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## A MODEL FOR EVALUATING THE FEASIBILITY OF AN EXTRACTION PROCEDURE FOR HEAVY METAL REMOVAL FROM CONTAMINATED SOILS

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**Abstract.** A model was developed that allowed for the evaluation of a soil metal cleaning technique in a rapid and cost effective manner. Metal flow (Pb, Cu, Zn, and Cd) during a counter-current soil-acid extraction procedure, consisting of a decarbonation, solubilisation, and washing step, was determined. Required input data are total soil metal content and metal equilibrium distribution coefficients, derived from batch equilibration experiments. The model was calibrated and validated against experimentally obtained results. Model predictions adequately described metal behaviour and removal in each of the extraction steps. Based on the results, optimum operating conditions for the steps involved in the extraction procedure were determined and the feasibility of the counter-current extraction procedure for heavy metal removal from a contaminated soil evaluated.

Keywords: soil remediation; extraction; heavy metals

### 1. Introduction

Decontamination of soils polluted with heavy metals is one of the most difficult problems of clean-up technology (Esposito *et al.*, 1989; Sheppard and Thibault, 1992). In our search for strategies for dealing with metal contaminated soils, we evaluated the feasibility of a counter-current soil-acid extraction procedure (Figure 1). In this procedure, soil metals are extracted in a three-step process including decarbonation, solubilisation, and washing. Metal mobilisation occurs in an acid solubilisation step. The acid extract is then used to pre-treat (decarbonate) the contaminated soil in the first step of the counter-current extraction procedure. The soil leaving the solubilisation step undergoes a final washing step. Washing the treated soil can occur with water or a salt.

For a soil cleaning process to be promising, several conditions need to be fulfilled. Metal concentrations need to be lowered in a cost effective manner to concentrations that are considered acceptable. Secondly, the restored or cleaned soil should have the potential to recover ecologically, spontaneously or after amelioration, to a viable soil. Post-extraction treatments for the counter-current soil acid procedure set forward above, could include liming and introduction of microbiota and plants.

When evaluating remediation technologies, feasibility studies and preliminary cost studies are a first step in determining the best cleaning strategy. Optimisation and full performance tests of promising treatments will eventually follow. The main goal of this paper is to describe a simple

model that can be used in a predictive way to describe metal flow in the counter-current soil-extraction procedure. In this manner, operating conditions of the three-step extraction procedure could be optimised and the feasibility of the soil remediation technology evaluated in a rapid and cost effective way. The approach taken here can easily be applied and extrapolated to other soil treatment technologies. This should avoid the promotion and use of soil sanitation techniques, without proper testing for possibilities and shortcomings.

## 2. Conceptual basis of the model

Figure 1 depicts a schematic of the metal extraction strategy put forward. Metal contaminated soil undergoes consecutively a decarbonation, a solubilisation, and a washing step. The three extractions occur in a counter-current manner. Washing liquid (water or a solution containing a salt) comes in contact with soil leaving the solubilisation step. After equilibration (washing) and phase separation, acid is added to the wash solution and the solution is brought in contact with soil leaving the decarbonation step. After solubilising the soil, the acidic liquid phase is added to contaminated soil entering the process. Symbols used in Figure 1 describe the mass flow of metals during the different steps of the soil cleaning process. The mass and metal content of solid phases in the process are described by  $S$  and  $X$ , respectively. In a similar manner  $L$  and  $C$  are used to denote the mass and metal concentration of the liquid phases involved. The subscripts describe the direction of the flow. The first letter represents the origin and the second the destination. For example,  $S_{sw}$  represents the mass of solid phase (soil) leaving the solubilisation step ( $s$ ) and entering the washing step ( $w$ ).

Metal flow is described by mass balance equations. For each step (decarbonation, solubilisation, and washing) the total input mass of a component must equal the total output mass. For example, for the solubilisation step the following partial mass balance equation can be written for a component (e.g. Pb):

$$S_{ds} X_{ds} + L_{ds} C_{ds} + S_{ws} X_{ws} + L_{ws} C_{ws} = S_{sw} X_{sw} + L_{sw} C_{sw} + S_{sd} X_{sd} + L_{sd} C_{sd} \quad (3)$$

where  $S_{ds}$  is the weight (kg) of the solid phase leaving the decarbonation step ( $d$ ) and entering the solubilisation ( $s$ ) step, and  $X_{ds}$  the concentration (mg kg<sup>-1</sup>) of a component. In a similar way  $L_{ds}$  represents the weight (kg) of the liquid phase leaving the decarbonation step ( $d$ ) and entering the solubilisation ( $s$ ) step, and  $C_{ds}$  the concentration (mg kg<sup>-1</sup>) of component therein. The notation "w" stands for washing step.

The model is based on the assumption that aqueous and sorbed concentrations reach equilibrium during the decarbonation, solubilisation, and washing steps. For each step the equilibrium distribution was described by the relation:

$$X = K C \quad (3)$$

where  $X$  is the steady-state concentration in the solid phase (mg kg<sup>-1</sup>) and  $C$  the equilibrium solution concentration (mg L<sup>-1</sup>).  $K$  (L kg<sup>-1</sup>) represents the distribution coefficient or solid surface affinity term and is function of pH and treatment (decarbonation, solubilisation, and washing).

The distribution coefficient may be incorporated in the mass balance (Equation 1). For the solubilisation step, for example,  $X_{sw} = K C_{sw} = K C_{sd}$ . As, moreover,  $S_{ws}$  and  $S_{sd}$  are equal to 0 as there is no solid phase in the liquid stream, Equation 1 can be simplified to

$$S_{ds} X_{ds} + L_{ds} C_{ds} + L_{ws} \cdot C_{ws} = C_{sw} (L_{sw} + L_{sd} + K S_{sw}) \quad (3)$$

Similar equations can be obtained for the decarbonation and washing steps.

Before evaluating metal flux in the counter-current extraction procedure, the following experimentally determined parameters were needed: total soil metal content, efficiency of solid-liquid phase separation, and equilibrium distribution coefficients for each metal in the 3 steps of the procedure. Data obtained in batch equilibration experiments were fitted to obtain mathematical expressions describing the distribution coefficients ( $K$ ) of the equilibrium expressions as a function of pH or reacting conditions.

### 3. Materials and methods

#### 3.1. SOIL SELECTION AND CHARACTERISATION

A metal polluted surface soil was collected at Tielrode, near the city of Antwerp in Belgium. Soil texture was determined by granulometric analysis. Using standard laboratory procedures (Cottenie *et al.*, 1982) soil pH, cation exchange capacity, C, N, and carbonate content were determined. Total soil metal (Cd, Zn, Pb, and Cu) content was determined after Aqua Regia digestion (Ure, 1990). Flame and graphite furnace atomic absorption spectrophotometry were used to quantify the amount of metals in solution.

#### 3.2. EXPERIMENTAL DETERMINATION OF EQUILIBRIUM DISTRIBUTION COEFFICIENTS

The distribution coefficients ( $K$ ) of the equilibrium expressions were experimentally determined in a series of batch equilibration experiments. All equilibrations were triplicated and occurred at a constant soil:liquid ratio of 1:5. After 1 hr equilibration, suspensions were filtered using a filter-vacuum system. The equilibrium pH of the filtrates was measured and the concentration of Cd, Zn, Pb, and Cu in the extracts determined. For each equilibration the dry weight and the Cd, Zn, Pb, and Cu content of the soil was determined before and after extraction. In this manner data (and  $K$  values) on the amount of metals in the solid phase ( $X$ ) in equilibrium with a concentration  $C$  in the liquid phase were obtained. The dry weight of the filtered soil reflects the efficiency of the solid-liquid phase separation.

For the decarbonation and solubilisation steps, the  $K$  values, termed  $K_{deca}$  and  $K_{sol}$ , respectively, were determined as a function of pH. In these batch equilibration experiments soil suspensions were acidified with increasing amounts of 2 M HCl. If controlled pH conditions were needed, addition of HCl occurred with an automatic pH stat/titrimeter. For  $K_{deca}$ , the batch equilibration experiments were conducted with original surface soil samples over a pH range 5.50 to 0.20 with increments of approximately 0.30 pH units. In order to determine  $K_{sol}$ , an amount of “decarbonated soil” was prepared by equilibrating original soil with metal laden acid extract, obtained after filtration of pH 1 acidified soil suspensions. Using the decarbonated soil, batch equilibrations were used to determine  $K_{sol}$  over a pH range 5.0 to 1.0.

Operating conditions in the washing step were determined by the ionic strength of the salt ( $\text{CaCl}_2$ ) added. Therefore,  $K_{was}$  was determined as a function of moles of  $\text{CaCl}_2$  added in the washing step. Soils acidified to pH 1 were washed with deionised water, 0.01, 0.05, 0.1, and 0.5 M  $\text{CaCl}_2$  and  $K_{was}$ , as affected by salt concentration, was determined.

### 3.3. MODEL VALIDATION

An array of batch equilibrations was used to simulate the counter-current extraction technique. Contaminated soil underwent consecutively decarbonation, solubilisation, and washing. Liquid phases obtained in the extractions were used as input (extractant) in the subsequent step of the process. A detailed description of the execution of the extraction scheme involved was described in an earlier contribution (Masscheleyn *et al.*, 1996). Solubilisation occurred at pH 1 and deionised water was used to wash the solubilised soil. Operating pH conditions of the decarbonation step were measured but not controlled. The efficiency of solid-liquid phase separation was assessed from the dry weight of the filtered soil. Metal analysis of contaminated soil and the different liquid phases of the process allowed the experimental determination of metal fluxes in the counter-current metal extracting process. Results obtained were compared to the model predictions.

## 4. Results and discussion

There have been numerous studies on metal sorption/desorption in both synthetic systems (Benjamin, 1983; Cowan *et al.*, 1991; Kinniburgh and Jackson, 1982) and soils (Kiekens, 1980; Sanders and Kherbawy, 1987). Results consistently show that pH is the dominant physicochemical parameter controlling metal solubility and that cation solubility drastically increases as pH decreases. Based on this knowledge, we designed a counter-current extraction scheme for the solubilisation and extraction of heavy metals from contaminated soils (Figure 1). The counter-current metal extraction scheme set forward in this paper makes optimal use of the acid added and it was hypothesised that this extraction procedure would result in a soil low in metal content. In order to test this hypothesis we developed a model that can be used to describe metal flow in the counter-current extraction procedure and, thereby, allows to determine operating conditions necessary for soil metal cleaning. Based on the results, conclusions can be made regarding feasibility and cost-effectiveness of the proposed soil cleaning strategy.

The soil used in our study was characterised by a silty clay texture, a pH 7.4, 2.00 % organic carbon, 4.87 % carbonate, and a cation exchange capacity of 19.5 cmol<sup>+</sup> per kg soil. The soil had a total Pb, Cu, Zn, and Cd content of  $236 \pm 6.0$ ,  $105 \pm 1.8$ ,  $1516 \pm 199$ , and  $8.65 \pm 0.3$  (n = 4) mg kg<sup>-1</sup> dry soil, respectively. The carbonate content of the Tielrode soil determined to a great extent the acid buffering capacity and governed acid requirement (Figure 2) and metal solubility as a function of pH.

### 4.1. MODEL CALIBRATION

For each metal, the pH dependent distribution coefficient  $K$  was determined experimentally for the decarbonation ( $K_{deca}$ ) and solubilisation ( $K_{sol}$ ) step using original soil and decarbonated soil, respectively. As mentioned before,  $K$  values were calculated as the ratio  $X:C$ . For example, Figures 3 and 4 depict the general type and shape of the experimental Pb equilibrium distribution data as a function of pH for the decarbonation and solubilisation step, respectively. The insets represent plots of  $\ln(K)$  versus pH. Partitioning coefficients for Pb decreased from 556 (pH 5.27) to 2.93 (pH 1.11) (Figure 4) and from 1176 (pH 5.50) to 0.305 (pH 0.21) (Figure 3). Similarly, for the other metals studied (Cu, Zn, and Cd), equilibrium distribution coefficients rapidly (exponentially) decreased as the pH decreased. The extent of decrease in both  $K_{deca}$  and  $K_{sol}$  with decreasing pH was as follows: Pb > Cu > Cd > Zn.

Experimental data sets were described by both polynomial and exponential regressions (PROC GLM, SAS, Statistical Analysis System, 1985). Although  $R^2$  values were similar for the polynomial and exponential equations, the standard error of the parameter estimates, a measure of the agreement between calculated and observed values (Steel and Torrie, 1980), was an order of magnitude smaller for the exponential equation. Also, possibility of linear approximation of the sorption equilibrium data substantially reduced the mathematical complexity of the modelling effort. Therefore, the exponential model was selected to describe the equilibrium distribution coefficients which are described by the slope and intercept of the linearised form. Parameter estimates, standard errors of the estimates, and  $R^2$  values relating  $\ln(K)$  values to pH for the 4 metals studied in the decarbonation and solubilisation steps are listed in Table I.

For the washing step (Figure 1) the metal equilibrium distribution coefficients ( $K_{was}$ ) were determined as a function of moles of  $\text{CaCl}_2$  added to solubilised soil (Figure 5). When describing the obtained partitioning constants, the  $\text{CaCl}_2$  solution added, pH after washing, and the interaction  $\text{CaCl}_2 \times \text{pH}$  were taken into account. While  $\text{CaCl}_2$  added was found to be significant, both the pH after washing and the  $\text{CaCl}_2 \times \text{pH}$  interaction were not significant in the GLM (Statistical Analysis System, 1985) model. This indicates that the amount of  $\text{CaCl}_2$  added was the main property controlling metal extractability during the washing step. The higher the amount of  $\text{CaCl}_2$  added the smaller metal  $K_{was}$  values became (Figure 5). Regression parameter estimates and  $R^2$ -values relating metal  $K_{was}$  with  $\text{CaCl}_2$  added are given in Table II. From these results it can be seen that, of the metals studied, Pb and Zn are most influenced by washing with a salt, and that Cu and Cd are the least affected

Although significant model expressions were found for the metal equilibrium distribution constants during the three steps of the counter-current extraction scheme (Figure 1), caution should be exercised in applying the equations because they may not be valid over pH (or  $\text{CaCl}_2$ ) ranges beyond those represented by the data to which they were calibrated. Taken this into account, mass balance equations for decarbonation, solubilisation, and washing step together with equilibrium distribution expressions were used to compute the mass flux of the contaminants in the counter-current extraction procedure.

Mass balance equations were set up in a spreadsheet file. Required input data are total soil metal content, data on the masses of liquids and solids involved, and the appropriate equilibrium expressions. The batch equilibration experiments were conducted at a soil:liquid ratio of 1:5. The vacuum-filtration technique used to separate solid from liquid phases resulted in a filtered solid phase with a dry weight of approximately 70%. As such, masses of both liquid and solid phases can be entered in the mass balance equations. For example, Equation 3 becomes

$$1 X_{ds} + 0.42 C_{ds} + 4.58 C_{ws} = C_{sw} (0.42 + 4.58 + K S_{sw}).$$

A similar mass balance expression can be set up for the decarbonation and washing step. In the spreadsheet, the mass balances for the different steps were connected, giving raise to a recursive calculation model. This was solved by iteration, until solutions to the mass balance equations converged within 2%. Less than 7 iterations were necessary.

#### 4.2. MODEL APPLICATION FOR THE TIELRODE SOIL

The model was used to describe metal flow during the counter-current metal extraction procedure (Figure 1) of the Tielrode soil. At the same time, operating conditions necessary for soil metal cleaning were determined and the feasibility of the extracting procedure evaluated. We considered

the treated soil to be decontaminated when metal levels became lower than the “A” reference values for soil metal content, as put forward by the Dutch Ministry of Housing, Physical Planning and Environment (VROM, 1990). These maximum permissible metal concentrations for “clean” soil are calculated as a function of clay and organic matter content. For the Tielrode soil “A” reference values amount to 78, 32, 0.64, and 126 mg kg<sup>-1</sup> soil for Pb, Cu, Cd, and Zn, respectively.

Acid requirement for the acidification of the Tielrode soil sharply increased as soil suspension pH values dropped below 1 (Figure 2). Therefore, the first runs of the model were done assuming a solubilisation pH of 1. This would somewhat limit the equivalents of acid needed and at the same time bring a considerable amount of metals in solution.

The influence of varying pH<sub>deca</sub> while solubilising at pH 1 and washing with deionised water, on the soil Pb content is shown in Figure 6. In this Figure, predicted soil Pb concentrations after decarbonation (Pb<sub>deca</sub>), solubilisation (Pb<sub>sol</sub>), and washing (Pb<sub>was</sub>) are represented. Lead contents of the native contaminated soil (236 mg kg<sup>-1</sup> dry soil) and the amount of Pb corresponding with an “A” reference soil (78 mg kg<sup>-1</sup> dry soil) are also indicated. From the results in Figure 6 it can be seen that it will be necessary to conduct the decarbonation step at pH values below 1.2 in order to extract Pb satisfactorily. Figure 6 clearly illustrates the importance of the pH extracting condition of the decarbonation step. According to the model predictions, Pb extracted in the solubilisation step would accumulate in soil entering the decarbonation step if pH<sub>deca</sub> is allowed to raise above 1.4. This would result in increased Pb concentrations of the decarbonated soil as compared to the native contaminated soil (Figure 6). Subsequent solubilisation of this decarbonated soil would not remove enough Pb to obtain a clean “A” reference soil. Moreover, when decarbonation would occur above pH 3.6, no net removal of Pb would occur (Pb<sub>was</sub>, Figure 6). From Figure 6 it can also be seen that the amount of Pb removed during the washing step with deionised water is expected to be small.

The increase in Pb extractability by replacing deionised water with a salt in the washing step of the procedure is illustrated in Figure 7. Concentrated salt solutions will be needed in order to significantly increase Pb removal in the washing step. The effect of a 0.05 M CaCl<sub>2</sub> wash is negligible compared to a wash with deionised water. The addition of 0.5 M CaCl<sub>2</sub> in the washing step, however, lowered the residual soil Pb content by approximately 16%.

The predicted behaviour of soil Cu (data not shown) during the counter-current metal extraction procedure was similar to that of Pb. With a solubilisation pH of 1, pH<sub>deca</sub>-values below 1.4 were required in order to obtain a “clean” soil, containing less than 32 mg Cu kg<sup>-1</sup> dry soil. At pH<sub>deca</sub> above 4.2, no net removal of Cu occurred. Again, washing with a salt was not predicted to be effective in removing extra Cu during the washing step.

In contrast to Pb and Cu, Cd was easily removed from the soil. Model calculations (data not shown) predicted Cd concentrations in the washed soil to be below 0.65 mg kg<sup>-1</sup> dry soil when the following operating parameters were used in the extraction procedure: pH<sub>sol</sub> = 1, deionised water as washing agent, and pH<sub>deca</sub> below 4.5. Cadmium never accumulated during the decarbonation step. Moreover, 47 (pH<sub>deca</sub> = 5.0) to 83 % (pH<sub>deca</sub> = 1.0) of the Cd present in the contaminated soil was already extracted during the decarbonation step. After the subsequent solubilisation step at pH 1, soil Cd concentrations were reduced to 0.62 (pH<sub>deca</sub> = 5.0) and 0.26 (pH<sub>deca</sub> = 1.0). On the average, soil washing with deionised water removed an extra 0.02 mg Cd kg<sup>-1</sup> dry soil.

The effectiveness of the counter-current metal extraction procedure for the removal of Zn was predicted to be limited. Zinc concentrations in the cleaned soil were reduced to only 1195 kg<sup>-1</sup> dry soil after extraction at pH<sub>deca</sub> = 1.0, pH<sub>sol</sub> = 1.0, and deionised water wash. Lowering pH<sub>sol</sub> to 0.6 and washing with 0.5 M CaCl<sub>2</sub> is not expected to significantly increase Zn removal (1180 mg kg<sup>-1</sup> dry soil). As for Pb and Cu, Zn accumulated in the soil during the decarbonation step. Zinc accumulation occurred at all pH<sub>deca</sub> values (5.2 to 1.0) studied. As long as pH<sub>deca</sub> was above 3.4, the decarbonated and solubilised soil had Zn concentrations higher than the native contaminated soil.

Acidification and solubilisation at pH 1, followed by a washing treatment, did not extract sufficient Zn to compensate for the enrichment that occurred in the decarbonation step. In all cases, final soil Zn concentrations remained far above the 126 mg kg<sup>-1</sup> dry soil “A” reference value for the Tielrode soil. As such, the counter-current acid extraction strategy does not appear to be able to remove Zn satisfactorily from the contaminated Tielrode soil.

Model predictions showed that of the metals studied Cd, Pb, and Cu will be extracted from the soil by the counter-current extraction procedure to a level for “clean” soils under the following operating conditions: pH<sub>deca</sub> = 1.2, pH<sub>sol</sub> = 1.0, and a deionised water wash. The overall removal efficiency for Zn was too low in order to reach acceptable soil levels for this contaminant.

In order to execute the soil metal cleaning strategy at pH<sub>deca</sub> = 1.2 and pH<sub>sol</sub> = 1.0, 2.5 mol HCl per kg dry soil are required. This leads to the need of approximately 200 L of conc. (12 M) HCl for each tonne of soil to be extracted.

#### 4.3. MODEL VALIDATION

Metal flux in the counter-current extraction procedure was experimentally determined in a series of batch equilibration experiments conducted with the Tielrode soil. In these experiments, solubilisation occurred at pH 1 and deionised water was used to wash the solubilised soil. Operating pH conditions of the decarbonation step were not controlled but measured to be 3.92. Metal analysis of contaminated soil and the different liquid phases of the process allowed the experimental determination of the metal flux in the extracting process. Experimental results were compared to results of model predictions in Table III. The model works well both qualitatively and quantitatively. The predicted accumulation of Pb, Cu, and Zn during the decarbonation step was confirmed by the experimental data. Furthermore, experimental data illustrate the effectiveness (or ineffectiveness) of the solubilisation and washing steps for soil metal removal, as predicted by the model. Taking the simplicity of the model into account, it adequately described metal flow in the soil extraction procedure. Shortcomings of the modelling approach are in a quantitative manner. While the accumulation of Cu and Zn during the decarbonation step were predicted within experimental errors, the amount of Pb and Cd accumulated in this step were overestimated and underestimated, respectively. Percentages of metals removed during the solubilisation and washing step were adequately described by the model. All predicted metal concentrations in the “cleaned” soil were well within the observed experimental variation.

In summary, a model was developed and used as evaluation tool for the feasibility of a counter-current metal extraction procedure from a contaminated soil. Model calculations allowed for the optimisation of extracting conditions. Although our results are limited to the specific experimental conditions used in our study, it must be clear that an approach similar to ours can be of help in predicting feasibility of other (metal) soil cleaning strategies, in a rapid and cost effective manner.

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## Tables

TABLE I: Calculated parameter estimates, standard error of the parameter estimates, and  $R^2$  values relating  $\ln(K)$  to pH

$\ln(K)$	Counter-current step	intercept	slope	$R^2$
Pb	Decarbonation	$0.237 \pm 0.29$	$1.246 \pm 0.08$	0.95
	Solubilisation	$-0.317 \pm 0.15$	$1.469 \pm 0.05$	0.96
Cu	Decarbonation	$-0.174 \pm 0.10$	$1.187 \pm 0.02$	0.99
	Solubilisation	$0.055 \pm 0.06$	$1.279 \pm 0.02$	0.99
Zn	Decarbonation	$3.086 \pm 0.08$	$0.198 \pm 0.02$	0.86
	Solubilisation	$1.648 \pm 0.10$	$0.601 \pm 0.03$	0.90
Cd	Decarbonation	$-0.460 \pm 0.17$	$0.277 \pm 0.05$	0.76
	Solubilisation	$-1.156 \pm 0.12$	$0.699 \pm 0.04$	0.91

TABLE II: Calculated parameter estimates, standard error of the parameter estimates, and  $R^2$  values relating  $\ln(K)$  to molars  $\text{CaCl}_2$  added

$\ln(K)$	Counter-current step	intercept	slope	$R^2$
Pb	Washing	$3.849 \pm 0.15$	$-3.461 \pm 0.61$	0.85
Cu	Washing	$3.349 \pm 0.09$	$-1.559 \pm 0.36$	0.75
Zn	Washing	$3.313 \pm 0.08$	$-1.748 \pm 0.32$	0.84
Cd	Washing	$1.989 \pm 0.11$	$-1.664 \pm 0.41$	0.73

TABLE III: Comparison between experimental results and model predictions

Metal	Soil	Experimental results	Model prediction
Pb	Contaminated	$236 \pm 6$	
	Decarbonated	$358 \pm 43$	473
	Solubilised	$221 \pm 56$	243
	Washed	$211 \pm 37$	239
Cu	Contaminated	$105 \pm 2$	
	Decarbonated	$166 \pm 45$	192
	Solubilised	$101 \pm 12$	108
	Washed	$95 \pm 14$	101
Zn	Contaminated	$1516 \pm 199$	
	Decarbonated	$1749 \pm 305$	1995
	Solubilised	$1396 \pm 117$	1594
	Washed	$1310 \pm 130$	1360
Cd	Contaminated	$8.65 \pm 0.2$	
	Decarbonated	$8.28 \pm 3.72$	3.25
	Solubilised	$1.67 \pm 2.36$	0.57
	Washed	$0.26 \pm 0.92$	0.52

## List of figures

Fig. 1. Counter-current metal extraction scheme

Fig. 2. Acid titration curve for the Tielrode soil (error bars denote the standard deviation of three replicates)

Fig. 3. Equilibrium distribution coefficients for Pb in the decarbonation step ( $K_{deca}$ ) of the counter-current metal extraction procedure as a function of pH.

Fig. 4. Equilibrium distribution coefficients for Pb in the solubilisation step ( $K_{sol}$ ) of the counter-current metal extraction procedure as a function of pH.

Fig. 5. Metal equilibrium distribution coefficients in the washing step ( $K_{was}$ ) of the counter-current metal extraction procedure as a function of  $\text{CaCl}_2$  added.

Fig. 6. Predicted Pb content in decarbonated ( $\text{Pb}_{deca}$ ), solubilised ( $\text{Pb}_{sol}$ ), and washed ( $\text{Pb}_{was}$ ) soil during the counter-current soil cleaning process as a function of the pH in the decarbonation step (pH solubilisation = 1, deionised water wash).

Fig. 7. Predicted Pb content of treated soil after washing with deionised water, 0.05 M  $\text{CaCl}_2$ , and 0.5 M  $\text{CaCl}_2$  as a function of the pH in the decarbonation step (pH solubilisation = 1).

Figure 1

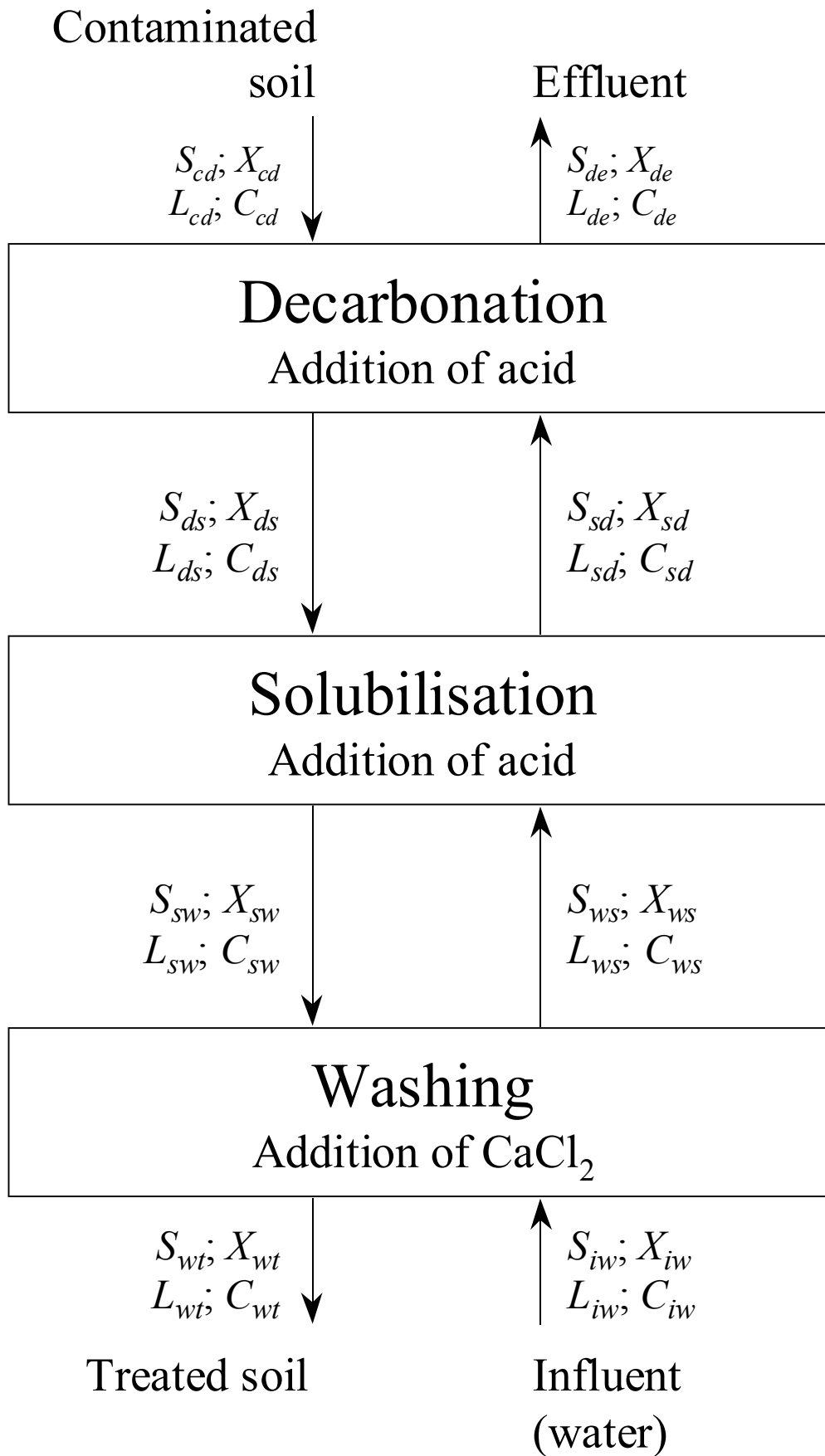


Figure 2

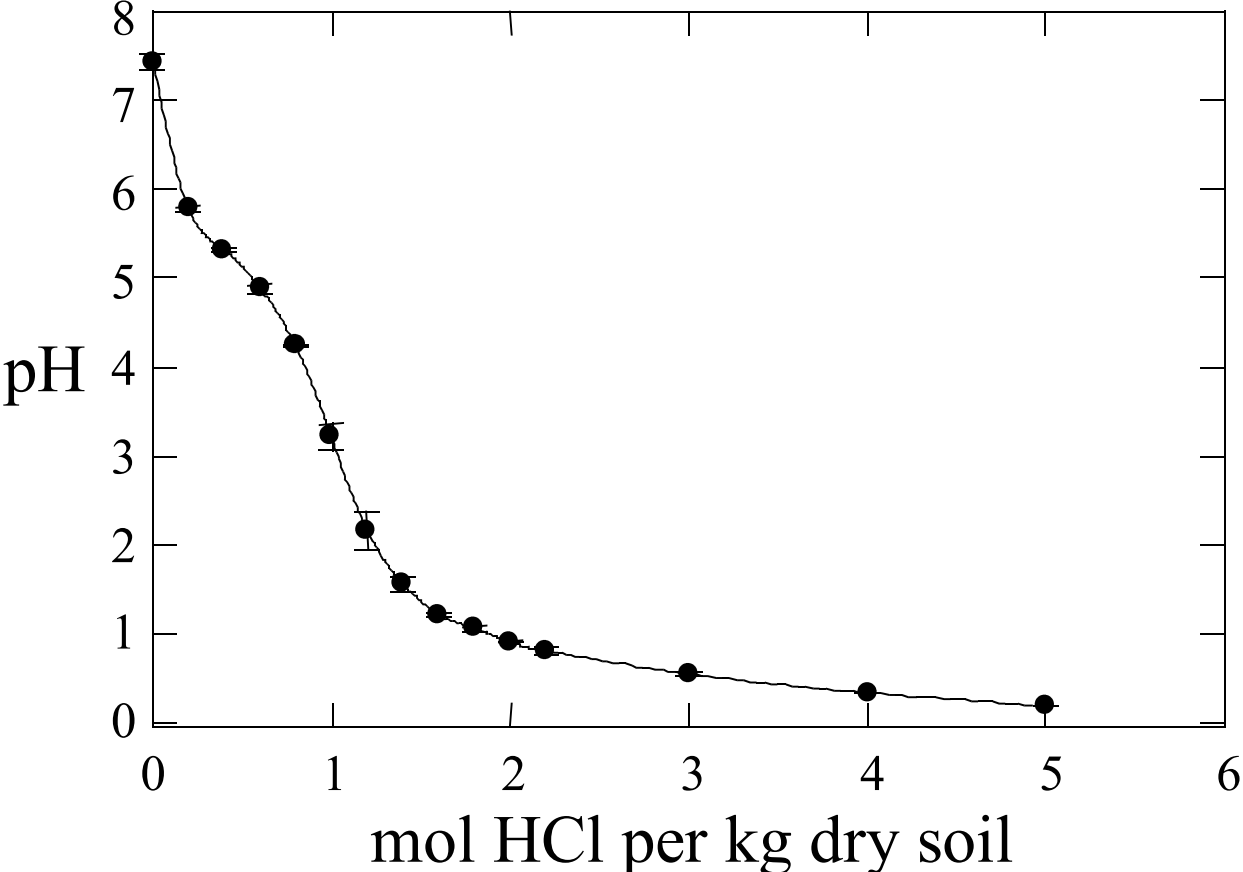


Figure 3

## Decarbonation step

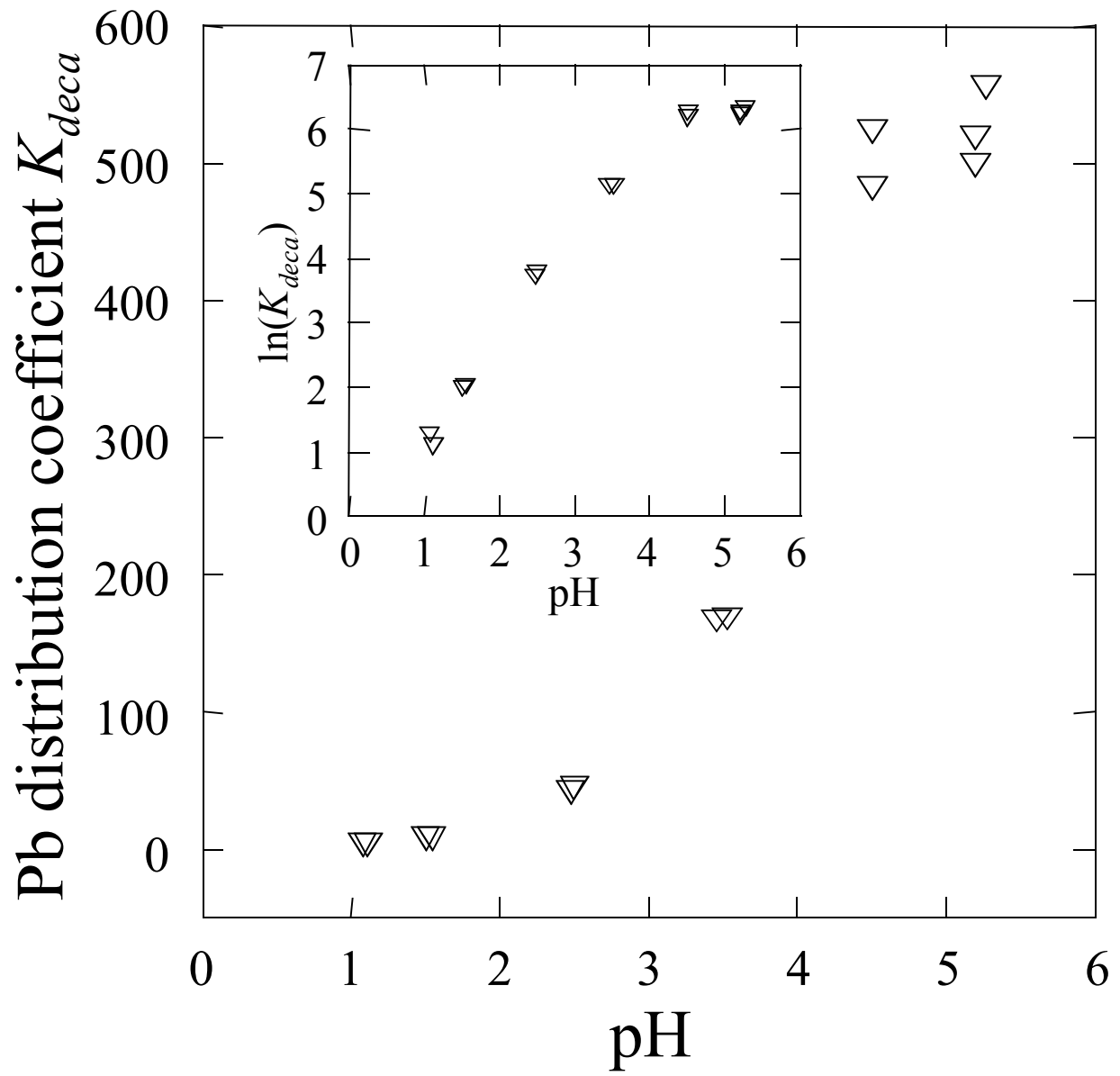


Figure 4

## Solubilisation step

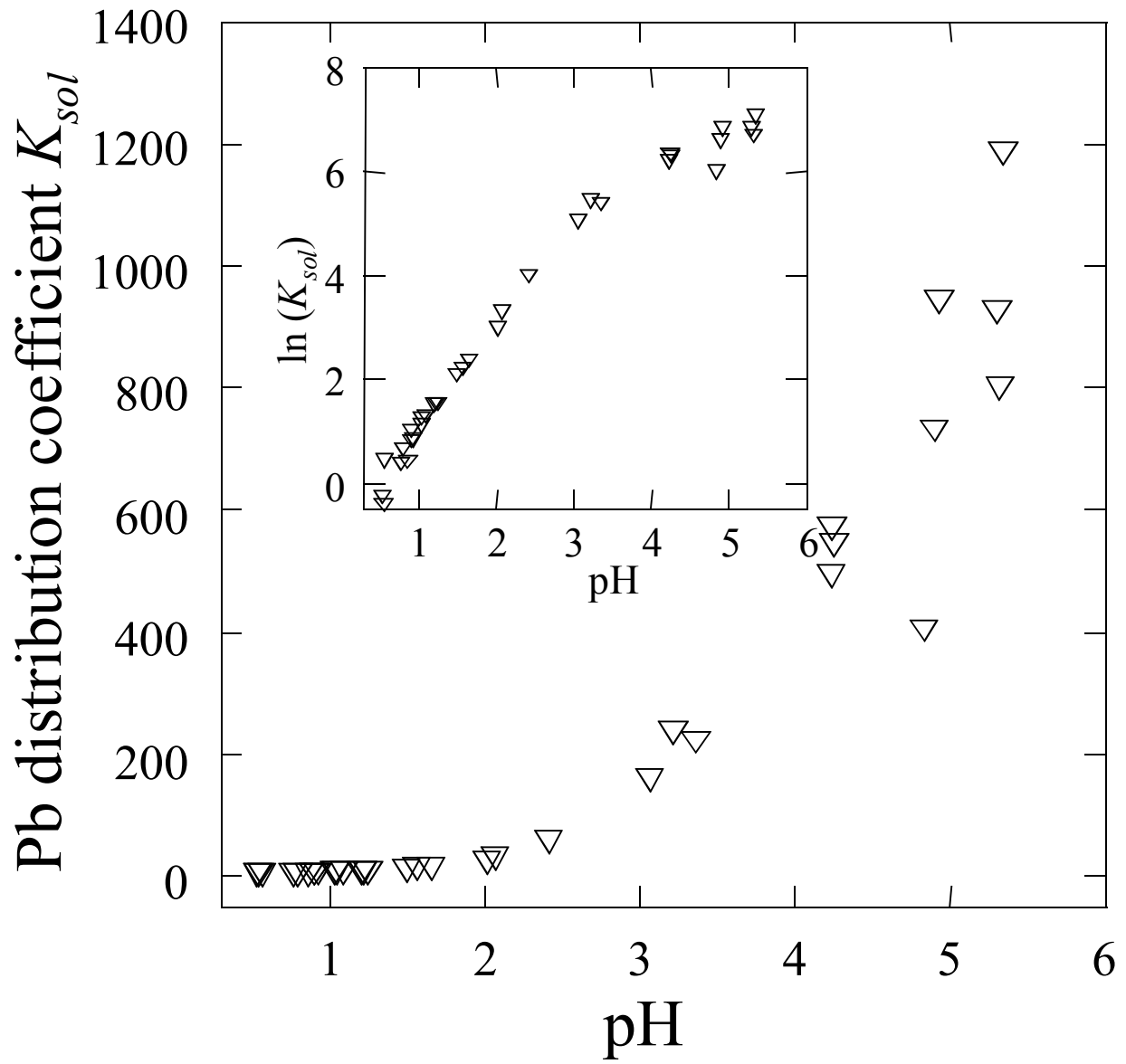




Figure 5

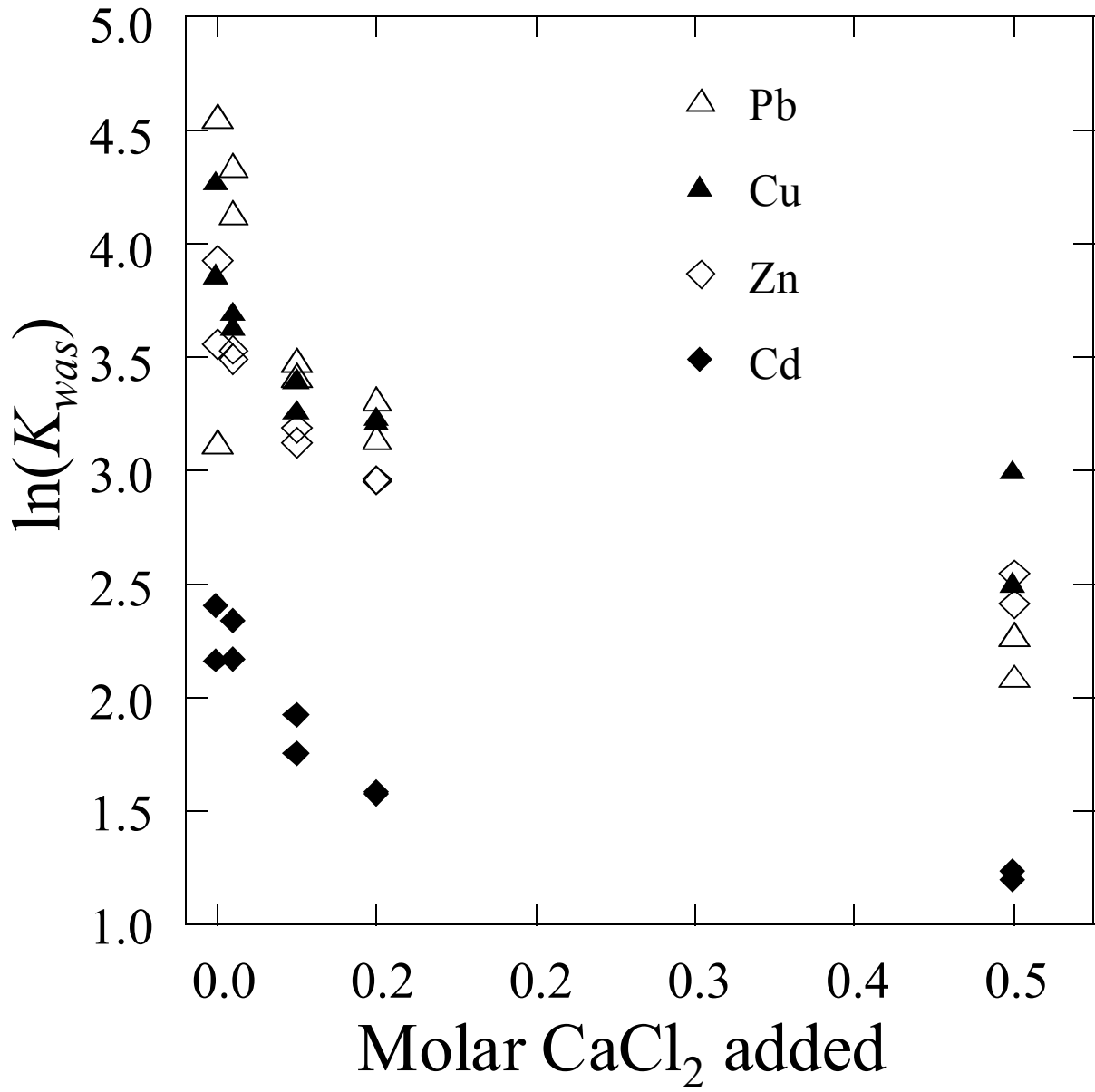


Figure 6

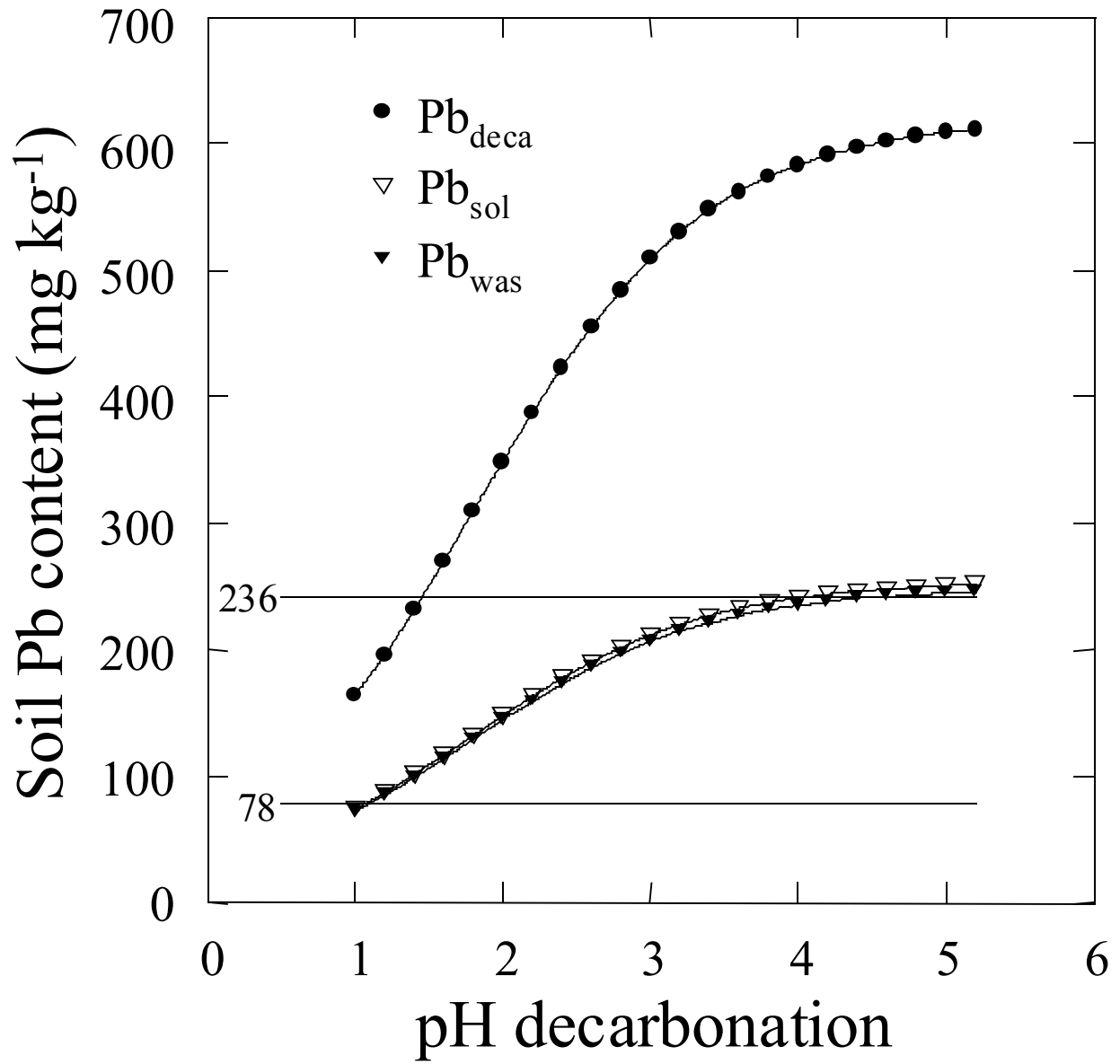


Figure 7

