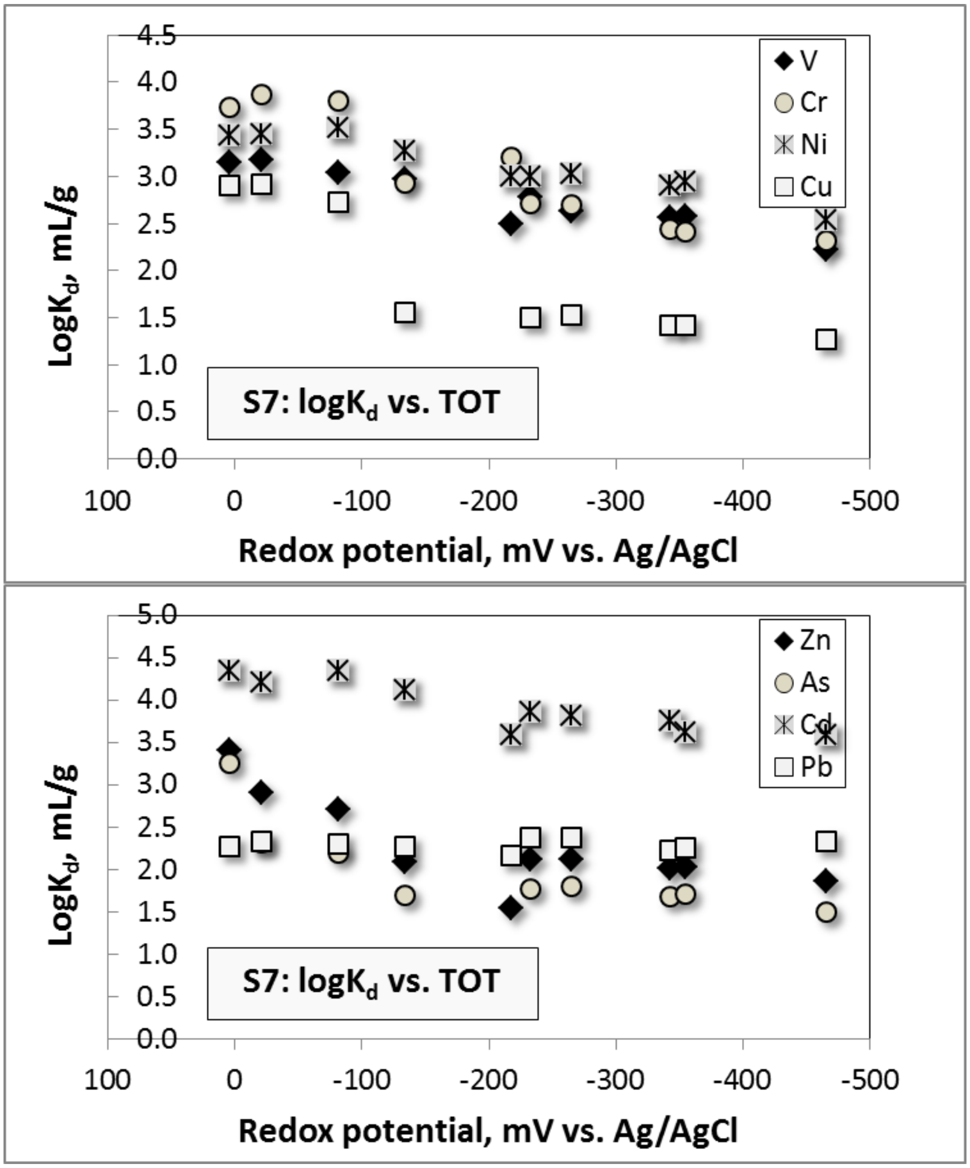

Figure 47 Effects of redox potential on logK$_d$ coefficients determined for soil S7 vs. total soil digestion condition. pH10, exposure time 7 days.

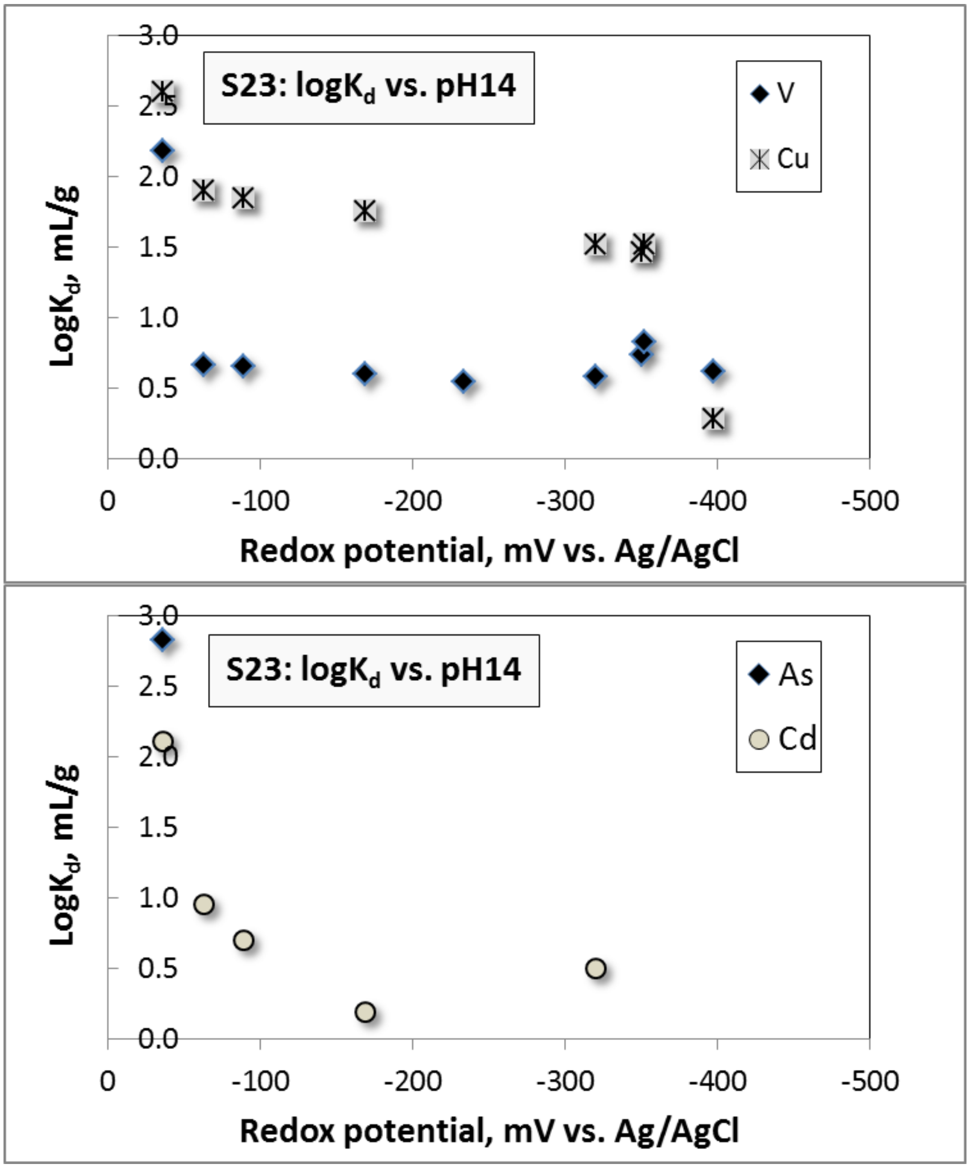

Figure 48 Effects of redox potential on logK$_d$ coefficients determined for soil S23 vs. pH 14 reference condition. pH10, exposure time 7 days.

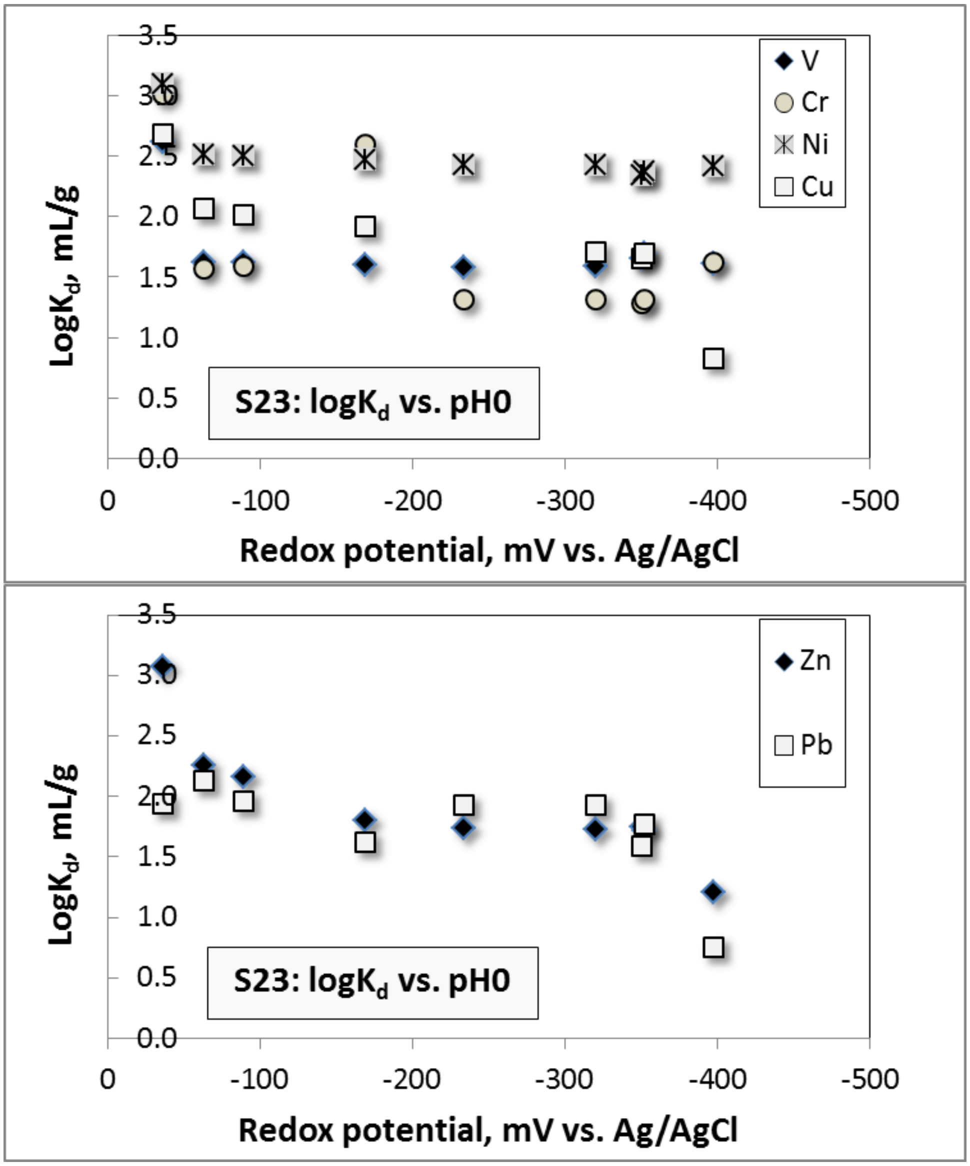

Figure 49 Effects of redox potential on logK$_d$ coefficients determined for soil S23 vs. pH 0 reference condition. pH10, exposure time 7 days.

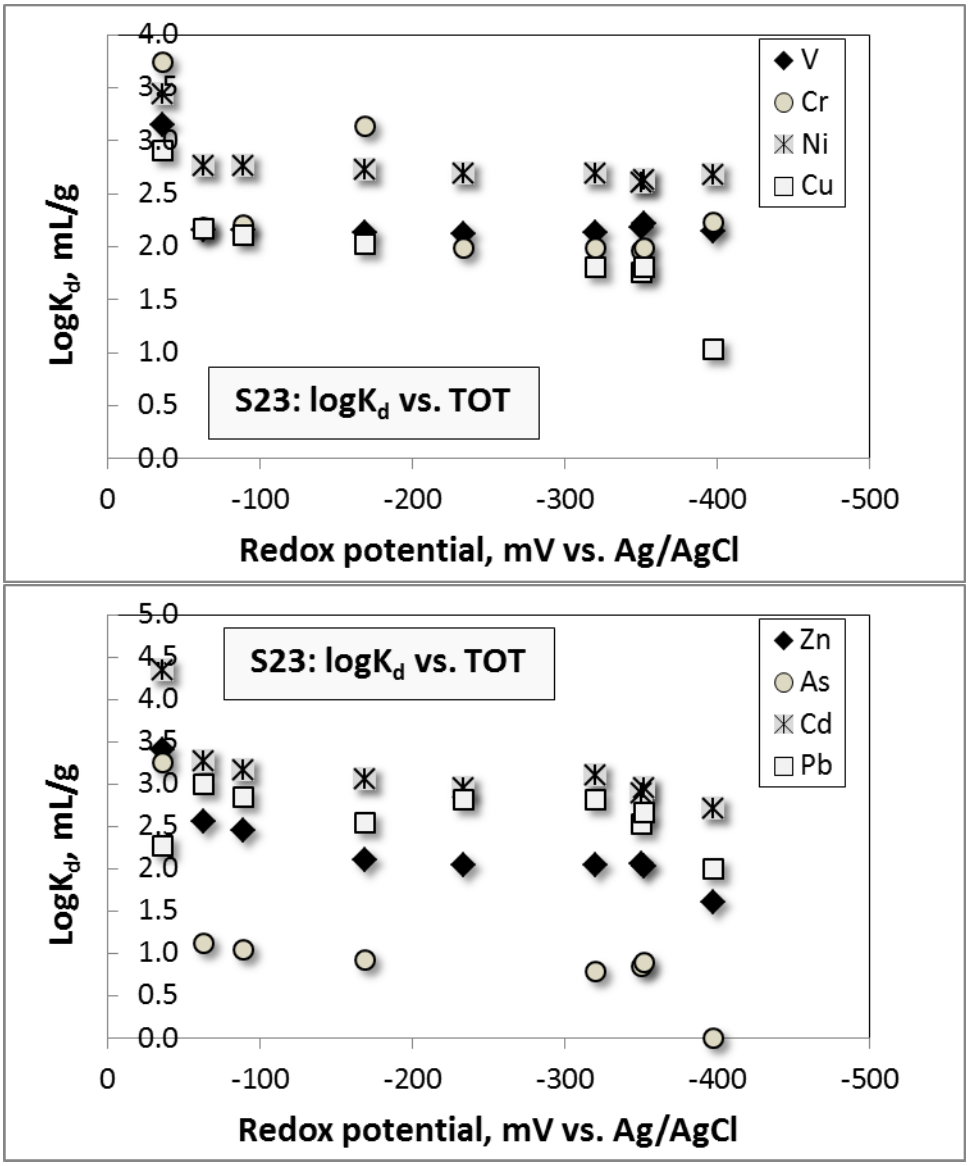

Figure 50 Effects of redox potential on logK$_d$ coefficients determined for soil S23 vs. total soil digestion condition. pH10, exposure time 7 days.

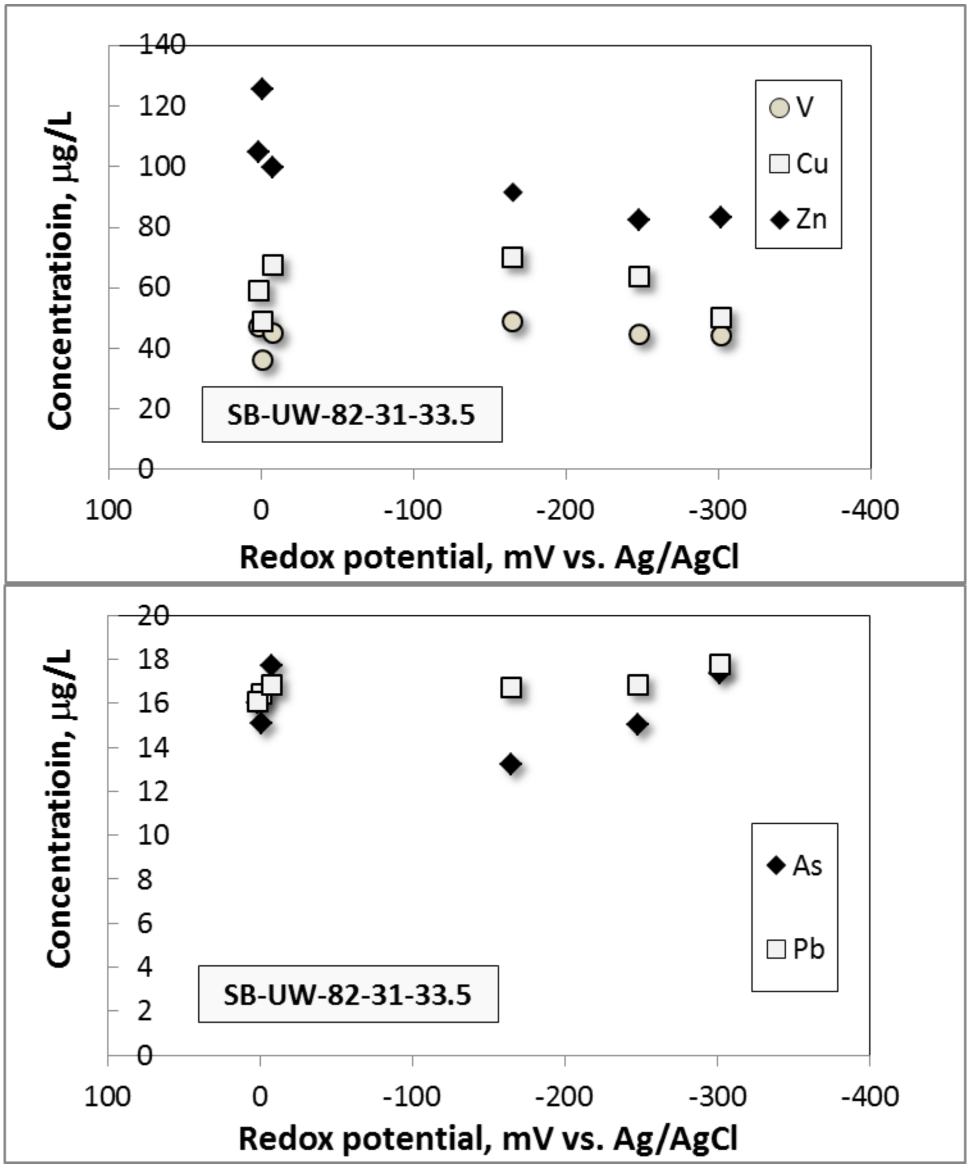

Figure 51 Effects of redox potential on metal release from soil SB-UW-82-31-33.5 extracted from the vicinity of Well 82 (high pH plume). pH10, exposure time 7 days.

Appendix

pH stability in experiments with varying target pH values and exposure times

Table A13 Measurements of pH stability in 7-day exposures of Oxy site soils (Samples S&, S8, S10, S11 and S25).

Sample 7	nominal pH values			
Time, days	pH 8	pH 10	pH 11	pH 12
1	7.5	8.8	10.2	11.8
2	6.3	8.6	10.8	11.9
3	7.5	9.0	10.9	11.9
4	7.3	9.4	10.9	12.0
5	7.8	9.9	11.0	12.0
6	7.8	9.8	11.0	12.0
7	7.9	9.8	11.0	12.0

Sample 8	nominal pH values			
Time, days	pH 8	pH 10	pH 11	pH 12
1	7.7	8.9	10.5	11.9
2	7.3	8.0	10.6	11.5
3	7.3	9.0	10.5	11.9
4	8.0	9.1	11.0	11.9
5	7.1	9.9	11.0	12.0
6	8.0	9.9	11.0	12.0
7	8.0	10.0	11.0	12.0

Sample 10	nominal pH values			
Time, days	pH 8	pH 10	pH 11	pH 12
1	7.9	9.3	10.9	11.9
2	7.1	9.3	10.3	12.0
3	7.5	9.4	10.6	12.0
4	7.7	9.4	10.6	12.0
5	8.0	10.0	10.6	12.0
6	8.0	10.0	11.0	12.0
7	8.0	10.0	11.0	12.0

Sample 11	nominal pH values					
Time, days	pH 0	pH 8	pH 10	pH 11	pH 12	pH 14
1	0.4	5.5	7.0	10.5	11.8	13.7
2	0.6	6.6	8.0	10.7	12.0	13.9
3	0.3	7.0	9.0	11.0	12.0	13.8
4	0.3	8.0	9.1	11.0	12.0	13.8
5	0.3	8.0	9.2	11.0	12.0	13.7
6	0.3	8.0	9.9	11.0	12.0	13.8
7	0.3	8.0	10.0	11.0	12.0	13.8

Sample 25	nominal pH values					
Time, days	pH 0	pH 8	pH 10	pH 11	pH 12	pH 14
1	0.3	8.1	8.7	10.8	11.8	13.6
2	0.4	7.2	9.0	10.3	11.9	13.5
3	0.4	7.3	9.0	10.5	12.0	13.5
4	0.4	7.7	9.0	11.0	12.0	13.6
5	0.3	8.0	9.4	11.0	12.0	13.6
6	0.3	8.0	10.0	11.0	12.0	13.6
7	0.3	8.0	10.0	11.0	12.0	13.6

Table A14 Measurements of pH stability in 7-day exposures of Oxy site soils (Samples S18, S23, S26 and S27).

Sample 18	nominal pH values				
Time, days	pH 8	pH 9	pH 10	pH 11	pH 12
0	8.0	9.0	10.0	11.0	12.0
1	8.6	9.4	9.8	10.9	11.9
2	8.8	9.4	9.8	10.6	11.8
3	8.4	9.2	10.0	10.5	11.9
4	8.3	9.1	10.0	10.9	12.0
5	8.6	9.2	9.9	11.0	12.0
6	8.2	9.1	9.9	11.0	12.0
7	8.1	9.1	10.0	11.3	11.9
Sample 23	nominal pH values				
Time, days	pH 8	pH 9	pH 10	pH 11	pH 12
0	8.0	9.0	10.0	11.0	12.0
1	9.7	9.6	10.0	11.4	11.6
2	9.9	9.7	10.6	11.3	11.5
3	9.2	9.2	10.2	11.4	11.9
4	9.0	9.3	10.2	11.2	11.9
5	8.3	9.3	10.3	11.0	11.8
6	8.3	9.3	10.0	11.3	12.0
7	8.2	9.0	10.2	11.0	12.0
Sample 26	nominal pH values				
Time, days	pH 8	pH 9	pH 10	pH 11	pH 12
0	8.0	9.0	10.0	11.0	12.0
1	9.0	9.6	10.0	11.2	11.8
2	8.9	9.5	10.0	11.1	11.6
3	8.4	9.6	10.9	10.8	11.9
4	8.5	9.4	10.4	11.2	11.9
5	8.3	9.3	10.4	11.0	12.0
6	8.3	9.0	10.1	11.0	12.1
7	8.2	9.0	10.3	11.3	12.0
Sample 27	nominal pH values				
Time, days	pH 8	pH 9	pH 10	pH 11	pH 12

0	8.0	9.0	10.0	11.0	12.0
1	9.0	9.4	9.3	10.6	11.9
2	7.9	9.4	9.5	10.6	11.8
3	7.9	9.5	9.3	10.7	11.9
4	8.4	9.0	9.4	10.9	11.9
5	8.3	9.2	9.8	11.0	12.0
6	8.3	9.0	10.0	10.8	12.0
7	8.2	8.9	10.2	10.9	12.0

Results of measurements of metal concentrations in exposures at varying pHs (7 day contact time)

Table A15 Soil sample S7. Results of measurements of metal release at varying pHs.

S7	Varying pH metal data (ug/L, 20 g solids exposed in 200 mL water)			
Element	***pH 8***	***pH 10***	***pH 11***	***pH 12***
Al	752.0	680.4	2066.2	10809.4
As	0.9	1.0	42.1	64.5
Ba	4.1	2.4	5.6	7.0
Ca	1889.2	1104.4	1075.8	1416.1
Cd	0.0	0.0	0.0	0.0
Cr	2.4	4.0	5.0	6.2
Cu	7.7	20.3	132.2	273.0
Fe	494.3	442.3	1504.9	2398.7
Mg	1554.7	936.5	265.4	248.0
Mn	23.9	2.5	9.4	22.1
Ni	3.5	6.3	7.3	9.4
Pb	13.4	13.3	13.7	14.0
Si	6039.4	7823.1	22848.1	127494.3
Tl	0.0	0.0	0.0	0.0
U	16.4	16.5	17.2	18.0
V	21.3	36.9	300.3	421.6
Zn	7.5	8.3	8.5	9.6

Table A16 Soil sample S8. Results of measurements of metal release at varying pHs.

S8	Varying pH metal data (ug/L, 20 g solids exposed in 200 mL water)			
Element	***pH 8***	***pH 10***	***pH 11***	***pH 12***
Al	892.7	7038.9	11298.0	40923.2
As	1.0	4.2	69.3	87.7
Ba	4.6	4.1	3.3	3.0
Ca	8809.0	7705.3	5505.0	1443.0
Cd	0.0	0.0	0.0	0.0
Cr	2.9	6.2	7.8	10.2

Cu	10.0	33.5	155.3	803.3
Fe	785.4	1202.8	3230.4	8830.2
Mg	2293.4	1530.3	778.4	179.2
Mn	19.2	22.4	24.9	33.4
Ni	3.3	7.4	11.9	20.9
Pb	14.4	13.3	13.4	15.0
Si	8102.7	10045.8	22039.6	138742.3
Tl	0.0	0.0	0.0	0.0
U	12.3	11.3	11.9	11.8
V	44.2	50.4	389.3	493.3
Zn	7.4	10.7	12.4	14.1

Table A17 Soil sample S10. Results of measurements of metal release at varying pHs.

S10	Varying pH metal data (ug/L, 20 g solids exposed in 200 mL water)			
Element	***pH 8***	***pH 10***	***pH 11***	***pH 12***
Al	737.6	1590.6	4872.4	11382.6
As	0.8	7.7	33.5	50.5
Ba	3.5	5.1	7.9	17.4
Ca	2355.8	1617.8	1180.4	1066.8
Cd	0.1	0.1	0.1	0.6
Cr	0.7	0.9	2.3	12.1
Cu	1.9	31.9	102.3	217.2
Fe	511.3	1083.6	2321.0	3808.8
Mg	6050.5	3132.2	2093.9	1384.3
Mn	13.0	5.8	8.3	25.4
Ni	0.4	0.8	1.1	4.6
Pb	13.2	13.5	13.6	14.4
Si	5722.1	9506.5	110982.4	130923.6
Tl	0.0	0.0	0.0	0.0
U	16.4	16.6	16.9	17.5
V	4.8	157.3	343.3	457.0
Zn	0.1	0.1	3.3	6.2

Table A18 Soil sample S11. Results of measurements of metal release at varying pHs.

S11	Varying pH metal data (ug/L, 20 g solids exposed in 200 mL water)			
Element	***pH 8***	***pH 10***	***pH 11***	***pH 12***
Al	2418.3	2337.4	44837.0	18804.5
As	0.7	0.9	12.9	24.8
Ba	7.2	5.8	8.4	42.7
Ca	835.6	583.4	552.9	406.1
Cd	0.0	0.1	0.1	0.1
Cr	0.2	0.3	11.0	20.4

Cu	0.6	5.0	87.5	151.6
Fe	2604.8	1883.7	10093.0	14664.2
Mg	1423.5	886.8	663.5	691.6
Mn	28.1	11.6	77.4	101.8
Ni	0.7	0.7	0.8	7.8
Pb	13.9	13.7	14.1	17.7
Si	9092.8	12285.9	22930.5	49118.6
Tl	0.0	0.0	0.0	0.0
U	16.4	16.6	18.0	19.6
V	1.0	15.0	109.4	248.3
Zn	26.2	0.7	0.9	1.0

Table A19 Soil sample S18. Results of measurements of metal release at varying pHs.

S18	Varying pH metal data (ug/L, 20 g solids exposed in 200 mL water)				
Element	***pH 8***	***pH 9***	***pH 10***	***pH 11***	***pH 12***
Al	4719.2	4001.1	4248.0	20000.1	47612.8
As	4.6	5.0	8.1	4.1	13.2
Ba	104.9	88.2	71.0	66.1	57.5
Ca	2478.3	1986.2	1073.7	1003.0	952.1
Cd	0.9	0.8	0.4	0.4	0.3
Cr	87.6	78.1	19.9	10.2	8.9
Cu	29.2	33.0	52.4	100.2	179.0
Fe	2499.6	766.1	879.8	1293.1	3477.1
Mg	688.6	444.0	207.2	162.1	87.3
Mn	167.9	102.3	44.5	22.1	4.2
Ni	100.1	43.1	1.7	1.2	1.0
Pb	26.6	26.1	26.4	26.5	26.7
Si	51357.2	63022.3	71754.3	207001.3	264017.2
Tl	0.1	0.1	0.0	0.0	0.0
U	118.6	119.1	116.5	120.0	124.5
V	117.1	121.0	138.7	158.1	160.3
Zn	174.0	140.1	65.0	30.2	5.0

Table A20 Soil sample S23. Results of measurements of metal release at varying pHs.

S23	Varying pH metal data (ug/L, 20 g solids exposed in 200 mL water)				
pH	***pH 8***	***pH 9***	***pH 10***	***pH 11***	***pH 12***
Al	49279.3	10765.1	12875.8	70333.0	103218.3
As	76.3	77.9	79.9	79.2	91.5
Ba	1088.0	402.9	80.1	73.0	56.1
Ca	1334.4	1235.1	1022.9	908.9	804.8
Cd	0.9	0.9	0.8	0.8	0.8
Cr	120.7	128.2	115.4	49.0	50.5
Cu	380.7	403.0	441.6	445.3	451.7

Fe	4008.1	3094.0	2824.1	8823.9	11327.5
Mg	1497.5	1539.1	273.5	225.4	201.8
Mn	382.4	108.3	31.0	19.0	3.8
Ni	55.7	50.0	21.4	27.2	18.0
Pb	26.8	27.0	26.7	27.0	27.3
Si	246205.6	290864.0	494164.2	798224.0	1166800.1
Tl	86.2	71.0	75.5	70.8	72.3
U	131.2	125.1	128.6	134.4	129.8
V	267.1	277.1	280.1	290.1	367.0
Zn	18.9	2.1	1.7	1.1	1.0

Table A21 Soil sample S25. Results of measurements of metal release at varying pHs.

S25	Varying pH metal data (ug/L, 20 g solids exposed in 200 mL water)			
Element	***pH 8***	***pH 10***	***pH 11***	***pH 12***
Al	1031.6	2662.4	10923.4	14321.9
As	0.9	1.2	4.2	29.3
Ba	7.9	9.8	11.3	27.3
Ca	2140.8	1086.0	1189.4	2494.9
Cd	0.7	0.7	0.9	1.5
Cr	0.6	3.9	4.4	30.5
Cu	23.6	37.5	88.3	208.6
Fe	867.9	2068.2	4418.3	7027.5
Mg	1115.9	722.7	663.5	73.3
Mn	11.8	9.3	22.8	32.5
Ni	1.0	1.6	1.1	2.1
Pb	13.6	14.2	14.9	16.6
Si	5683.8	7575.7	22983.2	43433.4
Tl	0.0	0.0	0.0	0.0
U	16.3	16.6	17.9	17.9
V	0.6	88.1	298.4	419.9
Zn	0.6	3.8	7.3	15.6

Table A22 Soil sample S26. Results of measurements of metal release at varying pHs.

S26	Varying pH metal data (ug/L, 20 g solids exposed in 200 mL water)				
pH	***pH 8***	***pH 9***	***pH 10***	***pH 11***	***pH 12***
Al	15293.4	8608.0	9986.0	20199.0	21433.9
As	26.6	30.0	32.6	30.1	27.9
Ba	180.9	154.1	44.1	34.0	8.1
Ca	799.8	704.0	665.5	487.0	383.6
Cd	0.7	0.6	0.5	0.4	0.4
Cr	46.3	47.9	44.1	40.1	35.9
Cu	637.6	778.9	822.2	1208.9	1381.2

Fe	17871.2	6729.1	7884.3	9028.1	9659.9
Mg	2082.7	510.0	478.6	44.1	32.9
Mn	139.0	98.1	9.3	9.0	8.4
Ni	58.0	55.1	44.1	38.9	34.0
Pb	28.9	29.1	29.4	29.1	28.8
Si	68408.1	78753.0	81674.0	160235.0	180568.9
Tl	0.0	0.0	0.0	0.0	0.0
U	7.2	7.9	7.3	8.6	7.2
V	55.5	58.1	60.8	60.1	63.0
Zn	88.0	80.1	76.5	60.0	55.3

Table A23 Soil sample S27. Results of measurements of metal release at varying pHs.

S27	Varying pH metal data (ug/L, 20 g solids exposed in 200 mL water)				
pH	***pH 8***	***pH 9***	***pH 10***	***pH 11***	***pH 12***
Al	1304.9	284.0	339.5	24973.1	25591.4
As	89.1	81.0	79.1	82.1	80.1
Ba	99.1	80.1	30.2	29.0	23.3
Ca	31818.9	29876.1	16789.8	3397.0	2490.1
Cd	3.0	4.0	3.2	1.9	1.3
Cr	54.1	44.1	39.1	39.0	33.0
Cu	1662.4	1809.9	2026.9	27.1	2741.3
Fe	1741.2	863.1	859.0	4931.1	4984.8
Mg	39645.8	19203.1	14082.6	476.9	352.7
Mn	409.4	293.8	50.8	34.0	32.1
Ni	116.9	98.3	88.0	73.1	68.1
Pb	26.2	26.1	26.1	27.9	26.5
Si	10680.5	11038.0	12062.2	99862.9	158577.5
Tl	0.0	0.0	0.0	0.0	0.0
U	28.4	28.1	28.4	29.1	29.6
V	20.1	29.1	56.9	709.1	810.5
Zn	1007.0	881.0	700.7	340.1	106.0

Correlations between pH of ambient water and mean logK_d values determined for Oxy site soils

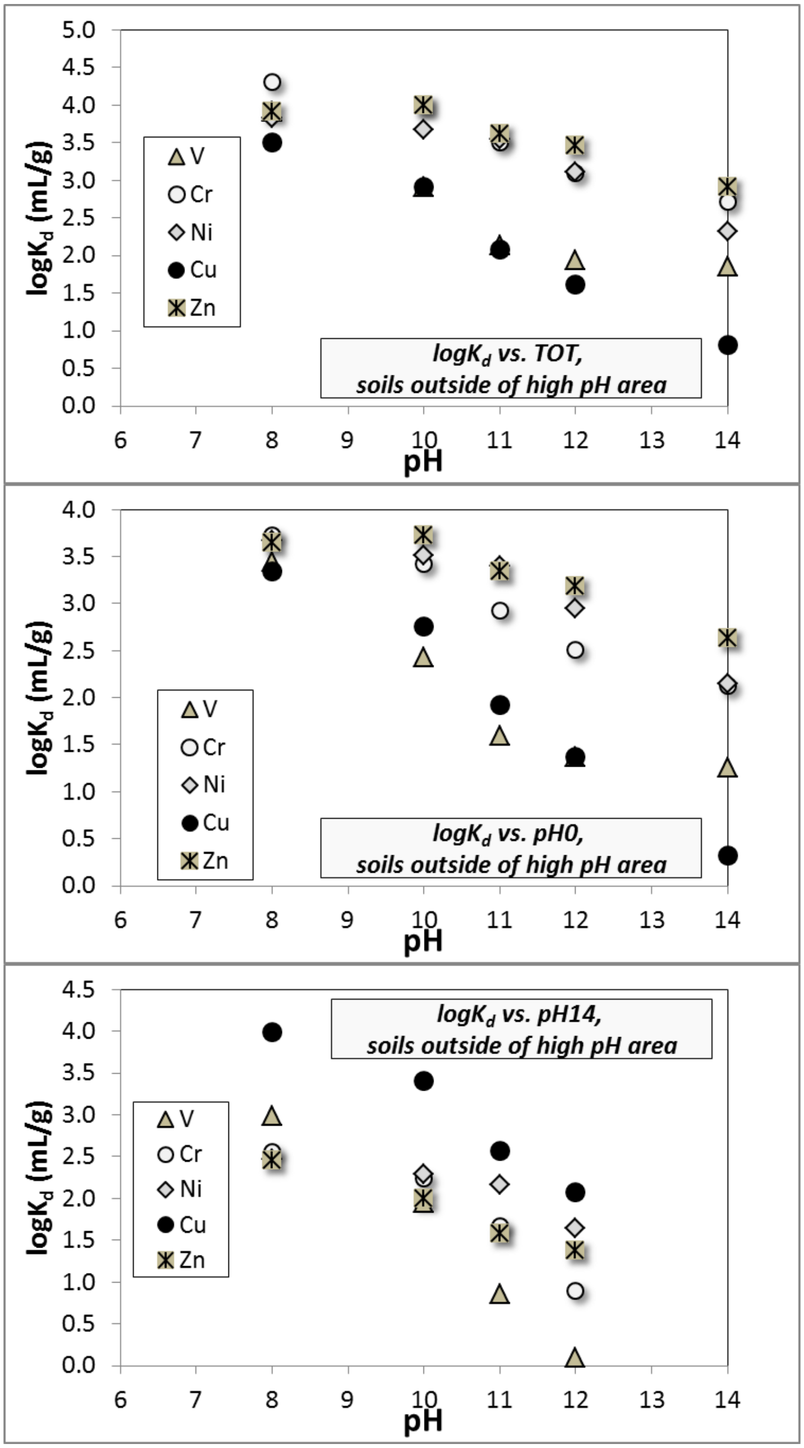

Figure A52 Effects of pH on sample-averaged pH-specific logK_d values for V, Cr. Ni. Cu and Zn for Oxy site soils deemed unaffected by high pH groundwater and three different reference states.

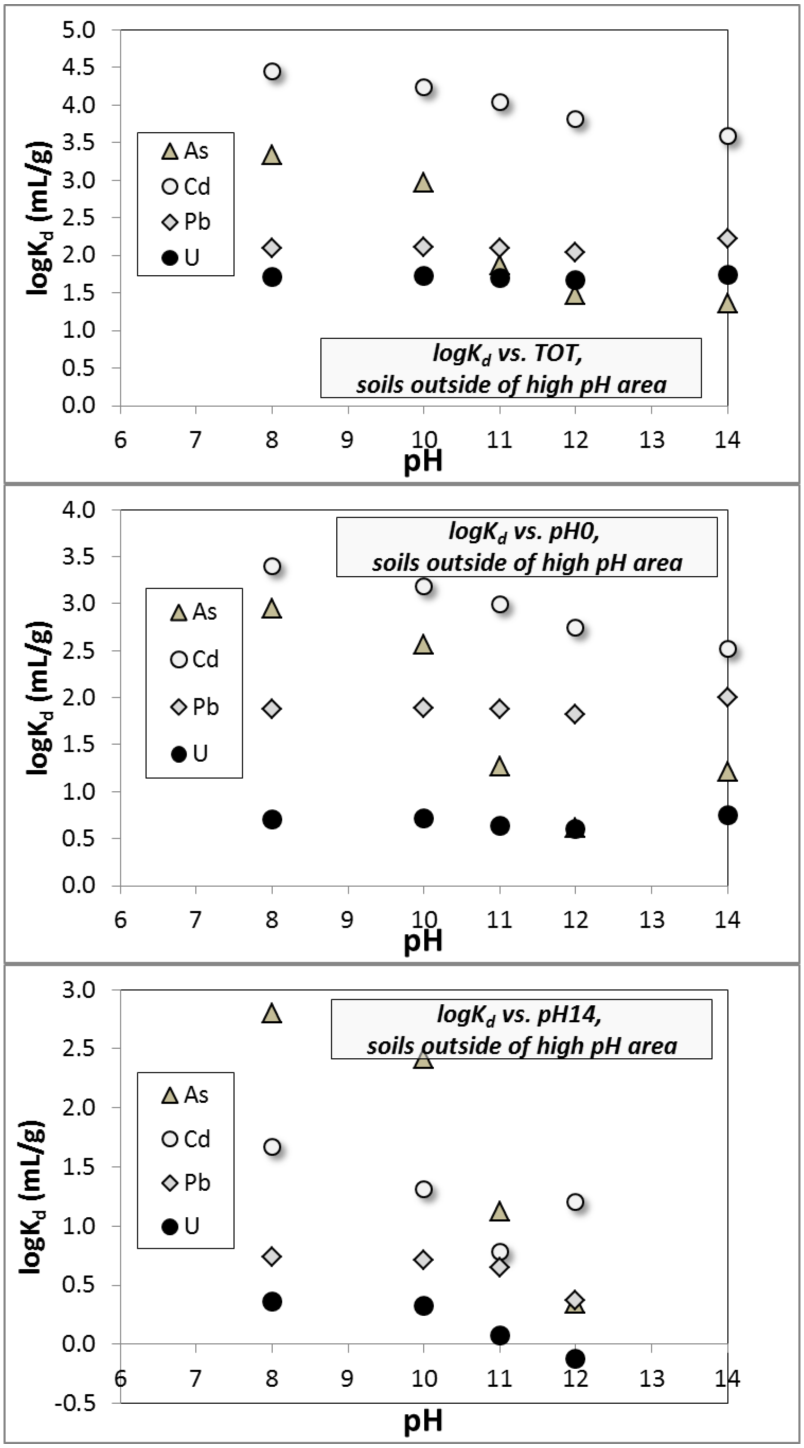

Figure A53 Effects of pH on sample-averaged pH-specific logK$_d$ values for As, Cd, Pb and U for Oxy site soils deemed unaffected by high pH groundwater and three different reference states

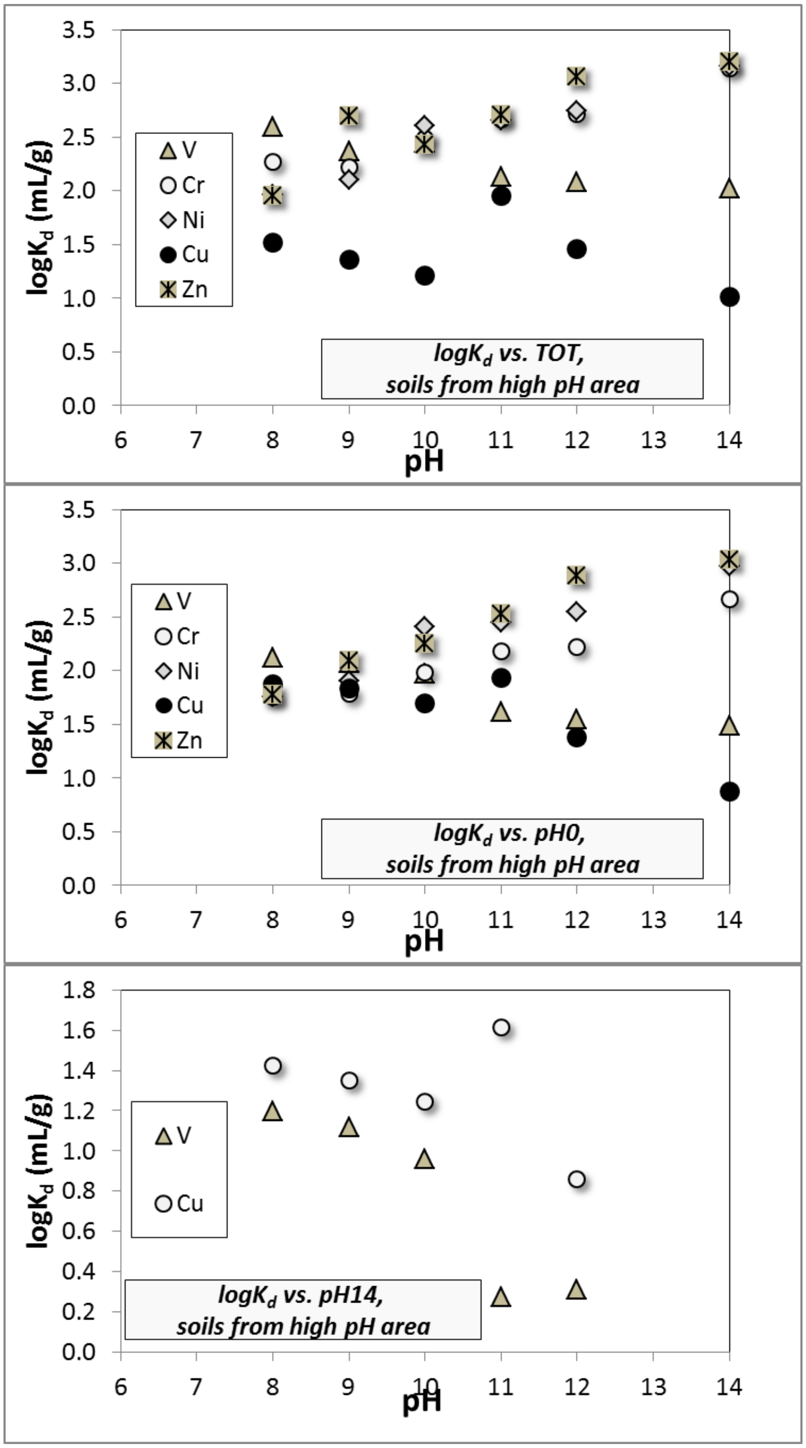

Figure A54 Effects of pH on sample-averaged pH-specific logK$_d$ values for V, Cr, Ni, Cu and Zn for Oxy site soils that are likely to have been affected by high pH groundwater and three different reference states.

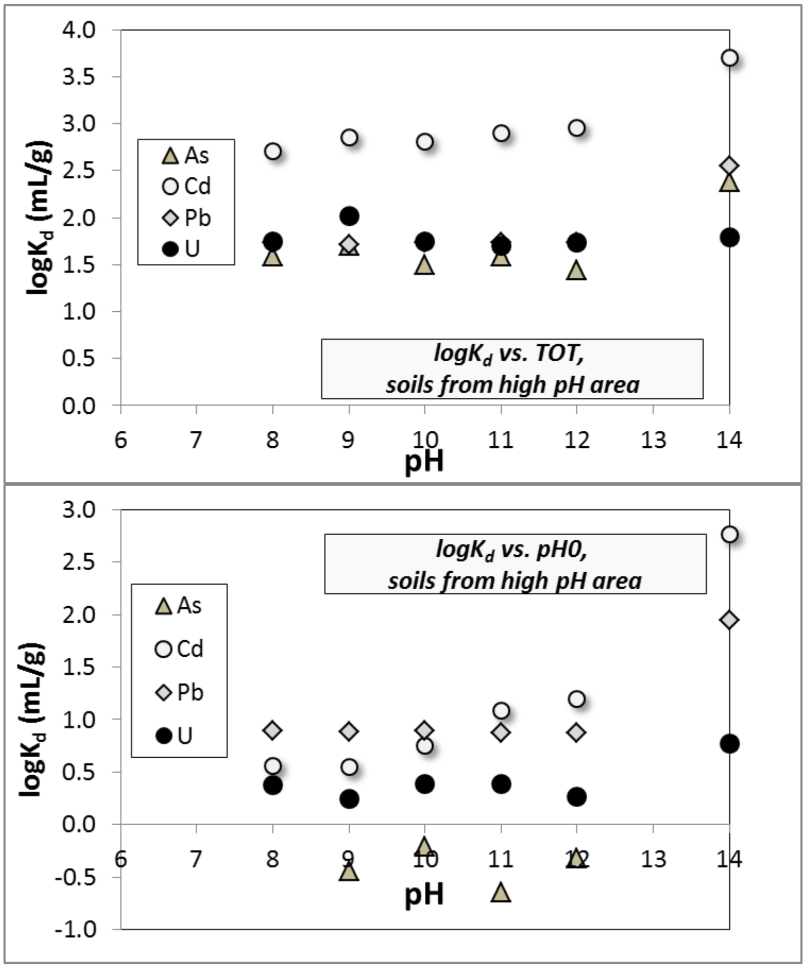

Figure A55 Effects of pH on sample-averaged pH-specific logK$_d$ values for As, Cd, Pb and U for Oxy site soils that are likely to have been affected by high pH groundwater and three different reference states.

Table A24 R^2 coefficients for linear correlations between pH of ambient water and mean logK$_d$ values calculated for Oxy site soils (samples S7, S8, S10, S11 and S25) deemed unaffected by high pH groundwater plumes.

Element	vs. TOT	vs. pH0	vs. pH14
V	0.98	0.86	0.98
Cr	0.88	0.96	0.88
Ni	0.81	0.88	0.81
Cu	0.95	0.98	0.95
Zn	0.98	0.84	0.98
As	0.88	0.66	0.88
Cd	0.55	0.98	0.55
Pb	0.65	0.26	0.65

U	0.82	0.00	0.82

Table A25 Slopes of linear correlations between pH of ambient water and mean $\log K_d$ values calculated for Oxy site soils (samples S7, S8, S10, S11 and S25) deemed unaffected by high pH groundwater plumes.

Element	vs. TOT	vs. pH0	vs. pH14
V	-0.356	-0.382	-0.729
Cr	-0.283	-0.287	-0.401
Ni	-0.255	-0.257	-0.186
Cu	-0.469	-0.523	-0.486
Zn	-0.178	-0.179	-0.277
As	-0.370	-0.358	-0.624
Cd	-0.149	-0.153	-0.158
Pb	0.014	0.015	-0.079
U	0.002	0.000	-0.120

Table A26 Estimates of $\text{Log}K_d$ values at pH 7.0 made based on the linear correlations between pH of ambient water and mean pH-specific $\log K_d$ for Oxy site soils (samples S7, S8, S10, S11 and S25) deemed unaffected by high pH groundwater plumes.

Element	vs. TOT	vs. pH0	vs. pH14
V	4.0	3.5	3.8
Cr	4.7	4.1	3.1
Ni	4.3	4.2	2.7
Cu	4.1	4.0	4.6
Zn	4.3	4.0	2.8
As	3.7	3.2	3.7
Cd	4.6	3.6	1.8
Pb	2.1	1.8	0.9
U	1.7	0.7	0.5

Table A27 R^2 coefficients for linear correlations between pH of ambient water and mean $\log K_d$ values calculated for Oxy site soils (samples S18, S23, S26 and S27) that are likely to have been affected by high pH groundwater.

Element	vs. TOT	vs. pH0	vs. pH14
V	0.86	0.88	0.86
Cr	0.00	0.97	
Ni	0.00	0.94	
Cu	0.24	0.74	0.24
Zn	0.00	0.96	

As	0.20	0.00	0.20
Cd	0.00	0.84	
Pb	0.00	0.55	
U	0.25	0.46	0.25

Table A28 Slopes of linear correlations between pH of ambient water and mean logK_d values calculated for Oxy site soils (samples S18, S23, S26 and S27) that are likely to have been affected by high pH groundwater.

Element	vs. TOT	vs. pH0	vs. pH14
V	-0.098	-0.122	-0.262
Cr	0.153	0.154	
Ni	0.198	0.199	
Cu	-0.050	-0.163	-0.087
Zn	0.186	0.217	
As	0.100	-0.008	-0.087
Cd	0.146	0.355	
Pb	0.117	0.149	
U	-0.014	0.060	-0.061

Table A29 Estimates of LogK_d values for pH 7.0 made based on the linear correlations between pH of ambient water and mean pH-specific logK_d calculated for Oxy site soils (samples S18, S23, S26 and S27) that are likely to have been affected by high pH groundwater.

Element	vs. TOT	vs. pH0	vs. pH14
V	2.6	2.3	1.6
Cr	2.0	1.5	
Ni	1.8	1.6	
Cu	1.6	2.2	1.6
Zn	2.0	1.6	
As	1.3	-0.4	0.0
Cd	2.5	-0.1	
Pb	1.4	0.5	
U	1.8	0.2	-0.1