Final Report (draft)

Soil-solution Partitioning of Trace Elements in Cropland Soils of California: Estimating the Plant Uptake Factors of As, Cd, and Pb

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Abstract

This report summarizes the outcomes of studies that assessed the appropriateness of the soil-solution partition coefficients, K_d, and the plant uptake factors, *PUF* that were used in the CDFA's risk based study on the plant accumulation of As, Cd, and Pb by food plants grown in California cropland soils (CDFA, 1998) through examinations of existing data, laboratory experiments, and field testing.

Under the field growing conditions, the K_d and *PUF* for any food crops did not appear to be constants with respects to the element, plant species, or soils of concern. Instead, the field obtained values for these two parameters followed the log-normal distributions and the range of the distributions appeared to be rather wide. The K_d and PUF_{total} employed for the CDFA risk-based study of As, Cd, and Pb uptake by food plants were similar in magnitudes, covered roughly the same ranges, and followed the log-normal distributions as those data we obtained independently from the field samplings. Since this is the case, we expect that the outcomes of CDFA's risk-based assessment on the maximum tolerable threshold for As, Cd, and Pb in the fertilizers to be comparable to the outcomes if the K_d and *PUF* were obtained based on the conditions of production fields in California. We conclude that the K_d and *PUF* used in the previous referenced study were appropriate.

The conclusions of the individual studies we conducted are summarized as follows:

1. The soil to solution partitioning coefficient, K_d, is an important parameter in assessing the environmental and health risks of potentially toxic metals in cropland soils. We examined the K_d, for As, Cd, and Pb in P fertilizers and cropland soils in the laboratory based on the conventional extraction of 1:10 soil to water ratio (w/v). In soils treated with P fertilizer and micronutrients, solution/solid phase partition of As, Cd, and Pb were comparable to those indigenous of the soils unless the amounts added became excessive. (Chapter 2)

2. Ideally, K_d, the ratio of the total (C_{total}) and solution concentrations ($C_{solution}$) of trace element in soil, is determined under the field moisture conditions. In reality, the soil solution concentration is represented by the concentration in extracts of a given soil to water ratio. We used cadmium as an example demonstrated the uncertainties in determining the soil solution Cd concentrations, thus the K_d because the soil solution concentration varied with the soil to water ratio. Results of extraction experiments showed that extracting the soils at the soil to water ratio of 1: 1 (w/v) was most representative of the field moisture contents and provided the most consistent results. Under this circumstance, the Cd concentration in soil solution tends to be probabilistic and follows a normal distribution. The probability density functions for K_d were established. If K_d is characterized in probabilistic terms, the risks of environmental and health harms of trace elements in the soils may be more appropriately assessed. (Chapter 3)

3. We assessed the K_d and *PUF* based on soil and plant tissue samples obtained from croplands in California several. Under the growing conditions of production fields, the K_d and *PUF* for any food crops did not appear to be constants with respects to the element, plant species, or soils confirming the laboratory findings summarized in Chapter 3. Instead, the field obtained values of these two parameters followed generally the log-normal distributions and the range of the distributions appeared to be rather wide. The K_d and *PUF* employed for the CDFA's risk-based study of As, Cd, and Pb uptake by plants were similar in magnitudes, covered roughly the same ranges, and followed the log-normal distributions as those we obtained from the field samples. Since this is the case, we expect that the outcomes of the risk-based assessment on the maximum tolerable thresholds for As, Cd, and Pb in the fertilizers and micronutrients to be comparable to the outcomes if K_d and PUF were obtained from data representing the conditions of production fields in California. (Chapter 4)

4. In soils, As, Cd, Pb in solution phase may be surface adsorbed or immobilized and precipitated into mineral phases and vise versa. These processes take place simultaneously and for K_d, they must be considered at the same time. We described the reaction kinetics by a two-site model combining linear instantaneous model for the surface adsorption and first order reaction kinetic model with forward and backward reaction constants for the immobilization and precipitation of the mineral phase. We developed the mathematical models and used the batch Cd adsorption experiments with two California to test the validity of the model. The method allowed us to distinguish the trace elements that are surface adsorbed and precipitated and determine the K_d and the precipitation and dissolution constants simultaneously. (Chapter 5)

5. A more reasonable approach to assess the impacts of trace element inputs on cropland soils is through the mass balance of trace elements in the soil profile. Based on the information obtained in the previous studies, we updated the model parameters of the mass balance model developed in the previous study and used the Monte Carlo simulations to assess CDFA's trace elements thresholds for fertilizers and micronutrients. Under the normal crop practice, applications of P fertilizers meeting California's trace element standards for fertilizers will results in gradual reduction of As and increase of Cd in the receiving soils over 100 year of continuous cultivation. The amounts of changes were considerably smaller than applying P fertilizers meeting the trace element thresholds of the regulations in Oregon and Washington and those recommended by APPFRO. Removal by plant uptake has the greatest impact in the mass balance of trace elements in soils. (Chapter 6)

6. Based on the outcomes of the model simulation, we designed a field experiment to examine the plant uptake of the trace elements under the growth conditions of field production. In this case Cd uptake by romaine lettuce was used as the example. The soil solution Cd concentrations the soils remain relatively constant throughout the plant growing season. At a given stage of growth, the rate of Cd uptake by Romaine lettuce plants is related to the soil solution Cd concentrations

according to the Michaelis-Menton kinetics model. However, the maximum influx rates J_{max} obtained in this manner would decrease with the length of the growing period. A second order kinetic model by integrating the time factor was developed to simulate the cumulative plant uptake of Cd over the growing season:

$$C_{plant}(t) = C_{Solution} PUF_{\max} \cdot e^{-b \cdot t}$$

where C_{Plant} and $C_{Solution}$ refer to the Cd content in plant tissue and soil solution, respectively,□PUF_{max} represents the uptake potential at time zero and b is a kinetic constant related to plant growth. The plant uptake factor, *PUF*, which is defined as the ratio of Cd in plant tissue to that in soil solution, follows the similar trend to that of C_{Plant}. The data from the field experiment showed that the Cd naturally occurring in the P fertilizers and Cd spiked P fertilizers were different. On a per unit total soil Cd basis, the absorption by Romaine lettuce were much higher for the indigenous Cd than the spiked Cd of the P fertilizers. This mathematical model is general and may universally be applicable to the assessment of uptake by other plant species or of other trace elements. (Chapter 7)

We improved the trace element model by coupling the trace element mass balance with the water flow algorithms of HYDRUS-1D to account for trace element distributions in the soil profiles. In the modified model, the simulated soil profile is discretized into a number of uniform adjoining sections. In each section, the same scheme as defined in the previous model was adopted. The external inputs are sorted into three categories. Inputs from atmospheric deposition and with irrigation water are added to the top element of the soil profile. Discrete sources from fertilizes, micronutrient and waste disposal are added uniformly to the plow layer. The model allows simulating plant root growth and distribution along the soil profile and the solute transport is simulated with the convective-dispersive equation. The model not only allows studying the pools and fluxes of trace element in cropland soils, but also assessing the distribution of trace elements along the soil profile. (Chapter 8)

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Chapter 1

Introduction

Trace elements, such as arsenic (As), cadmium (Cd), and lead (Pb) are ubiquitous in the natural environment. At the normal concentration ranges, the potentially hazardous trace elements referenced above do not pose significant threats to human and eco-system health. Their levels in cropland soils however may be affected by various cultivation activities such as fertilizer applications, irrigation, pesticide sprays, land application of organic wastes, re-incorporation of crop residues, and atmospheric fallouts (Chang and Page, 2000). Among them, the fertilizer and micronutrient applications are by far the most consistent inputs. While the amount of contaminant being added with each input may be small in comparison to the total volume of the receiving soil and their deposition and transformation in soils may not be readily detectable by the routine field soil sampling, long term continual inputs and a lack of removal mechanisms can lead to a gradual buildup of these trace elements in the agricultural soils especially if the soil amendments are inherently contaminated.

Krage (2002) reported that the As, Cd and Pb contents of irrigated cropland soils in California exhibited the rising trends in contrast to the respective baseline levels. Mulla et al. (1980) reported results of a long-term P fertility experiment at the University of California, Riverside that the Cd contents remained elevated in the surface soils several decades after the experiment ended and were in proportion to amounts of P-fertilizer the soils received over time. In Europe, fertilizers produced from phosphate rock represent a major contribution of Cd to cropland soils. In 1985, the Cd from P fertilizers constituted an estimated 74% of the total Cd load to European arable soils (EUROSTAT, 1995). With the subsequent control measures, phosphate fertilizer borne Cd remained as the major contributor, accounting for more than 50% of the total input in areas that were not heavily polluted or were not heavily industrialized according to a 1995 estimate (Meeus et al., 2002). Phosphate fertilizers have been the primary source of Cd in pasture soils in Australia and New Zealand (Andrewes et al. 1996). Mulla et. A. (1980) and Loganathan et al. (1995) showed a clear relationship between P-fertilizer use and Cd accumulation.

The enrichments in the soils may lead to inadvertent transfer of trace elements through the food chain to affect unsuspected consumers. The possible risks derived from the increasing amount of trace elements in cropland soils have resulted in growing public health concerns on the consumers of the harvested crops (Krishnamurti, et al. 1999, Meeus, et al. 2002) and the indigenous populations (Hinwood et al., 2004). It is imperative to understand the behavior of trace elements in cropland soils.

Soils often are repositories of fugitive trace element pollutants. In soil, most trace elements are not readily soluble. They are present in the soils indigenously and they may be introduced various mechanisms as solid phase minerals. In readily soluble forms, the trace elements are adsorbed by inorganic solid phases, organic matter and clays, associated with the primary minerals, or form insoluble precipitates (Gray et al. 2000). The behavior of trace elements in the soil-water-plant system is dependent on the interactive and dynamic processes in the soils. Trace elements in the soil solution are of special interest as they are readily accessible to plants and other soil organisms and are mobile through the vadose zone to reach underground waters. Knowledge on the partition of trace elements between the solid and solution phases are imperative for assessing environmental and health risks associated with the anthropogenic sources of trace elements in soils

Solid-Solution Partition

Plants absorb water, nutrients, and potentially toxic substances from those present in the solution phase of the soil. Consequently, the plant uptake of trace elements is a function of their concentrations in soil solution. In soils, the introduced trace elements tend to remain in the solid phases and therefore must first enter the soil solution before uptaking by plants. Trace element concentrations of the soil solution, however, are not readily determined. In risk assessment and solute transport modeling, the trace element transfer between the solid (C_{solid}) and solution ($C_{solution}$) phases of the soil is assumed to be in a steady state. Therefore, the element's solid-solution phase partition coefficient (K_d) would be a constant. The concentration in the solid phase may be represented by its total contents that (Sauve et al., 2000):

$$K_d = \frac{C_{total}}{C_{solution}} \qquad \text{[Eq. 1.1]}$$

where K_d (l kg^{-1}) is the solid and solution phase partition coefficient and C_{total} (mg kg^{-1}) and $C_{solution}$ (mg l^{-1}) are the total and solution concentrations of trace element of the soil, respectively. Unlike the total contents, the soil solution concentration of trace elements is frequently below the limit of detection of the commonly used analytical instruments and is seldom measured. The trace element contents of the soil solution are functions of soil properties. Equation 1 may be employed to quantitatively assess the mobility and biological availability (such as the uptake by plants) of trace elements in the soils if K_d is defined.

Environmental risk assessment has become a commonly employed procedure for establishing numerical limits in the fertilizer regulatory processes (TFI, 2000; USEPA, 2000; AAPFCO, 2002). In 1997, CDFA conducted a risk-based assessment on human health due to exposures to trace elements in fertilizers and/or micronutrients applications on cropland (CDFA, 1998). Through this process, CDFA established the safe limits for As, Cd, and Pb in fertilizer products that are used in food production. Subsequently, the numerical limits derived from this study were adopted as a part of the fertilizer regulations in California (California Code of Regulations, Title 3, Sections 2302 and 2303). The fertilizer regulatory agencies in California, Oregon, and Washington now track and, via Internet, publish the levels of non-nutritive substances in fertilizer and/or micronutrient products registered for sale in the states (http://www.cdfa.ca.gov/is/fert/, http://www.oda.state.or.us/dbs/heavy_metal/search.lasso,and http://www.wa.gov/agr/PestFert/Fertilizers/ProductDatabase.htm).

Plant Uptake

The plant uptake of trace elements may be affected by the soil properties. The interactive and dynamic processes of the soils on trace elements are reflected in their solution phase concentrations through which the plant uptake of trace elements may by normalized across soils of various physical and chemical properties. The *PUF* (l kg^{-1}) is defined as the element's ratio of plant tissue concentration (mg kg^{-1}) vs. soil solution concentration (mg l^{-1}) that:

$$PUF = C_{plant} / C_{solution} \qquad \text{[Eq. 1.2]}$$

where *PUF* denotes the plant uptake factor (l kg^{-1}), C_{plant} is the trace element concentration of harvested plants (mg kg^{-1}), and $C_{solution}$ has been previously defined. In this manner, the plant uptake attribute of soils of different characteristics may be standardized through the $C_{solution}$.

The K_d however was not readily available for cropland soils to establish the $C_{solution}$. In the risk-based assessment conducted by CDFA (1998), the plant uptake factors (*PUF'*) were estimated directly using soil and corresponding plant tissue concentrations data available from published technical literature that:

$$PUF' = C_{plant} / C_{total} \qquad \text{[Eq. 1.3]}$$

where C_{plant} and C_{total} were previously defined

Would the trace element concentration of the soil solution be a more appropriate estimator of the plant uptake factor? The uncertainties of the plant uptake factors that were employed in this risk assessment could introduce significant errors in the final outcomes. The values of K_d and *PUF* are susceptible to measurement uncertainties, even obtained under the most realistic situation. In addition, they must be generalized across different soil and plant species and management alternatives to represent scenarios often encountered in realistic situations. Ideally, K_d and *PUF* should be characterized in the probabilistic terms. In this manner, the outcomes of risk assessment may account for uncertainties in parameterization of K_d and *PUF*.

The trustworthiness of risk assessments is dependent on the reliability of the parameters used. Unless the partition coefficients (K_d) and the soil solution-based plant uptake factors (PUF) for the trace elements of cropland soils in California are systematically characterized, the accuracy of their outcomes on projecting the potential harm resulting from the application of fertilizers and micronutrient supplements cannot be validated and uncertainties associated with the projections can not be defined. Consequently, the numerical limits for non-nutritive elements of fertilizers adopted in the regulations can not be authenticated.

Objectives

This investigation characterizes of the As, Cd, and Pb partition coefficients, K_d, for cropland soils and the plant uptake factors, PUF, for crops in California.

During the course of the study, a series of laboratory experiments, computer-based modeling, and field investigations were conducted. The justifications for undertaking each study, methods used, results obtained, and implications derived will be deliberated in separately. At the end, the results will be integrated to evaluate the validity of K_d and *PUF* based on the overall outcomes.

Chapter 2

Solid – Solution Partition: K_d, Reagent-based vs. Fertilizer-based

In the scientific literature, the soil-solution partition coefficients of metals are defined according to the eq. 1. The batch metal adsorption experiments are often conducted to determine the resulting equilibrium solution concentrations with known amounts of metal inputs (Sauve et al., 2000, Jopony and Young, 1994; Butcher et al., 1989). The partition coefficients obtained in this manner provided a reasonable estimate of the values obtained for desorption of the metals by the dynamic continuous leaching systems (Allen et al., 1995). The behavior of K_d has been described for metal-contaminated soils of which the concentrations of trace metals in soils reached 10,000 mg kg^{-1} (Sauve et al., 2000).

In the crop production systems, As, Cd, and Pb are introduced into the soil primarily as a part of the P fertilizer and micronutrient supplements. The amounts of As, Cd, and Pb accumulated in the soils are considerably less than soils contaminated by industrial emissions and/or accidental spills (Krage, 2002). As a result, the K_d found in the published literature may not be representative of the K_d of inorganic fertilizer-borne trace elements in the soils because:

> Trace element inputs used in developing the adsorption isotherms may be considerably higher than inputs customarily expected from fertilizer applications.
>
> The dissolved elements commonly used in adsorption experiments may not be representative of the chemical forms of trace elements in fertilizer ingredients.

Under the circumstances, the trace element in the solution phase may not be a negligible portion of the total content. According to the definition of the partition coefficient, equation 1.1 would be rewritten as:

$$K_d = C_{solid}/C_{solution} \qquad \text{[Eq. 2.1]}$$

where C_{solid} is the concentration in the solid phase (mg kg^{-1}) and $C_{solution}$ has been previously defined. The trace elements introduced in the forms of fertilizers do not necessary reach equilibrium with the solid constituents of the soil in the same manner as those entering the soil in dissolved forms.

Experimental Procedures

We determine the K_d of the soils according to the conventional procedures as described by Sauve et al. (2000) and compare them with K_d derived from introducing As, Cd, and Pb into the soils via phosphate fertilizer and micronutrients and the As,Cd, and Pb inputs that covered a broad range of concentrations.

1. Soils

Soil samples from vegetable growing fields of production regions in Imperial Valley (VHL 3 and VHL 4), Oxnard/Ventura (B 5 and P 4), and Santa Maria (RB5 and RB 6) were used for the studies. Prior to the experiments, the total As, Cd, and Pb of the soils were determined according to US EPA Method 3052 using the atomic absorption spectrophotometry.

2. Sources of As, Cd, and Pb

The K_d of the soils was determined when the trace elements were introduced in comparable amounts in the solution form and as contaminants in P fertilizers and micronutrient supplements. For the solution forms of trace elements, the concentrations of As, Cd, and Pb in the solution varied from 1×10^{-7} to 1×10^{-4} M that corresponded to 0.007 to 7.492 mg l^{-1}, 0.011 to 11.24 mg l^{-1}, and 0.021 to 20.77 mg l^{-1}, for As, Cd, and Pb, respectively.

Commercially available super phosphate fertilizer, granulated Zn oxide micronutrient, and Ironite were used to provide the As, Cd, and Pb inputs from the amendments. They are hereafter designated as P fertilizer, Zn oxide, and Ironite, respectively. Prior to the experiments, the As, Cd, and Pb contents of these material were determined according to US EPA Method 3052 using the atomic absorption spectrophotometry.

3. K_d of As, Cd, and Pb in Solution Forms.

In the experiments, the K_d was determined by batch adsorption method described in Allen et al. (1995). Briefly, 1.00 ± 0.01 g aliquots of soil samples is immersed in 100 ml of 0.01 N $NaNO_3$ containing 0 (experimental control), 1×10^{-7}, 1×10^{-6}, 5×10^{-6}, 1×10^{-5}, 5×10^{-5}, and 1×10^{-4} M of As, Cd, or Pb. They provide up to 0.75 to 749, 1.12 to 1124, and 2.1 to 2070 mg kg^{-1} of As, Cd, and Pb inputs to the soils, respectively. At the lower concentration end, the inputs would be comparable to the amounts expected in the cropland soils, At the higher concentration ends, the inputs would resemble the polluted lands.

The mixtures were shaken for 24 hours on a reciprocating shaker at constant speed and at room temperature. Afterwards, the contents were filtered through 0.45 μm polypropylene fiber membrane filters. The As, Cd, and Pb concentrations in the filtrate were analyzed, using atomic absorption spectrophotometry (AAS). The difference between the amount of element remaining in the solution and the amount initially present in the solution was taken as the amount of element adsorbed by the soil. The K_d was calculated according to equation 1.

4. K_d of As, Cd, and Pb in P Fertilize or Micronutrient Forms

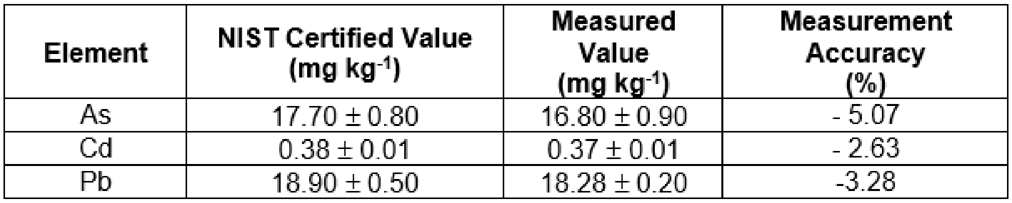
For trace elements that entered the soil in P fertilizer or micronutrient forms, 50 to 100 g aliquots of soil samples were mixed with various amounts of P fertilizer, Zn oxide, and Ironite. The mixtures were subjected to 5 cycles of wetting and drying in which the fertilizer or micronutrient amended soils are wetted to field capacity with de-ionized water and air dried in a growth chamber. Afterwards, 1.00 ± 0.01 g aliquots of soils were then equilibrated with 100 ml of 0.01 N $NaNO_3$ and filtered in the same manners as previously described. The difference between the amount of element remaining in the solution and the amount initially present in the solution was taken as the amount of element adsorbed by the soil. The K_d was calculated according to equation 1.

Results and Discussions

1. As, Cd, and Pb in the Experimental Material

The As, Cd, and Pb concentrations of the soils and soil amendments used in the experiments were determined. The reliability of the determinations was checked by including a NIST certified soil reference material (NIST SRM 2709) in the analysis. This soil reference was prepared from a San Joaquin Soil in California and the elemental contents of the standard reference material were determined by a neutron activation method. Table 2.1 compares the NIST certified values of As, Cd, and Pb in SRM 2709 with our measurements of the same material.

Table 2.1. Means and Standard Deviations of As, Cd, and Pb Measurements of NIST Standard Reference Material 2709 (San Joaquin Soil)

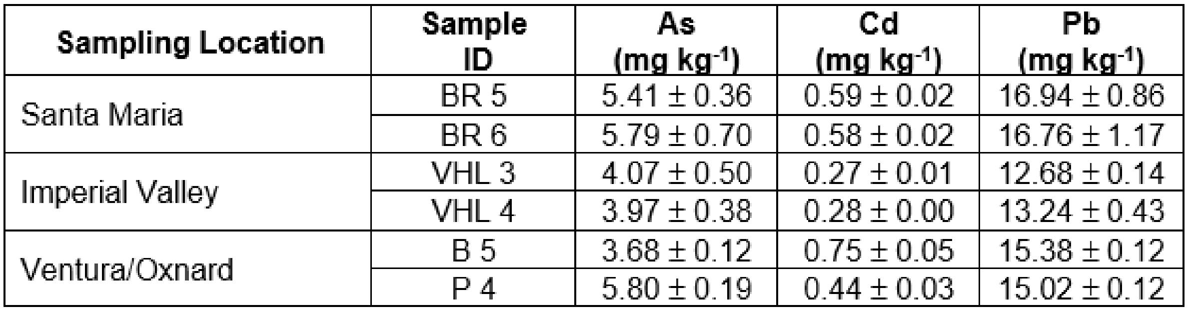


Element	NIST Certified Value ($mg\ kg^{-1}$)	Measured Value ($mg\ kg^{-1}$)	Measurement Accuracy (%)
As	17.70 ± 0.80	16.80 ± 0.90	- 5.07
Cd	0.38 ± 0.01	0.37 ± 0.01	- 2.63
Pb	18.90 ± 0.50	18.28 ± 0.20	-3.28

It illustrated the accuracy of our measurements of As, Cd, and Pb in soils using the EPA Method 3052 for soil digestion and atomic absorption spectroscopy for elemental analyses. Our measurements under estimated the contents of As, Cd, and Pb in the standard reference material by 5.1, 2.6, and 3.3%, respectively. The errors were well within the normally acceptable range that the measurement means were within ±10% of the true means. The comparisons of the standard deviations showed that the data dispersion measured in terms of the coefficients of variation for As, Cd, and Pb were 4.5, 2.6, and 2.6, respectively for the certified values and 5.3, 2.7, and 1.1, respectively for our determinations. The precision of the measurements was comparable to measurement errors of the certified values.

The As, Cd, and Pb concentrations of the soils used in the experiments are summarized in Table 2.2. The trace element concentrations in the soils used for the experiments were all at the baseline levels.

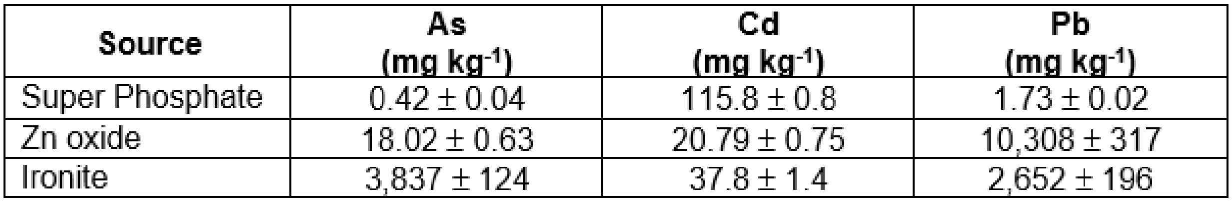
Table 2.2. Arsenic, Cd, and Pb Concentrations of Soils Used in the Experiments



Sampling Location	Sample ID	As (mg kg^{-1})	Cd (mg kg^{-1})	Pb (mg kg^{-1})
Santa Maria	BR 5	5.41 ± 0.36	0.59 ± 0.02	16.94 ± 0.86
	BR 6	5.79 ± 0.70	0.58 ± 0.02	16.76 ± 1.17
Imperial Valley	VHL 3	4.07 ± 0.50	0.27 ± 0.01	12.68 ± 0.14
	VHL 4	3.97 ± 0.38	0.28 ± 0.00	13.24 ± 0.43
Ventura/Oxnard	B 5	3.68 ± 0.12	0.75 ± 0.05	15.38 ± 0.12
	P 4	5.80 ± 0.19	0.44 ± 0.03	15.02 ± 0.12

The As Cd, and Pb contents of soil amendments, namely P fertilizer, Zn oxide, and Ironite were considerably higher than those of the soils (Table 2.3). The P fertilizer was high in Cd concentration (116 mg kg^{-1}) and was relatively free of As and Pb contaminations. Zn oxide was contaminated with high concentration of Pb (over 10,000 mg kg^{-1}) and its Cd concentration was approximately 100 times higher than those of the soils. The As, Cd, and Pb concentrations in Ironite, 3,837, 37.8, and 2,652 mg kg^{-1}, respectively were two orders of magnitude higher that the typical soils. When these amendments are applied routinely, they will produce noticeable increases of As, Cd, and Pb in the receiving soils.

Table 2.3.Arsenic, Cd, and Pb Contents of Three Commercially Available Amendments Used in the Experiments



Source	As (mg kg^{-1})	Cd (mg kg^{-1})	Pb (mg kg^{-1})
Super Phosphate	0.42 ± 0.04	115.8 ± 0.8	1.73 ± 0.02
Zn oxide	18.02 ± 0.63	20.79 ± 0.75	10,308 ± 317
Ironite	3,837 ± 124	37.8 ± 1.4	2,652 ± 196

Solution-based K_d for As, Cd and Pb

Based on the experimental data of summarized in Appendix A, the K_d were calculated and tabulated in Tables 2.4 to 2.6. In the control soil and soils receiving low solution-based trace element inputs, the concentration of the trace element was below the detection limits of 0.002, 0.0005, and 0.002 mg kg^{-1} for As, Cd, and Pb, respectively and the K_d was then reported as greater than a value that corresponded to the K_d as if the equilibrium concentration equaled the limit of detection.

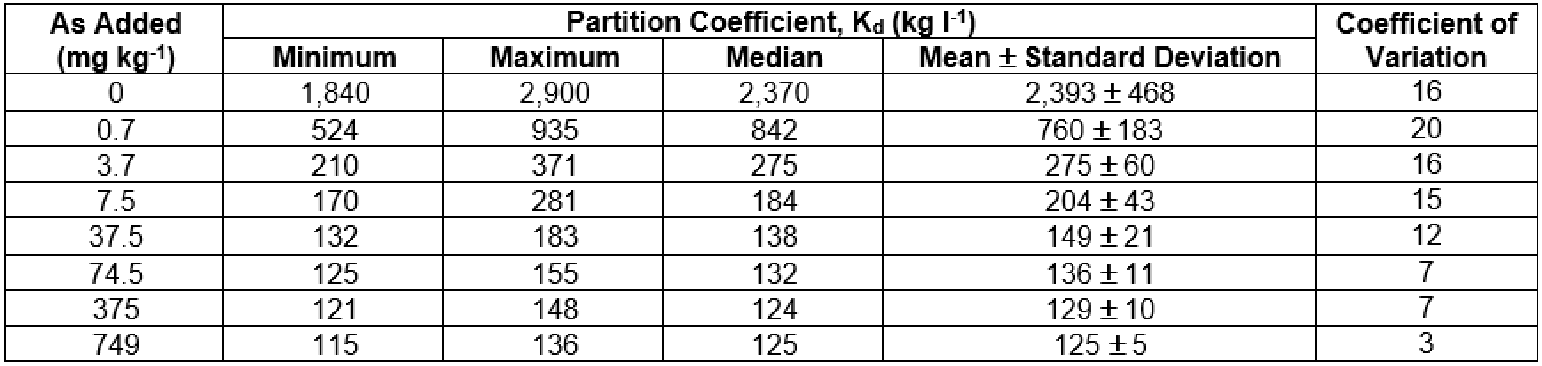
In this experiment, the trace element concentration of the equilibrating solutions therefore the trace element inputs varied by 1,000 times from 10^{-7} to 10^{-4} M. The resulting K_d values were element-dependent and they ranged from 10^2 to 10^3, 10^2 to 10^4, and 10^3 to 10^5 l kg^{-1} for As, Cd, and Pb, respectively. Overall, the K_d values of As are the lowest, indicating that larger amounts of the As remained in the solution phase than Cd and Pb when the soils received the same levels of trace element mass inputs. These values and their ranges were comparable to what have been reported in the literature (Sauve et al. 2000).

For As, the K_d values decreased by one order of magnitude while the As inputs increased by three orders of magnitude over the input range covered. The K_d value of the control soil was considerably greater than the soils treated with soluble As. It indicated that proportionally greater fractions of the added As remained in the solution phase while the As indigenous to the soil was considerably less soluble and had greater affinity to the solid phases. When the soluble As introduced rose, the solid – solution partition of As gradually approach steady state equilibrium that the As concentration of the solution phase rose, yet proportional amounts of As were adsorbed by the soils. As a result, K_d was relatively constant when the inputs exceeded 3.7 mg As kg^{-1} soil.

For Cd, the K_d value of the control soil was lower than those of the soils treated with soluble Cd, indicating that the added soluble Cd was tightly adsorbed by the soils. The Cd concentration of the solution phase however increased in proportion with the Cd inputs and the solution and solid phase partition of the Cd remained fairly constant over the entire Cd input range.

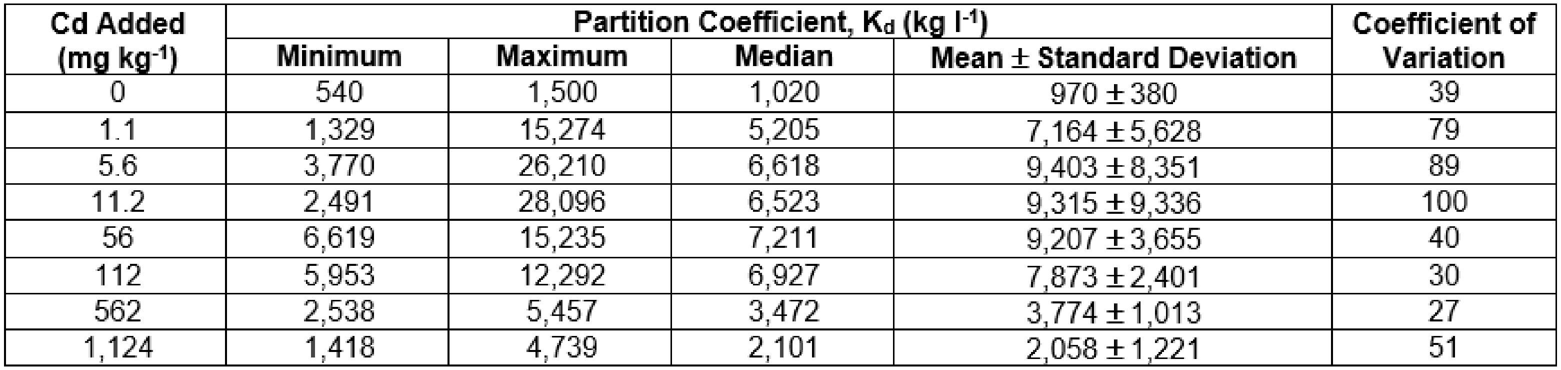
For Pb, the K_d values were on the average 1 to 2 orders magnitude higher than those of the As and Cd, indicating Pb is extremely insoluble regardless of it sources.

Table 2.4. Summary of Solution and Solid Partition Coefficient, K_d, of As in Three California Soils



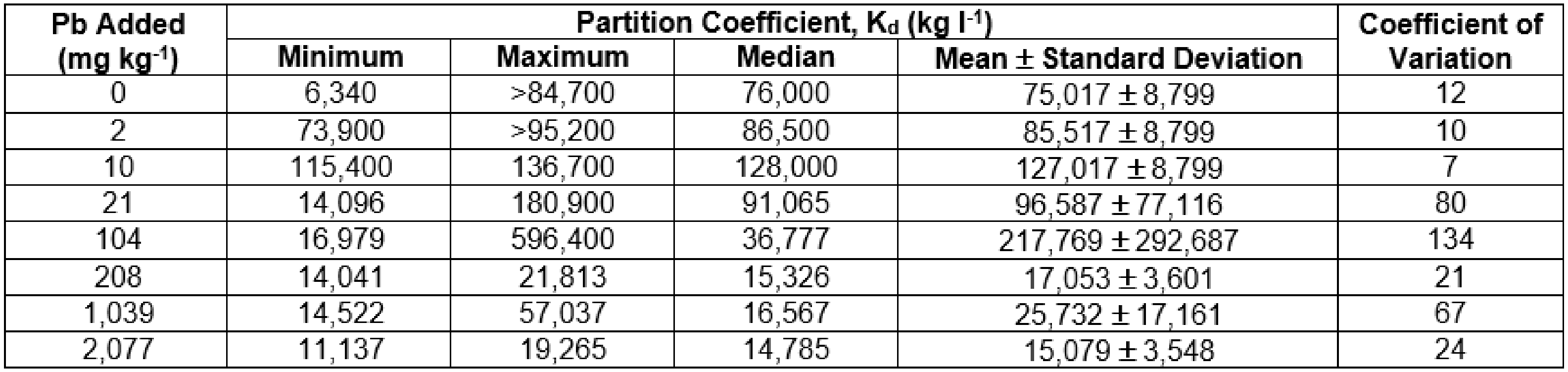
As Added (mg kg^{-1})	Partition Coefficient, K_d (kg l^{-1})				Coefficient of Variation
	Minimum	Maximum	Median	Mean ± Standard Deviation	
0	1,840	2,900	2,370	2,393 ± 468	16
0.7	524	935	842	760 ± 183	20
3.7	210	371	275	275 ± 60	16
7.5	170	281	184	204 ± 43	15
37.5	132	183	138	149 ± 21	12
74.5	125	155	132	136 ± 11	7
375	121	148	124	129 ± 10	7
749	115	136	125	125 ± 5	3

Table 2.5. Summary of Solution and Solid Partition Coefficient, K_d, of Cd in Three California Soils



Cd Added (mg kg^{-1})	Partition Coefficient, K_d (kg l^{-1})				Coefficient of Variation
	Minimum	Maximum	Median	Mean ± Standard Deviation	
0	540	1,500	1,020	970 ± 380	39
1.1	1,329	15,274	5,205	7,164 ± 5,628	79
5.6	3,770	26,210	6,618	9,403 ± 8,351	89
11.2	2,491	28,096	6,523	9,315 ± 9,336	100
56	6,619	15,235	7,211	9,207 ± 3,655	40
112	5,953	12,292	6,927	7,873 ± 2,401	30
562	2,538	5,457	3,472	3,774 ± 1,013	27
1,124	1,418	4,739	2,101	2,058 ± 1,221	51

Table 2.6. Summary of Solution and Solid Partition Coefficient of Pb in Three California Soils



Pb Added (mg kg^{-1})	Partition Coefficient, K_d (kg l^{-1})				Coefficient of Variation
	Minimum	Maximum	Median	Mean ± Standard Deviation	
0	6,340	>84,700	76,000	75,017 ± 8,799	12
2	73,900	>95,200	86,500	85,517 ± 8,799	10
10	115,400	136,700	128,000	127,017 ± 8,799	7
21	14,096	180,900	91,065	96,587 ± 77,116	80
104	16,979	596,400	36,777	217,769 ± 292,687	134
208	14,041	21,813	15,326	17,053 ± 3,601	21
1,039	14,522	57,037	16,567	25,732 ± 17,161	67
2,077	11,137	19,265	14,785	15,079 ± 3,548	24

2. Amendment-based K_d for As, Cd and Pb

The K_d of As, Cd, and Pb in the untreated control soils and the amendments were determined (Tables 2.7 and 2.8). For the P fertilizer, the K_d values of As and Cd (10 and 46 l kg^{-1}, respectively) were considerably lower than those of the soils (69 to 854 and 470 to >1,113 l kg^{-1}, respectively). It means that, at the same total trace element concentrations, the As and Cd in the P fertilizers are more soluble than the As and Cd indigenous to the soils. Since the solution concentration of Pb were below the detection limits, a comparison of the soil's and the amendments' K_d was not possible. For Zn oxides and Ironite, the K_d values for Cd (29 and 28 l kg^{-1}, respectively) were considerably lower than those of the soils while the K_d values for As and Pb were considerably greater than those of the soils. The amounts of amendments and trace elements added into the soils for the K_d experiments are summarized in Appendix B. The resulting K_d values were summarized in Tables 2.9 to 2.11. When the amendments are introduced into the soils, the interactions between the amendments and the soils will affect the resulting K_d.

For P fertilizer treated soils, the As and Pb contents of the soils were not affected significantly by the amendments as the levels of contamination were low. The K_d values for As and Pb of the P fertilizer treated soils were essentially the same as that of the control soil. At the low P fertilizer treatment levels, the Cd concentrations of the solution phase were below the detection limit and K_d values of Cd were similar to that of the control soils. At the higher Cd inputs, the K_d values lied between those of the control soils and the P fertilizer. It indicated that the soil attenuated the solubility of Cd added with the P fertilizers.

For Zn oxide treated soils, the As concentrations of the soil was not significantly affected by the amendment and the K_d of As was not affected by the Zn oxide amendments because Zn oxide was not contaminated by As. However, both the Cd and Pb concentrations of the Zn oxide treated soils increased significantly with incremental addition of the amendment. In both cases, the K_d values progressively decreased with the increases of amendment addition. This is an indication that the Cd and Zn added with the Zn oxide were rather soluble and considerable amounts remained in solution phase following the incorporation of the amendment.

For the Ironite treated soils, the Pb concentrations of the soils were not significantly affected by the amendment additions and the Pb concentrations in the solution phase were consistently below the detection limit. As a result, the K_d of Pb in the Ironite treated soils were similar to those of the control soils. On the other hand, the As and Cd contents of the Ironite treated soils were significantly increased. For As, the concentrations in the solution phase increased progressively, with the addition of Irointe. The K_d values of As in the Ironite treated soils lied between those of the soils and the Ironite again indicating that the soils attenuated a part of the soluble As that was added with the Ironite amendments. The Cd concentrations of the solution phase were below the detection limits when the Ironite inputs were low, indicating that most of the added Cd were immobilized by the soils. When the Ironite inputs were high, the K_d of Cd in the treated soils decreased rapidly indicating the accumulation of the soluble Cd.

Table 2.7. Partition Coefficient (K_d) of As, Cd, and Pb in untreated soils.

Site	As			Cd			Pb		
	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})
RB 5 (Santa Maria)	6.30	0.045	114	0.58	0.001	481	17.54	n.d.	>8,770
RB 6 (Santa Maria)	5.74	0.035	165	0.557	n.d.	>1,113	17.34	n.d.	>8,667
VHL 3 (Imperial Valley	3.738	0.052	71	0.243	n.d.	>486	13.57	n.d.	>6,787
VHL 4 (Imperial Valley	4.039	0.059	69	0.244	n.d.	>489	14.27	n.d.	>7,134
B 5 (Oxnard/Ventura)	4.167	0.006	666	0.705	0.001	470	19.745	n.d.	>9,876
P 4 (Oxnard/Ventura)	5.561	0.007	854	0.476	n.d.	>952	15.967	n.d.	>7,983

Table 2.8. Partition Coefficient (K_d) of As, Cd, and Pb of P Fertilizer, Zn Oxide, and Ironite Amendments.

Amendment	As			Cd			Pb		
	Solid (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Solid (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Solid (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})
P fertilizer	0.530	0.053	10	96.933	2.129	46	2.255	n.d.	>1,127
Zn oxide	17.964	n.d.	>8,973	20.313	0.700	29	11,234	0.872	12,880
Ironite	4186	0.468	8,956	30.290	1.064	28	3,698	n.d.	>1,849

Table 2.9. Arsenic Partition Coefficient (K_d) of Soils Treated with Various Levels of P Fertilizer, Zn Oxide, and Ironite Amendments.

1. P Fertilizer-Treated Soils

Treatment	BR 5			VHL 3$^+$			B 5		
	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})
1	5.424	0.067	81	-	-	-	3.682	0.014	263
2	5.640	0.071	80	-	-	-	3.912	0.019	206
3	6.010	0.076	80	-	-	-	3.812	0.029	130
4	5.488	0.085	64	-	-	-	3.370	0.024	140
5	5.414	0.054	100	-	-	-	2.891	0.029	99
6	5.072	0.073	69	-	-	-	3.860	0.037	103

$^+$This soil was not tested

2. Zn Oxide-treated Soils

Treatment	BR 5			VHL 3			B 5		
	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})
1	5.990	0.036	168	-	-	-	4.053	0.006	725
2	5.743	0.018	318	-	-	-	3.761	n.d.$^+$	>1880^{++}
3	5.224	0.017	3.11	-	-	-	3.567	0.007	531
4	5.101	n.d.$^+$	>2550^{++}	-	-	-	4.076	n.d.$^+$	>2038^{++}
5	5.976	n.d.$^+$	>2988^{++}	-	-	-	4.119	n.d.$^+$	>2247^{++}
6	6.462	n.d.$^+$	>3231^{++}	-	-	-	4.512	n.d.$^+$	>2462^{++}

3. Ironite-treated Soils

Treatment	BR 5			VHL 3			B 5		
	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})
1	6.777	0.052	127	6.402	0.207	31	4.573	0.030	150
2	9.575	0.147	65	8.922	0.370	24	7.519	0.122	62
3	13.400	0.792	50	11.628	0.601	19	11.430	0.237	48
4	42.466	0.792	54	42.441	1.222	35	36.653	0.786	47
5	77.305	1.070	72	82.720	1.167	71	78.246	1.039	75
6	457.522	0.399	1146	347.406	0.486	715	384.257	1.605	239
7	678.514	0.720	943	604.367	0.224	2698	637.889	2.204	289
8	1078.230	0.428	2522	979.273	0.109	8958	1040.390	2.465	422

Table 2.10 Cadmium Partition Coefficient (K_d) of Soils Treated with Various Levels of P Fertilizer, Zn Oxide, and Ironite Amendments.

1. P Fertilizer-Treated Soils

Treatment	BR 5			VHL 3			B 5		
	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})
1	0.063	n.d.$^{+}$	>1260^{++}	0.348	n.d.$^{+}$	>697^{++}	0.813	n.d.$^{+}$	>1627^{++}
2	0.689	n.d.$^{+}$	>1378^{++}	0.397	n.d.$^{+}$	>794^{++}	0.917	n.d.$^{+}$	>1828^{++}
3	1.060	n.d.$^{+}$	>2120^{++}	0.859	n.d.$^{+}$	>1719^{++}	1.350	0.002	541
4	1.687	n.d.$^{+}$	>3374^{++}	1.305	0.050	260	6.450	0.038	266

2. Zn Oxide-treated Soils

Treatment	BR 5			VHL 3			B 5		
	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})
1	0.600	0.001	430	0.271	n.d.[+]	>541[++]	0.778	n.d.[+]	>1556[++]
2	0.625	0.001	928	0.303	n.d.[+]	>606[++]	0.791	n.d.[+]	>1828[++]
3	0.635	0.003	220	0.341	n.d.[+]	>682[++]	0.847	n.d.[+]	>1693[++]
4	0.818	0.022	37	0.469	0.005	98	1.050	0.046	23
5	1.396	0.587	2.4	1.262	0.058	15	1.776	0.447	4
6	2.491	1.217	2	2.675	0.266	10	2.759	0.835	3
7	8.685	3.025	3	18.865	1.636	12	8.620	1.729	5

[+] Not detected, as the solution concentration of Cd was below the limit of detection of 0.0005 mg l^{-1}

[++] K_d determined based on the detection limit of Cd in solution phase

3. Ironite-treated Soils

Treatment	BR 5			VHL 3			B 5		
	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})
1	0.601	n.d.[+]	>1202[++]	0.290	n.d.[+]	>580[++]	0.803	n.d.[+]	>1607[++]
2	0.648	n.d.[+]	>1295[++]	0.314	n.d.[+]	>628[++]	0.768	n.d.[+]	>1537[++]
3	0.700	n.d.[+]	>1400[++]	0.366	n.d.[+]	>732[++]	0.846	n.d.[+]	>1693[++]
4	0.913	n.d.[+]	>1826[++]	0.696	n.d.[+]	>1392[++]	1.125	n.d.[+]	>2250[++]
5	1.256	n.d.[+]	>2512[++]	1.061	n.d.[+]	>2123[++]	1.497	n.d.[+]	>2994[++]
6	3.957	0.067	59	3.369	0.005	655	4.525	0.278	16
7	6.511	0.733	9	6.611	0.016	407	7.456	0.841	9
8	11.660	2.415	12	12.309	0.031	403	12.347	1.958	6

Table 2.11. Lead Partition Coefficient (K_d) of Soils Treated with Various Levels of P Fertilizer, Zn Oxide, and Ironite Amendments.

1. P Fertilizer-Treated Soils

Treatment	BR 5			VHL 3			B 5		
	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})
1	16.613	n.d.$^{+}$	>8307^{++}	13.743	n.d.$^{+}$	>6872^{++}	17.472	n.d.$^{+}$	>8763^{++}
2	17.248	n.d.$^{+}$	>8624^{++}	13.781	n.d.$^{+}$	>6890^{++}	17.189	n.d.$^{+}$	>8595^{++}
3	17.231	n.d.$^{+}$	>8616^{++}	13.334	n.d.$^{+}$	>6667^{++}	17.621	n.d.$^{+}$	>8811^{++}
4	17.057	n.d.$^{+}$	>8528^{++}	14.103	n.d.$^{+}$	>7297^{++}	17.350	n.d.$^{+}$	>8766^{++}
5	17.144	n.d.$^{+}$	>8572^{++}	14.585	n.d.$^{+}$	>7292^{++}	17.350	n.d.$^{+}$	>8675^{++}
6	15.057	n.d.$^{+}$	>7528^{++}	13.080	n.d.$^{+}$	>6540^{++}	16.521	n.d.$^{+}$	>8261^{++}

$^{+}$Solution concentration of Pb was below detection limit of 0.002 mg l^{-1}

$^{++}K_d$ determined based on the detection limit of Pb in solution phase

2. Zn Oxide-treated Soils

Treatment	BR 5			VHL 3			B 5		
	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})
1	17.160	n.d.$^{+}$	>8580^{++}	15.543	n.d.$^{+}$	>7111^{++}	19.606	n.d.$^{+}$	>9803^{++}
2	23.934	n.d.$^{+}$	>11967^{++}	20.464	n.d.$^{+}$	>10232^{++}	27.121	n.d.$^{+}$	>13560^{++}
3	32.420	n.d.$^{+}$	>16210^{++}	56.601	0.006	9357	51.797	n.d.$^{+}$	>25899^{++}
4	111.439	n.d.$^{+}$	>55719^{++}	91.927	n.d.$^{+}$	>45964^{++}	116.192	n.d.$^{+}$	>58096^{++}
5	399.098	0.036	11088	597.580	n.d.$^{+}$	>298790^{++}	504.170	0.046	11064
6	939.279	0.943	996	1108.517	0.072	15460	1379.451	0.151	9125
7	3855.826	8.793	439	3413.376	7.300	468	3068.906	4.568	672

3. Ironite-treated Soils

Treatment	BR 5			VHL 3			B 5		
	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})	Soil (mg kg^{-1})	Solution (mg l^{-1})	K_d (l kg^{-1})
1	21.469	0.043	504	17.723	0.018	969	24.501	n.d.$^{+}$	>12250^{++}
2	21.326	n.d.$^{+}$	>10663^{++}	18.315	n.d.$^{+}$	>9157^{++}	26.137	n.d.$^{+}$	>13068^{++}
3	26.019	0.004	6845	20.197	0.011	1899	37.439	n.d.$^{+}$	>18.719^{++}
4	47.622	0.044	1084	45.516	0.004	12609	52.451	n.d.$^{+}$	>26225^{++}
5	83.187	n.d.$^{+}$	>41594^{++}	85.437	n.d.$^{+}$	>42719^{++}	89.067	n.d.$^{+}$	>44533^{++}
6	308.729	n.d.$^{+}$	>154364^{++}	303.107	n.d.$^{+}$	151553	317.315	n.d.$^{+}$	>158657^{++}
7	607.235	n.d.$^{+}$	>303618^{++}	616.808	n.d.$^{+}$	>308404^{++}	649.142	n.d.$^{+}$	>324570^{++}
8	1186.442	n.d.$^{+}$	>593221^{++}	1099.833	n.d.$^{+}$	>549917^{++}	1136.603	n.d.$^{+}$	>568301^{++}

$^{+}$Solution concentration of Pb was below detection limit of 0.002 mg l^{-1}

$^{++}K_d$ determined based on the detection limit of Pb in solution phase

Implications

The outcomes of this set of experiments demonstrated that:

1. K_d derived for the outcomes of conventional batch adsorption experiments over estimated the concentration therefore the amounts of soil borne As, Cd, and Pb in the solution phase.

   The K_d representing the indigenous As, Cd, and Pb of the soils is considerably larger than those receiving spiked As, Cd, and Pb during the batch adsorption experiment. It indicated that greater percentages of the added trace elements would be in the solution phase.

2. Based on the K_d values obtained, greater percentage of the total Cd and Pb in P fertilizers and micronutrients (zinc oxide and Ironite) than in the soils remained in the solid phase.

Chapter 3

Laboratory Evaluations of K_d

The solid – solution partition coefficient, K_d, is the conventional approach to depict the trace elements in soluble and solid phases of the soils. Yet the theoretical basis and the chemical meaning of this parameter are not clear. The methods for determining the total and the dissolved contents of trace elements in the soils, however, have not been standardized. Depending on the methods employed, the resulting K_d may vary by several orders of magnitude (Peirjnenburg et al., 2001; Gooddy et al., 1995).

The solution concentration of trace elements in soils is customarily determined as the concentration in the extract of soil obtained at a given soil to solution ratio such as l:10 (w/v). There is growing recognition that K_d obtained in this manner may not be entirely representative as the conditions in which the soil solution is prepared are not realistic especially for the cropland soils. On the other hand, the solution concentration is dependent on the solid to solution ratio and the duration for which the soil suspensions are equilibrated. The plant roots where the food chain transfer processes initiates are hardly ever exposed to the trace element at the intensity levels mimicking the concentrations represented by the solid to solution ratio at 1: 10 (w/v). Under the normal circumstances, the solid to solution extraction ratio of 1:10 far exceeds the field moisture levels and yet is inadequate to bring all of the soluble fractions into the solution phase.

The chemical constituents of the soil solution are ideally determined by extracting soils at the field moisture range as it is most reflective of the realistic situations. At the field moisture levels, the soils contain little free water. The outcomes will not always be consistent because the mass transfer likely is diffusion limited and the equilibrium is localized around discrete the metal containing particles and only a small portion of the water can be extracted. Conceptually, the concentration of Cd in field soils should therefore be probabilistic in nature. When the plants absorb trace elements in the solution phase, the depletions are replenished by those remaining in the solid phase. It is imperative that the dissolution kinetics is factored in.

Customarily the soil solution is obtained at the water to soil ratios that the mixture forms a homogeneous soil paste that is conceptually defined as the largest amount of water to be added without significantly changing the concentration of dissolved constituents of soil solution, the soil saturation extract. The approach appeared to work well and provided consistent results if the constituents in question are readily soluble or the soils are heavy contaminated. The trace element concentrations obtained from the lower soil to water ratios are not representative of the realistic conditions in soils. If a limited quantity of a trace element is available for dissolution, a lower soil to water ratio (i.e. high-water volume with respect to amount of soil, such as 1:10) will results in the dilution of the chemical in solution. At higher soil to water ratios (i.e. low water volume with respect to amount of soil, such as 1:1 and higher), relatively large amounts of soil mass are needed to obtain small volumes of extract. Under the circumstances, the mass transfer of Cd from solid to solution phase will be short ranged and the equilibrium would be localized. The solution concentrations through the mixture may not be entirely uniform. The Cd concentrations in the extracted solutions would be probabilistic as a relatively small fraction of the total water added may be withdrawn. A logical approach is needed to define the K_d.

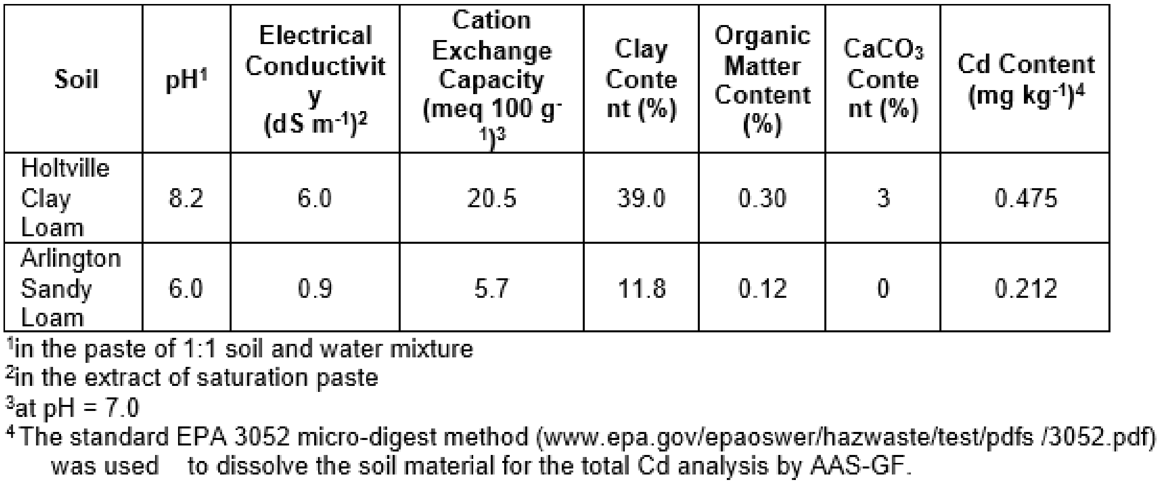
We used Cd as an example to characterize the nature of and develop the probabilistic model for K_d. The Cd concentrations in soil solutions were determined from the extracts that represent different solid to solution ratios. Relationships between Cd concentrations in solution and solid phases were fitted into a linear Langmuir isotherm equation. The most appropriate soil to water ratio for determining the Cd concentration in soil solution was select based on results from the batch extraction experiments. The probability partition of the solution concentrations hence the partitioning coefficient of Cd in two California cropland soils were investigated.

Materials and Methods

Materials

Two soils, the Arlington sandy loam soil at the University of California, Riverside Agricultural Experiment Station and the Holtville clay loam soil from University of California Meloland Field Station in Imperial Valley, were used in the batch extraction experiments. Selected physical and chemical properties of the two soils, as reported in the Soil Survey (http://websoilsurvey.nrcs.usda.gov) are given in Table 3.1.

Table 3.1. Selected physical and chemical properties of the two test soils.



Soil	pH[1]	Electrical Conductivity (dS m^{-1})[2]	Cation Exchange Capacity (meq 100 g^{-1})[3]	Clay Content (%)	Organic Matter Content (%)	$CaCO_3$ Content (%)	Cd Content (mg kg^{-1})[4]
Holtville Clay Loam	8.2	6.0	20.5	39.0	0.30	3	0.475
Arlington Sandy Loam	6.0	0.9	5.7	11.8	0.12	0	0.212

[1] in the paste of 1:1 soil and water mixture
[2] in the extract of saturation paste
[3] at pH = 7.0
[4] The standard EPA 3052 micro-digest method (www.epa.gov/epaoswer/hazwaste/test/pdfs /3052.pdf) was used to dissolve the soil material for the total Cd analysis by AAS-GF.

Preparation of Spiked Soils

Since the Cd concentration in natural soil solution is often too low to be routinely determined, especially at the higher soil to water ratios, we spiked the soil samples by adding approximately 0.4 μg Cd per gram soil. The spiked soil was allowed to undergo weathering through several cycles of wetting and drying during a period of 3 weeks. In soils, increasing the contact time has been shown to decrease the metal's subsequent ability to desorb from the soil (22-24). But the kinetics tends to be stable after two or three weeks thus have minor effect on studying the trend of Cd soil solution concentration at different extraction approach.

Batch Extraction Experiments

When the soil suspension changes from the dilute to concentrated forms, the trace element concentration in the soil solution will increase and approach the concentration in field moisture levels. The experiments are set up to test the hypothesis and determine the most appropriate soil to water ratio for determining the trace element concentration in soil solution.

Two sets of extraction at different soil to water ratios were conducted. In one set, different amounts of water were mixed with the spiked soil to form soil to water ratios of 1:100, 1:50, 1:20, 1:10, 1:5, 1:1 and 1:0.5. The second set of extraction experiments focused on the lower soil to water ratios and used the soils not spiked with Cd. Extractions at soil to water ratios of 1:0.3, 1:0.4, 1:0.5, 1:0.6 and 1:0.7 for the sandy loam soil and 1:0.4, 1:0.5, 1:0.6, 1:0.7 and 1:0.8 for the clay soil, respectively, were conducted. The samples were allowed to equilibrate for 48 hours on a reciprocating shaker. This desorption period was selected as a result of a preliminary study that showed little change in the amount of Cd desorbed from the soil after a 48-h equilibration at high soil to water ratio (at low water to soil ratio, the period is less). Following equilibration, samples were centrifuged, and the supernatant was decanted and filtered (0.45 μm Hydriohilic PVDF, Millipore Corporation, syringe driven filter). The sample solution is then determined by graphite furnace atomic absorption spectroscopy (AAS-GF).

The results of the first set of batch experiments illustrated the relationship between soil to solution ratios and amounts of Cd extracted through the desorption isotherms. An appropriate soil to water ratio for determining the trace element concentration in the soil solution was further selected based on the results of the second set of batch experiments. Then the probability distribution function of the Cd concentration in soil solution was established by extracting 20 replicates at the selected soil to water ratio. Since the Cd concentration in soil solution is very low (less than 0.5% of the total), the partitioning coefficient were calculated based on the Cd soil solution concentrations and the total Cd soil contents.

Quality Control

The Cd solution concentrations are expected to be very low at natural soil environment. One-time sterile polypropylene centrifuge tubes and high quality deionized water were used to avoid the contamination effects from the containers and extractant. The accuracy of the determinations was verified using a Trace Elements in Water standard (NIST 1640). The standard is certified to contain 22.79 □g Cd l^{-1}. Figure 3.1 shows the chronological recording of a 50-fold dilution of certified NIST 1640 standard. The mean value of 25 determinations, 0.428 □g Cd l^{-1}, is a little lower than the expected value 0.445 □g Cd l^{-1}, with CV of 4.4%. All the determinations are within ± 10% of the mean value. This standard was analyzed after preparing each calibration curve for the GFAAS to check the accuracy of the analyses. To study the possible effect from the filter system, the diluted NIST 1640 standard was past through the filter system. The mean value of 10 determinations is 0.438 µg Cd l^{-1}, no difference from the sample without passing through the filter system. The possible release from or sorption to the filter is negligible.

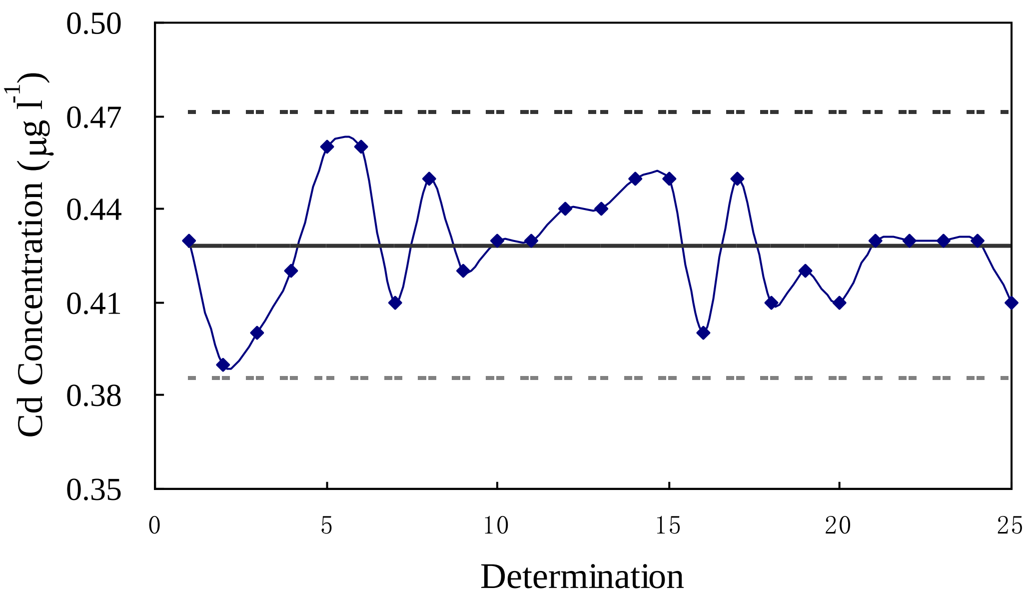


Figure 3.1. Chronological recording of Cd concentration of a certified NIST 1640 standard (0.445 □g l^{-1}), mean=0.428 □g l^{-1}, Standard Deviation=0.0188 □g l^{-1}.

Results and Discussion

Desorption Isotherms

For a given soil, the trace element concentration in the solution phase is expected to change with the soil to solution ratios employed for the extractions. The Cd concentrations in soil solution of the Cd spiked Holtville clay loam soil and Arlington sand sandy loam soil exhibited the same pattern and the solution concentrations increased while the total quantity of Cd extracted decreases as the soil to water ratio decreases from 1:100 to 1:0.5 (Figure 3.2).

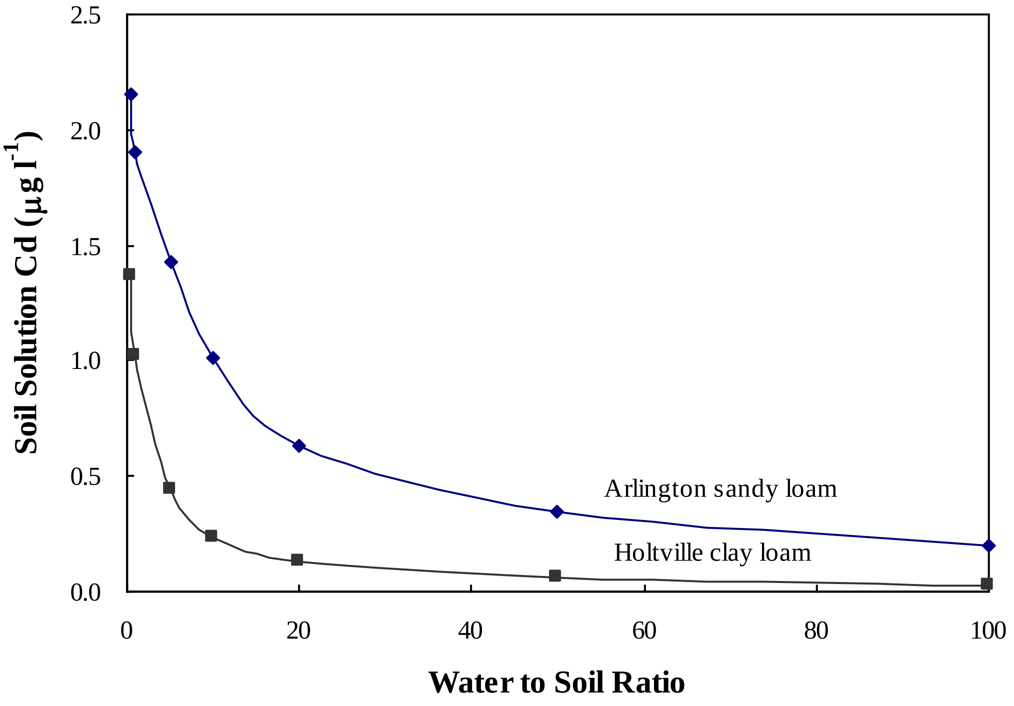


Figure 3.2. Cd concentration at different water to soil extraction ratio of the Cd spiked Holtville clay loam and the Arlington sandy loam.

Desorption of cations (i.e. Cd^{2+}) as a function of solution volume can be described by the Langmuir isotherms model. The linear form of Langmuir desorption isotherm is given by:

$$\frac{1}{C} = \frac{R}{S_{\max}} + \frac{a}{S_{\max}} \qquad \text{[Eq. 3.2]}$$

where C is the Cd concentration of the extracted solution (µg l^{-1}) at the water to soil ratio of R (ml g^{-1}); S_{max} is the maximum quantity that can be extracted per gram soil (µg g^{-1} soil); a is a constant. Plotting 1/C against R, a straight line with a positive nonzero intercept may be obtained if the desorption isotherm is linear (Figure 3.3). The extraction of Cd in the range of soil to water ratios from 1:0.5 to 1:100 fitted well into the linear Langmuir desorption isotherm (R^2 >0.99). Based on the slope of the linear regression, the maximum quantities that can be extracted for Cd in the Holtville clay loam and Arlington sandy loam are 0.0031µg g^{-1} and 0.022 µg g^{-1}, respectively. They are considerably smaller than the total Cd contents of the spiked soils, 0.88 and 0.61 µg g^{-1}, respectively.

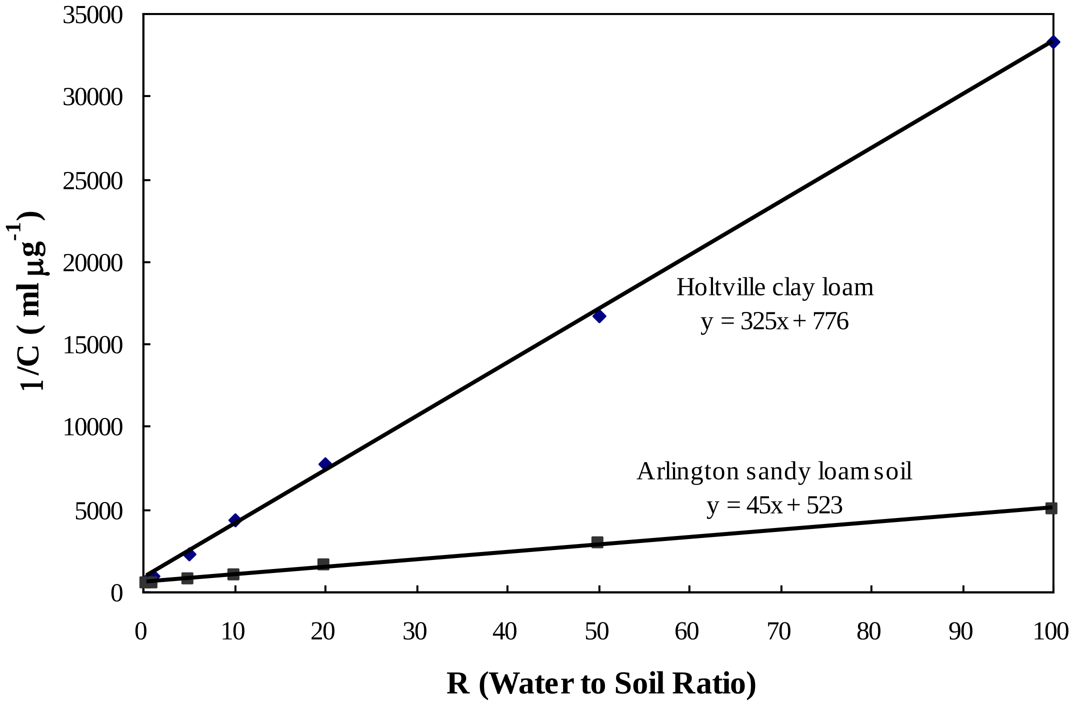


Figure 3.3. Influence of water to soil ratio (R) on Cd solution concentration (C) based on the equation 2, $1/C=R/S_{max} + a/S_{max}$

The soil solution pH for the Arlington sandy loam is lower than that of the Holtville clay loam. The percentages of clay and organic contents and the total cation exchange capacity in the Arlington sandy loam which contribute to the retention of Cd in soils are also lower than those in the Holtville clay loam (see Table 3.1). The chemical characteristics appeared to favor the Cd in Arlington sandy loam to have greater mobility and solubility. Based on the fitted S_{max} and the total Cd content of the spiked soils, 3.6% of the total soil Cd in the Arlington sandy loam may be desorbed, which is about 10 times greater than that of the Holtville clay loam, at 0.35%. The experiment was conducted on spiked soils with 3 weeks aging. Had the contact time increased, the fraction of Cd that can be dissolved should be smaller.

Soil to water ratio

Figures 4 and 5 showed the Cd concentrations of four replicated determinations at the soil to water extraction ratios from 1:0.3 to 1:0.8. For the same soil to water ratio, the outcomes were variable which indicates the uncertainties might be experienced in determining the soil solution concentration of Cd at the field moisture levels. However, based on the mean value of the four replicates, the solution Cd concentration in un-spiked soil tends to stabilize to a relatively constant level as the soil and water ratio of the extractions are 1:1 or higher. Based on the statistic results of t-test, there is no significant difference (at p =0.05) of the Cd concentration in soil solution extracted at all the selected soil to water ratios for the Holtville clay loam. For the Arlington sandy loam, there is no significant difference (at p =0.05) for using soil to water ratios of 1:0.3, 1:0.4 and 1:0.5 for the Arlington sandy loam. We chose to extract the soil solution at the soil to water ratio of 1:0.5 (w/v) that is reasonably representative of the stable range and the soil solution concentrations at the field moisture levels.

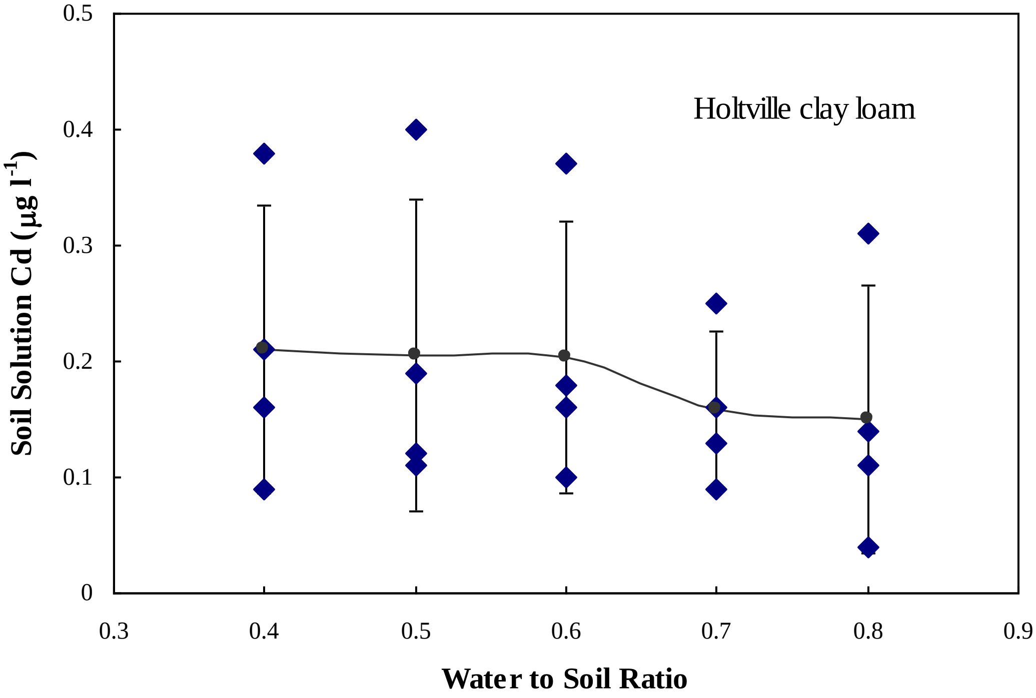


Figure 3.4. Soil solution Cd concentrations of Holtville clay loam soil extracted at different water to soil ratios.

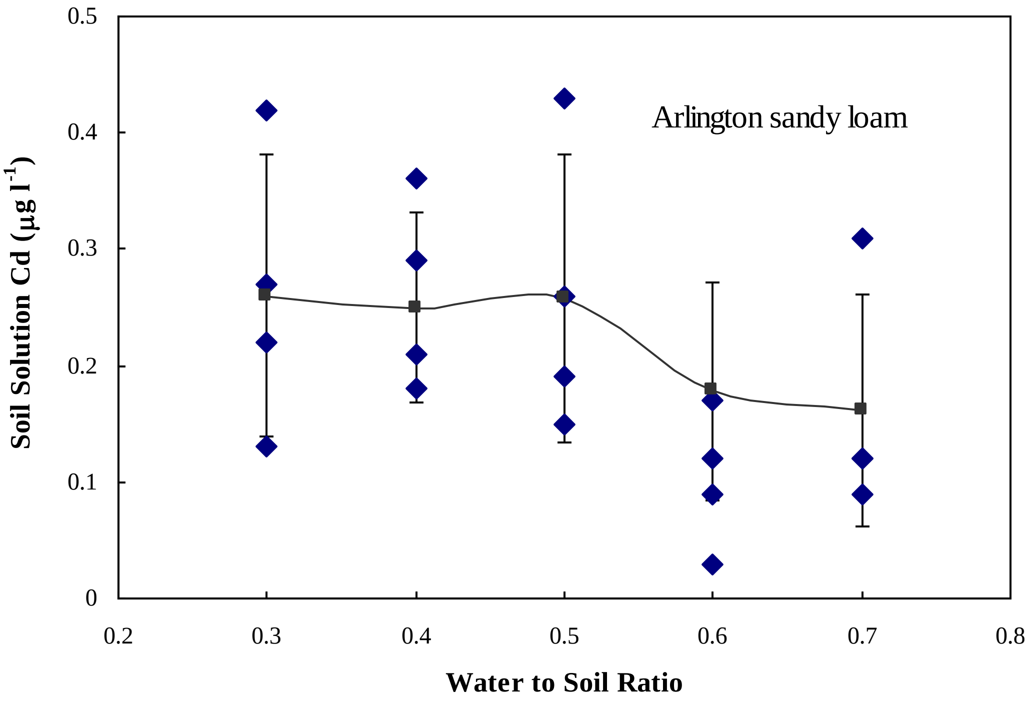


Figure 3.5. Soil solution Cd concentrations of Arlington sandy loam soil extracted at different water to soil ratios.

Probability Distribution of Soil Solution Concentrations and K_d

The attributes exhibited by the Cd in soil solutions (Figures 3.4 and 3.5) are typical of the outcomes from field-based measurements that are not entirely deterministic. Instead, they are often stochastic and may be quantitatively described by a probability distribution function. The distribution of Cd concentrations in soil solution was represented by 20 replicated measurements made at soil to water extraction ratio of 1:0.5 (w/v). Table 3.2 summarized the descriptive statistics characterizing the probability distributions for these two soils. The average soil solution Cd concentration of the Holtville clay loam and Arlington sandy loam are 0.216 and 0.319 μg l^{-1}, respectively. The lower quartile and upper quartile for Holtville clay loam soil are 0.143 and 0.275 μg $l^{-1,}$ respectively. For the Arlington sandy loam soil, they are 0.258 and 0.370 μg l^{-1}, respectively.

Table 3.2. Descriptive statistic of the distribution of Cd solution concentration in the two test soils.

Soil	Mean (□g l^{-1})	Standard Deviation	Minimum (□g l^{-1})	Maximum (□g l^{-1})	Skewness	Standard Error Skewness	Kurtosis	Standard Error Kurtosis
Holtville Clay Loam	0.216	0.0966	0.04	0.46	0.702	0.512	1.029	0.992
Arlington Sandy Loam	0.319	0.0908	0.13	0.55	0.327	0.512	1.434	0.992

The Cd concentrations of the soil solution for the Holtville clay loam and the Arlington sandy loam follow a normal distribution (Figure 3.6 and 3.7). The normality of the distribution was first evaluated based on the statistic description of skewness, kurtosis and their corresponding standard error. The calculated □ values (the skewness divided by its standard error and the kurtosis divided by its standard error) are less than 1.96. Therefore, the distribution of soil solution Cd concentrations in both soils follows a normal distribution with $p < 0.05$. The distribution is slightly skewed toward the lower values with relatively lower peak. The K-S (Kolmogorov-Smirnov) test indicated that the two tailed p values for Holtville clay loam and Arlington sandy loams are 0.936 and 0.961, respectively indicating the normality of the distributions is significant.

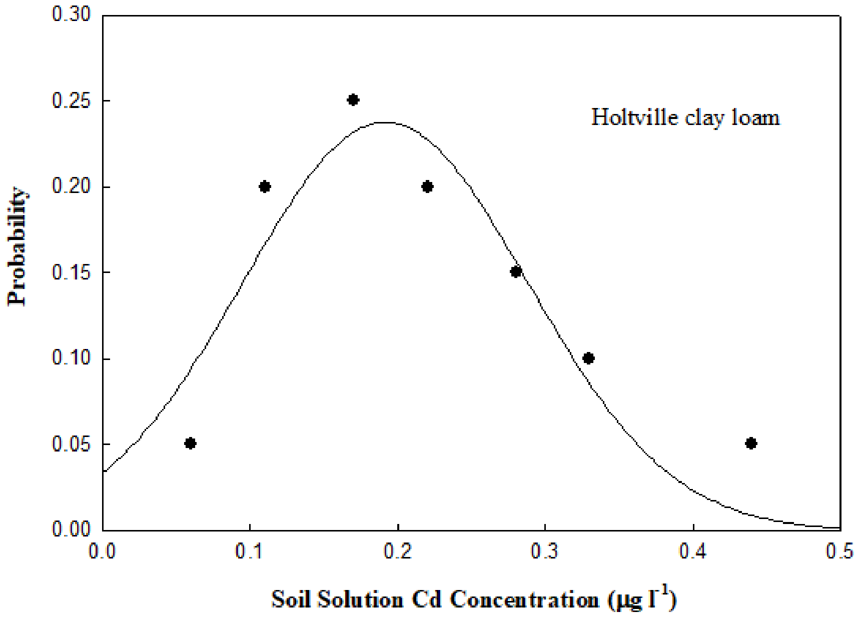


Figure 3.6. The probability distribution of soil solution Cd concentrations in the Holtville clay loam at a soil to water ratio of 1:0.5.

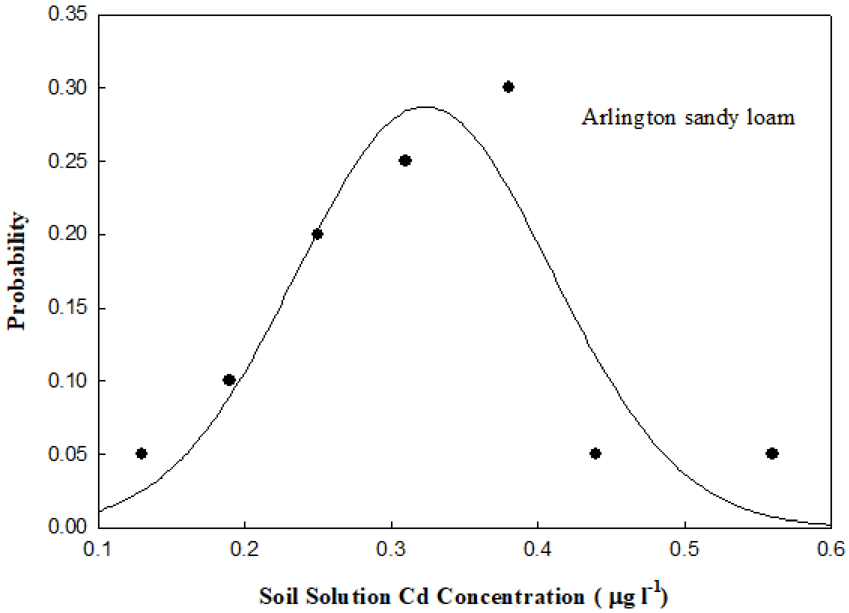


Figure 3.7. The probability distribution of solution concentrations of Cd in the Arlington sandy loam at a soil to water ratio of 1:0.5.

The histogram was fitted with a Gaussian distribution (Figure 3.6 and 3.7) in which the probability distribution function is described as:

$$f(x) = a \cdot \exp\left[-0.5 \cdot \left(\frac{x - x_0}{b}\right)^2\right] \qquad \text{[Eq. 3.3]}$$

where f(x) is the probability correspondence of x, x_0 and b are mean and standard deviation of the observed values. The fit is good for both soils (r >0.9). The fitted x_0 values are in close agreement to the mean values of the 20 replicated measurements and the b values are in close agreement to the standard deviations of the measurements. The probability distribution functions of Cd concentration in these two soil solutions are given,

For Holtville clay loam soil,

$$f(x) = 0.238 \cdot \exp\left[-0.5 \cdot \left(\frac{x - 0.192}{0.097}\right)^2\right] \qquad \text{[Eq. 3.4]}$$

and for Arlington sandy loam soil

$$f(x) = 0.287 \cdot \exp\left|-0.5 \cdot \left(\frac{x - 0.323}{0.087}\right)^2\right| \qquad \text{[Eq. 3.5]}$$

The K_d values for these two soils can not be simply calculated according to the conventional approach, dividing the total Cd content of the soils, C_{total}, by the soil solution, $C_{solution}$, Cd concentrations. The probability distribution of K_d of Cd for the Holtville clay loam and the Arlington sandy loam soil were plotted in Figures 3.8 and 3.9. The average K_d are 3,006 and 730□ l kg^{-1} for the Holtville clay loam and the Arlington sandy loam, respectively. The lower quartile and upper quartile for Holtville clay loam soil are 1,723 and 3,337□l kg^{-1}, respectively. For the Arlington sandy loam soil, they are 573 and 825□l kg^{-1}, respectively. There is one extreme value in each soil, resulting in greater skewness and kurtosis. The distributions of K_d are considerably skewed than those of soil solution Cd concentrations. The p values of the K-S tests are 0.225 and 0.294 for the Holtville clay loam and the Arlington sandy loam, respectively. Hence, the distribution of K_d in these two California cropland soils, while are visibly skewed, can still be described by a normal distribution. The probability distribution function of K_d in these two cropland soils is given, for Holtville clay loam soil:

$$f(x) = 0.416 \cdot \exp\left[-0.5 \cdot \left(\frac{x-1187}{437}\right)^2\right] \qquad \text{[Eq. 3.6]}$$

for Arlington sandy loam soil:

$$f(x) = 0.353 \cdot \exp\left[-0.5 \cdot \left(\frac{x-623}{134}\right)^2\right] \qquad \text{[Eq. 3.7]}$$

In this manner, the solid and solution phase distribution coefficients of Cd in cropland soils may be expressed in probabilistic terms and be used to characterize the uncertainties related to the fate and transport of trace elements in soils.

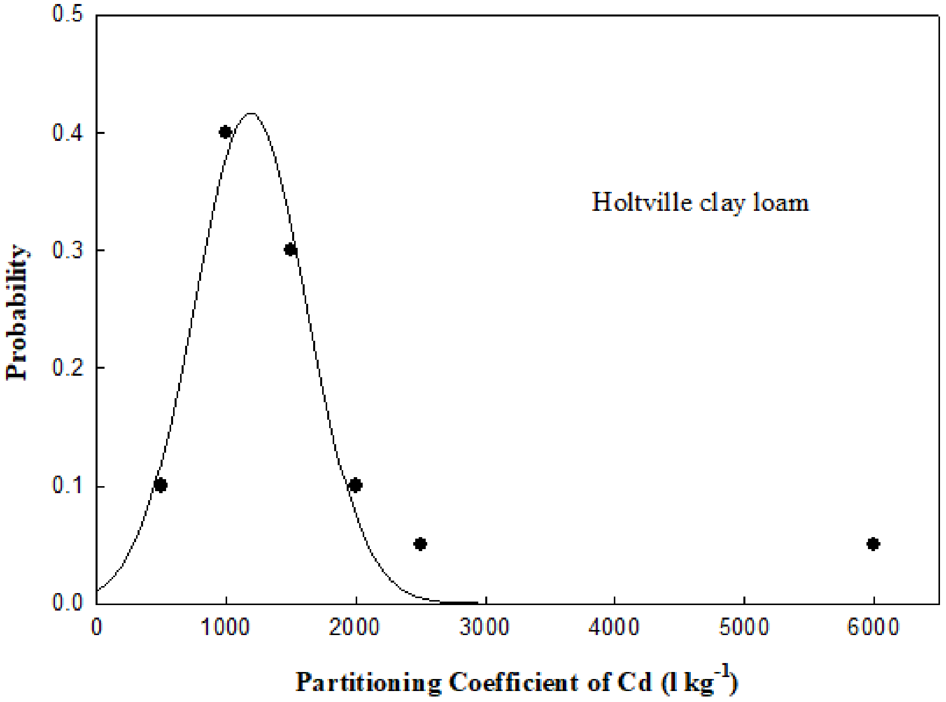


Figure 3.8. Probability distribution of partitioning coefficient (K_d) of Cd in the Holtville clay loam.

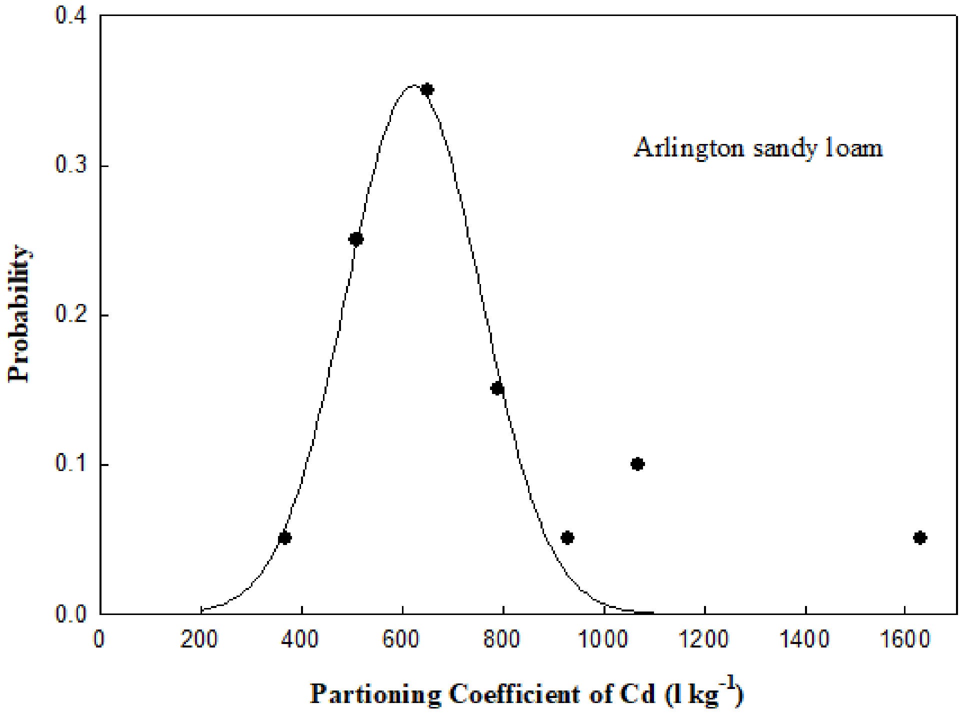


Figure 3.9. Probability distribution of partitioning coefficient (K_d) of Cd in the Arlington sandy loam.

Chapter 4

Assessing the Field Obtained K_d and PUF

Based on the information obtained from the analyses of laboratory derived K_d summarized in Chapter 3, we embarked on a study to determine the K_d and PUF based on soil and plant tissue samples obtained from the realistic crop production situations. All of the samples were obtained from production fields in California.

The samples were collected under different time framework and by separate individuals.

1. 45 sets of archived plant tissue and their corresponding soil samples, involving varieties of vegetable plants were used. These sampled were collected during the course of a previous CDFA supported study (Chang, A. C., A. L. Page, and N. J. Krage 2004. Role of Fertilizer and Micronutrient Applications on Arsenic, Cadmium, and Lead Accumulation in California Cropland Soils, http://www.cdfa.ca.gov/is/acrs/docs/CDFAFinalReport.pdf).
2. 25 sets of lettuce and the paired soil samples provided to us by Richard Smith of the University of California Cooperative Extension and Husein Ajwa of University of California, Davis**. (We gratefully acknowledge the assistances provided by our colleagues Husein Ajwa and Richard Smith)**
3. The California's portion of the Holmgren Dataset that was generated from the 1970's to 1980's U.S. Soil Survey national survey of trace elements in crops and crop production soils (Holmgren et al., 1993). The original data was provided by Dr. Rufus Chaney, USDA ARS, Beltsville, Maryland. This data set involved multiple sampling locations and multiple crops. However, only the total elemental concentrations of the plant tissue and the paired soil were available. **(We gratefully acknowledge our appreciation for the contributions of G. G. S. Holmgren and M. W. Meyer of U.S. Soil Survey and R. L. Chaney of USDA – ARS)**

Methods

Soil Analysis

As majority of the soil samples used were a subset of the samples collected in the previously study CDFA supported. We used the data of total As, Cd, and Pb contents of soils (C_{total}) that were determined for that study. In addition, the As, Cd, and Pb concentrations in the 1:1 (w/v) water extracts of the soils ($C_{solution}$) were determined using a ThermoFinnigan Element II Sector ICP-MS instrument at the research laboratory of Professor Cin-Ty Lee of Department of Earth Sciences, Rice University, Houston, Texas. The QA/QC protocols described in the previously reference CDFA report were followed. The remaining soil samples were processed, and the elemental contents were determined in the same manners.

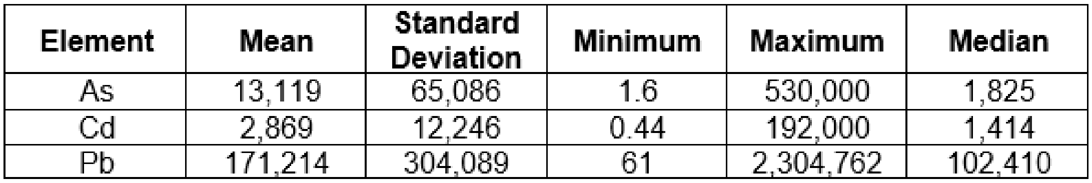
Plant Tissue Analysis

The plant tissues were digested and brought into solution by the microwave digestion procedure described in the previously referenced CDFA report. The As, Cd, and Pb contents of the solution were determined and converted to the plant tissue concentration on dry weight basis (C_{plant}). The QA/QC protocols described in the previously reference CDFA report were followed.

Solid –Solution Partition Coefficient. K_d

In the Development of Risk-based Concentrations for Arsenic, Cadmium and Lead in Inorganic Commercial Fertilizers (CDFA, 2002), the K_d summarized by Sauve et al. (2000) were used (Table 4.1).

Table 4.1 Descriptive statistics of partitioning coefficients, K_d (l kg^{-1}) of As, Cd, and Pb obtained by Sauve et al. (2000)

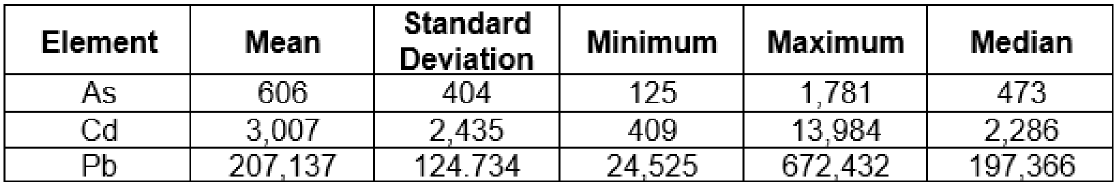


Element	Mean	Standard Deviation	Minimum	Maximum	Median
As	13,119	65,086	1.6	530,000	1,825
Cd	2,869	12,246	0.44	192,000	1,414
Pb	171,214	304,089	61	2,304,762	102,410

In the study (CDFA, 2002), the data was not used to estimate the plant uptake of As, Cd, and Pb. Instead, the solution concentrations estimated in this manner were employed to approximate the elemental concentrations in the solution phase and thus the losses through leaching and surface runoff.

In our analysis of the K_d for cropland soils in California, the results are as follows (Table 4.2):

Table 4.2 Descriptive statistics of partitioning coefficients, K_d (l kg^{-1}) of As, Cd, and Pb of cropland soils in California.



Element	Mean	Standard Deviation	Minimum	Maximum	Median
As	606	404	125	1,781	473
Cd	3,007	2,435	409	13,984	2,286
Pb	207,137	124.734	24,525	672,432	197,366

The K_d of As obtained from the cropland soils in California (Table 4.2) were two orders of magnitude less than those reported by Sauve et al. (2000) that means were 606 l kg^{-1}

and 13,119 l kg^{-1}, respectively and the ranges were 125 to 1,781 l kg^{-1} and 1.6 to 530,000 l kg^{-1}, respectively. The mean K_d of Cd obtained from the cropland soils in California (Table 4.2), 3,007 l kg^{-1}, was comparable to that reported by Sauve et al. (2000), 2,869 l kg^{-1}, yet the range for the cropland soils were considerably narrower than that reported by Sauve et al. (2000), 0.44 to 192,000 l kg^{-1}. The mean K_d of Pb obtained from the cropland soils in California (Table 4.2), 207,137 l kg^{-1}, was comparable to that reported by Sauuve et al. (2000), 171,214 l kg^{-1}, yet the ranges for both were wide although the later was considerably wider, 63 to 2,304,762 l kg^{-1} than the former, 24,525 to 672, 432 l kg^{-1}.

The data summarized in Sauve et al. (2000) represented a compendium of data in the published literature. Overwhelming majority of the data however represented soils contaminated by trace elements and required remediations. The chemistry in these soils tends to be dominated by the matrices of the contamination and the range of K_d values, varied by as much as five orders of magnitude, reflected the extent of the contaminations. Based on the K_d, the As, Cd, and Pb in the soils ranged from readily soluble (i.e. the low K_d) to extremely insoluble (i.e. the high K_d). For a contaminated soil, even a high Kd is not a guarantee that the solution concentration of the trace elements will be low and the reservoir of available elements may be exhausted quickly.

The amounts of As, Cd, and Pb in the cropland soils are relatively insignificant in contrast to those in the contaminated soils. For most cropland soils in California, the concentrations of As, Cd, and Pb were within the baseline range or slightly exceeded the upper range of the baseline. The concentration in soil solutions and their corresponding total concentrations in the soil did not appear to have a definitive correlation (Figure 4.1).

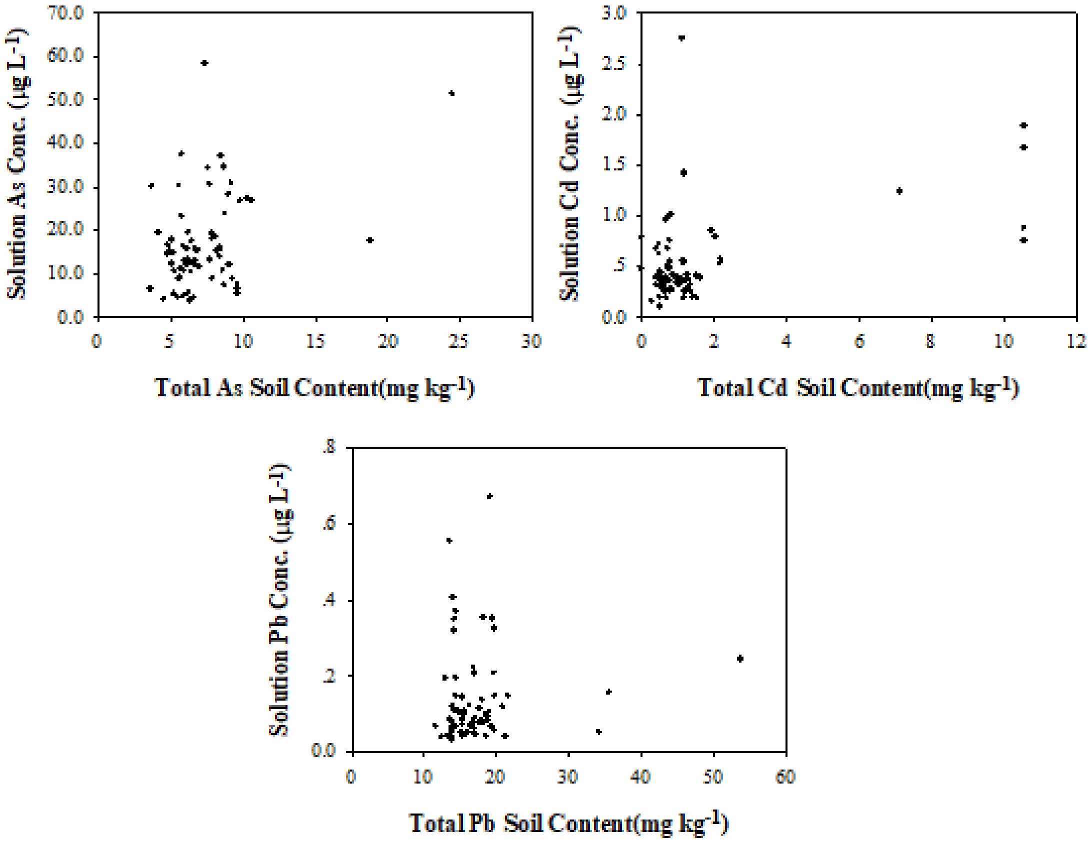


Figure 4.1. Distribution of As, Cd and Pb between solid and soil solution phase in 70 vegetable fields in California

The resulting K_d of the soils as summarized in Table 4.2 varied greatly. The K_d of As, Cd, and Pb for the cropland soils in California followed the log-normal distribution (Figure 4.2). The K_d of each element nevertheless remained in a much narrower ranges comparing to what was reported by Sauve et al. (2000). Instead of the K_d spanning across 5 orders of magnitude as reported by Sauve et al. (2000), the K_d for the cropland soils in California varied no greater than two orders of magnitudes. In this regard, the data summarized by Sauve et al. (2000) cast an extremely wide net and the K_d for the cropland soils represented a narrow subset within the ranges defined by Sauve et al. (2000). Based on the means, the CDFA study by considered a wider range overestimated risks in terms of dissolving the elements.

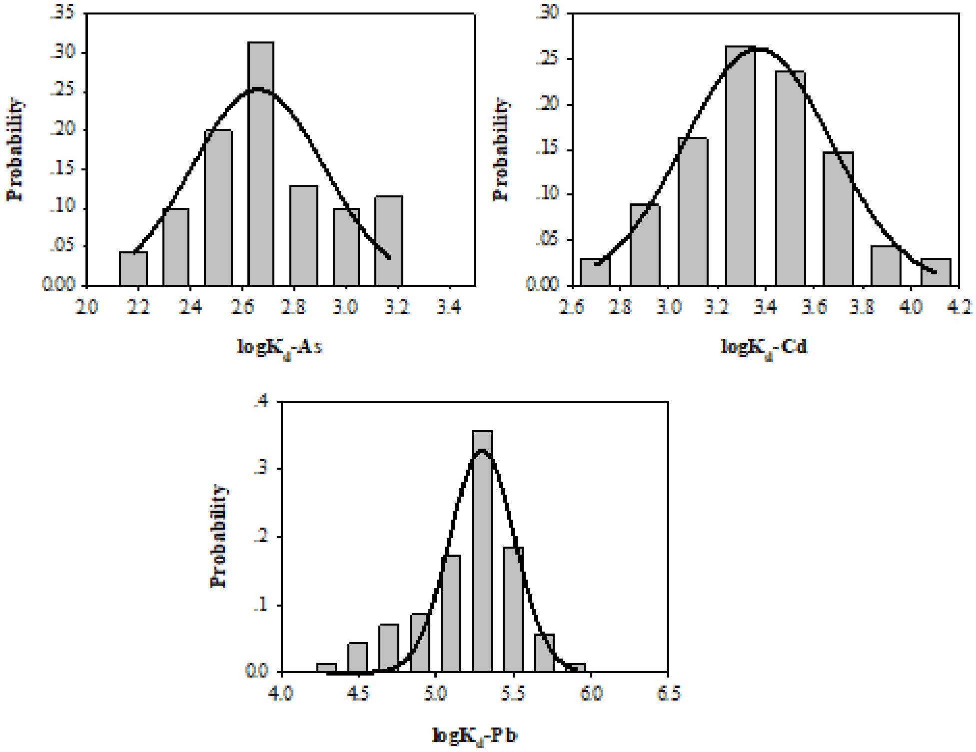


Figure 4.2 Probability distribution of K_d of As, Cd and Pb for the 70 vegetable fields in California

In direct comparisons of the K_d values summarized in Tables 4.1 and 4.2, the As in the cropland soils appeared to be significantly more readily soluble in the cropland soils and the Cd and Pb in the cropland soils were comparable to those reported. If the mean K_d were used to estimate the As, Cd, and Pb losses due to leaching and surface runoff, it would provide reasonable estimates of Cd and Pb losses due to leaching and surface runoff and would underestimate the As losses due to leaching and surface runoff. As the plant uptake would be estimated by the trace elements present in the soils, there would be a tendency for more As than expected to accumulate in the soil and thus an over estimation of As uptake by plants. The plant uptake of Cd and Pb will not be affected as the K_d used in the risk-based study (Table 4.1) were comparable to those obtained from cropland soils in California (Table 4.2)

Plant Uptake Factor, PUF

The soil solution and the corresponding plant tissue concentrations of As, Cd, and Pb in turn were used to define the plant uptake factor, PUF. Again, the plant tissue concentrations of As, Cd, and Pb did not appear to have a definitive correlation with their corresponding soil solution concentrations (Figure 4.3)

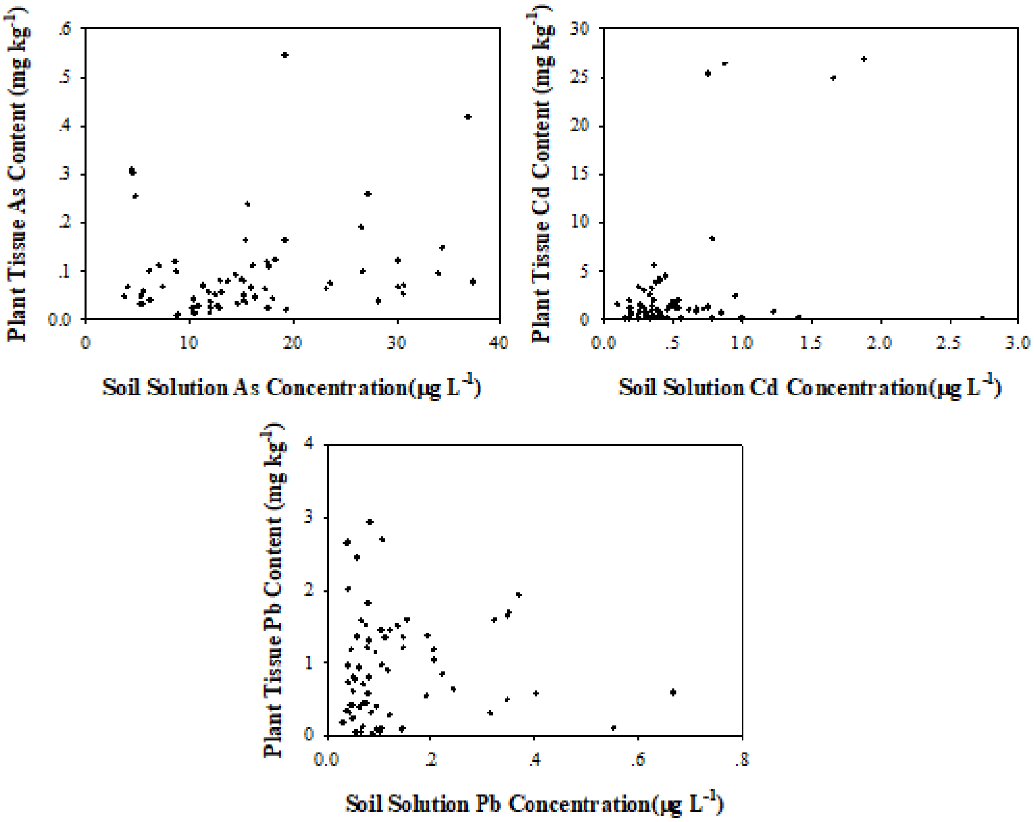


Figure 4.3 Relationships between soil solution concentration and plant tissue content of As, Cd and Pb for 70 CA vegetable fields

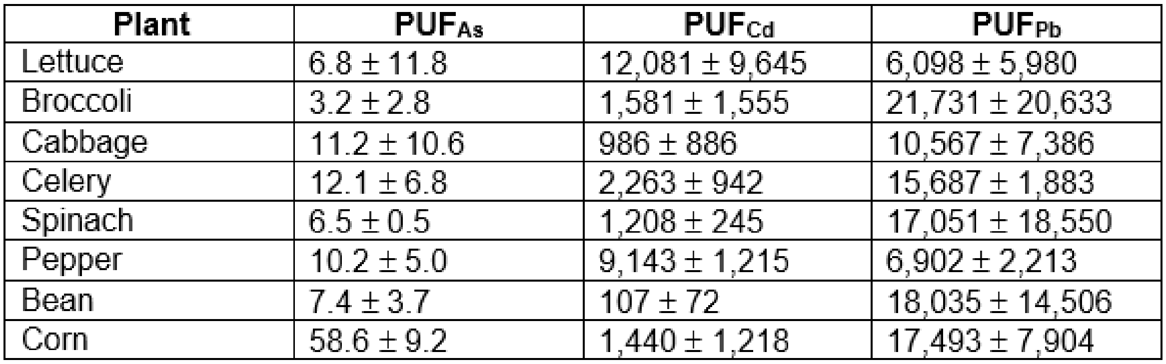
The resulting PUF calculated are summarized as follows (Table 4.3):

Table 4.3 PUF (l kg^{-1}) of crops grown on cropland soils in California

Element	Mean	Minimum	Maximum
As	8.22	0.8	68
Cd	6,782	19	32,177
Pb	11,375	181	68,261

While the descriptive statistics appeared to show wide range of variations, the PUF between plants did not appear to vary a great deal (Table 4.3) rather the PUF of the same element could varied by several orders of magnitude (Figure 4.4).

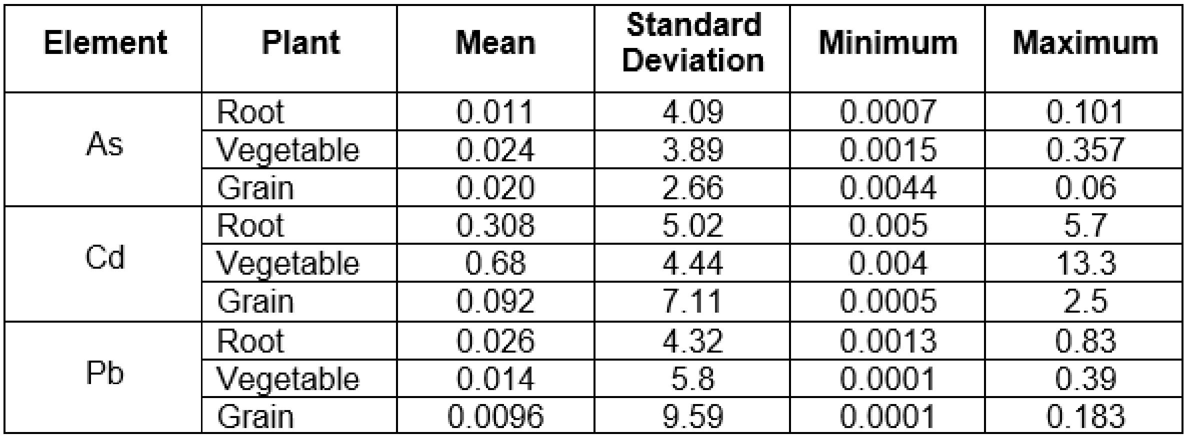
Table 4.4 PUF (l kg^{-1}) of selected vegetable plants in California



Plant	PUF$_{As}$	PUF$_{Cd}$	PUF$_{Pb}$
Lettuce	6.8 ± 11.8	12,081 ± 9,645	6,098 ± 5,980
Broccoli	3.2 ± 2.8	1,581 ± 1,555	21,731 ± 20,633
Cabbage	11.2 ± 10.6	986 ± 886	10,567 ± 7,386
Celery	12.1 ± 6.8	2,263 ± 942	15,687 ± 1,883
Spinach	6.5 ± 0.5	1,208 ± 245	17,051 ± 18,550
Pepper	10.2 ± 5.0	9,143 ± 1,215	6,902 ± 2,213
Bean	7.4 ± 3.7	107 ± 72	18,035 ± 14,506
Corn	58.6 ± 9.2	1,440 ± 1,218	17,493 ± 7,904

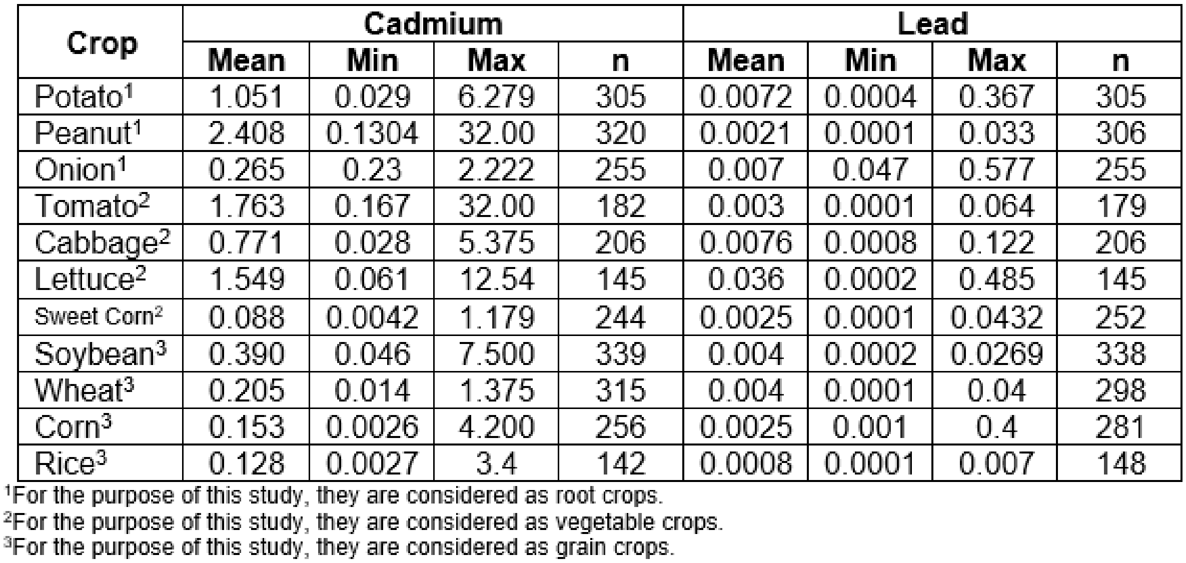
In the CDFA risk-based study (CDFA, 2002), the plant uptake of As, Cd, and Pb were estimated by the plant uptake factor, PUF, in which $PUF_{total} = C_{plant}$ (mg kg^{-1})/ C_{total} (mg kg^{-1}) where PUF_{total} referred to the plant uptake factor that was based on the total elemental content of the soils. As the total elemental content of the soil would be approximately 3 orders of magnitude larger than the soil solution concentrations, the PUF_{total} would be proportionally reduced. The data would not be comparable with those used for the study. In the following, the descriptive statistics of the PUF_{total} used in the study is summarized (Table 4.2). The data was compared with the PUF_{total} calculated by the data derived from the 1976 U. S. Soil Survey (only Cd and Pb data were available).

Table 4.5. Plant uptake factor, PUF (l kg^{-1}), used in the CDFA risk-based study (CDFA, 2002)



Element	Plant	Mean	Standard Deviation	Minimum	Maximum
As	Root	0.011	4.09	0.0007	0.101
	Vegetable	0.024	3.89	0.0015	0.357
	Grain	0.020	2.66	0.0044	0.06
Cd	Root	0.308	5.02	0.005	5.7
	Vegetable	0.68	4.44	0.004	13.3
	Grain	0.092	7.11	0.0005	2.5
Pb	Root	0.026	4.32	0.0013	0.83
	Vegetable	0.014	5.8	0.0001	0.39
	Grain	0.0096	9.59	0.0001	0.183

Table 4.3. Plant uptake factor (PUF_{total}) of Cd and Pb for root, vegetable, and grain crops grown in California (based on data provided by Dr. Rufus L. Chaney)



Crop	Cadmium				Lead			
	Mean	Min	Max	n	Mean	Min	Max	n
Potato[1]	1.051	0.029	6.279	305	0.0072	0.0004	0.367	305
Peanut[1]	2.408	0.1304	32.00	320	0.0021	0.0001	0.033	306
Onion[1]	0.265	0.23	2.222	255	0.007	0.047	0.577	255
Tomato[2]	1.763	0.167	32.00	182	0.003	0.0001	0.064	179
Cabbage[2]	0.771	0.028	5.375	206	0.0076	0.0008	0.122	206
Lettuce[2]	1.549	0.061	12.54	145	0.036	0.0002	0.485	145
Sweet Corn[2]	0.088	0.0042	1.179	244	0.0025	0.0001	0.0432	252
Soybean[3]	0.390	0.046	7.500	339	0.004	0.0002	0.0269	338
Wheat[3]	0.205	0.014	1.375	315	0.004	0.0001	0.04	298
Corn[3]	0.153	0.0026	4.200	256	0.0025	0.001	0.4	281
Rice[3]	0.128	0.0027	3.4	142	0.0008	0.0001	0.007	148

[1] For the purpose of this study, they are considered as root crops.

[2] For the purpose of this study, they are considered as vegetable crops.

[3] For the purpose of this study, they are considered as grain crops.

Comparing the data in Tables 4.2 and 4.3, it appeared that the PUF_{total} used in the risk-based study were similar in magnitudes and covered the similar range as those observed in the fields. However, based on the mean values, the risk-based PUF_{total} would underestimate the plant uptake of Cd and provided comparable PUF_{total} for plant uptake of Pb. The PUF_{total} observed in the field situations for each category of food crops followed the log-normal distributions and covered a range spanning approximately 3 orders of magnitude (Figure 4.4).

Conclusions

Under the field growing conditions, the K_d and PUF for any food crops did not appear to be constants with respects to the element, plant species, or soils as commonly assumed. Instead, the field obtained values of these two parameters followed generally the log-normal distributions and the range of the distributions appeared to be rather wide.

The K_d and PUF_{total} employed for the CDFA risk-based study of As, Cd, and Pb uptake by plants were similar in magnitudes, covered roughly the same ranges, and all followed the log-normal distributions as those we obtained from the field. If this is the case, we expect that the outcomes of the risk-based assessment on the maximum tolerable threshold for As, Cd, and Pb in the fertilizers to be comparable in values if the K_d and PUF based on K_d and PUF observed in the field production conditions.

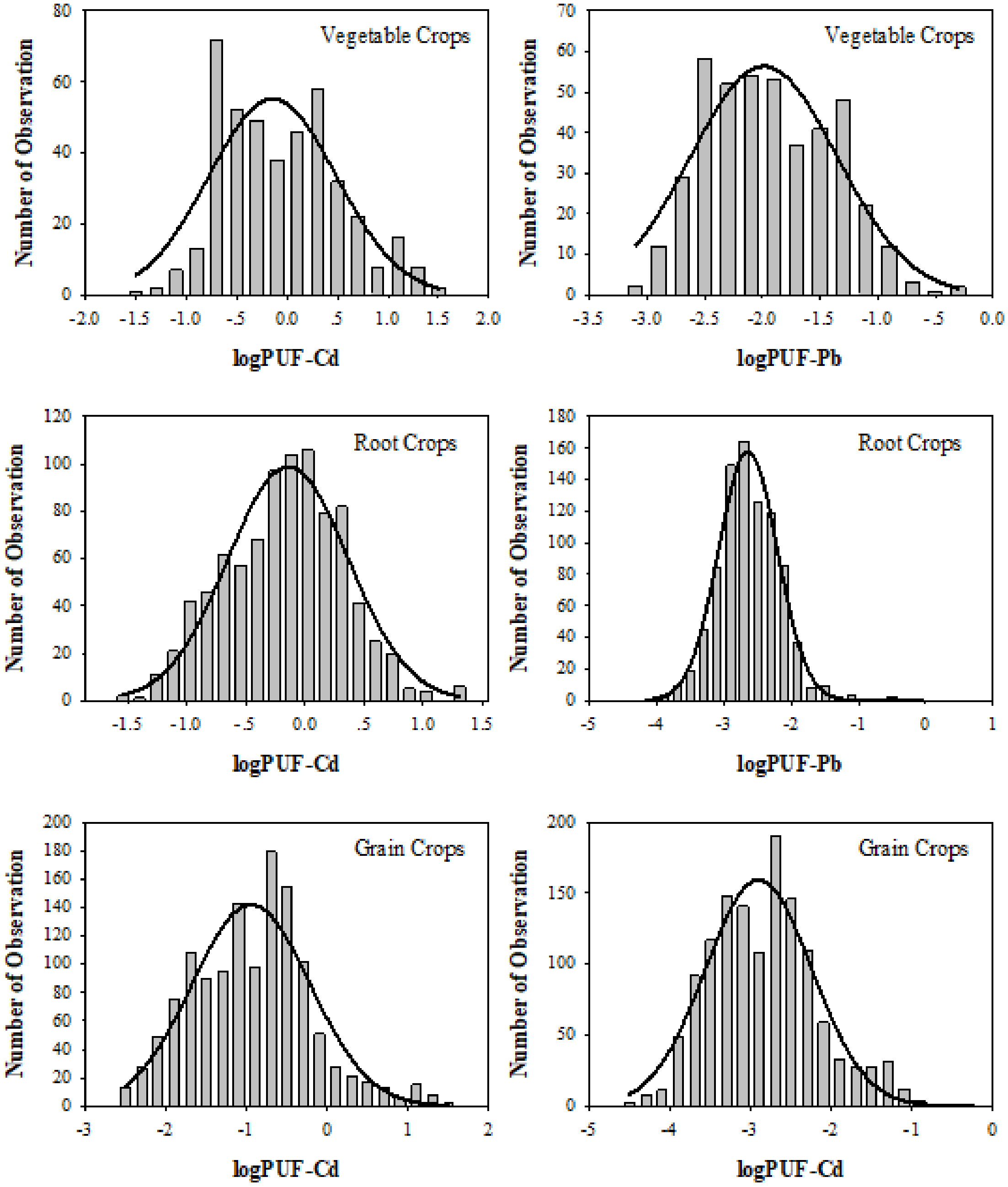


Figure 4.4 Probability distributions of PUF_{total} for Cd and Pb in root, vegetable, and grain crops.

Chapter 5

Dynamic Sorption-desorption of Cadmium in Cropland Soils

Conceptual Development

The sorption of Cd from solution by soil components usually consists of two steps: an initial rapid adsorption followed by a slow removal process. The initial rapid adsorption is generally ascribed to reversible adsorption at the interface. The characteristic time scale of trace element adsorption on soil surface is typically on order of seconds to minutes, and therefore is commonly quantified by thermodynamic equilibrium distribution models. The slow removal process may be due to surface precipitation, co-precipitation, or further diffuse into inert sites of soil particles, which is on time scale of hours to days and may describe by a first order kinetic reaction. Upon entering soil, the Cd undergoes these two types of reactions simultaneously. The distributions of Cd between the solution, surface adsorbed, and immobilized mineral phases are dependent on the Cd concentration of the solution phase at the start, C_0 and the time to equilibrium, t. In the two-site model, the different sorption reactions are ascribed either as surface adsorbed which is instantaneously in equilibrium with the Cd in solution phase or as occluded or co-precipitation with soil minerals which follows a first-order kinetic equilibrium with the solution phase or adsorbed phase. Consequentially, the Cd held on those solid soil components was defined as Cd in the adsorbed phase and mineral phase, respectively.

The mass balance in a Cd sorption experiment when these two processes occurred simultaneously can be described as follows:

$$C_t \cdot R + \mathrm{k_a} \cdot C(t) + MP_t = C_0 \cdot R \qquad \text{[Eq. 5.1]}$$

where R is the water to soil ratio (ml g^{-1}); k_a is the linear adsorption coefficient for Cd partition between the solution and adsorbed phase (ml g^{-1}); C_0 is the initial Cd concentration of the solution phase (□g ml^{-1}); C_t and MP_t is the Cd concentration in the solution phase and immobilized mineral phase at specific equilibration time, respectively. The slower reaction kinetics of the immobilized mineral phase can be described by the following first-order reaction equation that:

$$\frac{\partial MP}{\partial t} = k_f \cdot (R + K_d) \cdot C - \mathrm{k_a} \cdot MP \qquad \text{[Eq. 5.2]}$$

where k_f and k_b are the forward and backward reaction rate constants corresponding to immobilization and dissolution processes, respectively. Coupling the equations 4 and 5, the time dependent change of the Cd in solution phase and mineral phase is given by:

$$C_t = \left(\frac{C_0 \cdot R}{R + \mathrm{k}_a} - \frac{k_f \cdot C_0 \cdot R}{(k_f + k_b) \cdot (R + \mathrm{k}_a)} \right) + \frac{k_f \cdot C_0 \cdot R}{(k_f + k_b) \cdot (R + \mathrm{k}_a)} \cdot e^{-(k_f + k_b) \cdot t} \qquad \text{[Eq. 5.3]}$$

$$MP_t = \frac{k_f \cdot R \cdot C_0}{k_f + k_b} \cdot (1 - e^{-(k_f + k_b) \cdot t}) \qquad \text{[Eq. 5.4]}$$

If the equilibration time, t, is fixed, the right-hand side of equations 5.3 and 5.4 may be reduced to linear forms in terms of C_0. The Cd concentrations in the solution phase (C_t) and mineral phase (MP_t) at specific equilibration time (t) may be obtained for various initial solution concentrations (C_0) and C_t vs. t would be a straight line. When the initial solution concentration C_0 is fixed, the right-hand side of equations 5.3 and 5.4 may be reduced to an exponential form. The Cd concentration in solution phase, C_t will decrease exponentially with respect of equilibration time to the minimum and the Cd in mineral phase, MP_t will increase exponentially with respect to time to the maximum.

Typical batch Cd adsorption experiments may be conducted, and the data may be fitted into the equations 5.6 and 5.7 to evaluate the sorption kinetics, namely K_d, k_f and k_b.

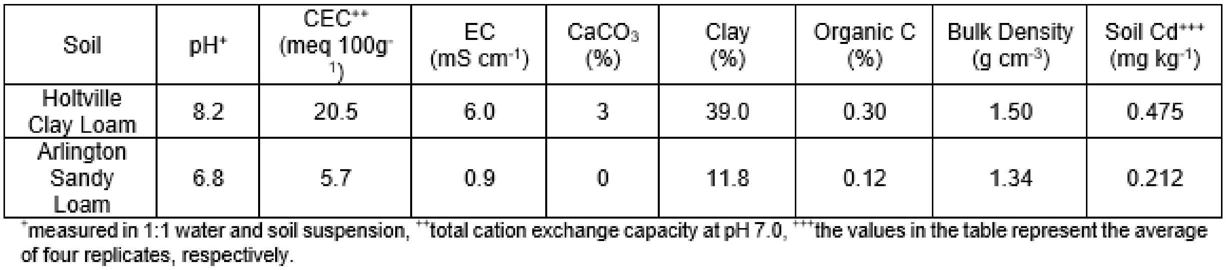
Methods

The experimental methods based on the above outlined model are summarized as follows:

Soils

Two soils, the Arlington sandy loam soil obtained at the University of California, Riverside Agricultural Experiment Station and the Holtville clay loam soil obtained at University of California Meloland Field Station in Imperial Valley, were used in the batch Cd adsorption experiments. Some physical and chemical properties of the two test soils are given based on the soil survey of USDA (http://websoilsurvey.nrcs.usda.gov) and the total Cd contents were analyzed by AAS-GF after dissolved based on the standard EPA 3052 micro-digest method (www.epa.gov/epaoswer/hazwaste/test/pdfs /3052.pdf).

Table 5.1. Selected characteristics of the soils used in study



Soil	pH^{+}	CEC^{++} (meq 100g^{-1})	EC (mS cm^{-1})	$CaCO_3$ (%)	Clay (%)	Organic C (%)	Bulk Density (g cm^{-3})	Soil Cd^{+++} (mg kg^{-1})
Holtville Clay Loam	8.2	20.5	6.0	3	39.0	0.30	1.50	0.475
Arlington Sandy Loam	6.8	5.7	0.9	0	11.8	0.12	1.34	0.212

$^{+}$measured in 1:1 water and soil suspension, $^{++}$total cation exchange capacity at pH 7.0, $^{+++}$the values in the table represent the average of four replicates, respectively.

<ins>Determine Cd in solid phases</ins>

The distribution of Cd in these solid phases can be examined with a sequential extraction procedure. Although the sequential extraction procedures are plagued with procedural shortcomings, they are practical tools to probe the behavior of trace element such as Cd that is present in soils mostly in solid phases. Many sequential extraction procedures have been developed to evaluate the distributions and chemical forms of Cd in different background matrices (Soon and Bates, 1982; Kuo et al. 1983; Miller and Mcfee, 1983; Xian, 1987 &1989; Ramos et al., 1994; Chlopecka, 1996; Sanchez et al., 1999; Ahnstrom and Parker, 1999).

Except the adsorbed and mineral phase defined in the previous section, Cd may form higher stability chelate complexes with soil organic matter which consist of a mixture of plant and animal products in various stages of decomposition. The decomposition of organic matter may release Cd into the solution phase. However, the kinetics is generally in scale of months and years and the organic matter content only accounts for a small portion of soils, thus the contribution from the mineralization may be negligible in a short time duration.

Based on outcomes reported in the published literature and results of preliminary experiments on material of known compositions, a sequential extraction procedure is devised to separate Cd in the soils into the adsorbed and mineral phases. In the sequential extraction procedure, the soil sample was first reacted with 20 ml of 1 M $CaCl_2$ at pH = 7.0 in a reciprocating shaker for 2 hr at room temperature (Young, 2000). The solution and solids were separated by centrifugation. The solution was saved and the recovered solid was treated two times with 10 ml deionized water, equilibrated for 30 minutes by shaking, and separated by centrifugation. The adsorbed phase Cd was obtained by determining the Cd concentration in the combined solutions. The residual solid was further treated by 20 ml of 1M HNO_3 (Soon and Bates, 1982) and equilibrated by shaking for 6 hr at room temperature. After centrifugation, the Cd in the solution was determined as the mineral phase Cd. The recovery rate based on this procedure may not be 100%, especially at higher loading of Cd. The fraction that is not dissolved in 1M HNO_3 generally is small and has a very low mobility thus has minor effects on the kinetics study.

Batch Cd Adsorption Experiments

The first set of batch adsorption experiments was conducted at initial Cd solution concentration of 50, 100, 200, 400, 600, 800, 1,000,1,500 and 2,000 □g l^{-1} with the equilibrium time equaled 48 hr. The second set of batch adsorption experiments was conducted at the initial Cd solution concentration of 100 □g l^{-1} and the equilibration time were 2 hr, 4 hr, 8 hr, 1 d, 2 d, 4 d, 6 d, 8 d, 10 d and 15 d. The different levels of Cd solution were obtained by diluting the Puro-Graphictm Calibration standard for atomic absorption (Buck Scientific, 1002 □g/ml Cd in 2% HNO_3) with 0.01 N $NaNO_3$. The soil to solution ratio of 1:20 (w/v) was used. The mixtures were allowed to equilibrate on a reciprocating shaker at room temperature. Following equilibration, samples were centrifuged, and the supernatant was decanted and filtered 0.45 □m Hydrophilic PVDF membrane filters. The sample solution is then determined by graphite furnace atomic absorption spectroscopy (AAS-GF). The solid phase was recovered and underwent the sequential extraction to recover those in the adsorbed phase and mineral phase.

Results and Discussion

Sorption at fixed equilibrium time:

Once introduced into the soil, Cd in solution phase will approach a dynamic equilibrium with those held on solid soil component. The adsorption isotherms of Cd for two California cropland soils, along with the contribution of the surface adsorbed and mineral phase, were plotted in Figure 5.1 and 5.2. The Cd adsorption isotherms are linear for the initial solution concentration ranging from 50 to 2,000 □g Cd l^{-1}. The slope for the Holtville clay loam soil and the Arlington sandy loam soil, namely the partitioning coefficient (K_d), is 7,760 and 5,554 l kg^{-1}, respectively. The K_d approach is the common way to describe the partition of trace elements between the solution and solid phase. However, not all of the Cd in the solid phases is available immediately. As shown in Figure 5.1 and 5.2, for both soils, most of the added Cd was present in the mineral phase, which means the release of this portion of Cd follows a kinetic reaction. The Cd in the adsorbed phase only account for a small portion. Based on the slope there, the linear partition coefficient (k_a in the equations) is 71- and 112-ml g^{-1} for the Holtville clay loam soil and the Arlington sandy loam soil, respectively, which is much less than the commonly used partitioning coefficient (K_d).

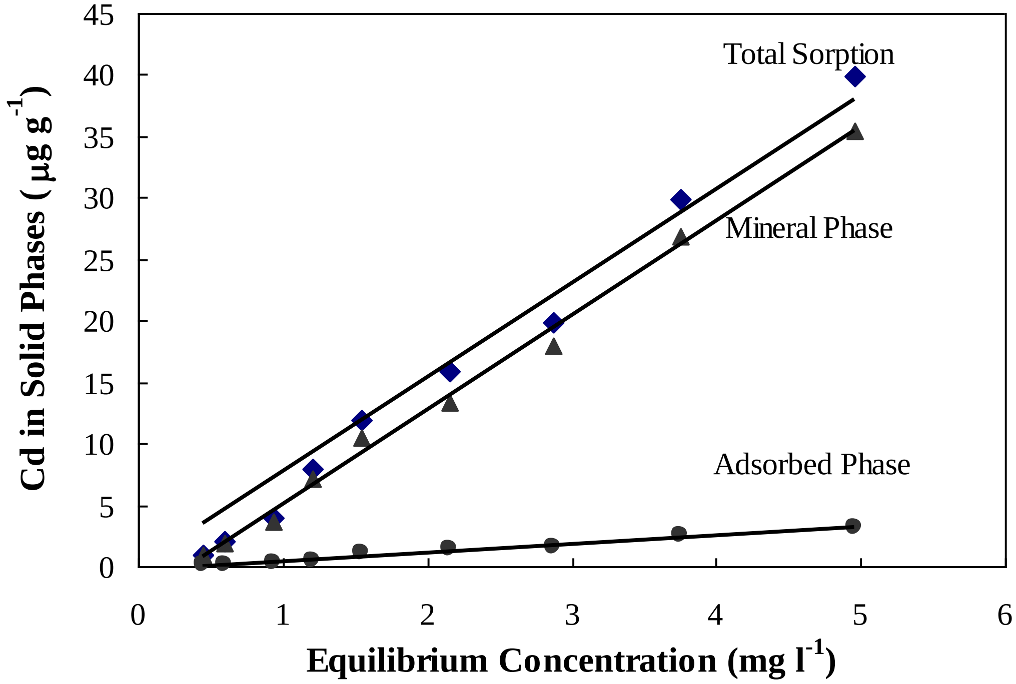


Figure 5.1. Adsorption isotherms of Cd for the Holtville clay loam soil equilibrated at 1:20 (w/v) for 48 hr at initial solution concentration ranging from 50 to 2,000 µg Cd l^{-1}.

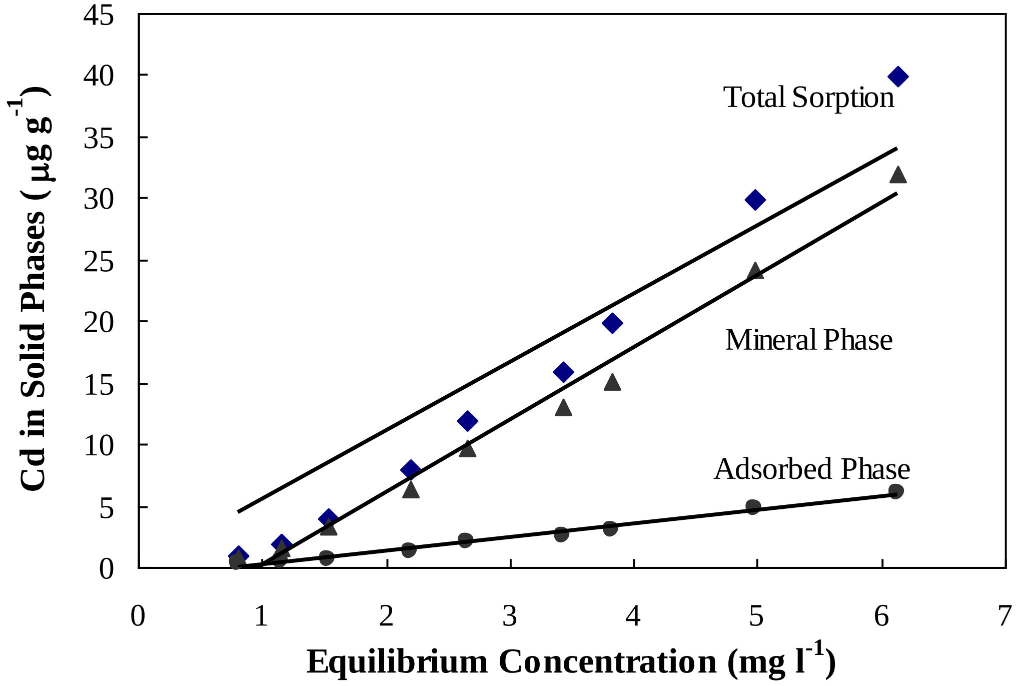


Figure 5.2. Adsorption isotherms of Cd for the Arlington sandy loam equilibrated at 1:20 (w/v) for 48 hr at initial solution concentration ranging from 50 to 2,000 µg Cd l^{-1}.

The kinetics parameters, k_f and k_b, can not be obtained since the equilibration time is fixed. As shown in equations 5.8 and 5.9, when t is fixed, equations 5.3 and 5.4 reduce to simply linear forms with zero intercept, which is given by:

$$C_{t=48} = a_1 \cdot C_0 \qquad \text{[Eq. 5.5]}$$

$$MP_{t=48} = a_2 \cdot C_0 \qquad \text{[Eq. 5.6]}$$

where a_1 and a_2 are functions of the water to soil ratio employed in the sorption experiment (R) and the kinetics parameters k_a, k_f and k_b. The equilibrium solution Cd concentration ($C_{t=48}$) and the amount of Cd retained in the mineral phase ($MP_{t=48}$) increase linearly in proportion to the initial solution concentration (C_0). The experimental results agreed with the theoretical prediction (Figure 5.3 and 5.4). The reaction kinetics in the Holtville clay loam was slightly faster than in the Arlington sandy loam, in which the equilibrium concentration is lower and much more Cd was retained in the mineral phase.

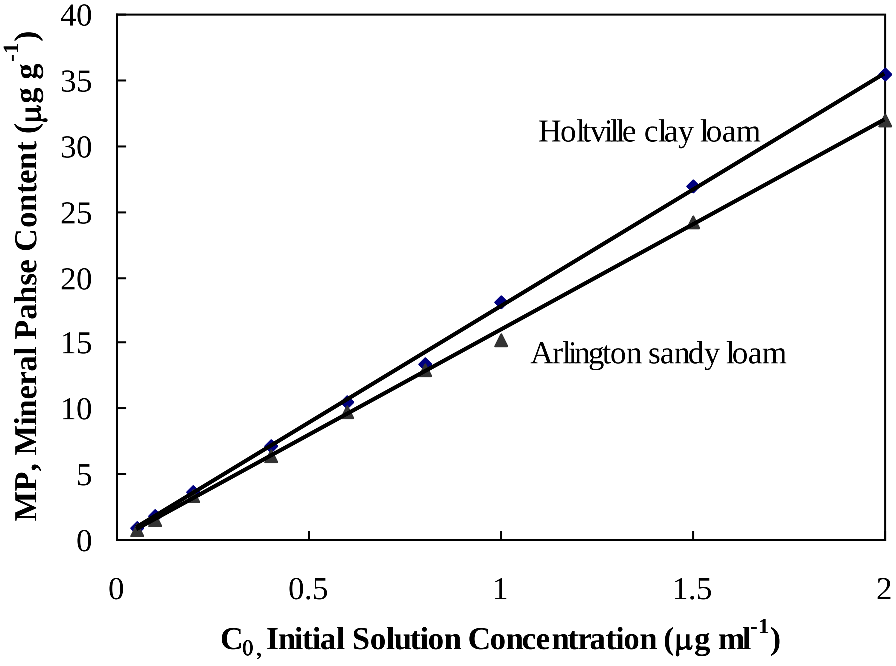


Figure 5.3. Cadmium adsorption: Retention in mineral phase (MP) against initial solution concentration (C_0), equilibrated at 1:20 (w/v) for 48 hr.

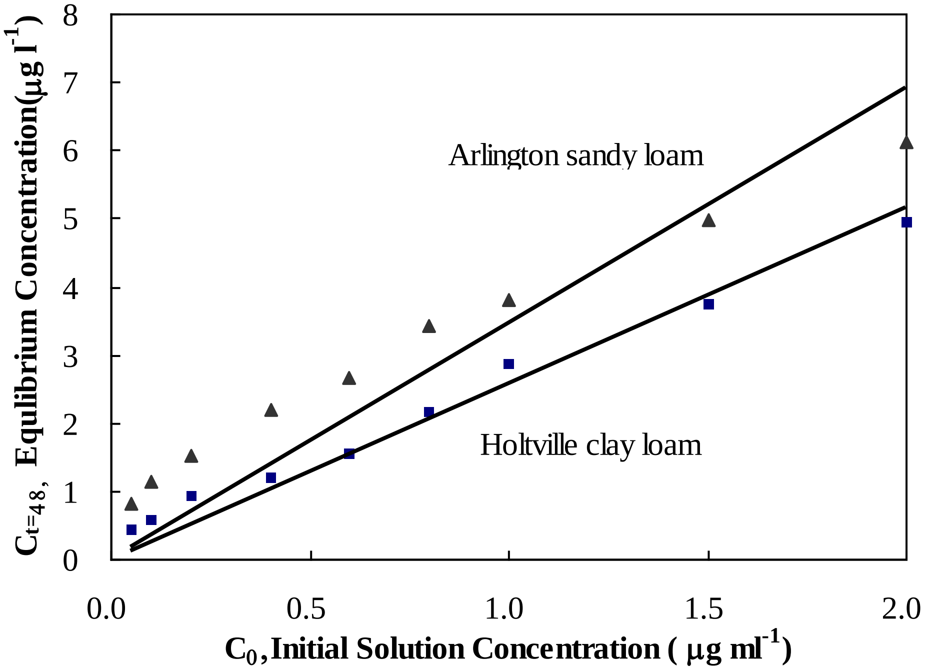


Figure 5.4. Cadmium adsorption: Equilibrium concentration against initial solution concentration, equilibrated of 1: 20 (w/v) for 48 hr.

Sorption at fixed initial solution concentration

To obtain the kinetic parameters, the batch adsorption experiments were conducted at initial Cd concentration in solution of 100 □g l^{-1} and equilibrated for periods from 2 hours to 15 days. Under the circumstances, the Cd solution concentration decreased exponentially to approach the equilibrium concentration and the amount of Cd in the mineral phase increased exponentially to approach the maximum with the time of equilibrating (Figures 5.5 and 5.6). The dynamic sorption can be described by Equations 5.3 and 5.4. When the initial solution concentration is fixed (C_0 = 0.1 □g ml^{-1}), equation 5.6 and 5.7 reduce to exponential forms, which are given by:

$$C_t = a_3 - a_4 \cdot (1 - e^{-b \cdot t}) \qquad \text{[Eq. 5.7]}$$

$$MP_t = a_5 \cdot (1 - e^{-b \cdot t}) \qquad \text{[Eq. 5.8]}$$

where a_3, a_4 and a_5 are functions of the water to soil ratio employed in the sorption experiment (R) and the kinetics parameters k_a, k_f and k_b, b are the sum of k_f and k_b.

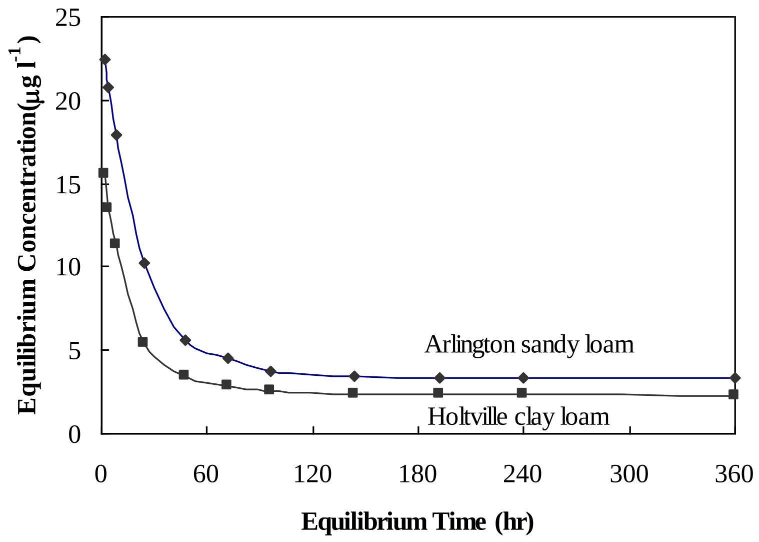


Figure 5.5. Cd solution concentration at different equilibration time of the Arlington sandy loam and Holtville clay loam, equilibrated at 1:20 (w/v) with initial concentration of 100 □g l^{-1}.

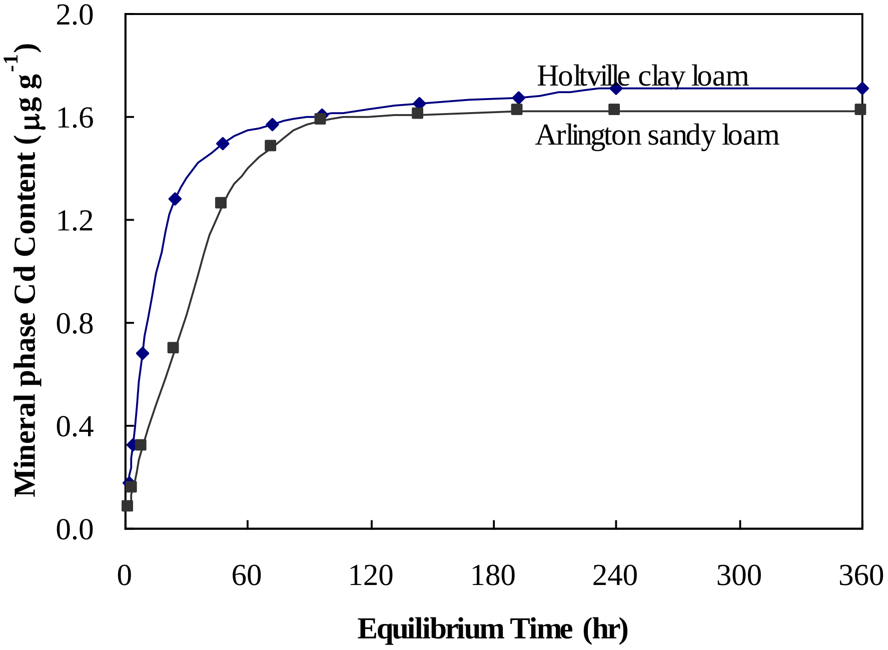


Figure 5.6. Cd in mineral phase of Arlington sandy loam and Holtville clay loam at different equilibration time, equilibrated at 1:20 (w/v) with 100□□g l^{-1}.

The experimental results agree with the conceptual framework defined by above equations. When the data is fitted into equation 5.5 or 5.6, the kinetic parameters of the forward and backward and reaction rates may be obtained if the linear Cd partition constant (k_a in the equation 5.6) was defined. The k_a values are the slope of linear regression of the Cd in the adsorbed phase vs. the equilibrium concentration (Figure 5.7), around 100 and 70 l kg^{-1} for the Holtville clay loam and the Arlington sandy loam, respectively. Table 5.2 summarizes the results for the forward and backward reaction rate constants (k_f and k_b) based on the solution concentration of Cd and Cd contents in the mineral phase.

Table 5.2. Fitting results of kinetic adsorption of Cd on the Holtville clay loam soil and the Arlington sandy loam soil

Parameter	Holtville Clay Loam		Arlington Sandy Loam	
	Based on Solution Conc. Data	Based on Mineral Phase Data	Based on Solution Conc. Data	Based on Mineral Phase Data
k_f (hr^{-1})	0.0517	0.0498	0.029	0.0229
k_b (hr^{-1})	0.0089	0.0105	0.005	0.0049
R^2	0.998	0.9939	0.9768	0.9949

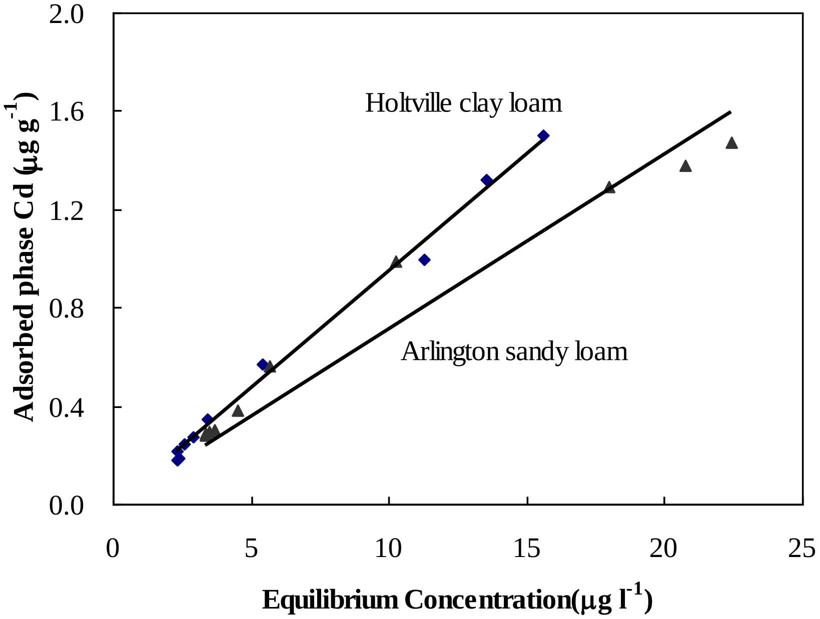


Figure 5.7. Cd in the adsorbed phase vs. equilibrium concentration of Arlington sandy loam and Holtville clay loam, equilibrated 1:20 (w/v) at 100 mg l^{-1}.

The k_f and k_b based on the solution concentration data and on the data of the mineral phase Cd contents are similar. The Cd adsorption experiments that varied the initial Cd solution concentration (fixed equilibration time) and experiments varied the equilibration time (fixed initial Cd solution concentration) produced the same outcomes. The precipitation dissolution kinetics of the Cd mineral phase in Holtville clay loam is approximately two times faster than that of the Arlington sandy loam. The ratios of k_f vs. k_b for Cd mineral phases are almost the same. For both, the forward reaction (dissolution) rate constant is about 5 times larger than the backward (precipitation) rate constant. Both sets of data are fitted well with the theoretical equations. The solution concentration data are easier to obtain and may be more reliable than the mineral phase Cd content data, since the latter may be affected by the extraction process of adsorbed phase. However, the fitted k_f and k_b are dependent on the value of k_a, which in turn dependent on extraction data of adsorbed phase. For example, if the k_a is 120 l kg^{-1} instead of 100 l kg^{-1}, the fitted k_f and k_b will be 0.06 hr^{-1} and 0.00024 hr^{-1}, respectively. For the mineral phase Cd content data, it is independent of k_a and the k_f and k_b can be obtained directly from the regression model.

The experiments were conducted at the 1:20 soil to water ratio and the mixtures were equilibrated with a reciprocating shaker. Unlike the field conditions, the contents were well mixed, and the reactions would be more complete. The reaction rate constants, k_f and k_b, are expected to be less in field conditions.

Conclusions

The developed two site model by combining a linear equilibrium reaction model and a first-order reaction kinetics model can describe the dynamic sorption of Cd in two California soils very well. The model can be further used to predict the fate and transport of trace elements in soils and assessed the hazard associated with the introduction of trace element containing compounds to the soil system. The characterized kinetic parameters can be obtained by conducting the batch adsorption experiments at fixed initial Cd solution concentration and fitting into the theoretical equations, based on either the solution concentration data or on the data of the Cd retained in mineral phase. Both approaches fitted well with the theoretical equations and give similar results. The solution concentration data are easier to obtain but the fitted k_f and k_b are dependent on the fitted K_d. Although the data of mineral phase content are harder to obtain and may affected by the extraction process, the fitted k_f and k_b are independent on the value of K_d.

Chapter 6

Risks Associated with Trace Element in Phosphate Fertilizers

The possible risks derived from the increasing amount of toxic trace elements such as arsenic (As) and cadmium (Cd) in cropland soils through application of fertilizers, irrigation water, and other amendments have resulted in growing public health concerns. The fate and transport of these trace elements in agricultural environments is greatly affected by the soil and plant characteristics. In this study, we used a generalized mass balance model previously developed to evaluate the long-term fate and transport of trace element in cropland soils. Based on the results of model simulation, the normal cropping practices do not have significant effect on the total soil As content, but the application of Cd-contaminated P-fertilizers could have a significant long term effect on soil Cd accumulation therefore risks of transfer through the food chain. The model simulation indicates that the existing regulations are not strict enough to avoid the accumulation of Cd in cropland soils. Sensitive analyses show the solid-solution partitioning coefficient (K_d) and the plant uptake factor are two key factors that affect the fate and transport of As and Cd in soil. Monte Carlo simulations show that a great deal of uncertainty is associated with the fate of trace elements in soils due to high variability of model parameters.

The details of the simulations and the findings are presented in the following sections.

Approach

For a trace element in soils, the one-dimension conservation equation of the transport may be written as:

$$\frac{\partial C_t}{\partial t} + \frac{\partial J_s}{\partial z} + r_s = 0 \qquad \text{[Eq. 6.1]}$$

where C_t is the total trace element content of soil, J_s is the flux of trace element in the direction of z and r_s is a production term representing sources and sinks of the species.

In soil, most trace elements are not readily soluble and remain mostly in solid phase. They are adsorbed by solid phases including clays and organic matter, associated with the primary minerals, or formed insoluble precipitates. Trace elements in the soil solution are of special interest as they are readily accessible to plants and mobile through the vadose zone to reach underground waters. The dynamic and interactive processes between solution and solid phases govern their concentrations. The formation of trace element solid phases may be represented by a two-site model to be articulated later (Eqs.6.3 and 6.4), in which the rapid reversible surface adsorption and desorption reaction is quantified by a thermodynamic equilibrium distribution model and the slower process of immobilization characterized by precipitation, co-precipitation with other minerals on surface and intra particle sites of soil solids and the dissolution is simulated by a first-order kinetic equilibrium (Chen, et al, 2006). In addition, a part of trace element uptaken by plants will return to soil as crop residues. Mineralization of the crop residues in the soil may release the trace elements back into the solution and surface adsorbed phases according to a first-order kinetic.

Correspondingly, the above-described trace element components in soils may be distributed into four phases and the total trace element content of the soil, C_t in equation 1 may be defined as:

$$C_t = \theta \cdot C + Ad + MP + Org \qquad \text{[Eq. 6.2]}$$

where θ is the volumetric water content (l water l soil^{-1}); C is soil solution concentration (μM); Ad, MP and Org refer to the element in the surface adsorbed phase, immobilized mineral phase and organic matter phase (μmol l soil^{-1}), respectively and C_t is in □mol l soil^{-1}. The kinetics between these phases is described by the following equations that:

$$Ad = K_d \cdot C \qquad \text{[Eq. 6.3]}$$

$$\frac{\partial MP}{\partial t} = k_f \cdot (K_d + \theta) \cdot C - k_b \cdot MP \qquad \text{[Eq. 6.4]}$$

$$\frac{\partial Org}{\partial t} = k_{im} \cdot Org \qquad \text{[Eq. 6.5]}$$

where K_d is the linear adsorption constant (l soil solution l soil^{-1}); k_f and k_b is the forward and backward first order reaction rate constants for immobilization and dissolution (hr^{-1}), respectively; k_{im} is the first order mineralization rate (hr^{-1}).

The solute transport through soils (Js term in Eq. 6.1) was modeled by using the convective-dispersive transport equation. For trace elements such as Cd and As, the transport due to dispersion is not significant as the solution concentrations are quite low. The solute transport through the homogeneous soil layer may be reduced to:

$$\frac{\partial Js}{\partial t} = \frac{K_h \cdot \theta \cdot C}{d} \qquad \text{[Eq. 6.6]}$$

where K_h is the percolation rate (cm hr^{-1}); d is the depth of soil layer (cm).

In cropland soils, the source and sink terms (r_s) may include the external input term (I), uptake of trace element by plant roots (U), surface runoff, weathering of bedrock, and possible volatilization as organic form. Compared to the annual inputs from irrigation, fertilizers, atmospheric deposition, the contribution from the weathering processes is very small and can be neglected. Relative to the loss term from plant uptake, the surface runoff in irrigated croplands may also be neglected (Chang and Page, 2000). Likewise, for most trace elements, the volatilization loss is negligible.

Applied above outlined mathematical terms (i.e. Eqs. 6.2 through 6.6) to the conservation equation and rearranged Eq. 5.1, the governing equation for the mass balance is as follows:

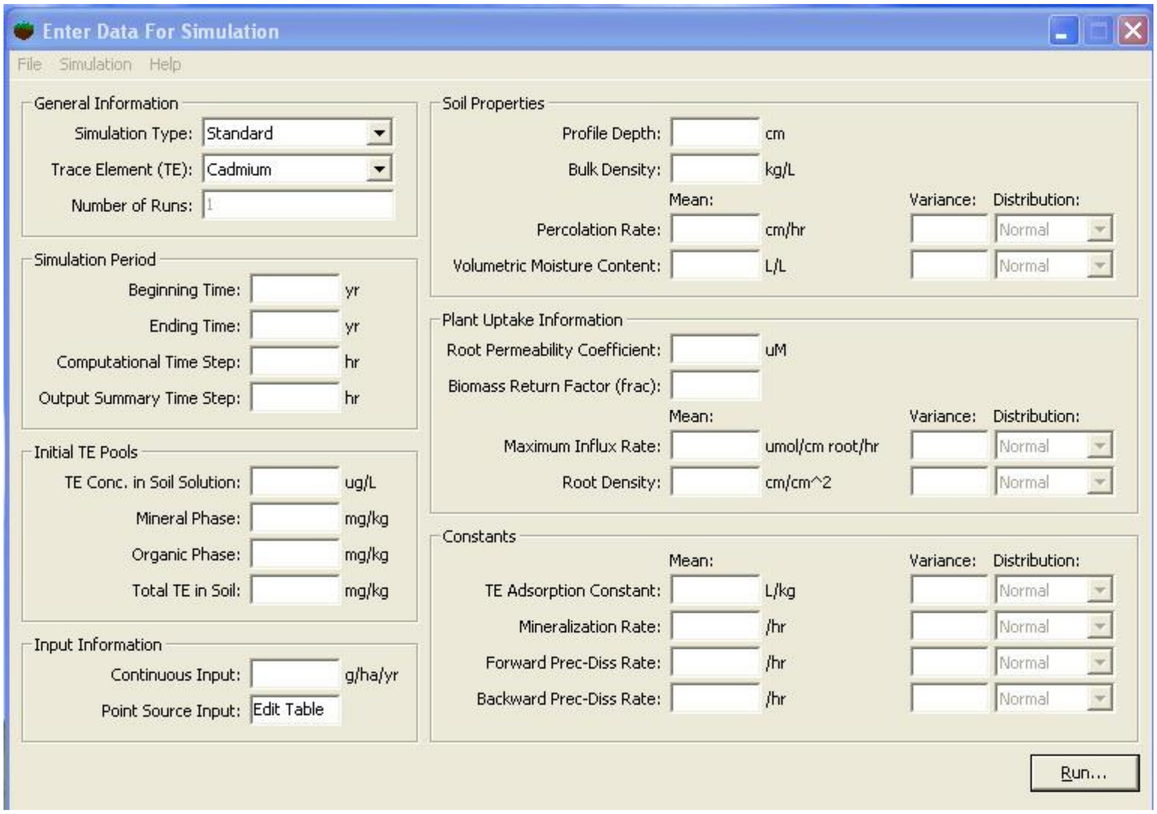
$$(K_d + \theta) \cdot \frac{\partial C}{\partial t} = I - U - K_h \cdot \theta \cdot \mathrm{C/d} + k_{im} \cdot Org - k_f (K_d + \theta) \cdot C - k_b \cdot MP \qquad \text{[Eq. 6.7]}$$

The plant uptake of elements from soil (*U*) depends on the plant demand (absorption) and the soil supply. In the model, the Michaelis-Menton type relation was used to simulate the absorption of elements at the root surface. The plant uptake rate (μmol cm^{-3}soil hr^{-1}) was described as:

$$U = \frac{R \cdot J}{d} \qquad \text{[Eq. 6.8]}$$

$$J = \frac{J_{max} . C}{K_m + C} \qquad \text{[Eq. 6.9]}$$

where R is root density (cm root cm^{-2}soil) in the soil layer of depth d (cm), J (μmol cm^{-1} root hr^{-1}) is the flux of trace element uptake by roots which is described by the Michaelis-Menten kinetics equation; J_{max} is the maximum J, K_m is the root permeability coefficient (μM) corresponding to the C at J = 50% J_{max}. R, J_{max}, and K_m are characteristics of the crop species. In addition, a biomass return factor was used to account for the biomass re-incorporation, in which part of trace element uptake by crops returns back into soil every 6 months. The fraction of biomass returned would be a function of the crops.



Simulation Type: Standard

Trace Element (TE): Cadmium

Number of Runs: 1

Point Source Input: Edit Table

Distribution: Normal

Figure 6.1. Input screen of the generalized mass balance model showing input parameters required for the calculations.

Model Parameters

The mass balance model is mathematically generic in nature as the distribution of any trace element in soils may be divided into the pools as outlined in the previously presented equations and the transformations between pools may be characterized by the same set of reactions. The model, therefore, may represent the mass balance of any trace element when the initial conditions of its distribution in soils and the reaction rate constants are defined accordingly. To demonstrate its efficacy, the model was used to evaluate the mass balance of As and Cd in cropland soils as affected by various soil properties and plant trace element uptake factors. Information extracted from the published literature and data from specially designed experiments were employed to define the initial conditions and the reaction rate constants needed for the computations.

1. Distribution and Kinetic Constants for As and Cd

The As and Cd concentrations of cropland soils vary considerably. The initial As and Cd in cropland soils is set to 7.6 and 0.22 mg kg^{-1}, respectively, based on the mean levels found in the benchmark soils of California. (Bradford et al, 1996; Krage, 2002). They represent the baseline concentrations in uncultivated soils

The kinetic parameter, k_a, k_f and k_b, may be obtained by fitting the batch adsorption experimental data to a two-site adsorption kinetics model (Eqs. 6.3 and 6.4). Based on results of separate experiments with cropland soils in California, the linear adsorption constant (k_a) is set to150 l kg^{-1} for As and 100 l kg^{-1} for Cd, the forward and backward precipitation/dissolution rate is set to 0.01 hr^{-1} and 0.001 hr^{-1} for As, and 0.01 hr^{-1} and 0.002 hr^{-1} for Cd respectively (Chen, 2006). In the model simulation, the organic to inorganic mineralization rate, k_{im}, is set to 10^{-6} hr^{-1} which was based on the equation provided by Ruhlmann (1999) with 1.5% of soil organic carbon content and 25% (by weight) of soil mineral particles that are less than 20 μm. Assuming that 5% of the total trace element is in the organic phase and the trace element in mineral phase and adsorbed phase are in kinetic equilibrium with the respective soil solution concentrations at the beginning of the simulation, the initial distribution of As and Cd in soils may be defined.

The distribution of As and Cd among the pools may be defined by outcomes of the sequential extractions (Chen, 2005). A general fractionation scheme separates the trace element in soil into water soluble, exchangeable, sorbed, carbonate, Fe/Mn oxides, organic and residual. Based on the premise of a sequential extraction, the fractions may be combined that the water soluble and exchangeable fractions represent the adsorbed phase (Ad), the sorbed, carbonate, and Fe/Mn oxides fractions represent the inorganic mineral phase (MP), and organic fraction corresponds to the organic phase (Org) in the simulation model.

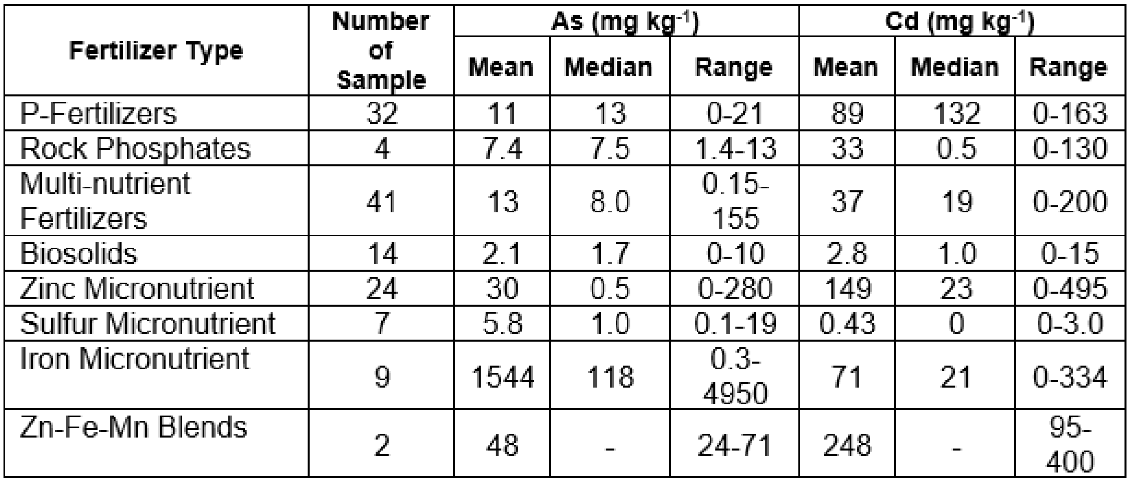
2. Input Sources

The As and Cd inputs to cropland soils come primarily from three sources, namely the atmospheric fallouts, irrigation and P fertilizers. Chang and Page (2000) estimated the atmosphere deposition of trace elements on the cropland soils in California based on the air quality monitoring data of the San Joaquin Valley and the settling velocity of airborne particulates. They reported the atmospheric fallout rates of 5 g As ha^{-1} yr^{-1} and 5 g Cd ha^{-1} yr^{-1}. The input from irrigation is dependent on the amount of water applied and trace element concentration of the irrigation water. The maximum contaminant levels (MCL) for As and Cd in drinking water are 10 and 5 μg l^{-1}, respectively (USEPA standard). The concentrations in the irrigation water are expected to be considerably lower. Chang and Page (2002) estimated that the As and Cd inputs from irrigation water are 25 and 2 g ha^{-1} yr^{-1}, respectively, assuming an application rate of 1.2 m yr^{-1} water and 2.08 μg l^{-1} As and 0.17 μg l^{-1} Cd, derived from the contents of the San Joaquin River. The values in Chang and Page (2002) were used for the concentrations in irrigation water.

The trace element contents of selective commercial fertilizers in California were reported by California Department of Food and Agriculture (CDFA, 1997). The As and Cd contents in the sampled phosphorus fertilizers are summarized in Table 6.1. Based on the collected data from U.S. EPA (1999), the P-fertilizer use on vegetable crops for the 1994 crop year in California may vary from less 70 kg P_2O_5 ha^{-1} for cucumber to as much as 454 kg P_2O_5 ha^{-1} for pepper (bell). The median application is around 110 kg P_2O_5 ha^{-1} yr^{-1}. The commonly used P fertilizers contain 45 – 55% of P_2O_5. Assuming an average of 50% P_2O_5 in P fertilizers, the mean input is around 2.5g As ha^{-1} yr^{-1} and 20 g Cd ha^{-1} yr^{-1}

The default As and Cd inputs for cropland soils are the sum of inputs from the three above-referenced sources and they amount to 32.5 g As ha^{-1} yr^{-1} and 27 g Cd ha^{-1} yr^{-1}. In the simulations, the atmospheric deposition is treated as a continuous input while the P fertilizers is a discrete input at the starting of each growing season and the irrigation is divided evenly into 5 discrete inputs over the growing season.

Table 6.1. As and Cd contents of selected commercial fertilizers of California (CDFA, 1997).



Fertilizer Type	Number of Sample	As (mg kg^{-1})			Cd (mg kg^{-1})		
		Mean	Median	Range	Mean	Median	Range
P-Fertilizers	32	11	13	0-21	89	132	0-163
Rock Phosphates	4	7.4	7.5	1.4-13	33	0.5	0-130
Multi-nutrient Fertilizers	41	13	8.0	0.15-155	37	19	0-200
Biosolids	14	2.1	1.7	0-10	2.8	1.0	0-15
Zinc Micronutrient	24	30	0.5	0-280	149	23	0-495
Sulfur Micronutrient	7	5.8	1.0	0.1-19	0.43	0	0-3.0
Iron Micronutrient	9	1544	118	0.3-4950	71	21	0-334
Zn-Fe-Mn Blends	2	48	-	24-71	248	-	95-400

3. Soil Property Parameters

The amount of water loss by deep percolation is dependent on factors such as soil type and irrigation. For the default simulation, the percolation rate, K_h, is set to 0.02 cm hr^{-1} and the field moisture content, θ, is set to 0.25 cm^3 cm^{-3}. In this case, the leaching fraction is 36.5%, assuming the annual irrigation application is 1.2 m.

4. Plant Uptake Parameters

In the model, the plant uptake rates are calculated in terms of the As and Cd concentrations in the soil solution (*C*), root density (*R*) and plant uptake flux (*J*), which is expressed in terms of the Michaelis-Menton kinetics maximum influx, J_{max} and root permeability factor, K_m. Studies on plant absorption of As (Meharg and Macnair, 1992;Abedin et al., 2002;Wang et al, 2002) and Cd (Cataldo et al.,1983; Mullins, 1986; Zhao et al., 2002) customarily employed hydroponics techniques and the As^{5+} and Cd^{2+} concentrations of the nutrient solutions were considerably higher than the concentrations in the soil solution of agricultural soils. In addition, absorption rates were often overestimated because corrections for metal binding by cell-wall materials in the root cell apoplasm were inadequate (Rauser, 1987). Moreover, most kinetic experiments were done with young roots. Nevertheless, the data illustrated the dynamic nature of the plant absorptive processes and the ranges where the kinetics parameters for plant absorption might lie. For the default simulation, we set the maximum influx rate, J_{max} to be

0.00001□□mol cm root^{-1} hr^{-1} for As and 0.0000005□□mol cm root^{-1} hr^{-1} for Cd, approximately one order of magnitude less than the report values in the technical literature. The root permeability coefficient, K_m, is set to be 30 □M for As and 0.1 □M for Cd. In addition, the root density is set to 5 cm root cm^{-2} of root zone, which is corresponding to the typical root density of matured crop plants. Each year is divided into two 6-month growing seasons. Fifty percent of the biomass harvest along with the proportional amounts of the plant-absorbed As and Cd is reincorporated as a discrete organic matter input at the starting of each growing season.

The default model parameter values based on the above discussions are summarized in Table 6.2.

Table 6.2. Parameter values for the default simulation of As and Cd mass balance of irrigated cropland soils.

Parameters	Arsenic	Cadmium
Initial Trace Element Pools of Soil		
Total Content (mg kg^{-1})	7.70	0.22
Mineral Phase (mg kg^{-1})	6.65	0.174
Organic Phase (mg kg^{-1})	0.385	0.011
Soil Solution Concentration (□M)	6.64	0.35
Soil Properties		
Profile Depth (cm)	30	30
Bulk Density (kg l^{-1})	1.40	1.40
Hydraulic Conductivity (cm hr^{-1})	0.02	0.02
Volumetric Water Content (l l^{-1})	0.25	0.25
Plant Uptake		
Root Permeability Coefficient (□M)	30	0.1
Maximum Influx (□mol cm^{-1} hr^{-1})	10^{-5}	5×10^{-7}
Root Density (cm cm^{-2})	5	5
Biomass Return Factor (-)	0.5	0.5
Reaction Constants		
Forward dissolution/Precipitation Rate (hr^{-1})	0.01	0.01
Backward dissolution/Precipitation Rate (hr^{-1})	0.001	0.002
Mineralization Rate Constant (hr^{-1})	10^{-6}	10^{-6}
Adsorption Constant (l kg^{-1})	100	100
Trace Element Inputs (g ha^{-1} yr^{-1})	32.5	27

Results and Discussion

Default Simulations

The temporal changes of soil As and Cd in 100 years of continuous cultivation under conditions defined by the default parameters (Table 6.2) are summarized as Figure 6.2.

It appears that the cropping practices do not have a significant long-term effect on the total As content of the cropland soils, but have an impact on total Cd content of the soils which will be significantly increased. Over the 100-year simulation period, the total soil arsenic content shows a decreasing trend despite of annual input of 32.5 g ha^{-1} yr^{-1}. The actual decrease from the initial level of 7.70 mg kg^{-1} to the final level of 7.66 mg kg^{-1} is mathematically distinguishable but realistically not measurable. This level of changes in total concentration would well be within the range of spatial variations expected in soil samplings. On the other hand, the soil Cd level almost increases three times over 100-year simulation period, from 0.22 to 0.62 mg kg^{-1}. The time needed to double the baseline concentration level of Cd is less than 50 years. The application of Cd-contaminated P-fertilizers could have a significant long-term effect on the Cd concentration of the soils therefore heightens the risks of transfer through the food chain. Krage (2002) showed through measurements made in field collected samples, the As contents of cropland soils in California were slightly less than that of the benchmark soils and the Cd contents of the cropland soils in California were significantly above that of the benchmark soils. The benchmark soils were typical soils in California that have not been previously cultivated.

The agricultural activities tend to increase the soluble fraction of As and Cd (Figure 6.2). The As concentration of the soil solution increases slightly from 6.64 to 6.74 □g l^{-1} while the total As content of the soil decreases. There is a significant increase of cadmium in soil solution. Over the 100-year simulation period, the Cd concentration of the soil solution increases from 0.35 to 0.87□□g l^{-1}. The higher solution concentration invariably indicates greater potential for the element to be absorbed by plants and to be leached below the root zone.

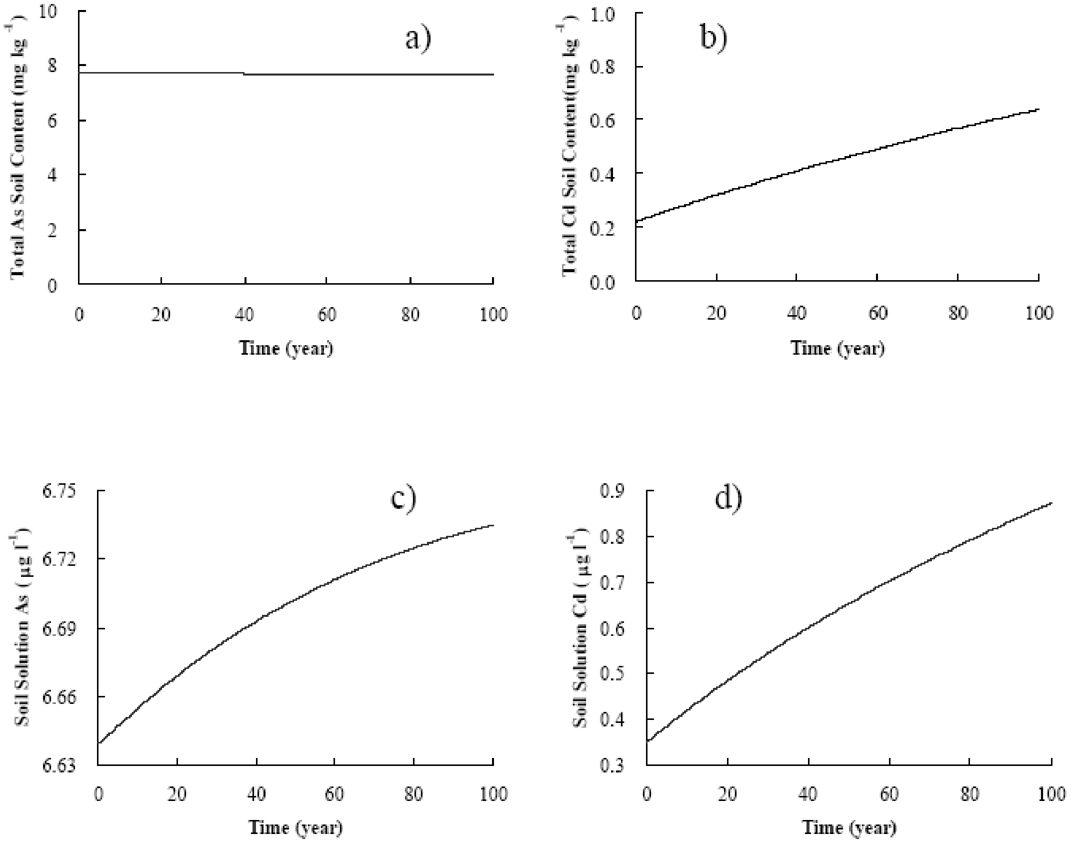
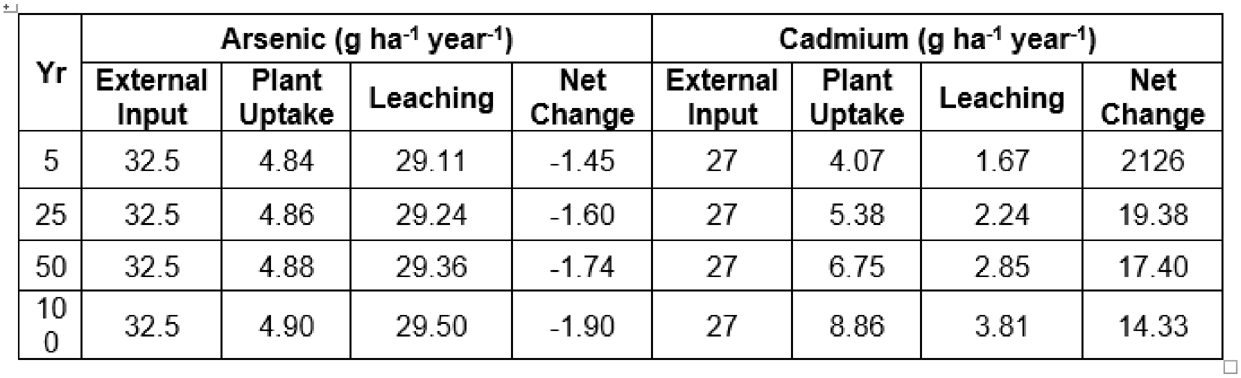


Figure 6.2. Temporal changes of soil As content (a), soil Cd content (b), As concentration of the soil solution, (c), and Cd concentration of the soil solution (d) in 100 years of continuous cultivation at the default parameters.

Data on the annual mass balance show over time the annual As and Cd uptake by plants and the leaching loss in proportion to the rise of their concentration in soil solution (Table 6.3). The rates appear to follow the first order reaction models. The fate of As and Cd in cropland soils is dominated by the leaching process and plant uptake process, respectively. In crop production systems, potentially there are higher risks for As being transported to the groundwater or surface water and for Cd being transferred through food chain.

Table 6.3. Annual As and Cd mass balances after selected years of cultivation.



Yr	Arsenic (g ha^{-1} year^{-1})				Cadmium (g ha^{-1} year^{-1})			
	External Input	Plant Uptake	Leaching	Net Change	External Input	Plant Uptake	Leaching	Net Change
5	32.5	4.84	29.11	-1.45	27	4.07	1.67	2126
25	32.5	4.86	29.24	-1.60	27	5.38	2.24	19.38
50	32.5	4.88	29.36	-1.74	27	6.75	2.85	17.40
100	32.5	4.90	29.50	-1.90	27	8.86	3.81	14.33

The simulated outcomes on leaching and plant uptake are in general agreements with the reported data of the cropland soils. Chang and Page (2000) estimated rate of removal for selected trace elements in soils of the San Joaquin Valley through subsurface drainage showing the leaching rate of As may range from 6 to 270 g ha^{-1} year^{-1} depending on the geological settings. For Cd, an estimated 3 g ha^{-1} year^{-1} was lost through subsurface drainage. Kabata-Pendias and Pendias (2001) showed that Cd leaching ranged from 0.3 g ha^{-1} year^{-1} for agricultural land in Denmark to 7 g ha^{-1} year^{-1} for a deciduous forest in Tennessee.

Chang and Page (2000) estimated that the alfalfa crop grown in San Joaquin Valley remove approximately 6 g ha^{-1} year^{-1} of both As and Cd. Beneš (1994) reported 9.4g As ha^{-1} yr^{-1} and 2.6 g Cd ha^{-1} yr^{-1} were removed by crops grown on uncontaminated soils. Jackson (1990) showed that lettuce and cabbage absorbed 0.25 to 21.67 g ha^{-1} yr^{-1} and 0.09 to 42.95 g ha^{-1} yr^{-1} of Cd respectively from the sludge-treated soils. Boo (1990) summarized data in technical literature and showed that the uptake of As and Cd selected crops were 1.20 and 1.40 g ha^{-1} year^{-1} for potatoes, 0.79 and 3.2 g ha^{-1} year^{-1} for winter oats and 0.79 and 4.50 g ha^{-1} year^{-1} for spring barley, respectively. Kabata-Pendias and Brümmer (1991) calculated the Cd budgets of agricultural soils in Poland and Germany. In Poland, the total Cd input from fertilizers, slurry, sludges, harvest residues and atmospheric depositions was around 10.5 to 13.5 g ha^{-1} year^{-1}, the outputs of crop removal and loss through seepage water were respectively 3 g ha^{-1} year^{-1} for each pathway. In Germany, the Cd inputs were 4.3 to 47 g ha^{-1} year^{-1} and the outputs were 1 to 5 g ha^{-1} year^{-1} for crop removal and 1to 2 (g ha^{-1} year^{-1}) for loss through seepage water.

In both cases, there were net inputs indicating over time Cd accumulation in the cropland soils.

While direct comparisons are uncalled for, leaching losses and plant uptake of As and Cd simulated by the model are in general agreements with data reported in the technical literatures. It appears to indicate results of the simulations were in the reasonable range.

Factors Affecting Trace Element Accumulation in the Cropland Soils

Loading rate. The input rates from different types of fertilizers to individual fields depend on the fertilizer type and application rate. The concentrations of trace elements in commonly used soil amendments vary considerably as shown by data summarized in Table 6.1. At extreme cases (based on the data from CDFA, 1997) that a type of blend N-P-K fertilizer (14.2-13-30.2) containing 155 mg As kg^{-1} is applied at rate of 2153 kg^{-1} ha^{-1} for root crops, the input for As may be as high as 330 g ha^{-1} yr^{-1} . For Cd, the input may be as high as 360 g ha^{-1} yr^{-1} when a type of phosphate rock containing 130 mg Cd kg^{-1} is applied at rate of 2800 kg ha^{-1} for root crops.

Guidelines and standards have been promulgated for maximum permissible trace element levels in phosphate fertilizers. The corresponding annual As and Cd inputs were calculated assuming an average of 50% P_2O_5 in phosphate fertilizers and annual application rate of 200 kg ha^{-1} yr^{-1}. The potentials for As and Cd to accumulate in cropland soils when P fertilizers containing the threshold levels of As and Cd are applied while inputs from irrigation water and atmospheric deposition remain unchanged may be simulated (Figures 6.3 and 6.4). At the extreme case, the total As content of the soil is almost doubled over 100 year period of time, from 7.70 to 15.04 mg kg^{-1} and the total Cd content of the soil increased to 0.22 to 7.34 mg kg^{-1}. The accumulation of As in the affected soils is not significant when the mass balances are evaluated based on the thresholds established by various entities. The cadmium enrichment over time, however, is substantial even under the most restrictive thresholds (i.e. California). the European Union (EU) has adopted the stepwise limit on the Cd content of P fertilizers that below 60 mg Cd kg^{-1} P_2O_5 by 2006, 40 mg Cd kg^{-1} P_2O_5 by 2010 and 20 mg Cd kg^{-1} P_2O_5 by 2015. At the conventional annual application rate of 250 kg P_2O_5 per hectare, they are equivalent to inputs of 16.8, 11.2 and 5.6 g Cd ha^{-1} yr^{-1}, respectively. The final target at 2015 is similar to Cd input rate used in the default simulation (i.e. 6 g Cd ha^{-1}yr^{-1}).

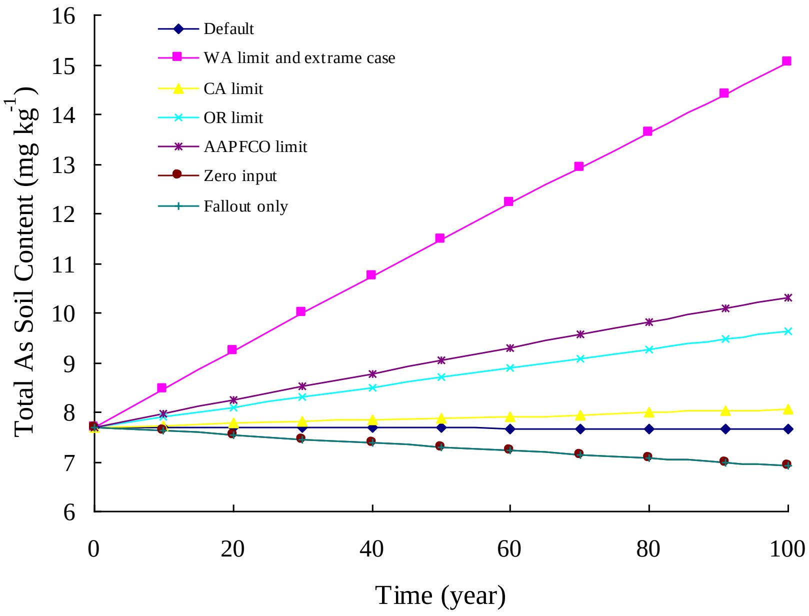


Figure 6.3. Temporal changes of arsenic at different loading rate cases.

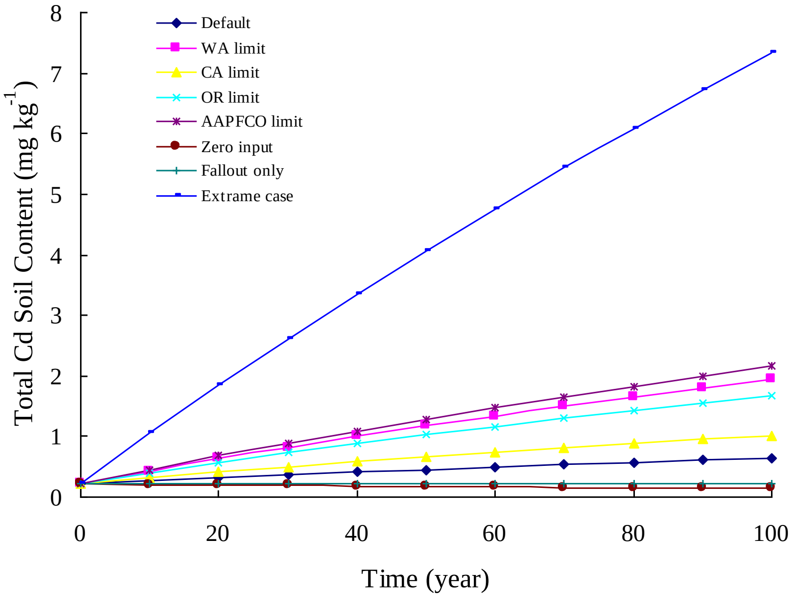


Figure 6.4. Temporal changes of cadmium at different loading rate cases

Correlation analyses show that the total As and Cd contents of the receiving soils after 100 years of continuing P fertilizer applications is in direct proportion to the annual inputs.

Current guidelines and standards were established based on the risk assessments and tolerated slow rise of the trace element contents in the receiving soils. To avoid the accumulation in receiving soils, the input rate of As and Cd should not exceed 33 and 3 g ha^{-1} yr^{-1}, respectively.

Soil and plant characteristics. The leaching potential of the soils may vary more than 100 folds from those in sand to those in clay. Absorption of As and Cd by plants is highly dependent on plant species. The concentration of Cd in plant tissues may vary from trace amounts in barley and oat to as high as 0.5 mg kg^{-1} fresh weight in spinach and lettuce. Three parameters: the solid and solution phases partitioning coefficient K_d, percolation rate K_h, and maximum influx rate J_{max} are representative of the spectra of soils and plant species. In simulations, different types of soils may be represented, by specifying different values for the parameters denoting the soil properties. By the same token, the parameters characterizing the plant uptake of trace elements are representatives for different plant species.

The linear solid-solution distribution coefficient, K_d, characterizes the soil's ability to retain the As or Cd in the solid form. It has direct impact on the amount of As and Cd accumulated in the soils, especially when the K_d is less than 1000 (Figure 6.5). As the K_d rises (i.e. soil retains incrementally more trace elements), the amounts held in the sinks of the mass balance of the soil, leaching and plant uptake, diminish and the amounts accumulate in the soils proportionally increase. When K_d exceeds 1000, the total As and Cd contents of the receiving soils rapidly approach a plateau indicating a steady state in the mass balance.

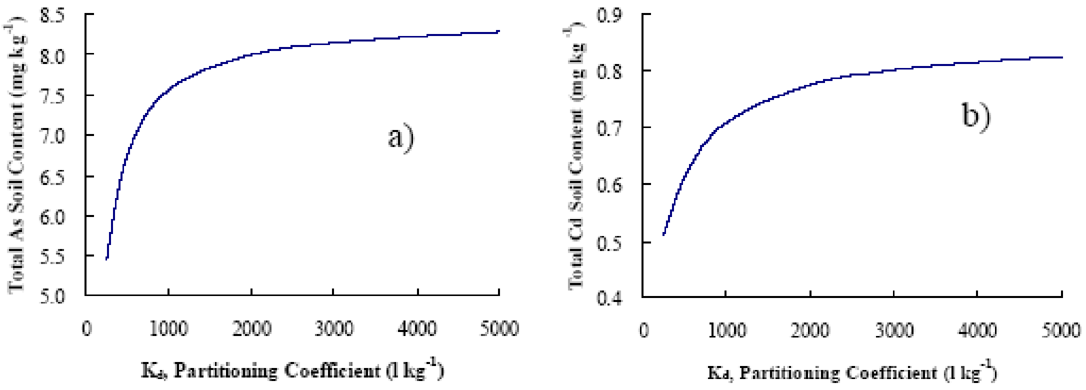


Figure 6.5. Effect of partitioning coefficient (K_d) on accumulation of (a) As and (b) Cd in cropland soils

The sensitivity analysis of the parameters showed that the accumulation in the soil, plant uptake and leaching loss are inter-related (Figures 6.6 and 6.7). The extent of leaching losses decreases as the percolation rate decreases, in turn, results in a higher concentration in the soil solution and greater level of plant uptake. Consequently, the percolation rate, K_h, has minor effects on the total As and Cd contents of the receiving soils when plant uptake rate, J_{max}, is high (i.e. plants accumulate trace elements). Leaching loss will have pronounced effect on the accumulation of As and Cd in the receiving soils when the plant uptake rate, J_{max}, is low (i.e. plants not accumulating trace elements). In food chain, the transfer of potentially toxic elements is customarily evaluated by the steady state transfer factor between the soil solution and plant tissue that the plant uptake factor, PUF = [Concentration in plant tissue (mg kg^{-1})]/[Concentration in soil solution (mg l^{-1})] (CDFA, 1997). The plant uptake is dynamic process and inter-related to other attributes in the soils. Judging from the outcomes of the parameter analyses, it may not be an appropriate approach.

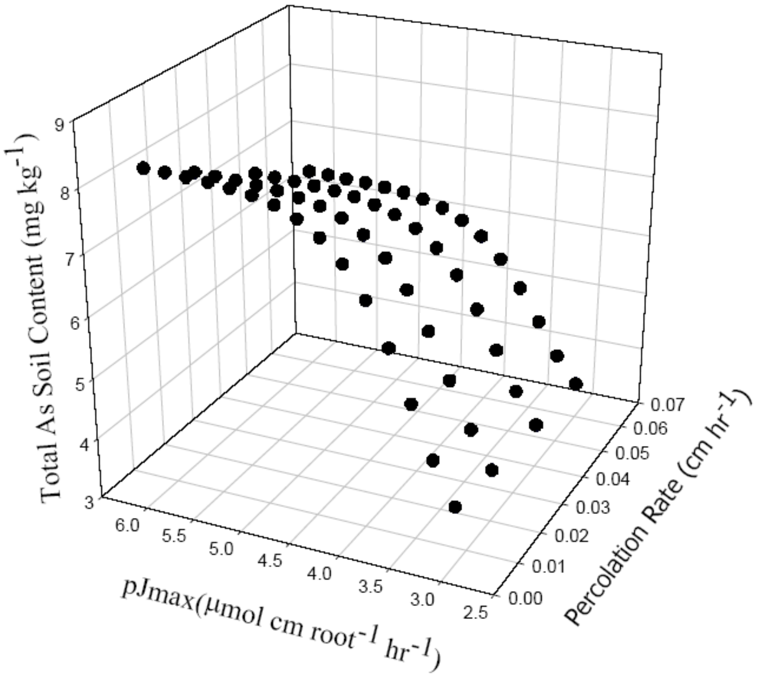


Figure 6.6. Effect of percolation rate and maximum influx rate on accumulation of As (pJ_{max}: negative log of the maximum influx rate).

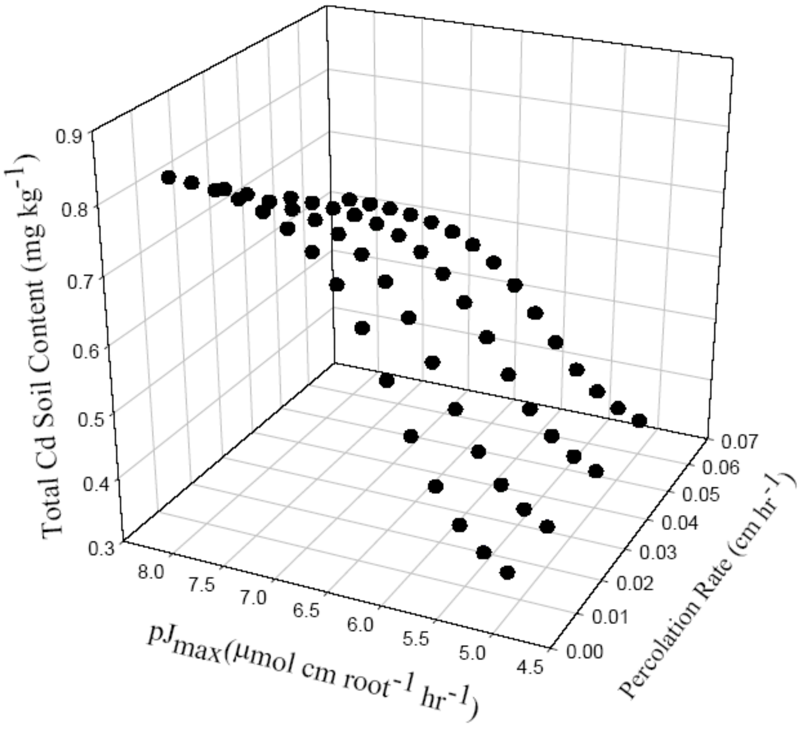


Figure 6.7. Effect of percolation rate and maximum influx rate on accumulation of Cd (pJ$_{max:}$: negative log of the maximum influx rate).

Uncertainty Analysis

The mass balance of As and Cd in the receiving soils are sensitive to the chemical property of the soils, K_d and plant uptake factor, J_{max}, which exhibited a high degree of variability and would be different for different plant species and soil types. Monte Carlo simulation was employed to evaluate the uncertainty associated with the model predictions for 100 years of fertilizer application (Figures 6.8 and 6.9). The statistical attributes of each parameter included in the Monte Carlo simulation are summarized in Table 6.4. The means total As and Cd contents of soil estimated by 10,000 Monte Carlo simulations is similar with the outcomes of the default simulation. The coefficient of variation (CV) for the estimated total soil arsenic and cadmium contents is 15%, the range of normal variations for soils that are sampled spatially over the landscape. The 95% confidence interval for As and Cd are from 0.53 to 0.99 mg/kg and from 5.3 to 9.5 mg/kg, respectively. Based on the outcomes, there is 60% probability that the As content of the soils receiving P fertilizer applications for 100 years will remain equal to or below the initial As concentration of the soil and there is 10% probability that the Cd of the soils receiving

100 years of P fertilizer application will remain equal to or below the initial As concentration of the soil. The estimated total As and Cd contents of the soils followed log-normal distributions and is skewed toward the high concentration end.

Table 6.4. Statistical attributes of parameters included in the Monte Carlo simulation

Uncertain Parameter	Arsenic			Cadmium		
	Mean	Variance	Distribution	Mean	Variance	Distribution
K_h (cm hr^{-1})	0.02	0.0004	Lognormal	0.02	0.0004	Lognormal
□□(cm^3 cm^{-3})	0.25	0.0025	Normal	0.25	0.0025	Normal
J_{max} (□mol cm root^{-1} hr^{-1})	10^{-5}	4×10^{-10}	Normal	10^{-6}	4×10^{-12}	Normal
k_a (l kg^{-1})	150	5625	Normal	100	2500	Normal
k_f (hr^{-1})$^+$	0.01	4×10^{-4}	Lognormal	0.01	4×10^{-4}	Lognormal
k_{im}(hr^{-1})	10^{-6}	4×10^{-12}	Lognormal	10^{-6}	4×10^{-12}	Lognormal

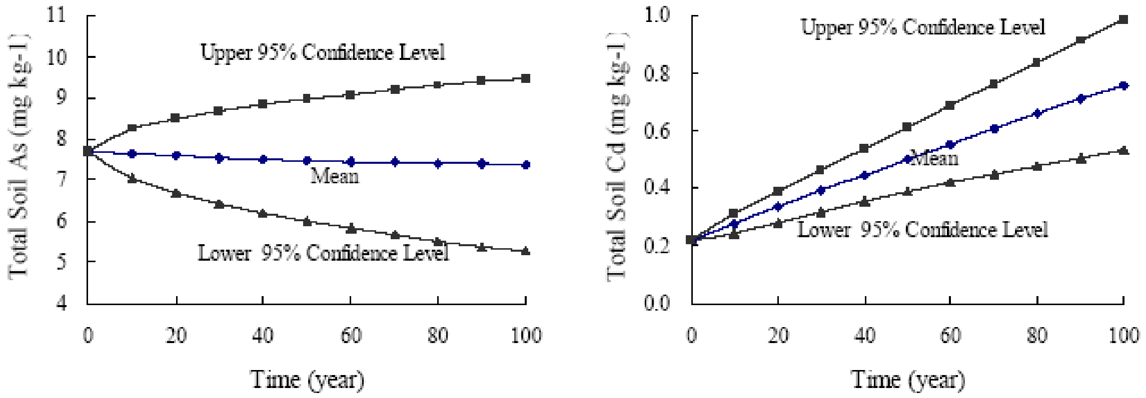


Figure 6.8. Mean and 95% confidence interval of estimated total As and Cd content of soil for 100 years as calculated by 1000 Monte Carlo simulations.

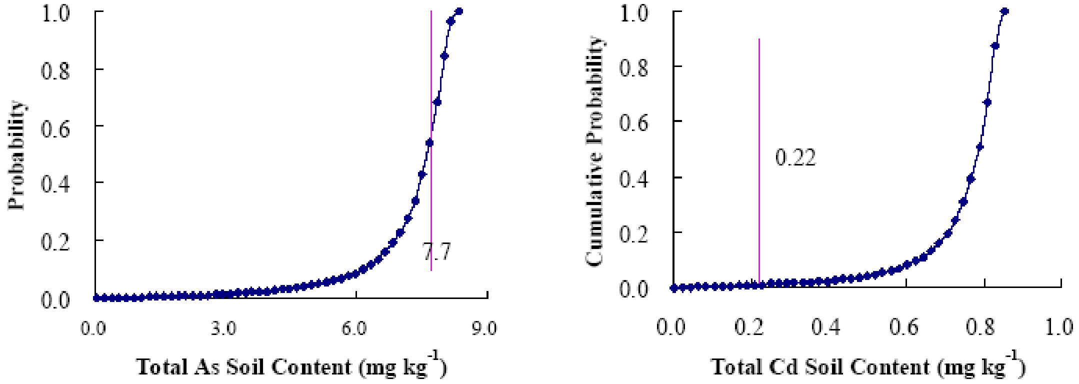


Figure 6.9. Cumulative probability distribution of total As and Cd content at the end of 100-year simulation

Chapter 7

Modeling the Uptake Kinetics of Cadmium by Field-grown Lettuce

The potentially toxic trace elements such as cadmium may accumulate in cropland soils through fertilizer applications and other cultivation practices (Krishnamurti et al., 1999, Chang and Page, 2000; Krage, 2002; Meeus, et al. 2002). Enhanced plant tissue Cd concentrations have been found in crops receiving P-Fertilizers containing high Cd levels (He and Singh, 1994; Grant and Bailey, 1998; Guttormsen *et al*., 1995; Huang *et al*., 2004).

The food chain transfer of trace elements, such as Cd, is customarily characterized by first estimating the soil solution concentration via the linear solid-solution partition coefficient, K_d ($l\ kg^{-1}$) and then the plant tissue concentrations through the plant uptake factor, PUF ($l\ kg^{-1}$) (CDFA, 1998; Renaud et al, 1999 and references therein). The K_d denotes the ratio of total elemental content of the soil, C_{Total}, ($mg\ kg^{-1}$) to that in soil solution, $C_{Solution}$, ($mg\ l^{-1}$). The PUF denotes the ratio of the concentration of a chemical in plant tissue, C_{Plant}, ($mg\ kg^{-1}$) to that in soil solution, $C_{Solution}$, ($mg\ l^{-1}$). The empirical approach assumes the steady state transfer of the element across the solid-solution-plant continuum. No dynamic factors are incorporated in the relationship. However, the element dissolution and dispersion as well as plant uptake of trace elements from soils are unsteady processes and their rates may vary over the growing period. To accurately characterize the plant uptake process, it is imperative to develop kinetic models integrating the interactive soil-plant processes.

Models have been developed to simulate solute uptake by plant roots (Barber and Cushman, 1981; Mullins and Sommers, 1986; Wu et al., 1994; Rao and Mathur, 1994; Gardiner and Christensen, 1997, Darrah and Staunton, 2000; Seuntijens et al., 2004). The Michaelis-Menten kinetics and its derivations are often used to predict solute uptake by plants, J ($g\ cm^{-1}$ root day^{-1}), that:

$$J = \frac{J_{\max} \cdot C_{Solution}}{K_m + C_{Solution}} \qquad \text{[Eq.7.1]}$$

where J_{max} is the maximum solute uptake influx (g cm^{-1} root day^{-1}), $C_{Solution}$ is the trace element concentration in soil solution (μg L^{-1}), and K_m is the root permeability coefficient (μg L^{-1}) denoting the $C_{Solution}$ when J = 50% of J_{max}.

Describing the plant uptake in terms of the Michaelis-Menten kinetics presents several issues. Firstly, it is difficult to obtain the kinetic parameters that represent the uptake at field conditions. Although the kinetics of Cd uptake by plants has been studied (Cataldo et al., 1983; Mullins et al., 1986; Hart et al., Costa and Morel, 1993; 1998; Zhao et al., 2002; Lombi et al., 2002), most of the data were obtained from limited exposure time in the hydroponics solutions. In the field cultivation, the Cd supply to the plant root may be limited by the solute diffusion and mass flow; while the Cd transport to plant roots in a hydroponics solution is virtually unrestricted. Secondly, it assumes that J_{max} and K_m are constants for a plant species and the actual uptake is simply a function of the solute concentration in the solution phase. The root uptake activities, however, may vary greatly over the growing period therefore the uptake kinetics as the plant growth and nutrient uptake are dynamic and unsteady processes. As most of the above referenced experiments were conducted for a short duration, the data generally fitted the Michaelis-Menten kinetics model well. If the kinetic parameters are evaluated based on observations through the entire growing season, they, especially J_{max}, may become time dependent. As a result, the Michaelis-Menten kinetics may not be suitable to evaluate the solute uptake by plants grown under field conditions.

The objective of this study was to develop and test a field-based kinetic model for plant uptake of trace elements. The Cd uptake by Romaine lettuce (*Lactuca savita var. longifolia*) grown under field conditions over the entire growing season are used in the model development.

Materials and Methods

Field Experiment

The field is located in the University of California's Meloland Field Station in the Imperial Valley, California. The soil is Holtville clay loam (Fine, smectitic, calcareous, hyperthermic Vertic Torrifluvent). The experimental field was 60 m long and 32 m (beds) wide. There were 20 sampling plots (made in the middle 20 beds) randomly assigned to receive one of the 5 P fertilizer treatments that each was replicated 4 times. Each sampling plot consists of 4 m ×15 m field-scale beds for lettuce growing. Each plot received 4.2 kg of ammoniated phosphate (11-52-0) fertilizers that contain various amounts of Cd. For the control group, un-spiked P-fertilizer was applied. For treatment level I through IV, the Cd spiked P-fertilizers were applied. The spiking was done, by spraying solutions containing 160, 320, 640 and 1280g $CdCl_2$ (in 1.5L water) to into 23 kg (50 lbs) of the P-fertilizers in a rotary mixer, respectively. After spiking, the fertilizers were allowed to undergo several cycles of wetting and drying during a period of several weeks. The background soil Cd content was 0.85 mg kg^{-1}; while for the treatment levels I through IV, they were 2.89 mg kg^{-1}, 5.00 mg kg^{-1}, 9.91 mg kg^{-1} and 19.38 mg kg^{-1}, respectively. Romaine lettuce was planted following the standard cultivation practices described in the *Guidelines to production costs and practices for Imperial County 2004-2005 vegetable crops* (Meister, et al. 2004).

Plant Sampling and Analysis

The plant tissue of the center 2 m (two beds) × 10 m area in each sampling plot was taken on 34, 49, 62, 70, 78, 88, 95 day after planting. After sampling, the plant tissues were dried in an oven at 65°C for 48 hr. The plant tissues were grounded for use in determining the Cd concentration, based on microwave digestion procedure in which4.0 ml HNO_3, 4.0 ml H_2O_2 and 2.0 ml of de-ionized water were added to about 0.5 g of grounded plant tissue sample in a Teflon vessel. Then the vessel was put in a microwave even (1200 watts) to digest for 15 minutes. After dilution, the Cd content was analyzed by graphite furnace atomic absorption spectroscopy (AAS-GF, Perkin Elmer AAnalyst 600). To verify the accuracy of the sample digestion, a standard reference material (NIST 1547) was analyzed in every batch of digestion. The accuracy of the Cd determinations was verified using the Trace Elements in Water standard (NIST 1640). The standard was analyzed after preparing each calibration curve for the AAS-GF to check the accuracy of the analyses.

Model Approach

The flux of Cd uptake by roots (g cm^{-1} root day^{-1}) are often expressed in terms of the Michaelis-Menton kinetics (see equation 7.1). To obtain the unit area uptake rate (g ha^{-1} day^{-1}), the root density must be known. However, the root growth and distribution is difficult to measure and/or simulate. The root density may be treated as a function of above-ground biomass (Casper et al., 1998). Thus, the plant uptake kinetics can be given by:

$$\frac{\partial U_t}{\partial t} = BM_t \frac{J_{\max} \cdot C_{Solution}}{K_m + C_{Solution}} \qquad \text{[Eq. 7.2]}$$

where U_t represents the amount of uptake (g ha^{-1}) at time t, BM_t refers to the biomass (kg ha^{-1}) at time t, and J_{max} is expressed in terms of the biomass (g kg^{-1} biomass day^{-1}). The amount of uptake (*U*) at certain time is calculated based on the Cd content in the plant tissues, C_{Plant} (mg kg^{-1}), and the corresponding biomass (BM_t).

The soil solution concentration of Cd is generally very low compared to the root permeability coefficient K_m. Thus, the Michaelis-Menton kinetics equation may be reduced to a linear relationship with a plant uptake coefficient α (= J_{max}/K_M). The plant uptake coefficient, α (L solution kg^{-1} biomass day^{-1}), generally decreases with time. We can hypothesize that it follows an exponential pattern, given by:

$$\alpha(t) = \alpha_{\max}.e^{-b \cdot t} \qquad \text{[Eq. 7.3]}$$

where α_{max} represents the maximum uptake potential at the planting when $t = 0$, *b* is a rate constant (day^{-1}) related to plant growth.

The soil solution Cd concentration, based on water to soil ratio of 0.5 (w/v) (Chen et al., 2007) were not significantly different (at $p < 0.05$) throughout the growing season and might be assumed as. Separate evaluations based on model simulations (Chen, 2006) indicated that the changes of soil solution Cd concentration over one growing season (half year) were less than 1%. By assuming $C_{Solution}$ is constant during the growing period and the plant growth (BM_t) follows an exponential growth model, we can integrate equation 7.2 and the change of Cd content in plant tissues (C_{Plant}) with time is obtained as:

$$C_{Plant}(t) = C_{Solution} PUF_{\max} \cdot e^{-b \cdot t} \qquad \text{[Eq. 7.4]}$$

The above equation can be further simplified as:

$$PUF(t) = PUF_{\max} \cdot e^{-b \cdot t} \qquad \text{[Eq. 7.5]}$$

where *PUF(t)* (L solution kg biomass^{-1}) is the plant uptake factor of time *t*, defined as the ratio of the Cd content in plant tissues (C_{plant}) to that in the soil solution ($C_{Solution}$) and PUF_{max} represent the PUF at *t* = 0.

Results and Discussion

Michaelis-Menton Kinetics. The uptake of Cd may involve both active and passive transport mechanism(s) (Arduini et al., 1996). The Cd^{2+} in soil solution may cross the plasma membrane of root cells via a cation channel for divalent cations such as Ca^{2+} or Mg^{2+}. It may also be transported by a Cd-specific membrane transport protein (McLaughlin and Singh, 1999). As with most cations, the kinetics of Cd^{2+} adsorption by roots would approach saturation as the Cd^{2+} activity in the soil increases. Therefore, the uptake of Cd by plants is customarily simulated by the Michaelis-Menton kinetics (Eq. 7.1) in which the Cd uptake, *J*, increases as the soil solution Cd concentration, $C_{Solution}$, increases and it approaches a saturation level, J_{max}, when $C_{Solution}$ rises.

The experimental data on plant uptake and soil solution Cd concentrations obtained at various stage of plant growth all fitted the Michaelis-Menton kinetics model (Figure 7.1). The model parameters, K_m and $J_{max,}$, changed with the stage of plant growth (Table 7.1). The root permeability coefficients, K_m, varied from 9.3 to 31.1 nM, are in general agreement with those reported in the literature, varied from 20-40 nM for bread and durum wheat (Hart et al., 1998), 88 nM for soybean, (Cataldo eal., 1983), and 30 to 100 nM for maize (Mullins and Sommers, 1986). The maximum uptake flux rate, J_{max}, on the other hand, decreases exponentially by approximately 15 times from the early stage of plant growth to maturity (Figure 6.2). The results indicate that the Michaelis-Menton kinetics, depicting a steady state equilibrium, is not appropriate in modeling the plant uptake process over the entire growing season, although it may produce good fitness for any single point of time in the growing period. The decrease of J_{max} fitted the exponential decay model ($R^2 > 0.99$). It is reasonable that the plant uptake coefficient, □, follow the first order reaction kinetics as described as equation 6.3.

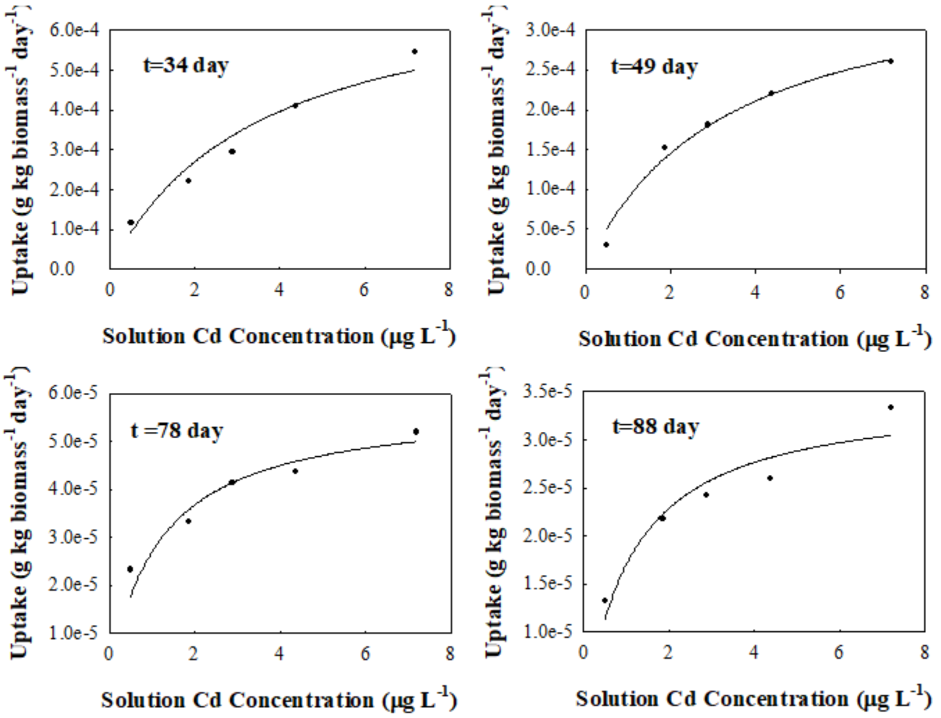


Figure 7.1. Michaelis-Menton Kinetics (Eq. 6.1) depiction of cadmium uptake by Romaine lettuce grown for four time periods.

Table 7.1. Cadmium uptake kinetics of Romaine lettuce grown for 34 to 95 days, according to Michaelis-Menton model (Eq. 7.1)

Time (day)	**34**	**49**	62	**70**	**78**	**88**	**95**
J_{max} (g kg^{-1} day^{-1})	7.4×10^{-4}	3.8×10^{-4}	1.2×10^{-4}	1.1×10^{-4}	5.8×10^{-5}	3.5×10^{-5}	2.8×10^{-5}
K_m (μg L^{-1})	3.50	3.25	1.48	1.91	1.15	1.05	1.11
R^2	0.9843	0.9938	0.9741	0.9741	0.9897	0.9895	0.9819

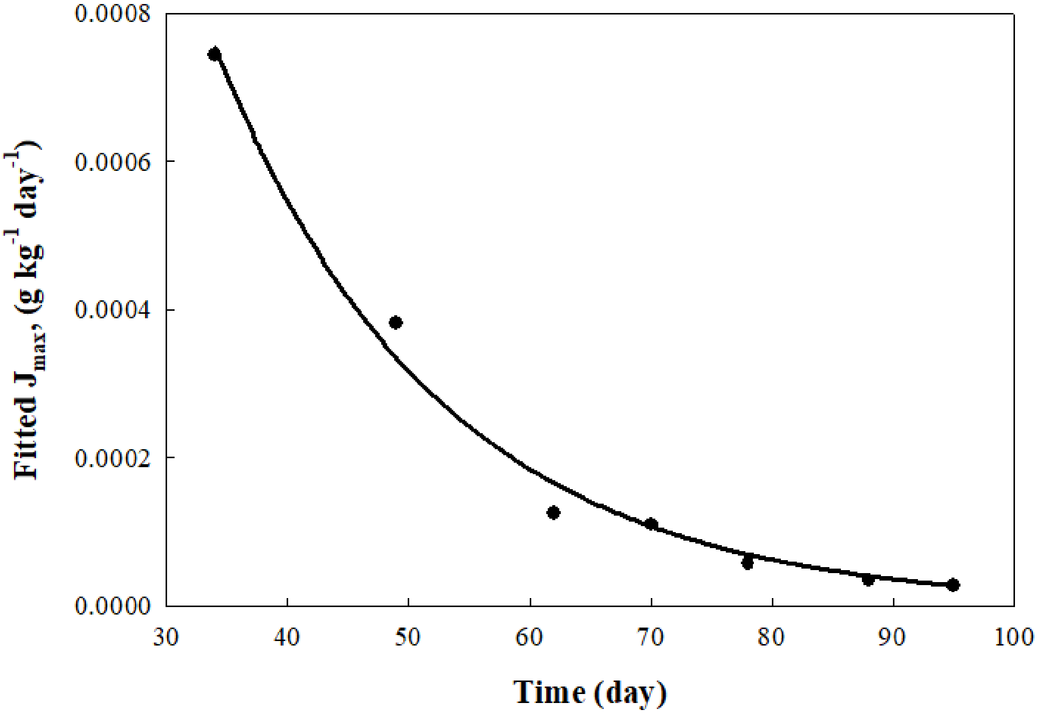
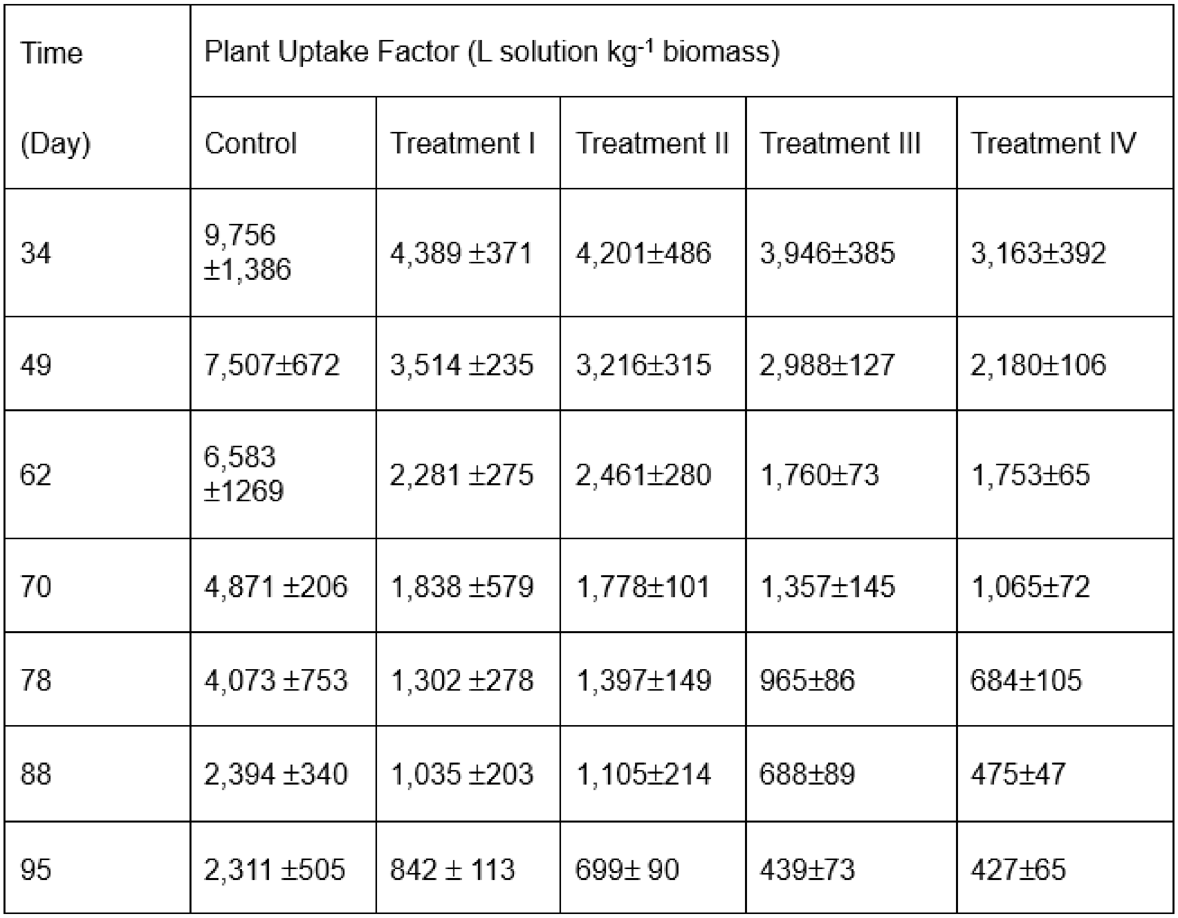


Figure 7.2. Michaelis-Menton maximum Cd uptake, J_{max}, for Romaine lettuce grown for various time period.

Plant Uptake Factors.

The plant uptake factors (PUFs) corresponding to plants at different growing periods (Table 6.2) fitted well with the equation 6.5 in which the PUF of plants follow the first order reaction kinetics (Figure 6.3 and 6.4). Under a given soil Cd level, the PUF decreases exponentially over the growing season, indicating a mass dilution that the biomass accumulated is more rapid than the absorbed of Cd by roots. This behavior may be contributed to the changes of the root morphology. The above-ground biomass increases proportionally to the root density, L_v, in the soil, while as described in Barber-Cushman (1981) described that the half-distance between root, r_1, is rekated to L_v that $r_1=1/(\pi L_v)^{1/2}$. When the root density rises, the distance between root axes would drop below a critical level and, the competition between root uptake begins (Barber, 1984). Consequentially, the plant uptake is limited by the soil supply (diffusion) and the solute uptake rate decreases as the r_1 decreases (i.e. plant grows). Little is known about Cd translocation from plant root cells to aerial parts. As plant grows, the translocation rate may decrease due to decreasing activities of Cd transporter or stronger binding with mature roots.

Table 7.2. Means and standard deviations of Cd plant uptake factor, PUF (L solution kg^{-1} biomass), for Romaine lettuce grown for 34 to 95 days.



Time	Plant Uptake Factor (L solution kg^{-1} biomass)				
(Day)	Control	Treatment I	Treatment II	Treatment III	Treatment IV
34	9,756 ±1,386	4,389 ±371	4,201±486	3,946±385	3,163±392
49	7,507±672	3,514 ±235	3,216±315	2,988±127	2,180±106
62	6,583 ±1269	2,281 ±275	2,461±280	1,760±73	1,753±65
70	4,871 ±206	1,838 ±579	1,778±101	1,357±145	1,065±72
78	4,073 ±753	1,302 ±278	1,397±149	965±86	684±105
88	2,394 ±340	1,035 ±203	1,105±214	688±89	475±47
95	2,311 ±505	842 ± 113	699± 90	439±73	427±65

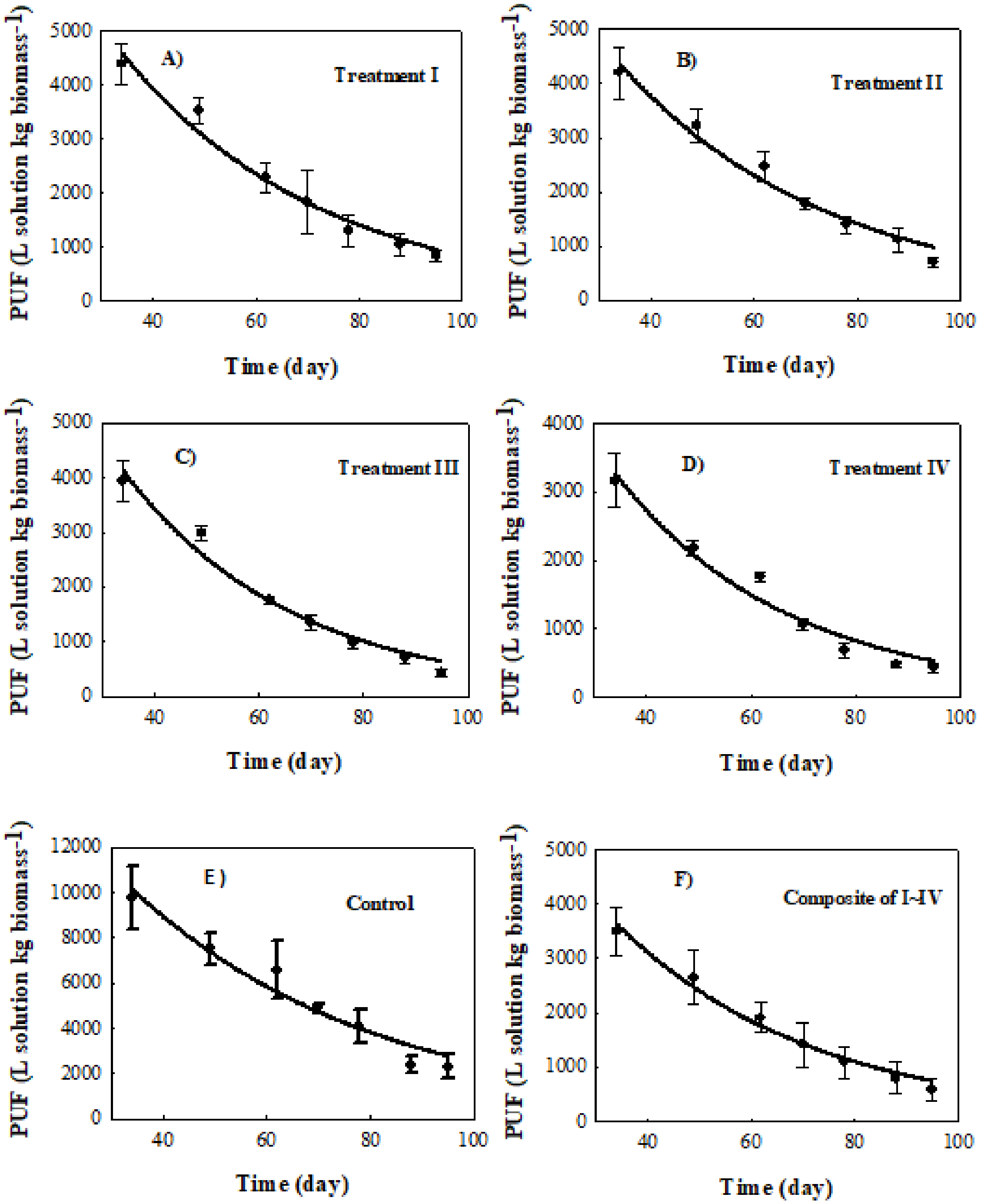
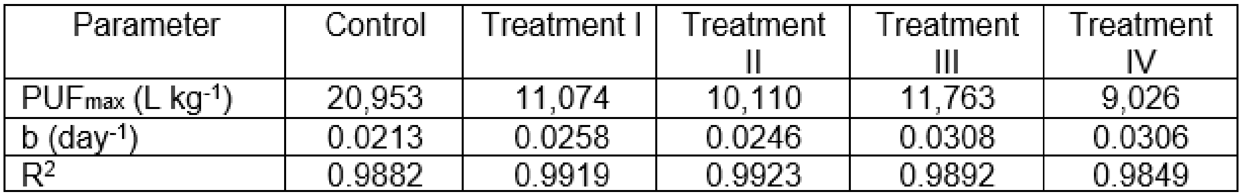


Figure 7.3. **Cd plant uptake factor for Romaine lettuce over the growing season**

For Cd concentrations of soil received Cd spiked P fertilizers, the resulting kinetic parameters (Table 7.3) are not significantly different regardless of the actual Cd inputs and data were pooled (Figure 7.3). The PUF_{max} for the soils receiving P fertilizers with the baseline level Cd level is about two times greater than that of plants grown in soils received spiked P fertilizers, indicating that indigenous Cd of the P fertilizers and soils in a unit concentration basis is twice likely be absorbed by plants. The bioavailability of Cd in soils is source dependent. The average K_d of the soils increases from 1,738, to 1,973, 2,435, and 2,894 l kg^{-1} as the Cd inputs incrementally increases. It is an indication that the solution phase Cd per unit amount of soil Cd significantly decreased.

Table 7.3. Cadmium uptake kinetic of Romaine lettuce grown for 95 days based on $PUF_t = PUF_{max} . exp[-b \cdot t]$, Eq. 6.5.



Parameter	Control	Treatment I	Treatment II	Treatment III	Treatment IV
PUF_{max} (L kg^{-1})	20,953	11,074	10,110	11,763	9,026
b (day^{-1})	0.0213	0.0258	0.0246	0.0308	0.0306
R^2	0.9882	0.9919	0.9923	0.9892	0.9849

Conclusions

The soil solution Cd concentrations the soils remain relatively constant throughout the plant growing season. At a given stage of growth, the rate of Cd uptake by Romaine lettuce plants is related to the soil solution Cd concentrations according to the Michaelis-Menton kinetics model. However, the maximum influx rates J_{max} obtained in this manner would decrease with the length of the growing period. A second order kinetic model by integrating the time factor was developed to simulate the cumulative plant uptake of Cd over the growing season:

$$C_{plant}(t) = C_{Solution} PUF_{\max} \cdot e^{-b \cdot t}$$

where C_{Plant} and $C_{Solution}$ refer to the Cd content in plant tissue and soil solution, respectively,□PUF_{max} represents the uptake potential at time zero and b is a kinetic constant related to plant growth. The plant uptake factor, *PUF*, which is defined as the ratio of Cd in plant tissue to that in soil solution, follows the similar trend to that of C_{Plant}. The data from the field experiment showed that the Cd naturally occurring in the P fertilizers and Cd spiked P fertilizers were different. On a per unit total soil Cd basis, the absorption by Romaine lettuce were much higher for the indigenous Cd than the spiked Cd of the P fertilizers. The mathematical model is general and may universally be applicable to the assessment of uptake by other plant species or of other trace

Chapter 8

Soil Profile Distribution of Trace Elements - Modeling

Model Structure

The simulated soil profile is discretized into a number of uniform adjoining elements (sections). In each element, the same trace element mass balance scheme as we defined in the previous chapter was adopted. Namely, there are four interactive phases, solution, adsorbed, mineral and organic phases, which are subjected to three fluxes including inputs from external sources and/or other sections, leaching out the section and plant uptake removal. The schematic diagram of the model is depicted in Figure 8.1.

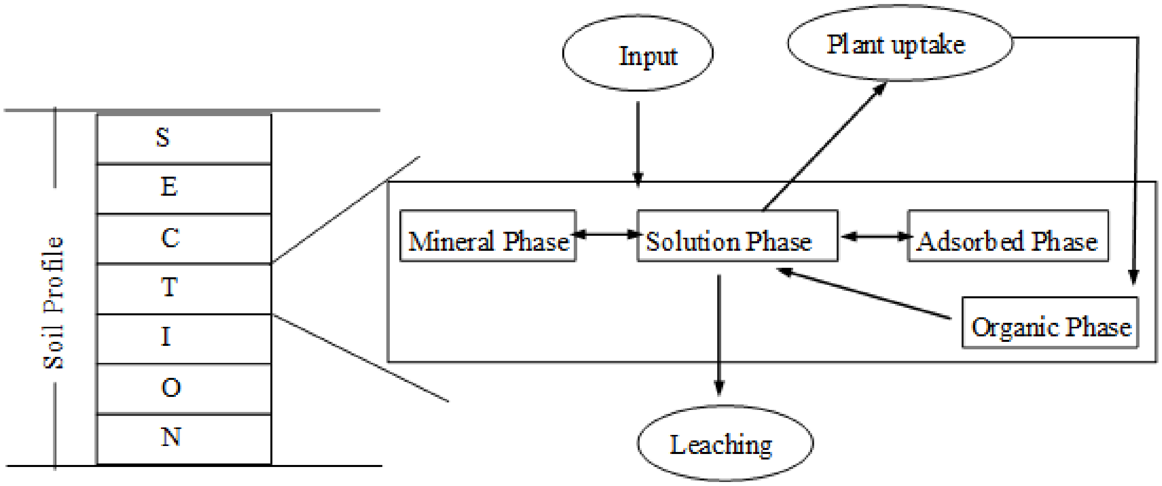


Figure 8.1. Schematic depiction of the profile distribution model.

The governing equation is given as:

$$(K_d + \theta) \cdot \frac{\partial C}{\partial t} = -\frac{\partial}{\partial z}[q \cdot C - \theta \cdot D(\theta, q)\frac{\partial C}{\partial z}] - U + I + k_{im} \cdot Org - k_f(K_d + \theta) \cdot C - k_b \cdot MP$$

[Eq. 8.1]

where K_d is the linear partition coefficient (l kg^{-1}); □□is the soil water moisture content (cm ^{3} solution cm^3 $soil^{-1}$); C is the concentration in soil solution (□M); q is water flux (cm hr^{-1}); D is the hydrodynamic dispersion coefficient (cm^2 hr^{-1}); U is the plant uptake term; I is the external input term; k_{im} is the mineralization rate (hr^{-1}) of organic phase (Org); k_f and k_b are the forward and backward rates (hr^{-1}) of precipitation/dissolution of mineral phase (MP).

The governing equation may be solved numerically at temporal and spatial scale.

HYDRUS – 1D

The temporal changes of soil water content (θ) and water flux (q) for each element must be obtained. This is accomplished by coupling the water flow subroutine from HYDRUS - 1D. In addition, the effective dispersion coefficient and the time dependant plant uptake and input term must be defined.

HYDRUS-1D is a one-dimensional finite element model simulating the movement of water, heat, and multiple solutes in variably saturated heterogeneous or layered soils subject to a variety of atmospheric and other boundary conditions (Simunek et al., 1998). The water flow simulation part of HYDRUS-1D was integrated into the profile distribution model. In HYDRUS-1D, the water flow is modeled by a modified form of the Richards' equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left[K(h)\left(\frac{\partial h}{\partial z} + \cos\alpha\right)\right] - S \qquad \text{[Eq. 8.2]}$$

where h is the water pressure head; θ is the volumetric water content; t is time; x is the spatial coordinate; α is the angle between the flow direction and the vertical axis (cosα is set to 1, which is for the vertical flow case); K(h) is the unsaturated hydraulic conductivity function; S is the root water uptake term.

The Richards' equation can be solved only when soil hydraulic properties and root water uptake model are defined, and the boundary conditions are set. Multiple choices are included in HYDRUS-1D. To simply the model, some choices are selected:

Soil Hydraulic Properties

Soil hydraulic properties, including the soil water retention curve and hydraulic conductivity function (K (h)), are the main attributes for determining the water retention and movement in soils. Three types of soil hydraulic models are available in the HYDRUS modeling package (i.e. van Genuchten, Brooks and Corey and modified van Genuchten type equations). The van Genuchten soil hydraulic functions have been implemented correctly for estimating hydraulic properties of unsaturated soils in many cases and are selected as the default model for defining the soil hydraulic properties. The equations are given by:

$$\theta(h)=\begin{cases}\theta_r+\dfrac{\theta_s-\theta_r}{\left[1+|\alpha h|^n\right]^m} \\ \theta_s\end{cases} \qquad \text{[Eq. 8.3]}$$

$$K=K_s\sqrt{S_e}\times\left[1-\left(1-S_e^{\ 1/m}\right)^m\right]^2 \qquad \text{[Eq. 8.4]}$$

$$S_e=\frac{\theta-\theta_r}{\theta_s-\theta_r} \qquad \text{[Eq. 8.5]}$$

$$m=1-\frac{1}{n} \qquad \text{[Eq. 8.6]}$$

where the above equations contain five independent parameters: θ_r is the residual water content; θ_s is saturated water content; α is the inverse of the air-entry value or bubbling pressure; n is a pore-size distribution index; K_s is the saturated hydraulic conductivity. These parameters can be obtained based on the database from Carsel and Parrish (1988), which are soil texture specified and summarized as Table 8.1. They can also be obtained based on the neural network prediction from Rosetta Lite (Schapp et al., 2001).

Table 8.1. Average values of selected soil water retention parameters (Carsel and Parrish, 1988).

Soil Texture	θ_r	θ_s	α (cm^{-1})	n	K_s (cm hr^{-1})
Sand	0.045	0.43	0.145	2.68	29.70
Loamy sand	0.057	0.41	0.124	2.28	14.59
Sandy loam	0.065	0.41	0.075	1.89	4.42
Loam	0.078	0.43	0.036	1.56	1.04
Silt	0.034	0.46	0.016	1.37	0.25
Silt loam	0.067	0.45	0.020	1.41	0.45
Sandy clay loam	0.100	0.39	0.059	1.48	1.31
Clay loam	0.095	0.41	0.019	1.31	0.26
Silty clay loam	0.089	0.43	0.010	1.23	0.07
Sandy clay	0.100	0.38	0.027	1.23	0.12
Silty clay	0.070	0.36	0.005	1.09	0.02
Clay	0.068	0.38	0.008	1.09	0.20

Root Water Uptake

In HYDRUS software package, the root water uptake (the S term in Eq. 7.4) is calculated based on a root-water uptake stress response function (α(h)) and the potential water uptake rate (S_p), which defined as:

$$S = \alpha(h) \cdot S_p \qquad \text{[Eq. 8.7]}$$

There are two options for the water stress response function: Feddes root water uptake model (Feddes et al., 1978) and an S-shaped function (van Genuchten, 1980). The root water uptake stress response function by Feddes (1978) is selected since there is a database for many plants, without considering the salinity stress (Figure 8.2). This function may be schematically described as in Figure 12. Four parameters are necessary to define the water stress response function. Pressure head h_1 (corresponding to P_0 in the model interface of HYDRUS) represents the pressure head below which roots start to extract water from the soil. Pressure head h_2 (corresponding to P_{opt} in the model interface of HYDRUS) represents the pressure head below which roots start to extract water at the maximum possible rate. Pressure head h_3 represents the pressure head below which the roots cannot extract water at the maximum rate. Pressure head h_4 (corresponding to P_3 in the model interface) represents the pressure head below which root water uptake ceases. Instead of giving h_3 directly, the model makes h_3 as a function of the potential transpiration rate (T_p). The linear interpolation scheme is given by:

$$h_3 = \begin{cases} P_{2H} + \dfrac{P_{2L} - P_{2H}}{r_{2H} - r_{2L}}(r_{2H} - T_p) & for \quad r_{2L} < T_p < r_{2H} \\ P_{2L} & for \quad T_p \le r_{2L} \\ P_{2H} & for \quad T_p \ge r_{2H} \end{cases} \qquad \text{[Eq. 8.8]}$$

where r_{2H} and r_{2L} are the high (0.5 cm day^{-1} as default) and low potential transpiration rate (0.1 cm day^{-1} as default); P_{2H} and P_{2L} are the corresponding pressure head for r_{2H} and r_{2L}. In summary, seven parameters are necessary for simulating root water uptake. A database for different plant type is available in HYDRUS.

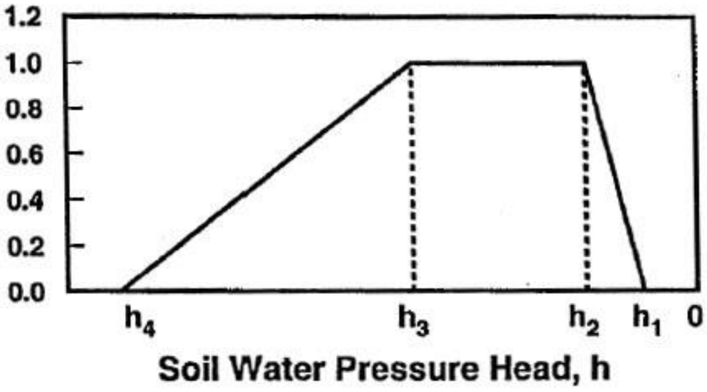


Figure 8.2 Schematic of the plant water stress response function used by Feddes et al. (1978)

Furthermore, the potential water rate (S_p) is related to the potential transpiration rate (T_p) with a normalized water uptake distribution function (b(x)), which describes the spatial variation of the potential extraction term, Sp, over the root zone.

$$S_p = b(x)T_p \qquad \text{[Eq. 8.9]}$$

The distribution function can be constant with depth, linear, or an exponential function with a maximum at the soil surface. In HYDRUS, a linear distribution function was used.

Boundary Conditions

There are six types of upper boundary conditions and seven types of lower boundary conditions are possible in HYDRUS. To simplify the model, only one option of upper and lower boundary conditions is selected. The option, atmospheric boundary condition with surface layer, is selected as the upper boundary condition and the lower boundary condition is set as free drainage.

After setting the initial conditions (initial distribution of the pressure head within the flow domain) and necessary parameters, the water content and water flux distribution within the flow domain can be obtained.

Effective Dispersion Coefficient

The effective dispersion coefficient (θD in Eq. 8.4) is consisted of the mechanical dispersion and the molecular diffusion. Molecular diffusion is a process whereby constituents move from areas of high concentration to areas of low concentration. Diffusion is independent of advection that the constituents of interest are carried by the flow of water and will occur as long as a concentration gradient exists. The coefficient of molecular diffusion is often negligible compared to the dispersivity term in the calculation of the effective dispersion coefficient and is commonly ignored. However, diffusion can be an important contributor to the overall dispersive process when flow rates are low. According to Tucker and Nelken (1982), molecular diffusion can probably be ignored in determining hydrodynamic dispersion when pore water velocities exceed 0.002 cm sec^{-1}. The longitudinal dispersivity is the characteristic length that defines spatial extent of dispersion of solutes, measured in the longitudinal direction, that is, along the flow path. Longitudinal dispersivity is dependent upon grain size distribution but independent of grain shape. When a constituent moves in the water, not every molecule is traveling at the same velocity, due to differences in pore size and flow path length and friction along pore walls, resulting in a probabilistic distribution along the flow path. In the model implement, the longitudinal dispersivity is commonly assumed to be uniform.

In the model, the equation suggested by Bear (1972) is used to calculate the effective dispersion coefficient:

$$\theta \cdot D = D_L \cdot |q| + \theta \cdot D_w \cdot \tau_w \quad \text{[Eq. 8.10]}$$

where D_W is the molecular diffusion coefficient in free water (cm^2 hr^{-1}); τ_W is a tortuosity factor in the liquid phase; |q| is the absolute value of the Darcian fluid flux density (cm hr^{-1}) and D_L is the longitudinal dispersivity (cm). Furthermore, the tortuosity factors are evaluated as the function of water content using the relationship of Millington and Quirk [1961]:

$$\tau_w = \frac{\theta^{7/3}}{\theta_s^2} \quad \text{[Eq. 8.11]}$$

For most chemicals at normal temperatures, the molecular diffusion coefficient is about 10^{-5} cm^2 sec^{-1} in water and the values increase with higher temperatures and with smaller molecules. A calculation equation suggested by the WATER9 model (U.S. EPA, 2001) is given by:

$$D_w = 0.0001518 \times \left(\frac{T + 273.16}{298.16}\right) \times \left(\frac{MW}{\rho}\right)^{-0.6} \quad \text{[Eq. 8.12]}$$

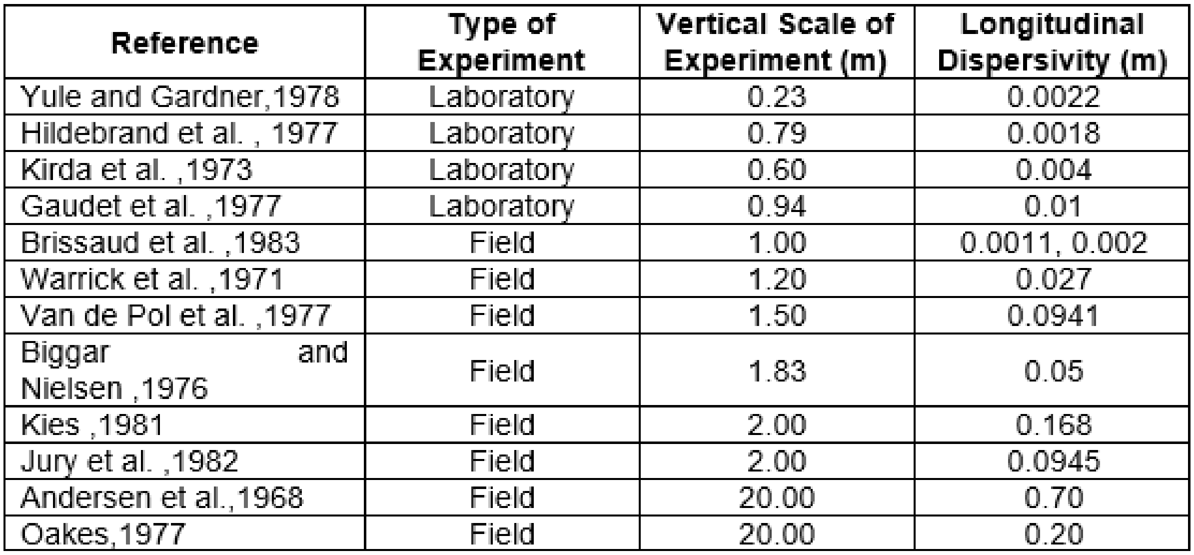
where D_W is diffusion coefficient in water (cm^2 sec^{-1}); T is temperature (°C); MW is molecular weight (g mol^{-1}) and ρ is density of the chemical (g cm^{-3}). When the chemical's density is not available, the equation from *Process Coefficients and Models for Simulating Toxic Organics and Heavy Metals in Surface Waters (Process Coefficients)* (U.S. EPA, 1987) can be used, which only requires knowledge on the molecular weight:

$$D_w = 0.00022 \times MW^{-2/3} \quad \text{[Eq. 8.13]}$$

Based on the above equation, the molecular diffusion coefficient for As and Cd are 1.24×10^{-5} cm^2 sec^{-1} (0.045 cm^2 h^{-1}) and 9.45×10^{-6} cm^2 sec^{-1} (0.034 cm^2 h^{-1}), respectively.

According to Lyman et al (1992), dispersivity values that are measured in the field are usually greater than those measured in the laboratory, and typically they range from 0.01 to 2 cm. Table 8.2 summarized some of field and laboratory dispersivity values.

Table 8.2. Longitudinal dispersivity values at field and laboratory conditions (based on Gelhar, et al. 1985)



Reference	Type of Experiment	Vertical Scale of Experiment (m)	Longitudinal Dispersivity (m)
Yule and Gardner,1978	Laboratory	0.23	0.0022
Hildebrand et al. , 1977	Laboratory	0.79	0.0018
Kirda et al. ,1973	Laboratory	0.60	0.004
Gaudet et al. ,1977	Laboratory	0.94	0.01
Brissaud et al. ,1983	Field	1.00	0.0011, 0.002
Warrick et al. ,1971	Field	1.20	0.027
Van de Pol et al. ,1977	Field	1.50	0.0941
Biggar and Nielsen ,1976	Field	1.83	0.05
Kies ,1981	Field	2.00	0.168
Jury et al. ,1982	Field	2.00	0.0945
Andersen et al.,1968	Field	20.00	0.70
Oakes,1977	Field	20.00	0.20

Root Growth and Plant Uptake

Simulation of root growth and distribution is an important element of the model. Several root growth models are available in the literature (see Acock and Pachepsky, 1996, and the references therein). However, these 'developmental' (Rose, 1983) or 'architectural' (Pages et al., 1989) models that explicitly simulate proliferation and spatial distribution of root segments belonging to different root classes are too complicated to be coupled into the trace element model. **Empirical equations that described the** root state variables (root depth or root length density) as function of time or depth are preferred. The increase in rooting depth with time typically follows a sigmoid pattern. Empirical models have been developed (Rasmussen, 1978; Hanks and Hill, 1986; Brog and Grimes, 1987; Schouwenaars, 1988; Subbaiah and Rao, 1993). Most of these empirical models require the maximum rooting depth and time at which the crop attains its maximum rooting depth as input data. In HYDRUS, the classical Verhulst-Pearl logistic growth function, which is frequently utilized in modeling of population growth, was used to simulate the root growth. The same equation was selected in the profile distribution for the root depth and root mass development. The root mass was represented by the root length per unit of soil volume, namely, root length density. These equations are given by:

$$RD(t) = \frac{RD_0 \cdot RD_m}{RD_0 + (RD_m - RD_0)e^{-rt}} \qquad \text{[Eq. 8.14]}$$

$$R(t) = \frac{R_0 \cdot R_m}{R_0 + (R_m - R_0)e^{-rt}} \qquad \text{[Eq. 8.15]}$$

where RD_0 is the initial value of the rooting depth (cm); RD_m is the maximum rooting depth (cm); R_0 is root length density (cm root cm^{-3} soil) at the beginning of the growing season; R_m is the maximum root length density (cm root cm^{-3} soil); r is the growth rate (hr^{-1}) which is calculated based on the assumption that 50% of the rooting depth or density will be reached after 50% of the growing season has elapsed. The root mass is distributed according to an exponential distribution function with a maximum at the soil surface (Raats, 1974):

$$b(x) = a \cdot e^{-a \cdot x(R)} \qquad \text{[Eq. 8.16]}$$

where a is an empirical constant; x(R) is the root depth.

The amount of plant root uptake in each soil element (□mol l $soil^{-1}$ hr^{-1}) is calculated based on root density in current soil element and the trace element flux describing by the Michaelis-Menton equation, which is given by the equation:

$$U(z,t) = B(z,t) \cdot R(t) \cdot \frac{RD(t)}{dz} \cdot \frac{J_{\max} \cdot C}{K_m + C} \qquad \text{[Eq. 8.17]}$$

where B (z, t) is the normalized root distribution coefficient; R (t) is the root density (cm root cm^{-3} soil); RD(t) is the root depth; C is the trace element concentration in soil solution (□M); J_{max} is the maximum influx rate (□M cm $root^{-1}$ hr^{-1}) and K_m are the root permeability coefficient (□M).

Source Inputs

The external trace element inputs are sorted into three categories: 1) Continuous source from atmospheric deposition, which is added to the top element of the studied soil profile as the mineral phase or mobile phase (solution phase plus adsorbed phase); 2) Discrete sources from fertilizers, micronutrient, and waste disposal and so on, which are added uniformly as the combinations of mobile, mineral and/or organic phases to the plow layer; and 3) Inputs from irrigation, calculated by the flux and trace element concentration in irrigation water, go into the solution phase of top section. Moreover, depending on the direction, the trace element transport with water fluxes and diffusion are considered as input or leaching for the specified section.

Spatial and Temporal Discretization

The space and time scheme must be defined before the implementation of numerical solution. Basically, the space discretization is defined by two variables. One is the profile depth, which specifies the depth of the soil profile simulated in the model. The other is the number of element (section). Since the model structure is based on number of uniform adjoining element, the quotient of soil profile depth and number of section will decide the thickness of each element. In addition, a plow layer is specified. At the beginning of each crop season, trace element in the plow layer will be mixed and redistributed uniformly. The biomass return and inputs from discrete source will be distributed uniformly in this layer, too. Furthermore, more than one soil texture type is allowed in the model. If there are more than one soil texture types in the soil profile, the corresponding parameters are necessary for each soil texture, including the depth, initial trace element pools, and soil hydraulic properties.

The temporal discretization is decided by four variables: simulation duration, initial time step, minimum time step and maximum time step. The model will adjust the time step internally according to the pressure head gradient. Since we choose atmospheric boundary condition with surface layer as the upper water flow boundary condition, smaller initial and minimum time step is necessary to reduce the errors. The water balance is correlated tightly with trace element balance. Therefore, if the water balance is not good, the resulting trace element balance may be incorrect. Generally, the relative errors of water balance should not greater than 0. 1%. If it does, it means the time step setting for computation is not appropriate and needs to be adjusted.

Coupling the water flow simulation, plant growth and uptake, different external sources, and effective dispersion coefficient into the governing equation for each element (Eq. 8.4) and solved by the 4th order Runge-Kutta at the spatial and temporal scale, the distribution of trace element in the soil profile may be realized. A Window-based computation algorithm was programmed and the interface is as shown below (Figure 8.3):

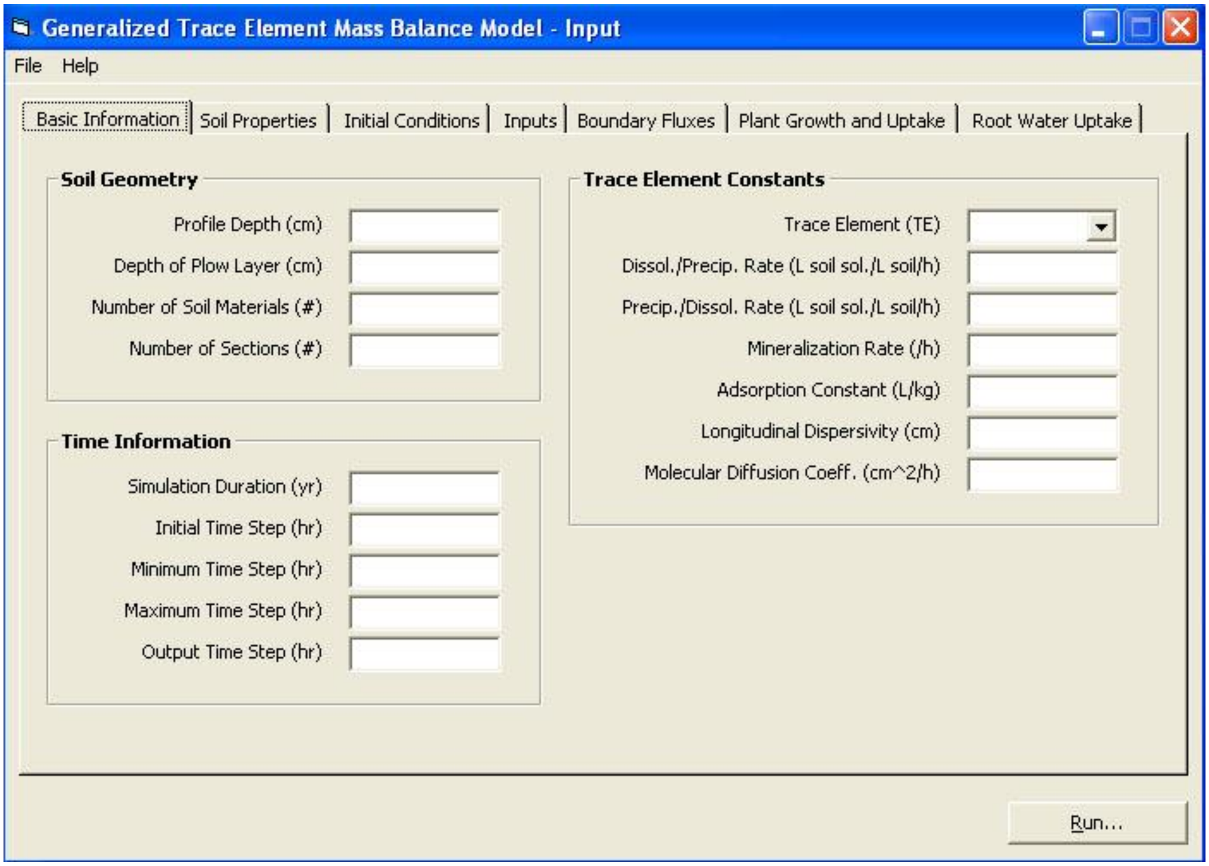


Figure 8.3 Windows interface of the trace element mass balance model with profile description.

Model Parameters

The model parameters and initial values were sorted into seven tabs in the Windows interface (Figure 8.3), namely, basic information, soil properties, initial conditions, input, boundary fluxes, plant growth and uptake, and root water uptake.

Basic Information

The soil geometry and time information must be specified firstly to define the Spatial and Temporal Discretization. These parameters are user-specified. The others are trace element specific, including the reaction rate constants and parameters for defining the dispersion coefficient, which have already been discussed in the previous sections.

Soil Properties

Five Parameters of the van Genuchten soil hydraulic model need to be specified in the soil properties tab. Alternatively, the parameters for 12 major soil textural groups are available in a database. For the default simulation, data for the loamy soil is selected. In addition, the soil bulk density must be specified for unit conversion inside the model. The same value as used in the previous model, 1.41 kg l^{-1}, is set as the default soil bulk density.

Initial Conditions

To make sure the results from the two models are comparable, the same initial trace element pools are used. In addition, the initial pressure head for each section must be known to couple the water flow simulation part of HYDRUS. The model will linearly interpolate the initial pressure head for each section within the soil profile based on the initial top and bottom soil pressure heads. For the default simulation, the initial pressure head is set to -100 cm for both the top and bottom soil pressure head.

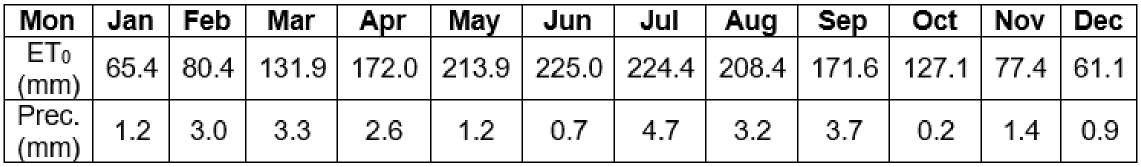
*Input***s**

As discussed, and summarized in previous chapters, there are regional differences in the sources of trace element in agriculture ecosystem. The profile distribution version of the model sorts the different external input sources into three catalogs: continuous sources, discrete sources, and addition with irrigation water. Continuous source from atmospheric deposition can be a significant input source to cropland soils, particularly when the background soil As and Cd levels are low. We will take the default value defined in Chapter 3 (5 g ha^{-1} yr^{-1}) for atmospheric deposition of As and Cd. Discrete sources from fertilizers, micronutrient, and waste disposal vary considerable depending by fertilizers type and the application rates. For the default simulation, the input from fertilizers is set to 0.5 g ha^{-1} and 2.5 g ha^{-1} per application for As and Cd, respectively. The application takes place at the beginning of each crop season and goes into the mobile phase. The input from irrigation is calculated based on the amount and trace element concentration of the irrigation water. Irrigation is not only an important source of trace element input (especially for As), but also one of the most important fluxes that control water balance in the soil profile, therefore the solute transport. The input with irrigation water is set in the boundary fluxes tab.

Boundary Fluxes

The time-dependent boundary water fluxes, including precipitation (irrigation or rainfall), evaporation and transpiration, must be specified for the model simulation. The evaporation and transpiration can be obtained based on the reference evapotranspiration (ET$_0$) and the crop coefficients for specific crop growth periods. The reference ET in different region of California can be obtained from CIMIS. Table 8.3 shows an example of the monthly reference ET and precipitation in Imperial County based on the CIMIS.

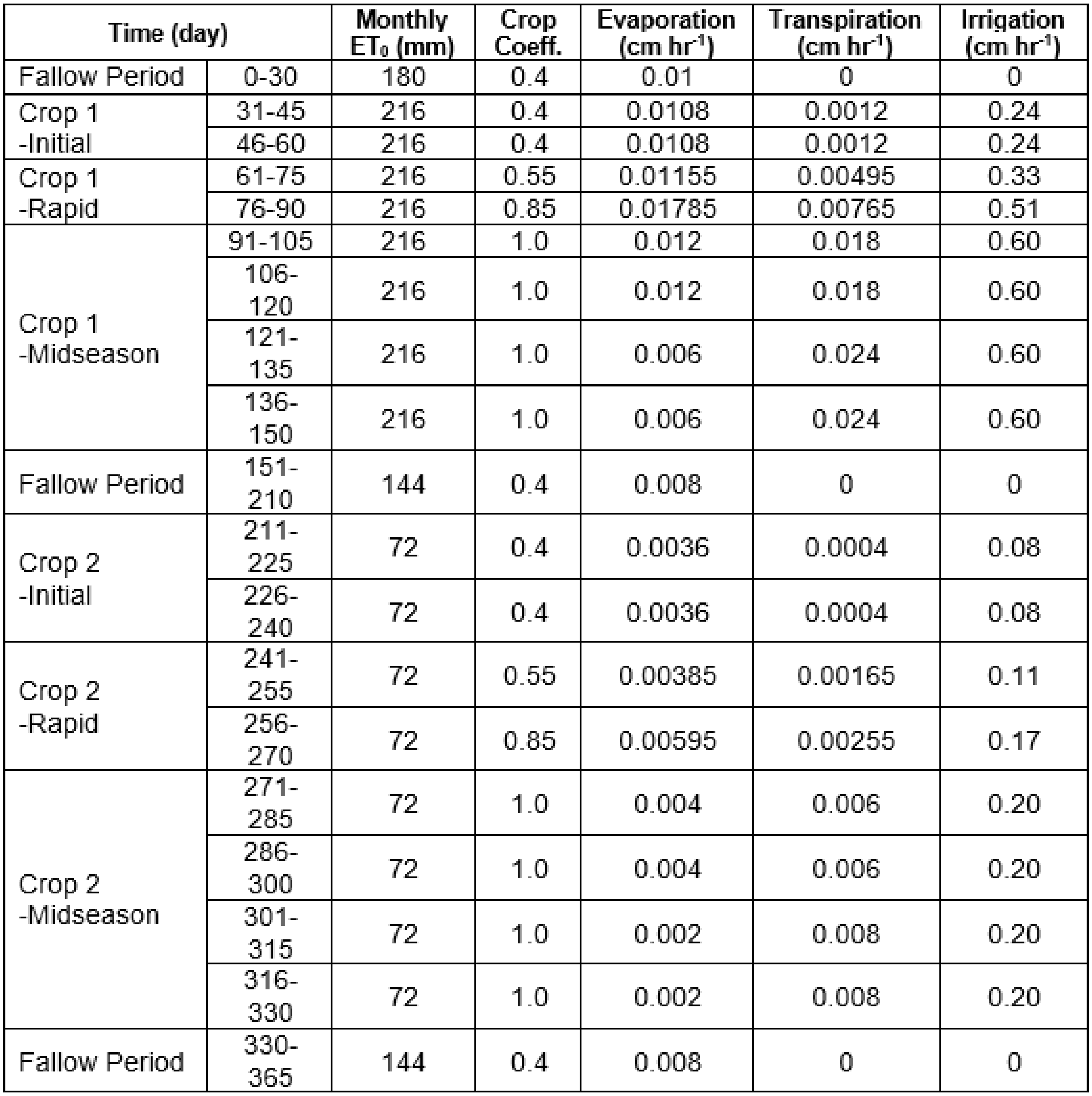
Table 8.3. Monthly reference evapotranspiration (ET$_0$) and precipitation in Imperial County Region (Data from CIMIS).



Mon	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
ET$_0$ (mm)	65.4	80.4	131.9	172.0	213.9	225.0	224.4	208.4	171.6	127.1	77.4	61.1
Prec. (mm)	1.2	3.0	3.3	2.6	1.2	0.7	4.7	3.2	3.7	0.2	1.4	0.9

For the default model simulations, there are two 120-day crop seasons. The summer crop is from May to August with a constant monthly ET$_0$ of 216 mm and the winter crop growing season is from November to February (the following year) with a constant monthly ET$_0$ of 72 mm. The percentage of the initial, rapid and midseason growth period is 25%, 25% and 50%, respectively. The crop coefficients are set based on the generalized crop coefficient curve for field vegetable crops from Snyder and Schulbach (1992). The actual crop evapotranspiration (ET$_c$) is calculated based on the ET$_0$ and the crop coefficients. The soil evaporation is assumed to account for 90% of the ET$_c$ at the beginning month of the growing season and then decrease to 70%, 40% and 20% for the continuous months. Irrigation occurs at every 15 days and continues for 24 hours. The irrigation efficiency is set to 75%. The actual amount of water applied can be obtained by dividing the ET$_c$ for the previous period by the irrigation efficiency. The annual irrigation is around 1.2 m. To make the total annual input from different sources equal the total annual input used in the previous model (13 g ha^{-1} yr^{-1} for Cd, 30 g ha^{-1} yr^{-1} for As), the trace element concentration in the irrigation water for As and Cd is set to 2.016 and 0.252 □g l^{-1}, respectively. The designed default boundary fluxes were summarized in Table 8.4.

Table 8.4. Default boundary fluxes for a typical crop year.



Time (day)		Monthly ET_0 (mm)	Crop Coeff.	Evaporation (cm hr^{-1})	Transpiration (cm hr^{-1})	Irrigation (cm hr^{-1})
Fallow Period	0-30	180	0.4	0.01	0	0
Crop 1 -Initial	31-45	216	0.4	0.0108	0.0012	0.24
	46-60	216	0.4	0.0108	0.0012	0.24
Crop 1 -Rapid	61-75	216	0.55	0.01155	0.00495	0.33
	76-90	216	0.85	0.01785	0.00765	0.51
Crop 1 -Midseason	91-105	216	1.0	0.012	0.018	0.60
	106-120	216	1.0	0.012	0.018	0.60
	121-135	216	1.0	0.006	0.024	0.60
	136-150	216	1.0	0.006	0.024	0.60
Fallow Period	151-210	144	0.4	0.008	0	0
Crop 2 -Initial	211-225	72	0.4	0.0036	0.0004	0.08
	226-240	72	0.4	0.0036	0.0004	0.08
Crop 2 -Rapid	241-255	72	0.55	0.00385	0.00165	0.11
	256-270	72	0.85	0.00595	0.00255	0.17
Crop 2 -Midseason	271-285	72	1.0	0.004	0.006	0.20
	286-300	72	1.0	0.004	0.006	0.20
	301-315	72	1.0	0.002	0.008	0.20
	316-330	72	1.0	0.002	0.008	0.20
Fallow Period	330-365	144	0.4	0.008	0	0

Plant Growth and Uptake

In the model, the root development is simulated by the classical Verhulst-Pearl logistic growth function with the assumption that the rooting depth will be reached half of the maximum root depth at the middle of the growing season. In the model simulations, the initial root depth is generally set to a small number and the crop season is 120 day. Thus the root growth in the profile with time can be obtained only if the maximum rooting depth is known. Similarly, the maximum root length density in the specified soil profile is needed to simulate the root mass development. In addition, a root partition coefficient is needed for distributing the root length density exponentially with soil depth. The root partition coefficient is set to 0.2. Figure 8.4 shows an example of the root mass distribution along a 30 cm root depth. The parameters related to plant uptake kinetics were already summarized in the previous chapters. We will use the same plant uptake kinetic parameters as used in the previous model in the default simulation. The default root growth and uptake parameters were summarized in Table 8.5.

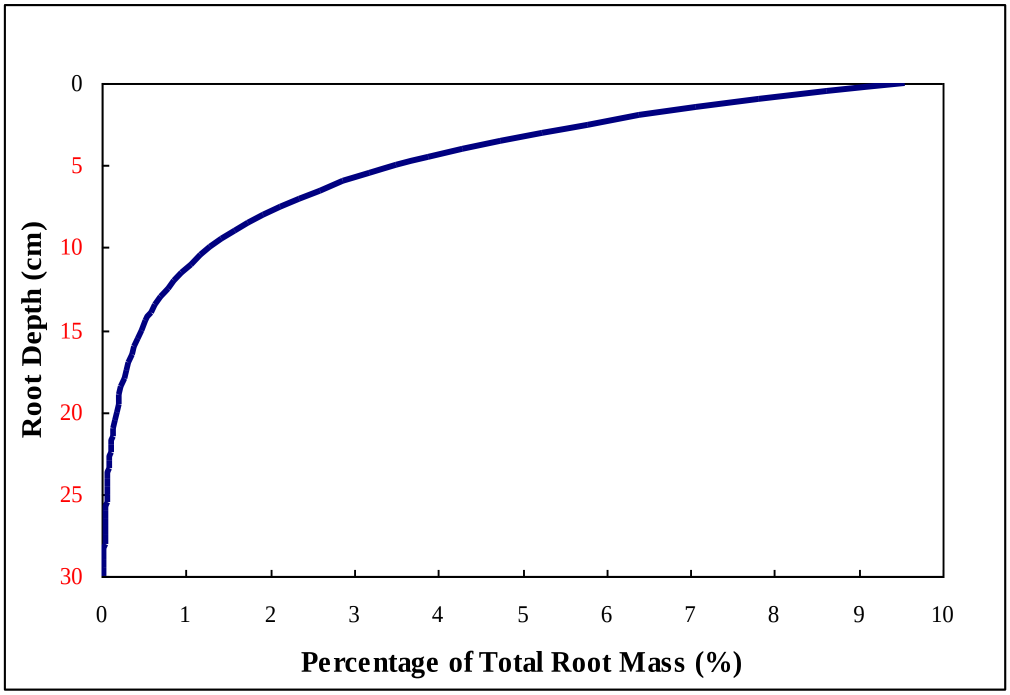
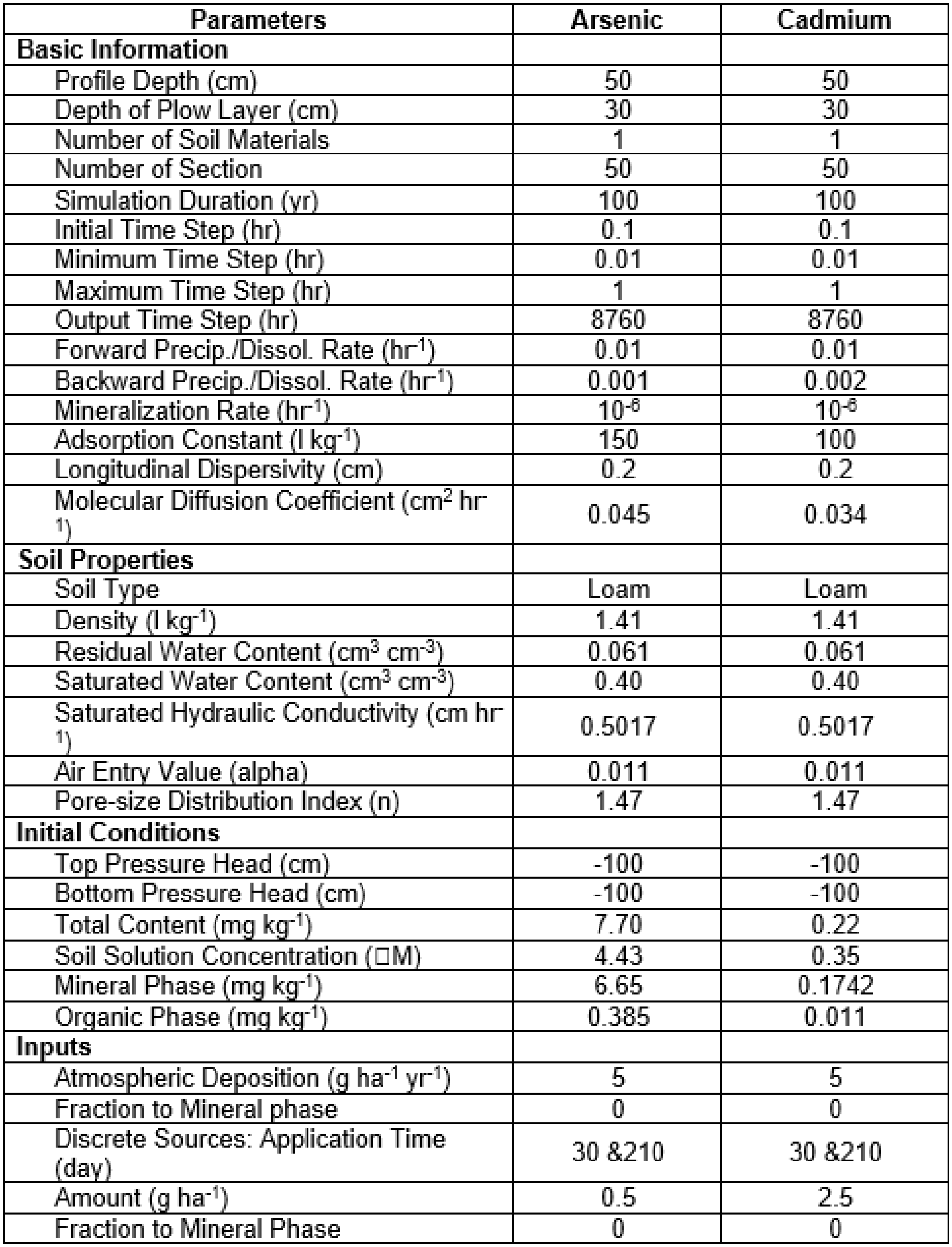


Figure 8.4. Distribution of the root mass along a 30 cm root depth when root distribution coefficient equals 0.2

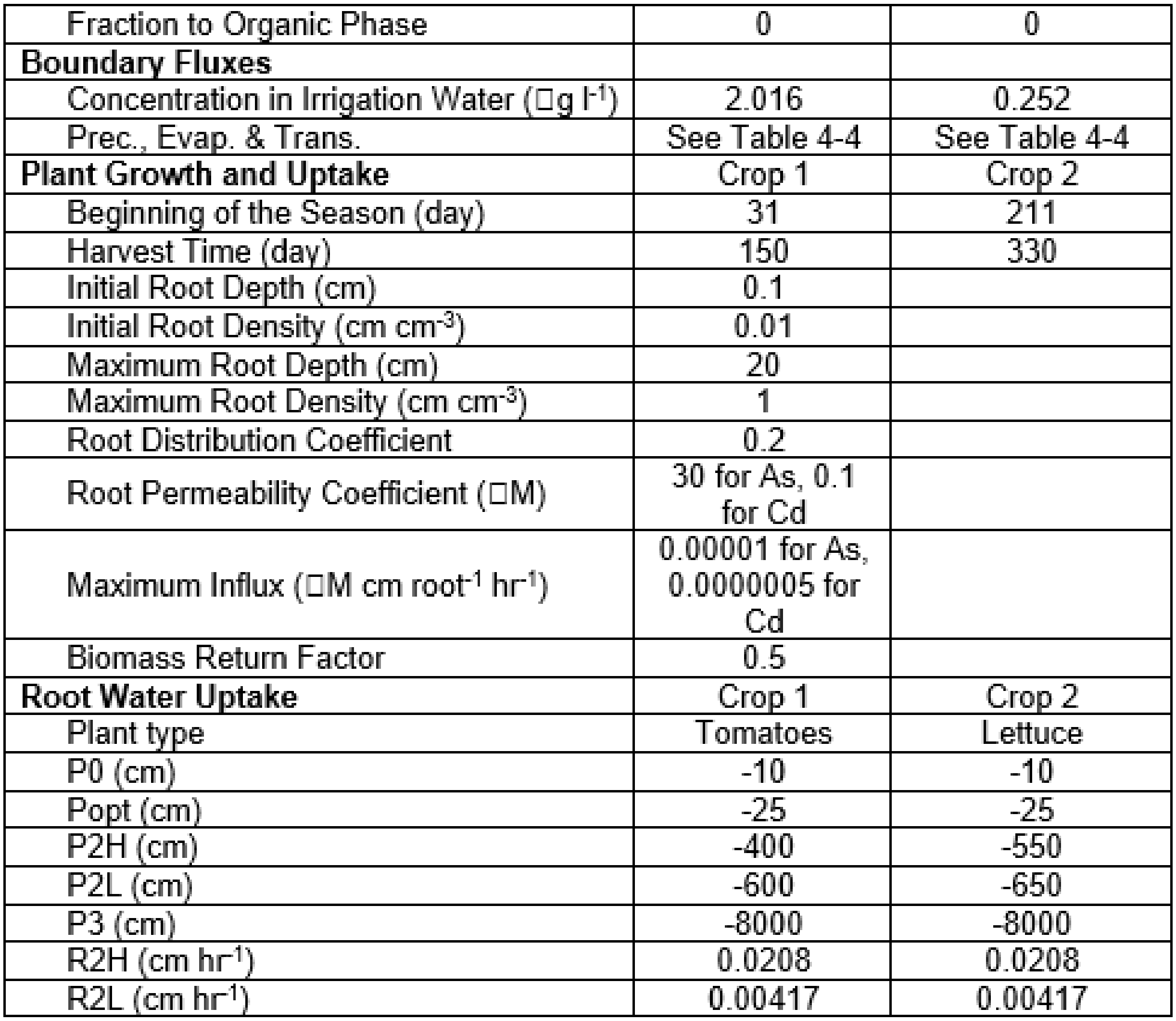
Root Water Uptake

In the model, water uptake is simulated by Feddes et al. (1978) root water uptake model. Seven crop specific parameters are necessary for simulating the root water uptake model. There is a database available in the model for the parameters of different crops. The parameters for tomatoes and lettuce in this database are employed for the default simulation. The default parameter values for As and Cd are summarized as Table 8.5.

Table 8.5. Parameter values for the default simulation of As and Cd.



Parameters	Arsenic	Cadmium
Basic Information		
Profile Depth (cm)	50	50
Depth of Plow Layer (cm)	30	30
Number of Soil Materials	1	1
Number of Section	50	50
Simulation Duration (yr)	100	100
Initial Time Step (hr)	0.1	0.1
Minimum Time Step (hr)	0.01	0.01
Maximum Time Step (hr)	1	1
Output Time Step (hr)	8760	8760
Forward Precip./Dissol. Rate (hr^{-1})	0.01	0.01
Backward Precip./Dissol. Rate (hr^{-1})	0.001	0.002
Mineralization Rate (hr^{-1})	10^{-6}	10^{-6}
Adsorption Constant ($l\ kg^{-1}$)	150	100
Longitudinal Dispersivity (cm)	0.2	0.2
Molecular Diffusion Coefficient ($cm^2\ hr^{-1}$)	0.045	0.034
Soil Properties		
Soil Type	Loam	Loam
Density ($l\ kg^{-1}$)	1.41	1.41
Residual Water Content ($cm^3\ cm^{-3}$)	0.061	0.061
Saturated Water Content ($cm^3\ cm^{-3}$)	0.40	0.40
Saturated Hydraulic Conductivity ($cm\ hr^{-1}$)	0.5017	0.5017
Air Entry Value (alpha)	0.011	0.011
Pore-size Distribution Index (n)	1.47	1.47
Initial Conditions		
Top Pressure Head (cm)	-100	-100
Bottom Pressure Head (cm)	-100	-100
Total Content ($mg\ kg^{-1}$)	7.70	0.22
Soil Solution Concentration (□M)	4.43	0.35
Mineral Phase ($mg\ kg^{-1}$)	6.65	0.1742
Organic Phase ($mg\ kg^{-1}$)	0.385	0.011
Inputs		
Atmospheric Deposition ($g\ ha^{-1}\ yr^{-1}$)	5	5
Fraction to Mineral phase	0	0
Discrete Sources: Application Time (day)	30 &210	30 &210
Amount ($g\ ha^{-1}$)	0.5	2.5
Fraction to Mineral Phase	0	0



Fraction to Organic Phase	0	0
Boundary Fluxes		
Concentration in Irrigation Water (□g l^{-1})	2.016	0.252
Prec., Evap. & Trans.	See Table 4-4	See Table 4-4
Plant Growth and Uptake	Crop 1	Crop 2
Beginning of the Season (day)	31	211
Harvest Time (day)	150	330
Initial Root Depth (cm)	0.1	
Initial Root Density (cm cm^{-3})	0.01	
Maximum Root Depth (cm)	20	
Maximum Root Density (cm cm^{-3})	1	
Root Distribution Coefficient	0.2	
Root Permeability Coefficient (□M)	30 for As, 0.1 for Cd	
Maximum Influx (□M cm $root^{-1}$ hr^{-1})	0.00001 for As, 0.0000005 for Cd	
Biomass Return Factor	0.5	
Root Water Uptake	Crop 1	Crop 2
Plant type	Tomatoes	Lettuce
P0 (cm)	-10	-10
Popt (cm)	-25	-25
P2H (cm)	-400	-550
P2L (cm)	-600	-650
P3 (cm)	-8000	-8000
R2H (cm hr^{-1})	0.0208	0.0208
R2L (cm hr^{-1})	0.00417	0.00417

Results and Discussion Outcomes of the model simulations based on the modified parameters are summarized as follows:

Default Simulation

The default model parameters for As and Cd are set based on values in Table 8.9 The default simulation depicts the mass balance of trace elements in a typical loamy soil growing two crops each year with a four- month growing season that receives 30 g As ha^{-1} yr^{-1} and 13 g Cd ha^{-1} yr^{-1} from various sources of atmospheric deposition, fertilizer application and irrigation. All the inputs are added to mobile phase and fifty percent of the previous crop uptake will be reincorporated as a discrete input in the organic form at the beginning of next crop season. After setting the basic information, soil properties, initial conditions, input, boundary fluxes, plant growth and uptake, and root water uptake, the mass balance was simulated for 100 years. The outputs of the model simulations illustrated the change and distribution of the trace elements pools in the soil profile, the pattern of plant uptake, and leaching below soil profile.

Total As Concentration of Soils

Under the normal crop growing conditions with a typical annual input of 30 g ha^{-1} of As from atmospheric deposition, fertilizers and irrigation, the total As content increases slowly from the initial value of 7.70 mg kg^{-1} to approximately 7.77 mg kg^{-1} in the 50 cm soil profile and to approximately 7.82 mg kg^{-1} in the 30 cm root zone over the 100-years simulation period (Figure 8.5). The similar trend as from the previous version of the model is obtained, in which the total Soil As content is slightly increase over 100 year. However, the total As concentration of the soil is again magnified when plotted as the left Y-axis of Figure 12. If the graph is re-plotted on a full 0 to 8 mg kg^{-1} scale (the dash line, right Y-axis of Figure 8.5), the same conclusion can be drawn that the change of total Soil As content over the 100-year simulation is not noticeable and the change is well within the range of variations expected in the soils and not measurable by routine soil sampling.

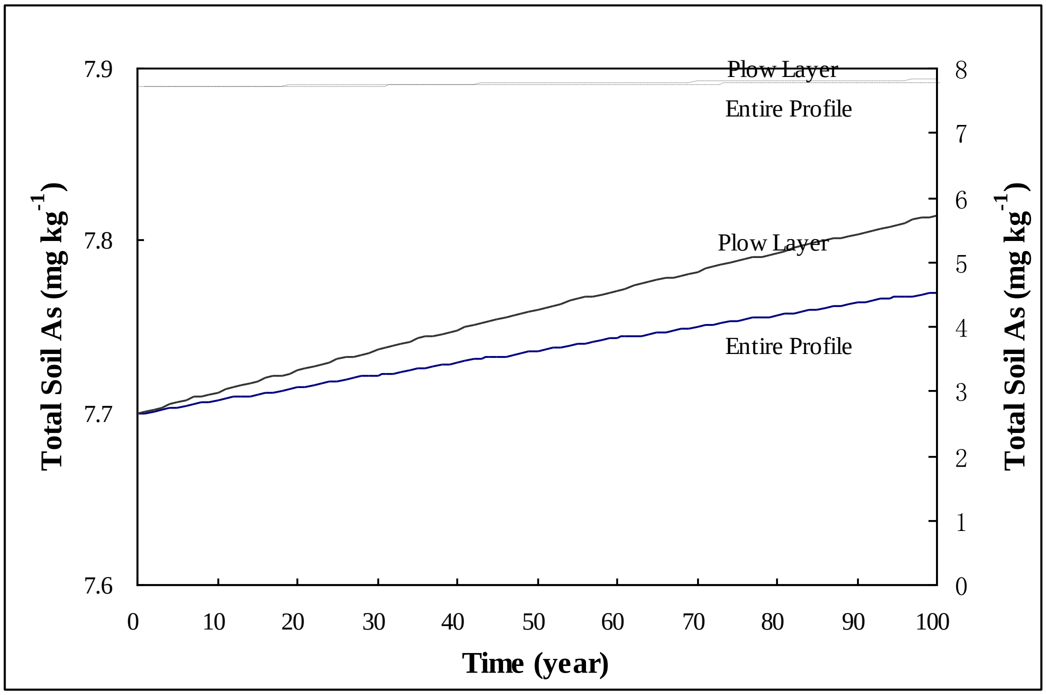


Figure 8.5. Simulated total As concentration of cropland soil at default parameter values for 100 years (expended and full scale).

Arsenic Concentration in Soil Solution

The trace element concentration in the solution phase is a deciding factor in controlling plant uptake and leaching and thus the total soil trace element content. Similarly, to the results from the previous version of the model, the change of As concentration in soil solution over the 100-year simulation period is unnoticeable (Figure 7.6). Again, the graph is somewhat misleading. The entire Y-axis scale represents only a 0.2 □g l^{-1}

concentration range. In the entire soil profile, it slowly increases from 4.43 □g l^{-1} to 4.59 □g $l^{-1.}$ The solution As concentration in the plow layer is a little greater than that of the entire soil profile. The change is quite small.

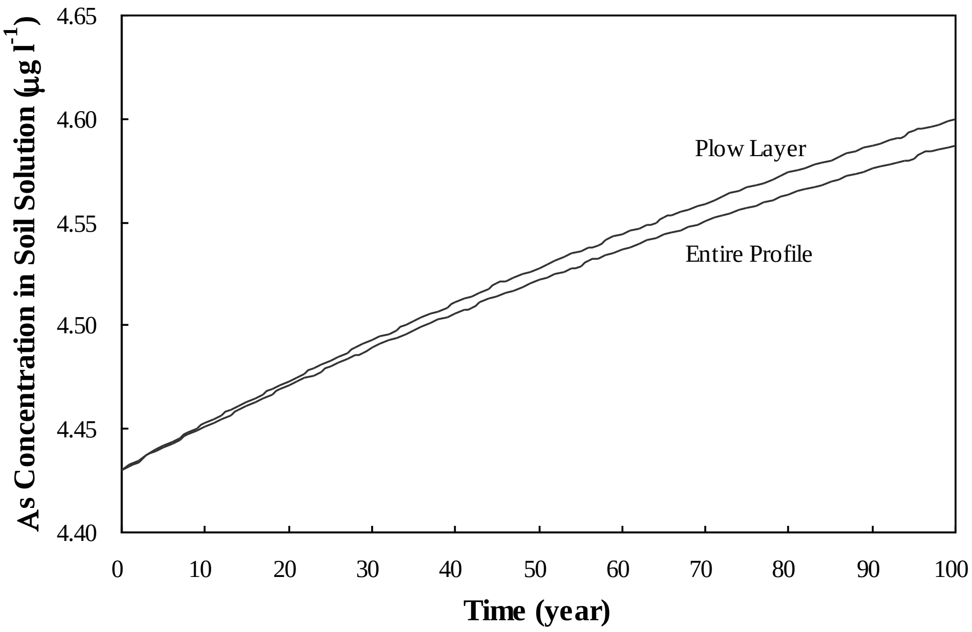


Figure 8.6. Simulated As concentration in soil solution of cropland soil at default parameters values for 100 years.

Arsenic Concentrations in Different Phases

The lack of significant changes in the total and solution concentrations of As in soil is indicative that the major As solid phase pools of the soil remained relatively constant for much of the 100-year simulation period, despite of the continuous external inputs of As. Figure 8.7 shows that change of the As phases over the 100 years. The results are similar to those from the previous version of the model. The As in mineral phase and adsorbed phase slightly builds up over the 100 years. The increase of the mineral phase and adsorbed phase As content is, however, less than 4%. At the same time, the organic phase As continuously declines even with a 50% of the plant uptake being reincorporated into soils as organic form. In the 100-year simulation, around 50% of organic phase As is depleted.

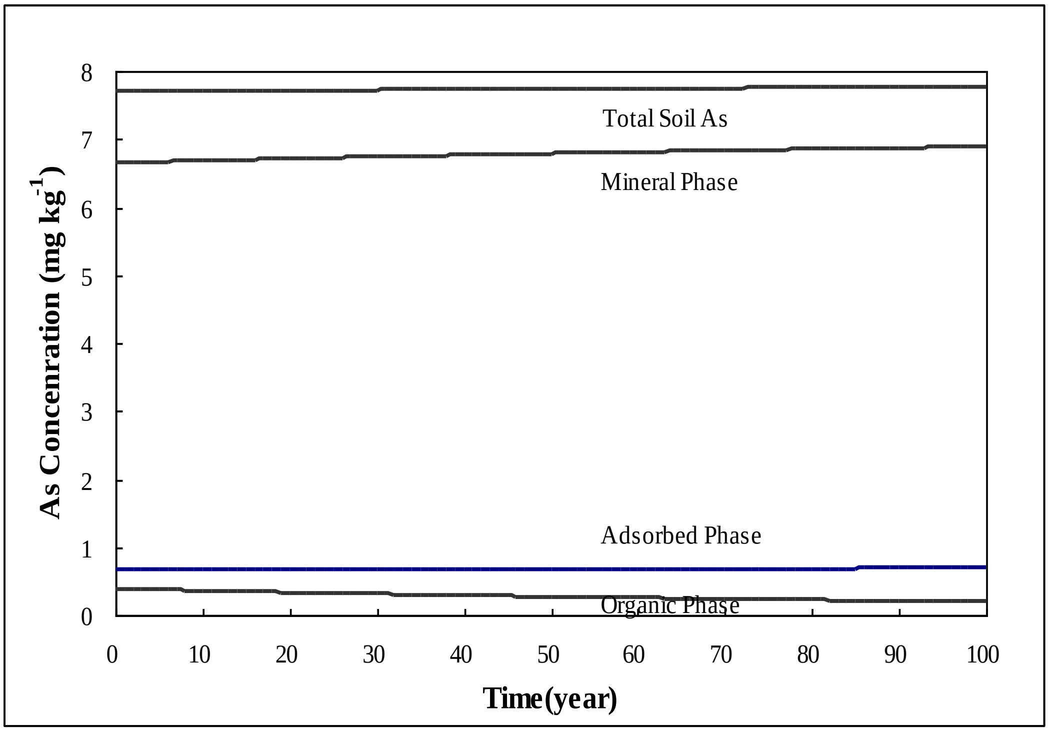


Figure 8.7. Concentrations of major As pools in the cropland soils at default parameters values for 100 years.

Profile Distribution of As Phases

The new version of the model allows studying the distribution of trace element along the soil profile at any specific time. Figure 8.8 shows the profile distribution of As phases at the end of 100-year simulation. At the beginning of simulation, the trace element pools are distributed uniformly along the 50 cm soil profile. Before the beginning of each crop season, the trace element pools in the plow layer (top 30 cm) are mixed and redistributed. Compared to the initial uniform distribution (dash line in Figure 8.6), there is a small accumulation of the total soil As content in the plow layer at the end of 100-year simulation due to inputs and the continuous mineralization of organic phase of As, which is consequentially leached out the soil profile or removed with plant uptake. The changes of adsorbed phase along the soil profile are unnoticeable. In the model, the biomass reincorporation only occurs in the plow layer. Thus As content of the organic phase below the plow layer is lower. The change of total As content below the top 35 cm is negligible and the accumulation of mineral phase As content below the top 35 cm is mainly attributed to the mineralization of the organic phase As.

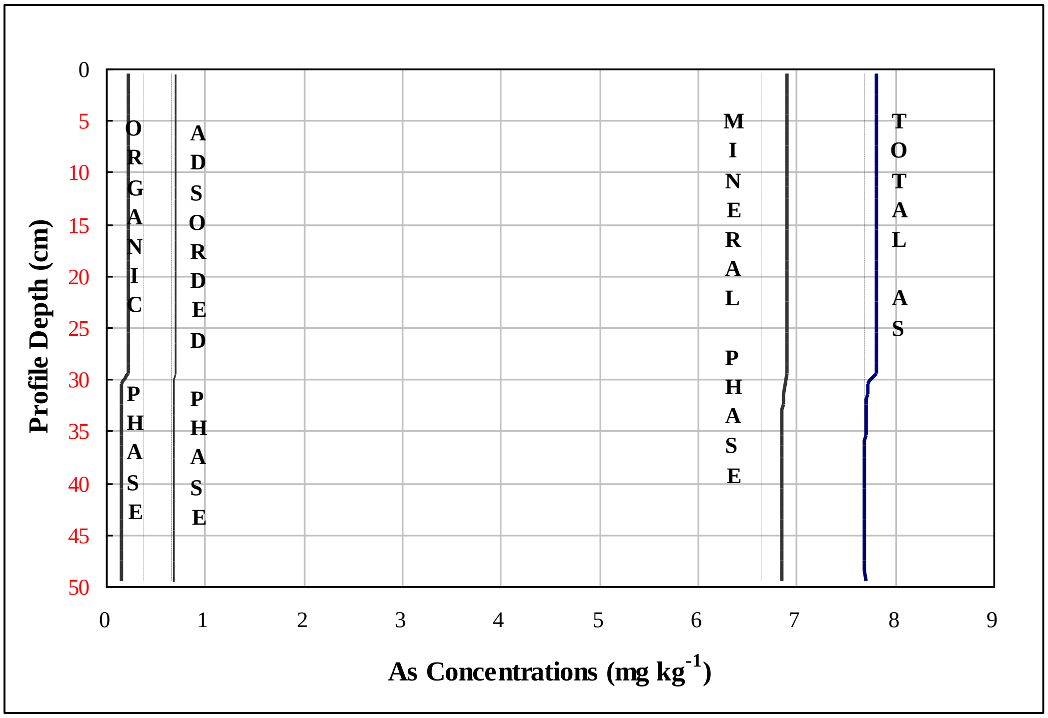
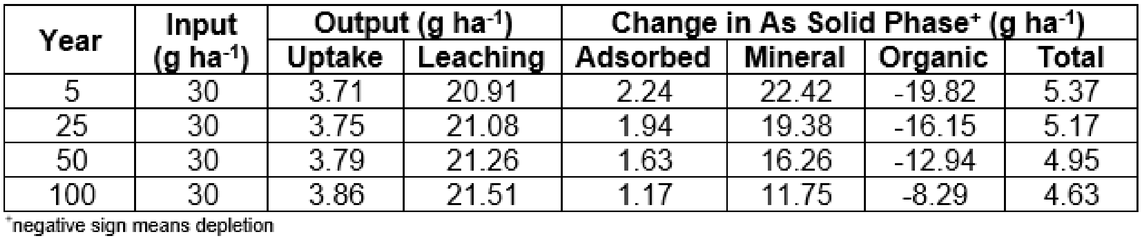


Figure 8.8. Profile distribution of As pools at the end of 100-year default simulation compared to the initial distribution (dash lines).

Mass Balance of As

The model allows studying the two type of mass balance at any specific time, namely the trace element fluxes and pools distribution. For a given input, the total trace element content with the change of pools in the studied soil profile is determined by two primary sink terms: the plant uptake and the leaching below soil profile. Table 8.6 illustrated the annual mass balance table at the 5th, 25th, 50th and 100th year. At the fifth year of receiving 30 g ha^{-1}, 3.71 g ha^{-1} of As is uptake by plants and 20.91 g ha^{-1} of As is leached, 5.37 g ha^{-1} of As is accumulated, which results in the increase of As in the adsorbed phase and mineral phase. The increase of As content in the adsorbed phase and mineral phase is not only due to the external inputs but also due to the mineralization of organic phase. Over time, the leaching loss and plant uptake of As increase in proportion to the rise of the As concentration in soil solution (as shown in Figure 7.8). Consequentially, the annual depletion of As over time increases slightly from 5.37 g ha^{-1} at fifth year to 4.63 g ha^{-1} at the 100th year. The annual deposit of As into the adsorbed and mineral phase decreases with decline of the annual mineralization rate of the organic phase As. By the 100th year, the annual plant uptake is 3.86 g ha^{-1} and the annual leaching loss is 21.51 g ha^{-1}, resulting in an annual accumulation of 4.63 g ha^{-1}. At this time, the annual deposition in adsorbed phase and mineral phase is 1.17 g ha^{-1} and 11.75 g ha^{-1}, respectively, with an annual depletion of 8.29 g ha^{-1} of organic phase As content. The As fate in cropland soils is dominated by the leaching process. The accumulation of As is mainly contributed to the buildup of mineral phase As.

Table 8.6. Simulated annual As mass balance of cropland soil in 50 cm soil profile for the 5th, 25th, 50th and 100th years.



Year	Input ($g\ ha^{-1}$)	Output ($g\ ha^{-1}$)		Change in As Solid Phase^{+} ($g\ ha^{-1}$)			
		Uptake	Leaching	Adsorbed	Mineral	Organic	Total
5	30	3.71	20.91	2.24	22.42	-19.82	5.37
25	30	3.75	21.08	1.94	19.38	-16.15	5.17
50	30	3.79	21.26	1.63	16.26	-12.94	4.95
100	30	3.86	21.51	1.17	11.75	-8.29	4.63

$^{+}$negative sign means depletion

Total Soil Cd Concentration

The changes of total soil Cd concentration in the plow layer and entire soil profile over 100 year of simulated crop growing conditions with a typical annual input of 13 g ha^{-1} are summarized in Figure 8.9. Unlike the total As concentration of the simulated cropland soils, the total Cd of the receiving soil increase from 0.22 mg kg^{-1} to approximately 0.31 mg kg^{-1} over the 50 cm profile. The increase represents a more than 140% increase of the Cd concentration in the soil. The inputs from the atmospheric deposition and irrigation are added to top layer of the soil profile and the inputs from fertilizers are added uniformly to plow layer. Thus the accumulation of total Cd in the plow layer is more pronounced. Over the 100-year simulation, the total soil Cd concentration increases from the baseline of 0.22 mg kg^{-1} to 0.36 mg kg^{-1} in the 30 cm plow layer. The rising trend is steady over the 100-year simulation period, although the rate of rise decreases slightly with time. The normal cropping practice of the irrigated agriculture could have a significant long term effect on the Cd concentration of the soils.

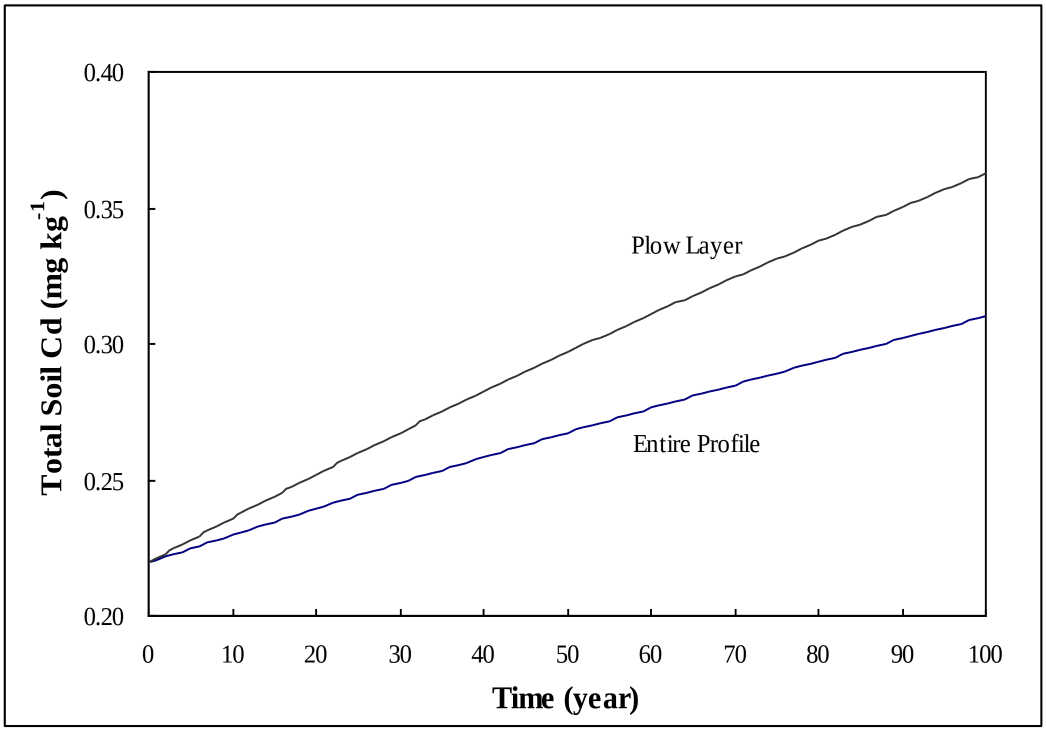


Figure 8.9. Simulated total As concentration of cropland soil at default parameter values for 100 years.

Cadmium Concentration in Soil Solution

Trace element in the soil solution phase is the core of the dynamic interactions of the element between different phases and a deciding factor that determines the amount of trace element removal from the soil profile by leaching and by plant uptake thus the total soil trace element content at specific external input level. Figure 8.10 shows the change of Cd concentration in soil solutions in the 30 cm plow layer and entire 50 cm soil profile over the 100-year simulation period. Due to the inputs only occurring in the plow layer, the increase of Cd concentration in soil solution in the plow layer is more significant. It increases from 0.35 □g l^{-1} to 0.47 □g l^{-1} over the 100-year simulation period. For the entire 50 cm profile layer, the Cd concentration in soil solution increases from 0.35 □g l^{-1} to 0.43 □g l^{-1}. Consequentially, there is a greater potential for the element to be uptaken by plants and to be leached below the soil profile due to the higher solution concentrations.

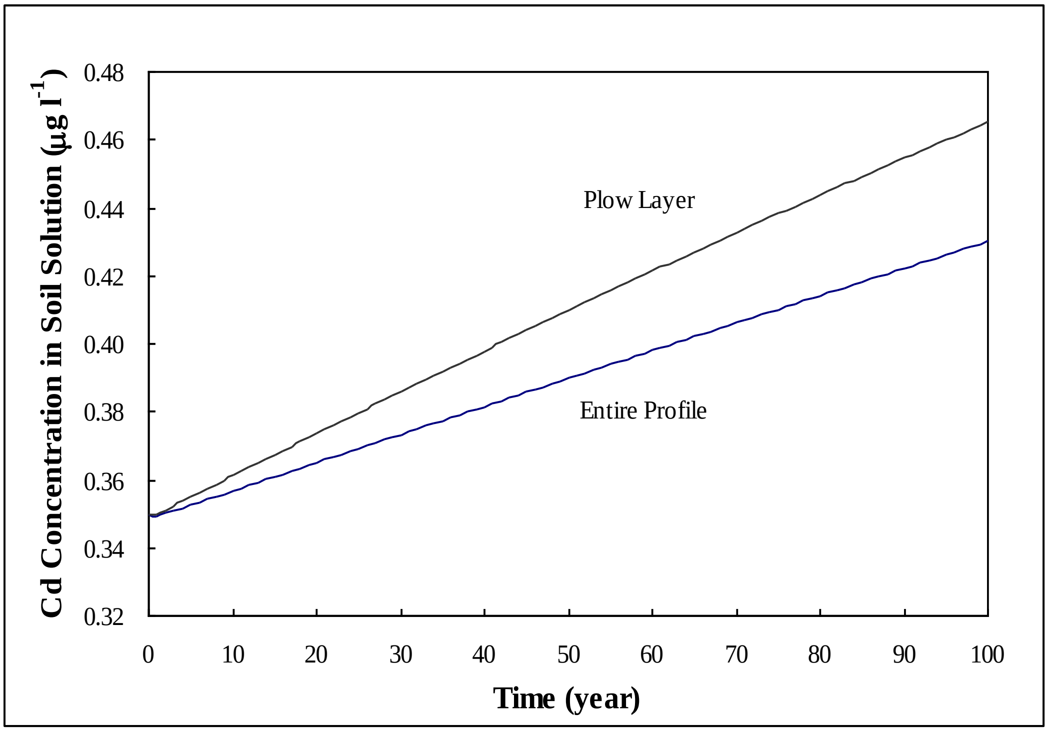


Figure 8.10. Simulated Cd concentration in soil solution of cropland soil at default parameter values for 100 years.

Cadmium Concentrations in Different Phases

The dynamic changes of the Cd pools in the soil are illustrated in Figure 8.11. The accumulation of Cd in the soil profile is mainly attributed to the build up in the mineral phase and organic phase. Over the 100 years, the Cd content in mineral phase increases from 0.17 mg kg^{-1} to 0.22 mg kg^{-1}. The Cd content in organic phase increases from 0.011 mg kg^{-1} to 0.052 mg kg^{-1}, which represent around 5 times increase. At the same time, the adsorbed Cd built up slightly. Over the 100-year simulation, the adsorbed Cd increases from 0.035 to 0.043 mg kg^{-1}. The absolute change of the adsorbed phase Cd is negligible when compared to the change of mineral phase and organic phase. It however represents a 23% increase.

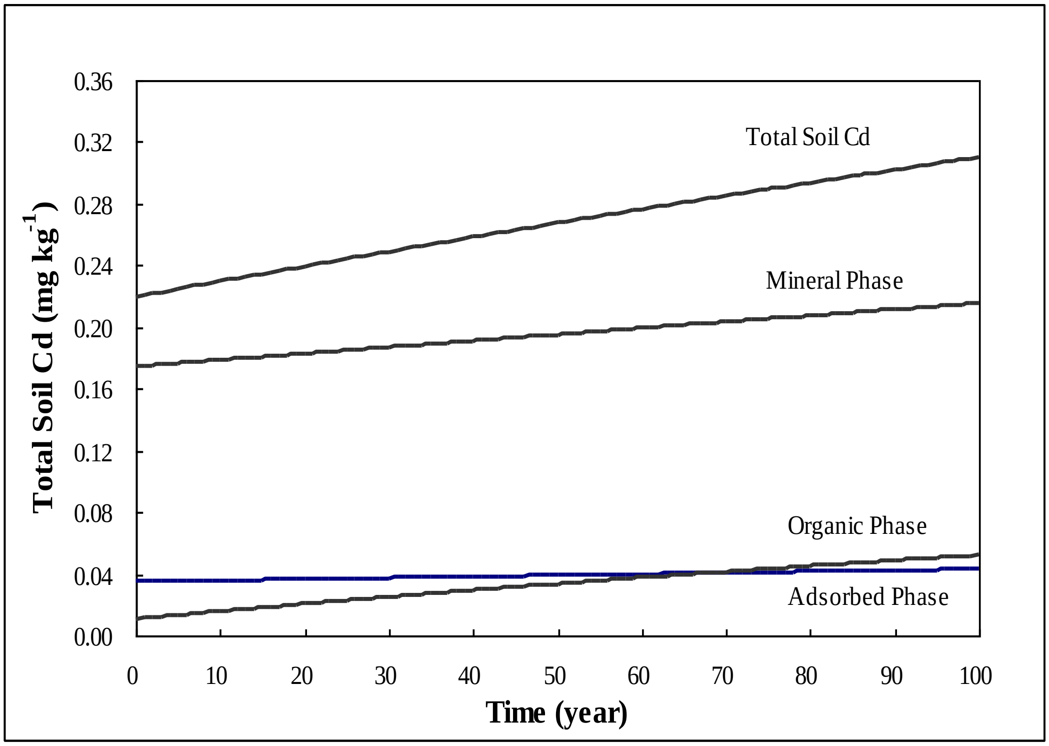


Figure 8.11. Concentrations of major Cd pools of cropland soil at default parameter values for 100 years.

Profile Distribution of Cd Phases

The profile distribution of Cd phases at the end of 100-year simulation is summarized in Figure 8.10. The significant increase of the total soil Cd content is indicative that there is an important shift of distribution of Cd pools along the soil profile. Compared to the initial uniform distribution (dash line in Figure 8.12), there is a significant accumulation of total soil Cd content in the plow layer at the end of the 100 year, with the continuous inputs from atmospheric deposition, fertilizers and irrigation and relative small loss with plant uptake removal and leaching. Consequently, there is a significant increase of organic phase and mineral phase content in the plow layer. The adsorbed phase Cd in the plow layer also increases, but the increase is not pronounced. In the mean time, the organic phase Cd below the plow layer declines due to the continuous mineralization without biomass reincorporation. The adsorbed phase Cd content below the plow layer increases somehow due to the diffusive and dispersive transport, resulting in an increase of Cd in mineral phase, which is in equilibrium with the Cd in adsorb phase, and consequently the total Cd soil content. The change of total Cd content becomes unnoticeable below the top 45 cm.

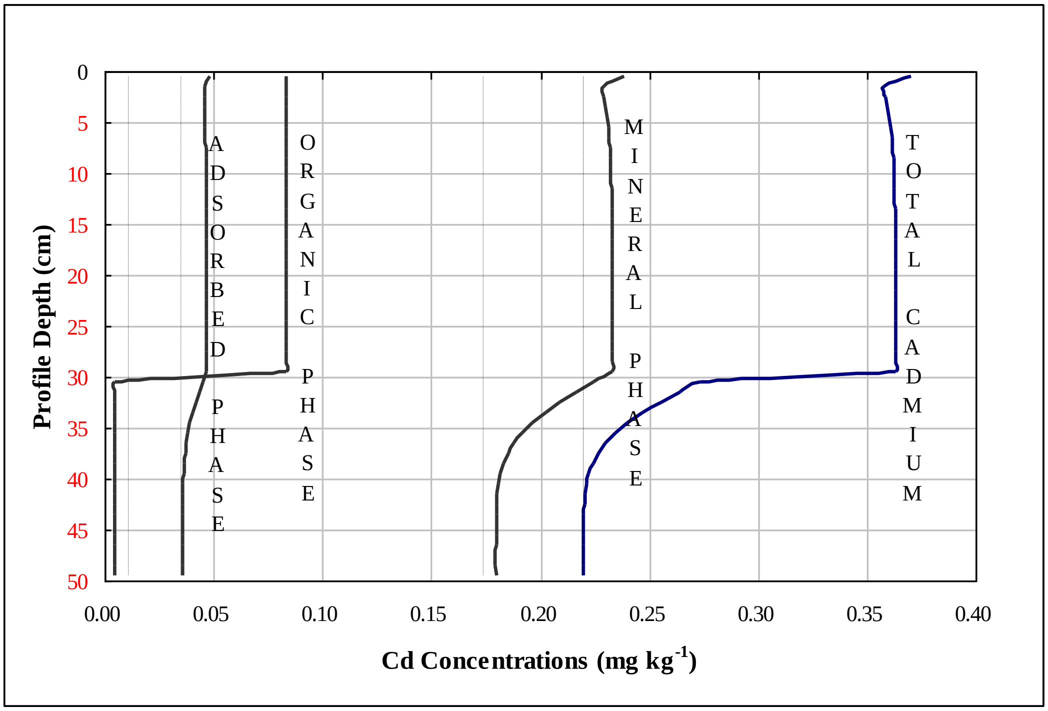


Figure 8.12. Profile distribution of Cd pools at the end of 100-year simulation compared to the initial distribution (dash lines).

Mass Balance of Cd

Table 8.7 illustrates the annual mass balance of Cd in the studied soil profile at 5th, 25th, 50th and 100th years. At the fifth year of receiving 13 g Cd ha^{-1}, 4.33 g ha^{-1} of Cd is uptaken by plants and 1.64 g ha^{-1} of Cd is leached out of the soil profile. The resulting net accumulation of 9.95 g Cd ha^{-1} is distributed among the adsorbed phase, mineral phase and organic phase. Over time, the annual Cd uptake by plants increases from 4.33 g ha^{-1} at the fifth year to 5.60 at the 100th year, which is in proportion to the rise of the Cd concentration soil solution in the plow layer (as shown in Figure 8.7). The annual leaching loss of Cd remains, however, unchanged through out the simulation period, and is correlated with the relative steady soil solution Cd concentration in the bottom section of the model. Consequentially, the annual deposit of Cd decreases slightly from 7.03 g ha^{-1} at fifth year to 5.71 g ha^{-1} at the 100th year with the annual deposits into the adsorbed phase and mineral phase decreasing. At the mean time, the annual deposits into the organic phase increases over time due to the increase of annual plant uptake and correspondingly greater inputs through biomass reincorporation. In the 100th year, the plant uptake accounts for 5.60 g ha^{-1} and leaching accounts for 1.69 g ha^{-1} of Cd removal, with an annual buildup of 0.56 g ha^{-1}, 2.38 g ha^{-1} and 2.78 g ha^{-1} of adsorbed phase, mineral phase and organic phase, respectively. The plant uptake is the predominant process controlling Cd fate in cropland soil. The accumulation of Cd in cropland soils is mainly caused by the buildup of the organic phase and mineral phase Cd content.

Table 8.7. Simulated annual Cd mass balance of cropland soil for 5, 25, 50 and 100 years in the entire 50 cm soil profile.

Year	Input (g ha^{-1})	Output (g ha^{-1})		Change in As Solid Phase (g ha^{-1})			
		Uptake	Leaching	Adsorbed	Mineral	Organic	Total
5	13	4.33	1.64	0.59	2.93	3.51	7.03
25	13	4.62	1.66	0.59	2.93	3.21	6.73
50	13	4.96	1.67	0.58	2.90	2.89	6.36
100	13	5.60	1.69	0.56	2.38	2.78	5.71

Factors Affecting Trace Elements Accumulation in the cropland Soils

Accumulation of trace element in the cropland soils is determined by the amount of external inputs and its removal with plant uptake and leaching. In the previous version of model, the leaching loss is determined by two parameters, the field hydraulic conductivity (K_h) and the field volumetric moisture water content (□), both were set as constants for the simulation period. The trace element concentration in soil solution of the soil profile, however, is dependent the dynamic transformation between different trace element phases. In the modified version of the model, the amount of leaching is characterized by the time dependent water flux and the dynamic trace element concentration in solution at the bottom section. Therefore, the boundaries fluxes and the soil hydraulic properties, which are deciding factors of the bottom water flux, may have significant impacts on the amount of trace element leaching out of the soil profile, consequentially on the mass balance of trace element in the cropland soils. Although the same kinetic equation is employed for calculating the plant uptake in both version of the model, the new profile distribution model allows simulating of the plant growth and root distribution in the soil profile. The root density is not a constant any more. It is a function of growing time and the characteristics of plant species. Therefore except for the parameters of the Michaelis-Menton kinetics model, the mass balance of trace element in the cropland soils may be affected by plant growth and the root distribution parameters.

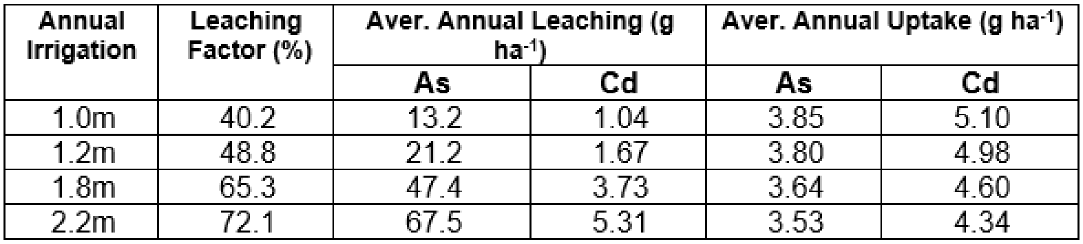
Most of the factors that govern the trace element transformations between phases in the soils, leaching and plant uptake of trace elements were already studied in the previous chapter. Since the similar model structure is adopted, the resulting accumulation should have the same trends. Therefore, we will not repeat the parameter sensitivity study. We will focus the effect of boundary fluxes including irrigation, evaporation and transpiration, plant growth, soil hydraulic properties and input forms on trace element accumulation in the cropland soils.

Irrigation Practice

In mass balance, the water balance and trace element balance go hand in hand. The water balance is mainly determined by the crop evapotranspiration and the amounts of irrigation/precipitation. Appropriate irrigation management is an important part of agricultural product activities. If insufficient water is applied, the plant development thus the productivity may be impaired. If more water than needed is applied, it not only wastes water and resources, but also can cause nutrients and other amendments to be leached. In the default simulation, the irrigation is designed based on the climate data (ET_0) of Imperial Valley County using a 75% irrigation efficacy. The total annual irrigation is around 1.2 m. In practice, the water application is often greater. If the irrigation efficacy was reduced to 50% and 40% or increase to 90% with all the other parameters remaining the same, the annual water application would be around 1.8 m, 2.2 m, and 1.0 m, respectively. As the annual irrigation increases, the bottom flux increases proportionally. The leaching factor, the percent of the applied irrigation water that drains below the soil profile, increases from 40.2%, to 48.8%, 65.3%, and 72.1% as the annual irrigation increases from 1.0 m, to 1.2 m, 1.8 m and 2.2 m, respectively. Consequentially, the leaching loss would increase proportionally (Table 8.8). When the annual irrigation increases from 1.0 m to 2.2 m, the average annual leaching loss of As and Cd increases by more than 4 times. In the mean time, the amount of plant uptake declines slightly since more irrigation results in a lower trace element concentration in the soil solution. Compared to the increase of leaching loss, the decrease of plant uptake of As and Cd is negligible. Therefore, less amount of trace elements is accumulated in soils as irrigation amount increases. The changes of total soil As and Cd contents at different irrigation practices over the 100-year simulation are illustrated in Figures 8.13 and 8.14. For the most efficient irrigation, namely, 1.0 m of annual irrigation, the change of total soil As is negligible. Over the 100-year simulation, the total soil As content increases lightly from the baseline level of 7.70 mg kg^{-1} to 7.88mg kg^{-1}. The input with the irrigation, fertilizers and atmospheric deposition is either removed by crop harvest or leaching out of the soil profile. When the annual irrigation increased from 1.0 m to 2.2 m, the total Soil As content at year 100 decreased from 7.88 to 7.12 mg kg^{-1} that represents a 10% of decrease.

The impact of irrigation practices on the total soil Cd content is more pronounced than that of the As. When the annual irrigation increased from 1.0 m to 2.2 m, the total soil Cd content at year 100 decreased from 0.32 to 0.27 mg kg^{-1}. The accumulation of Cd in soils is significant even with heavy irrigation. In summary, the irrigation practice may have great effect on the accumulation of trace elements in cropland soils by affecting the amount of plant uptake, and more important the amount of leaching out of soil profile.

Table 8.8. Average annual plant uptake and leaching at different irrigation practices.



Annual Irrigation	Leaching Factor (%)	Aver. Annual Leaching (g ha^{-1})		Aver. Annual Uptake (g ha^{-1})	
		As	Cd	As	Cd
1.0m	40.2	13.2	1.04	3.85	5.10
1.2m	48.8	21.2	1.67	3.80	4.98
1.8m	65.3	47.4	3.73	3.64	4.60
2.2m	72.1	67.5	5.31	3.53	4.34

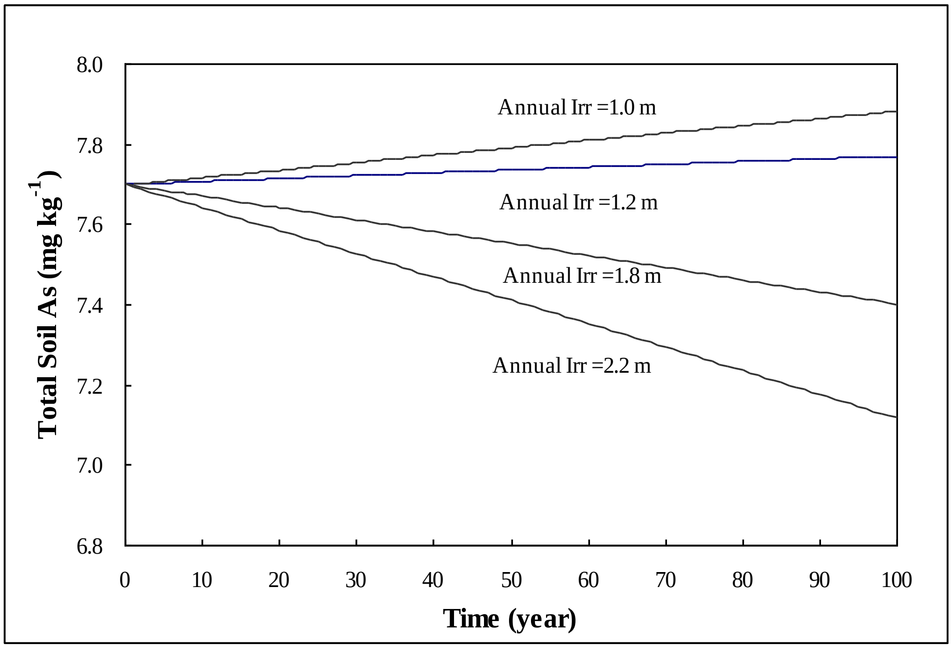


Figure 8.13.Simulated total Soil As content of cropland soil at different irrigation practices for 100 years.

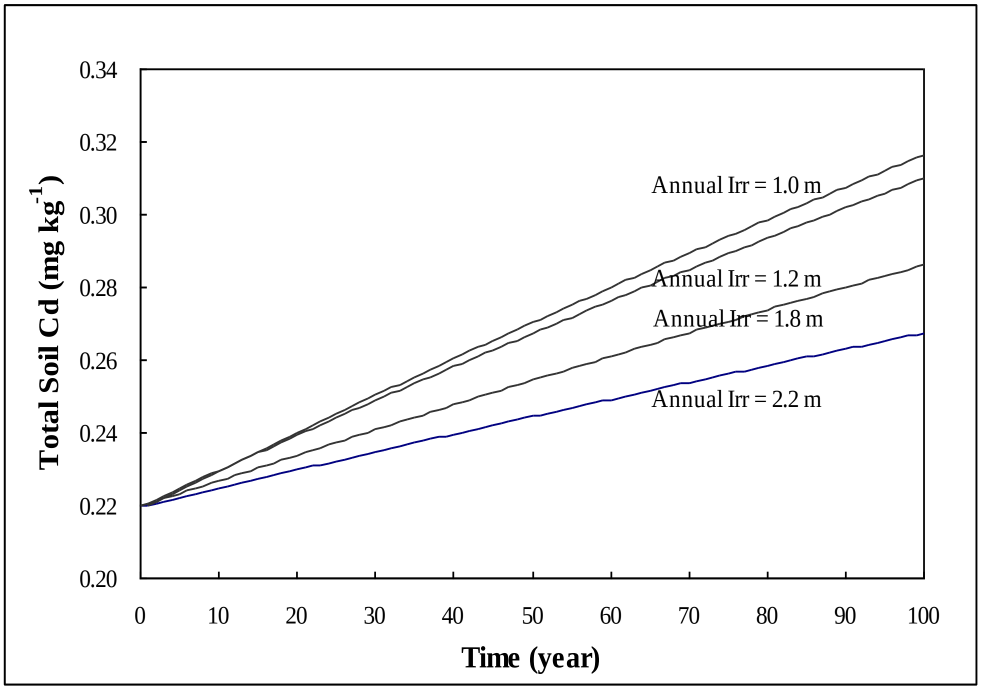
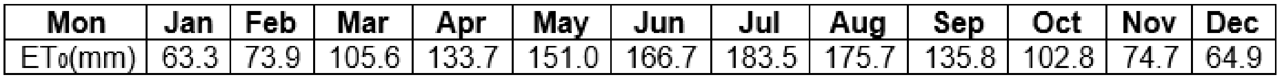


Figure 8.14. Simulated total Cd of cropland soil at different irrigation practices for 100 years.

Evaporation and Transpiration

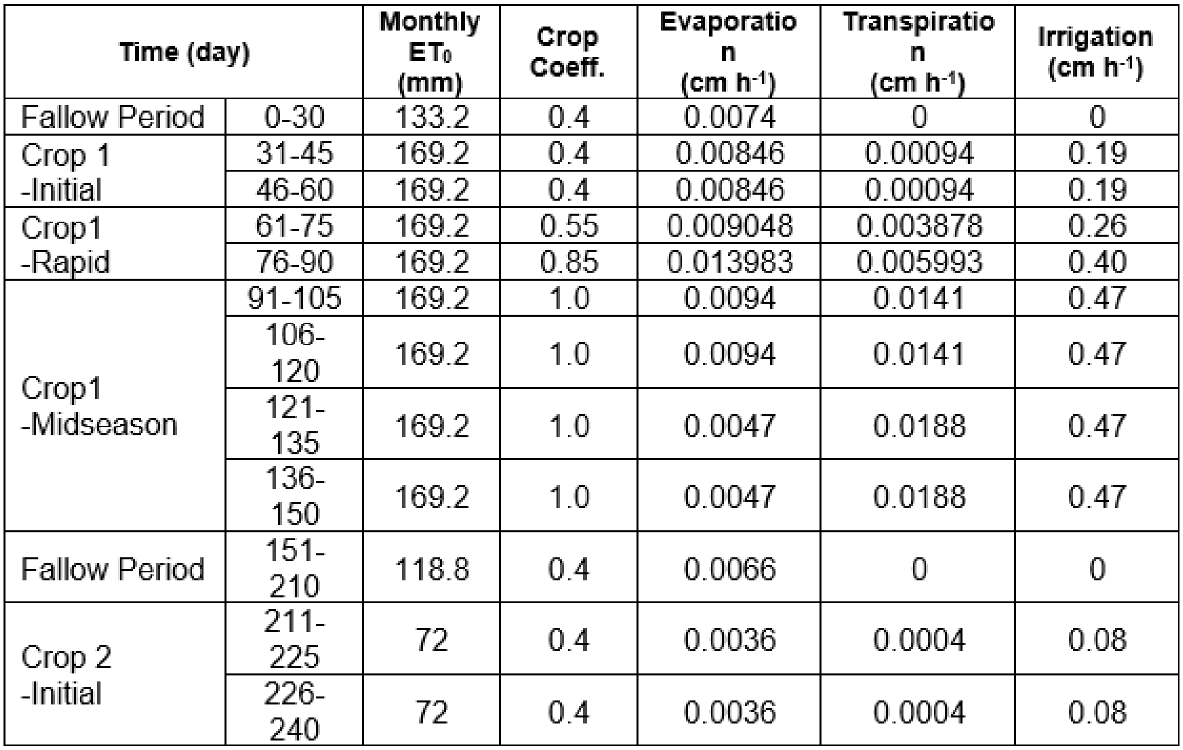
As summarized in the previous sections, the boundary fluxes are designed based on the climate data from Imperial Valley County. If the climate data (monthly ET_0) changed, all the boundary fluxes should change accordingly. The resulting accumulation of trace elements in soils may be different. Table 8.9 shows the average monthly ET_0 from the CIMIS weather station at UC, Riverside. Keeping all the other parameters and assumptions, the new designed boundary fluxes are summarized as Table 8.10. In this case, the annual irrigation is 1.0 m.

Table 8.9. Average monthly reference evapotranspiration (ET_0) in UC, Riverside area (data from CIMIS).



Mon	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
ET_0(mm)	63.3	73.9	105.6	133.7	151.0	166.7	183.5	175.7	135.8	102.8	74.7	64.9

Table 8.10. Designed boundary fluxes for a typical crop year based on climate data of UC, Riverside.



Time (day)		Monthly ET_0 (mm)	Crop Coeff.	Evaporation (cm h^{-1})	Transpiration (cm h^{-1})	Irrigation (cm h^{-1})
Fallow Period	0-30	133.2	0.4	0.0074	0	0
Crop 1 -Initial	31-45	169.2	0.4	0.00846	0.00094	0.19
	46-60	169.2	0.4	0.00846	0.00094	0.19
Crop1 -Rapid	61-75	169.2	0.55	0.009048	0.003878	0.26
	76-90	169.2	0.85	0.013983	0.005993	0.40
Crop1 -Midseason	91-105	169.2	1.0	0.0094	0.0141	0.47
	106-120	169.2	1.0	0.0094	0.0141	0.47
	121-135	169.2	1.0	0.0047	0.0188	0.47
	136-150	169.2	1.0	0.0047	0.0188	0.47
Fallow Period	151-210	118.8	0.4	0.0066	0	0
Crop 2 -Initial	211-225	72	0.4	0.0036	0.0004	0.08
	226-240	72	0.4	0.0036	0.0004	0.08

The accumulations of As and Cd at different evaporation and transpiration, which is set based on the climatic data at UCR and Imperial Valley, are illustrated in Figures 8.15 and 8.16. When the annual irrigation is the same, less water is leached out of the bottom soil profile due to greater evapotranspiration, thus less leaching and more As and Cd are accumulated in the soil (Imperial Valley Case). The difference between these two cases is, however, negligible. In summary, the effect of evaporation and transpiration on accumulation of As and Cd in cropland soil is limited.

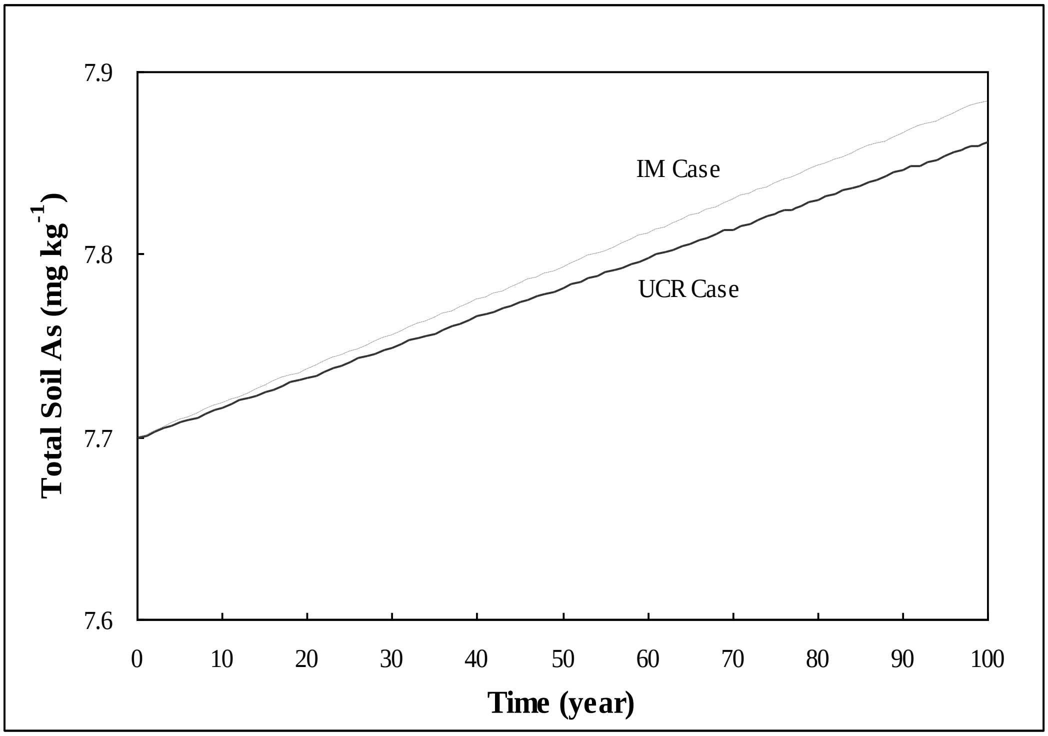


Figure 8.15. Simulated total As content of cropland soil at different boundary conditions for 100 years.

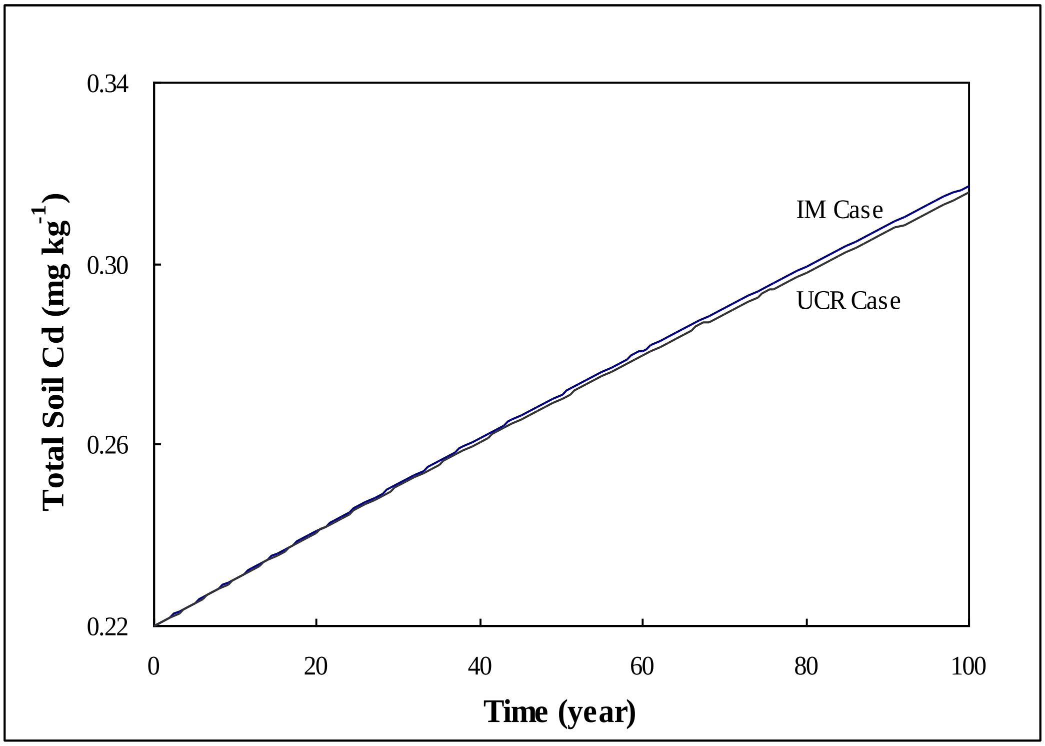


Figure 8.16. Simulated total Cd content of cropland soil at different boundary conditions for 100 years.

Soil Hydraulic Properties

Trace element mass balance is greatly dependent on water balance. Except for the boundary fluxes, the water retention and movement in soils are mainly controlled by soil hydraulic properties, namely the soil water retention curve and hydraulic conductivity function. The van Genuchten soil hydraulic functions are employed in the model and consequentially five independent parameters are required (i.e. Eq. 8.6). These parameters can be set based on the database from Carsel and Parrish (1988) or based on the prediction from the pedotransfer functions of Rosetta (Schapp et al., 2001). When the soil properties from the database are used, the model works well for most cases. But in cases that the saturated hydraulic conductivity is less than the irrigation flux such as clay soils, all of the soils are saturated after certain time of irrigation and the water flow simulation part from the HYDRUS will terminate. To make it work for clay soils, the designed flux of irrigation is decreased by 50% with 48 h irrigation each time. Figures 8.17 and 8.18 illustrated the change of total soil As and Cd content over the 100-simulation in different types of soils. The soil hydraulic properties for the loam are set based on the default database from Carsel and Parris (1988). The soil hydraulic properties for clay soil and sandy soil are set based on the predictions from the pedotransfer functions of Rosetta (Schapp et al., 2001). As soil type changes from clay to sandy, the soil hydraulic conductivity increases rapidly. More water is retained in the clay soils. The leaching factor for clay, loam and sandy soil is 80.6, 49.3, and 42.8%, respectively (Table 8.11). Consequentially, more trace elements are leached out of the soil profile in the clay soil. When the soil type changes from clay to sandy, the average annual leaching increases from 22.9 g ha^{-1} to 43.3 g ha^{-1} for As, and from 1.80 g ha^{-1} to 3.40 g ha^{-1} for Cd. In the mean time, the plant uptake decreases from 3.79 g ha^{-1} to 3.67 g ha^{-1} for As, from 4.95 g ha^{-1} to 4.67 g ha^{-1} for Cd. The effect of soil hydraulic properties on the plant uptake is limited. In summary, the total As and Cd contents of the soils at the end of the 100-year simulation period increases from 7.46, 7.70, to 7.75 mg kg^{-1}, and from 0.290^1, 0.305, to 0.309 mg kg^{-1}, respectively, for sandy, loam and clay soils.

Table 8.11. Average annual plant uptake and leaching at different soil hydraulic properties based on soil type.

Soil Type	Leaching Factor (%)	Average Annual Leaching (g ha^{-1})		Average Annual Uptake (g ha^{-1})	
		As	Cd	As	Cd
Clay	42.8	22.9	1.80	3.79	4.95
Loam	49.3	26.4	2.08	3.77	4.91
Sandy	80.6	43.3	3.40	3.67	4.67

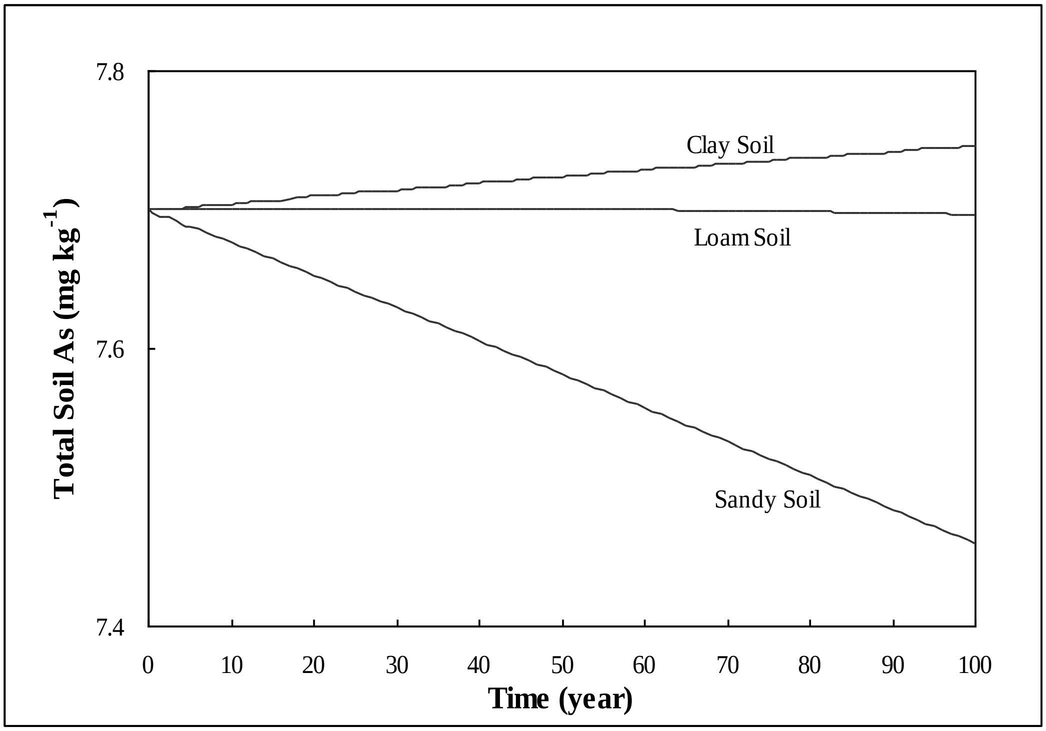


Figure 8.17. Simulated total Soil As content of cropland soil at different soil hydraulic properties based on soil type for 100 years

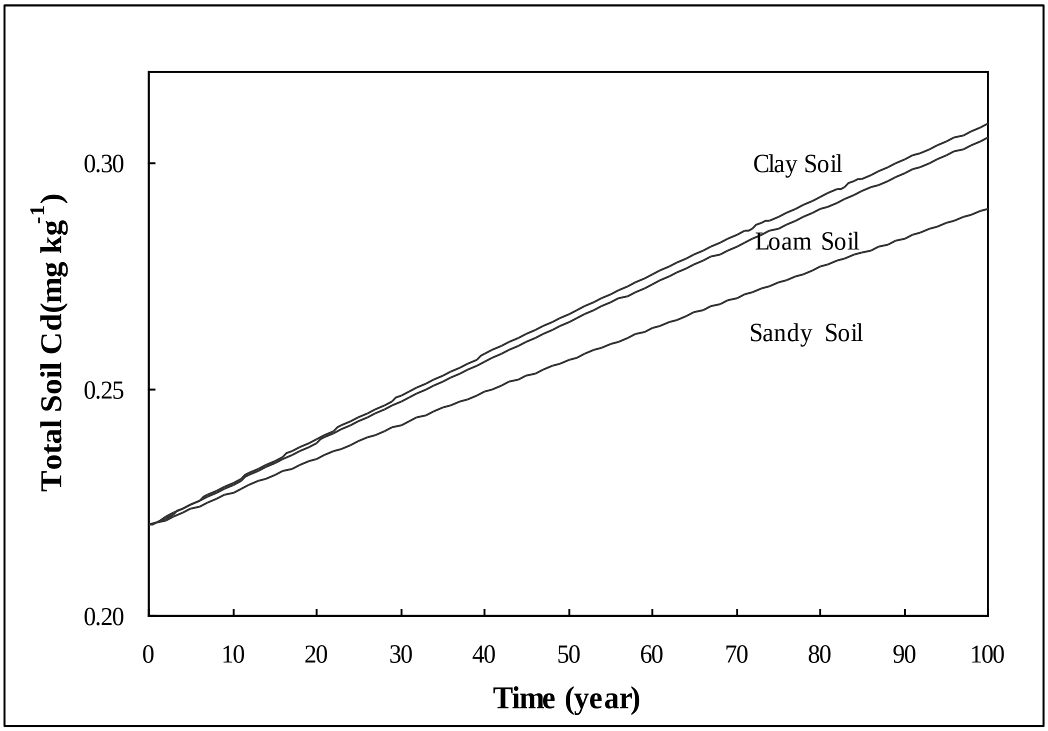


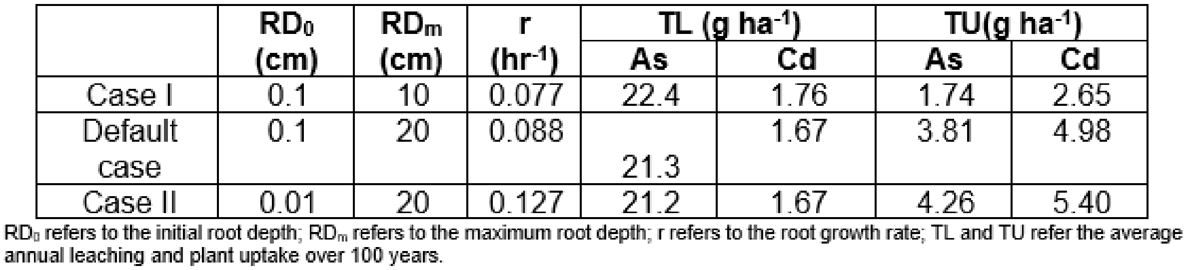
Figure 8.18. Simulated total Soil Cd content of cropland soil at different soil hydraulic properties based on soil type for 100 years

Plant Growth and Uptake

As one of the primary sinks through which trace elements in the soil may be lost, plant uptake may have significant effects on the trace element accumulation in cropland soils. The amount of plant uptake is determined by the root density and the influx rate represented by the Michaelis-Menton kinetics. The effect of maximum influx rate on trace element accumulation in soils is already discussed in the previous chapter. To assess the impact of the plant growth, the accumulation of As and Cd at different sets of root growth parameters, namely the initial root depth and root density, the maximum root depth and root density were studied. The root depth development doesn't directly correlate with the amount of crop uptake. However, the root growth rate and root distribution in the model are calculated based on the data of root depth. The growth rate is calculated based on the assumption that 50% of the rooting depth will be reached after 50% of the growing season has elapsed and the root mass distribution declines exponentially as a function of root depth. More important, the total root length in the soil profile, which is one of the deciding factors for calculating the amount of plant uptake, is determined by the root length density and the depth of the root zone (the root depth). Figures 7.19 and 7.20 summarized the accumulation of As and Cd using different root depth development parameters. As the root growth rate increases from 0.077 hr^{-1}(case I, in which the maximum root depth decrease from the default 20 cm to 10 cm), to 0.088 hr^{-1} (default case), and to 0.127 hr^{-1} (case II, in which the initial root depth decreases from the default 0.1 cm to 0.01 cm), the average annual plant uptake increases accordingly (Table 8.12).

In the mean time, the leaching decreases slightly. The decrease of leaching is not significant comparing with the increase of plant uptake. Therefore, the total soil As and Cd content decreases slightly from 7.78, 7.77, to 7.76 mg kg^{-1}, and from 0.34, 0.31, to 0.30 mg kg^{-1}, respectively, as the root depth development parameters change from case I to the default case to and case II. The effect of root depth development on the accumulation of Cd in cropland soils is more pronounced as the fate of Cd is dominated by the plant uptake. In summary, the effect of the root depth development on the accumulation of trace element in cropland soils is limited, especially the maximum root depth.

Table 8.12. Average annual leaching and plant uptake at different root depth development cases.



	RD_0 (cm)	RD_m (cm)	r (hr^{-1})	TL (g ha^{-1})		TU(g ha^{-1})	
				As	Cd	As	Cd
Case I	0.1	10	0.077	22.4	1.76	1.74	2.65
Default case	0.1	20	0.088	21.3	1.67	3.81	4.98
Case II	0.01	20	0.127	21.2	1.67	4.26	5.40

RD_0 refers to the initial root depth; RD_m refers to the maximum root depth; r refers to the root growth rate; TL and TU refer the average annual leaching and plant uptake over 100 years.

When the initial root density increases from the default 0.01 cm root cm^{-3} soil to 0.1 cm root cm^{-3} soil (Case III) or the maximum root density increases from the default 1 cm root cm^{-3} soil to 2 cm root cm^{-3} soil (Case IV), the plant uptake changes proportionally. The average annual uptake over the 100- year increases from 3.81, 4.24, to 7.03 g ha^{-1}, and from 4.98, 5.38 , to 7.39 g ha^{-1} for As and Cd as the root density parameters changes from the default case to the Case I and to the Case II, respectively. Consequentially, the total As and Cd contents of soils at the end of the 100-year simulation decreases slightly from 7.77, 7.76, to 7.72 mg kg^{-1}, and from 0.31, 0.30, to 0.28 mg kg^{-1}, respectively ss illustrated in Figures 8.21 and 8.22. Since the mass balances of As in cropland soils are controlled by the leaching process, the amount of plant uptake is infinitesimally small on an annual basis compared to the total soil trace element pool, the effect of root mass development on accumulation of As is not pronounced. For Cd, the mass balance is controlled by the plant uptake process. Thus, the effect of root mass development on accumulation of Cd is more significant.

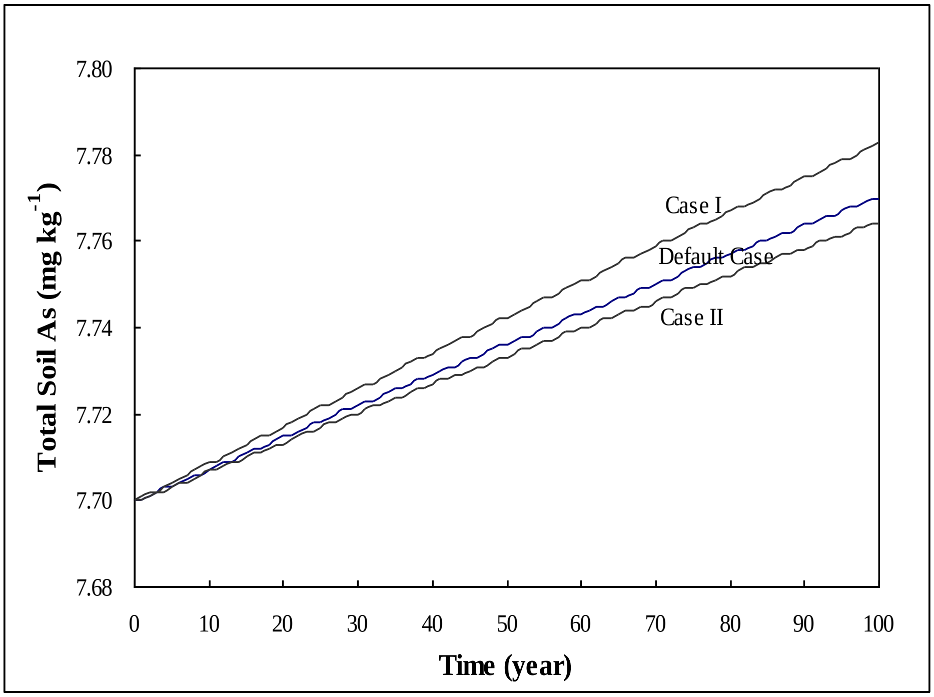


Figure 8.19. Simulated total Soil As content of cropland soil at different root depth development for 100 years

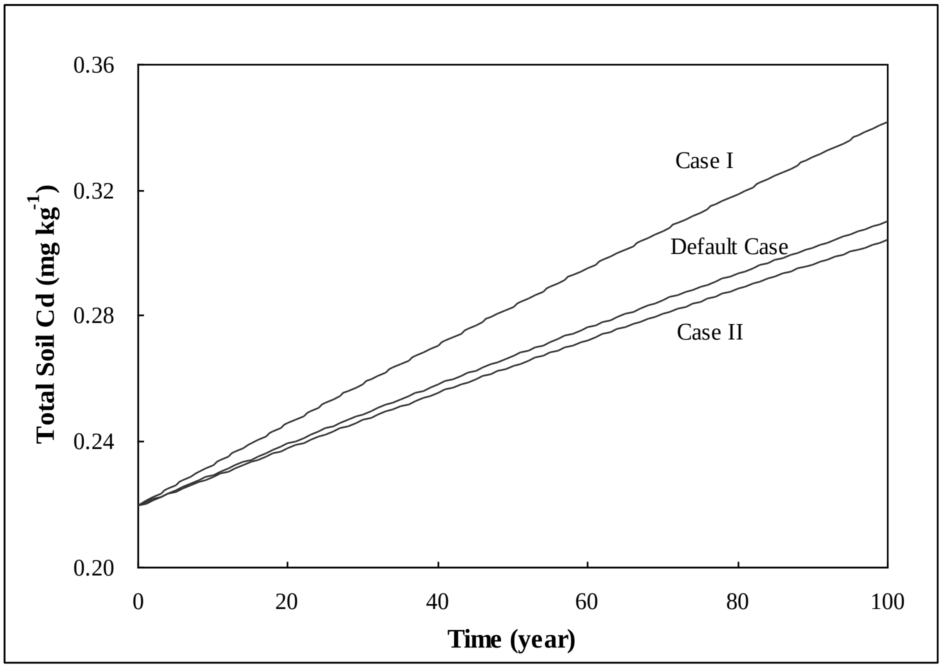


Figure 8.20. Simulated total Soil Cd content of cropland soil at different root depth development for 100 years

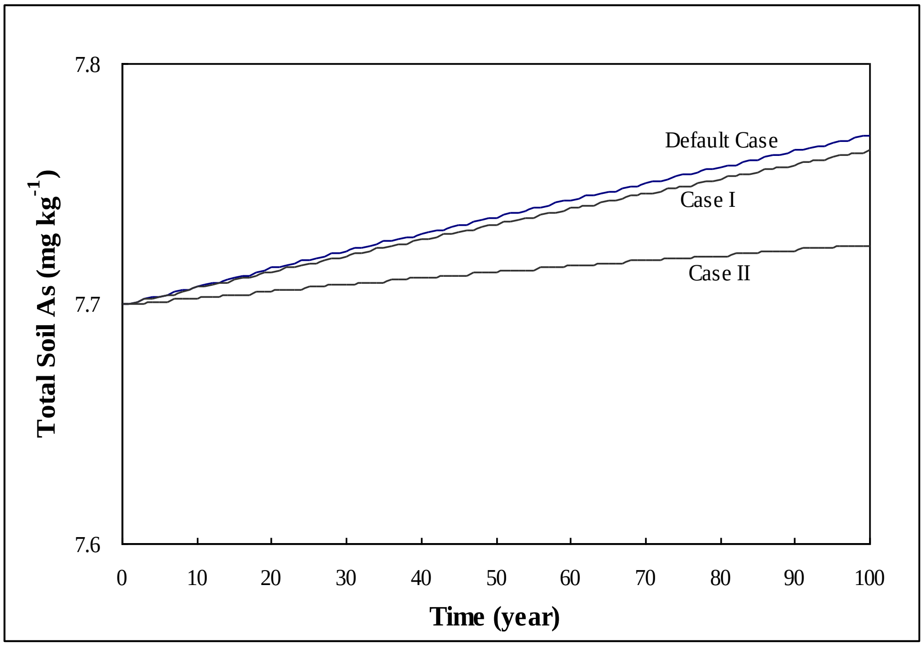


Figure 8.21. Simulated total Soil As content of cropland soil at different root mass development for 100 years

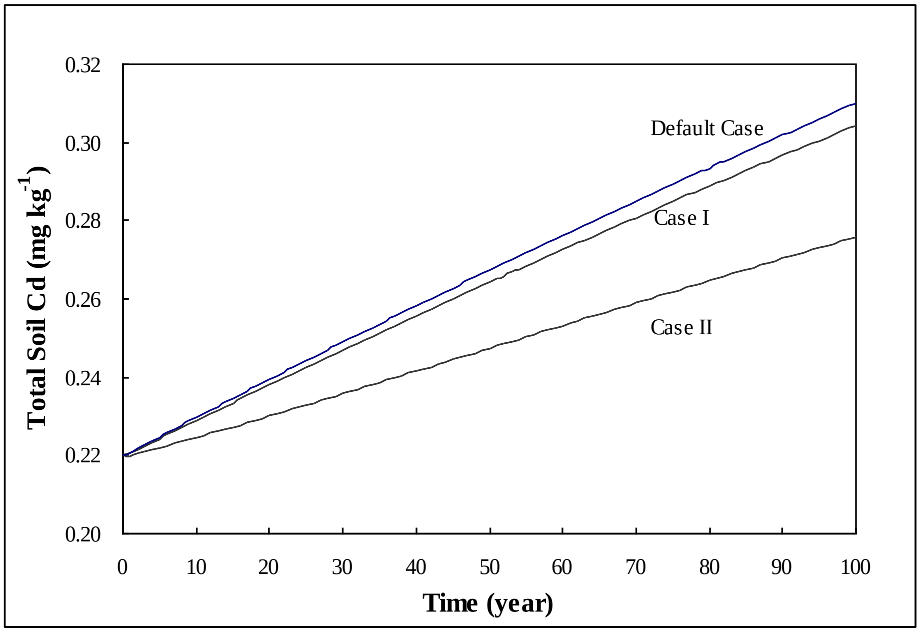


Figure 8.22. Simulated total Soil Cd content of cropland soil at different root mass development for 100 years

Chemical Forms of Trace Element Inputs

In the profile model, the external inputs are sorted into three categories: inputs from atmospheric deposition and with irrigation water are added to the top element of the soil profile, discrete sources from fertilizes, micronutrients and waste disposal are added uniformly to plow layer. In addition, the chemical forms of the inputs from the continuous atmospheric deposition and discrete sources inputs were considered in the model. The inputs can be added to mobile phase, mineral phase or organic phase. For default simulation, all the inputs from the deposition and fertilizers are added to mobile phase directly. In the real situation, part of these inputs may be in mineral phase or organic phase.

When 50% (or any other random number) of the inputs from atmospheric deposition and fertilizers is added to soil profile as mineral phase, there is no change in the mass balance of As and Cd in soil during the 100 years. Although it may affect the trace element distribution in a short time, its effect on trace element fluxes is quite limited. Rather than dependent on the form of the solid phase, plant uptake is dependent on the trace element concentration in the solution phase, which is relatively steady since the mobile phase and the mineral phase are in relatively faster kinetic equilibrium. The amount of leaching is dependent on the water flux at the bottom of the soil profile and corresponding trace element concentration in soil solution there, thus it is independent of the input forms.

The inputs can be in organic form when biosolids are applied. The kinetic of mineralization is several orders less than that of the precipitation-dissolution process. Therefore, when part of the inputs is added as the organic phase, it will not only affect trace element distribution in the profile, but also the mass balance of trace element in cropland soils. Figures 8.23 and 8.24 illustrate the change of total As and Cd contents when 0% or 80% of the discrete source of 55 g As ha^{-1} and 21 g Cd ha^{-1} is added as organic phase, while keeping all the other parameters the same except that the input for irrigation is set to zero. When 80% of the discrete source is added as organic phase, less amount of trace elements is removed by plant uptake. Thus, more trace elements are accumulated in soil. However, the effect is quite limited. The difference of total As and Cd contents of soils between two cases is negligible.

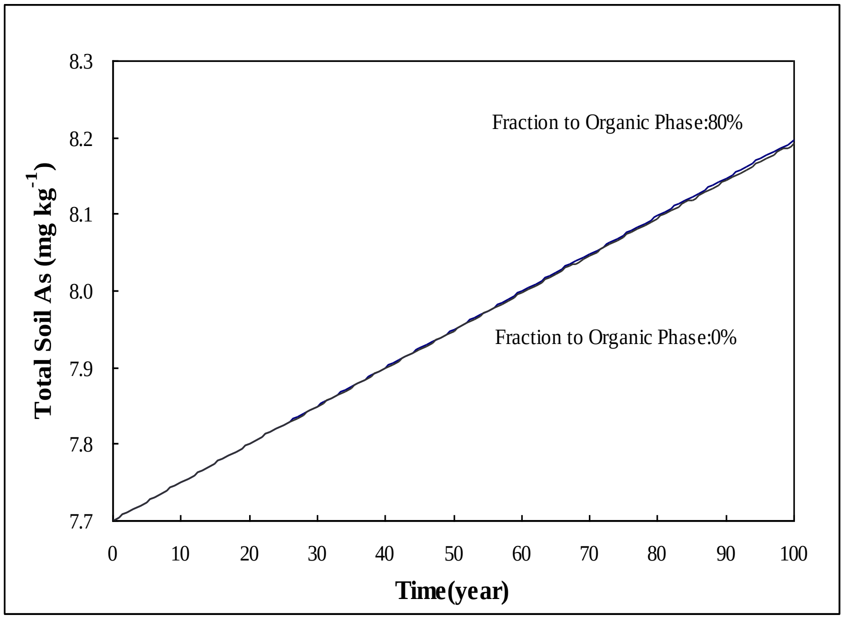


Figure 8.23. Simulated total Soil As content of cropland soil at different fraction to organic phase of discrete source for 100 years

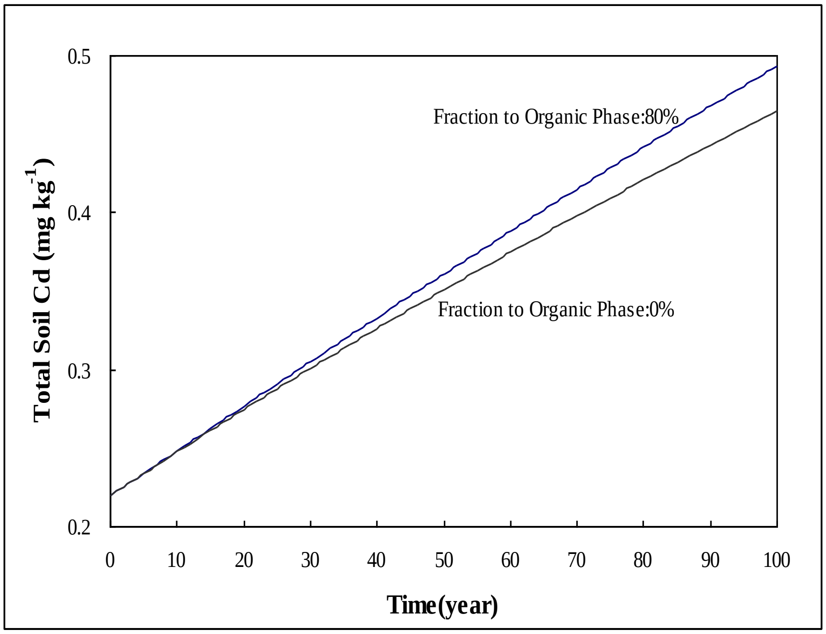


Figure 8.24. Simulated total Soil As content of cropland soil at different fraction to organic phase of discrete source for 100 years

Conclusions

By coupling the trace element mass balance with the water flow algorithms of HYDRUS-1D, the model was modified to account for trace element distributions in the soil profiles. In the modified model, the simulated soil profile is discretized into a number of uniform adjoining sections. In each section, the same scheme as defined in the previous model was adopted. The external inputs are sorted into three categories. Inputs from atmospheric deposition and with irrigation water are added to the top element of the soil profile. Discrete sources from fertilizes, micronutrient and waste disposal are added uniformly to the plow layer. The model allows simulating plant root growth and distribution along the soil profile and the solute transport is simulated with the convective-dispersive equation. The model not only allows studying the pools and fluxes of trace element in cropland soils, but also assessing the distribution of trace elements along the soil profile.

Under the normal crop practice that typically receives 30 and 13 g $ha^{-1}yr^{-1}$ of As from sources of atmospheric deposition, fertilizer application and irrigation, similar results as the previous model are obtained. The cropping practices do not have significant effect on the total As content of the soils therefore the distribution of different pools, but on total Cd content of the soils. The accumulation of Cd in the root zone is more than 60% over the 100-year simulation. Mass balance study shows the accumulation of Cd is mainly due to the buildup of Cd in the mineral phase and organic phase. The mass balance of As and Cd in cropland soils is dominated by the leaching process and by plant uptake process, respectively. Due to the diffusive and dispersive transport, the total Cd content below the plow layer is somewhat elevated.

The accumulation of trace element in the cropland soils at different irrigation practice, climate environment, soil hydraulic properties and plant growth conditions were studied specifically. The amount of As and Cd leaching is characterized by the water flux and the trace element concentration in soil solution at the bottom section. When heavy irrigation is applied, more trace elements are leached out the soil profile. In the meantime, less amount of trace elements is removed by plant uptake since more solute is moved out of the root zone with water. However, the effect of irrigation on uptake is limited. When the annual irrigation increase from 1.0 m to 2.2 m, the total soil As and Cd contents decrease from 7.88 to 7.12 mg kg^{-1}, and from 0.32 to 0.27 mg kg^{-1}, respectively.

Except the amount of water applied, the soil hydraulic properties are deciding factors for controlling the water movement in the soil profile. As the soil type changes from clay to sandy, the soil hydraulic conductivity increases rapidly. More water is retained by a clay soil, which will affect the amount of leaching out of the soil profile and the plant uptake. The effect of soil hydraulic properties on plant uptake is, however, limited. Consequentially, more trace elements are accumulated due to less leaching. Over the 100 years, the total As and Cd contents of soils increases from 7.46 mg kg^{-1}, 7.70 mg kg^{-1}, to 7.75 mg kg^{-1}, and from 0.290 mg kg^{-1}, 0.305 mg kg^{-1}, to 0.309 mg kg^{-1}, respectively, for the sandy, loam, and clay soils.

The water balance may also be affected by the evaporation and transpiration. When the annual irrigation is the same, less water is leached out of the bottom soil profile if evapotranspiration is high, thus less leaching and more trace elements are accumulated.

The case studies based on climatic data of UC Riverside and the Imperial Valley CIMIS stations show that the effects of evaporation and transpiration on trace element accumulation in the soils are limited.

The amount of plant uptake is characterized by the root density, which is a function of time and position, and the influx rate, representing by the Michaelis-Menton kinetics. The amount of plant uptake is affected by the root depth development parameters since they determine the root growth rate and root distribution. Plant uptake increases as the root growth rate increases. The total soil As and Cd content decreases slightly from 7.78, 7.77, to 7.76 mg kg^{-1}, and from 0.34, 0.31, to 0.30 mg kg^{-1}, respectively, as the root depth development parameters changes from the case that the maximum root depth decreases from the default 20 cm to 10 cm, to the case that the initial root depth decreases from the default 0.1 cm to 0.01 cm. As the initial or maximum root density increases, the amount of plant uptake increases proportionally. The effect of root mass development on accumulation of Cd is more pronounced than that of As, in which the mass balance is dominated by the plant uptake process. Over the 100 years, the total As and Cd contents of soils decreases slightly from 7.77, 7.76, to 7.72 mg kg^{-1}, and from 0.31, 0.30, 0.28 mg kg^{-1}, respectively when the root mass development parameters change from the default case to the case that the initial root density increases from the default 0.01 cm root cm^{-3} soil to 0.1 cm root cm^{-3} soil, and to the case that the maximum root density increases from the default 1 cm root cm^{-3} soil to 2 cm root cm^{-3} soil. Overall, the effect of root growth on the trace element accumulation in cropland soils is limited.

References

AAPFCO (Association of American Plant Food Control Officials). 2002. Statement of Interpretation and Policy (SUIP) 25. Metals in Fertilizers. http://aspfco.org/SUIP25Aug02.htm

Abedin M. J., J. Feldmann, and A. A. Mecharg. 2002. Uptake kinetics of arsenic species in rice plants. Plant Physiology, 128:1120-1128.

Acock B., and A. Pachepsky. 1996. Convective-diffusive model of two-dimensional root growth and proliferation, Plant Soil 180: 231-240.

Ahnstrom, Z. S., and D. R. Parker. 1999. Development and assessment of a sequential extraction procedure for the fractional of soil cadmium. Soil Sci. Soc. Am. J. 63:1650-1658.

Allen, H. E., Yu-Tung Chen, Yimin Li, C. P. Huang, and P. F. Sanders. 1995. Soil Partition Coefficients for Cd by Column Desorption and Comparison to Batch Adsorption Measurements. Environmental Science and Technology 29(8):1887-1891.

Andrewes, P., R. M. Town, M. J. Hedley and P. Loganathan. 1996. Measurement of plant available cadmium in New Zealand soils. Australian Journal of Soil Research, 34:441-452.

Arduini, I., Gotbold, D. and Onnis, A.: 1996, Cadmium and copper uptake and distribution in Mediterranean tree seedlings, Physiol. Plant. 97, 111–117.

Barber, S. A. and J. H. Cushman. 1981. Nitrogen uptake model for agronomic crops. In Modeling waste water renovation, Iskander I.K., ed., 382-409.

Bear J. 1972. Dynamics of Fluid in Porous Media. Elsevier, New York, NY.

Beneš, S. 1994. Contents and Balance of Elements in the Compartments of the Environment. Part II, Czech Ministry of Environment, 154 pp. (in Czech).

Borg, H. and D. W. Grimes. 1986. Depth development of roots with time: an empirical description. Trans of ASAE, 29:194-197.

Bradford, G. R., A. C. Chang, A. L. Page, D. Bakhtar, J. A. Frampton and H. Wright. 1996. Background concentrations of trace and major elements in California soils. Kearney Foundation Special Report, University of California, Riverside.

Butcher, B., B. Davidoff, M. C. Amacher, C. Hinz, I. K. Iskandar, and H. M. Selim. 1989. Correlation of Freundlich K_d and n Retention Parameters with Soils and Elements. Soil Science 148(5):370-379.

Carsel, R. F. and R. S. Parrish. 1988. Developing joint probability distributions of soil water retention characteristics. Water Resources Research, 24:755-769.

Cataldo, D. A., T. R. Garland and R. E. Wildung. 1983. Cadmium uptake kinetics in intact soybean plants. Plant Physiol, 73:844-848.

CDFA (California Department of Food and Agriculture). 1997. Development of Risk-Based Concentrations for Arsenic, Cadmium, and Lead in Inorganic Commercial Fertilizers. Prepared for the California Department of Food and Agriculture and the Heavy Metal Task Force by the Foster Wheeler Environmental Corporation.

CDFA (California Department of Food and Agriculture). 1998. Development of Risk-based Concentrations for Arsenic, Cadmium, and Lead in Inorganic Fertilizers. The Report of The Heavy Metal Task Force, Agricultural Commodities and Regulatory Services, California Department of Food and Agriculture.

CDFA (California Department of Food and Agriculture). 2002. Supplement to The Development of Risk-based Concentrations for Arsenic, Cadmium, and Lead in Inorganic Fertilizers. Report prepared for California Department of Food and Agriculture by MWH, 3321 Power Inn Road, Suite 300, Sacramento, California 95826.

Chang, A. C., A. L. Page and N.J. Krage 2004. Role of Fertilizer and Micronutrient Applications on Arsenic, Cadmium and Lead Accumulation in California Cropland Soils. CDFA November 2004, 143 pages.

Chang, A. C., and A. L. Page. 2000. Trace elements slowly accumulating, depleting in soils. California agriculture, 54(2):49-55.

Chen, W., 2005, Modeling trace element mass balance in cropland soils**.** Ph.D. dissertation, Department of Environmental Sciences, University of California, Riverside.

Chen, W., A. C. Chang, L. Wu, and A. L. Page. 2006. Modeling Dynamic Sorption of Cadmium in Cropland Soils. Vadose Zone Journal. (Accepted).

Chlopecka, A., J. R. Bacon, M. J. Wilson and J. Kay. 1996. Forms of cadmium, lead, and zinc in contaminated soils from southwest Poland. J. Environ. Qual. 25:69-79.

Costa, C. and J. L. Morel. 1993. Cadmium uptake by Lupinus albus (L.): cadmium excretion, a possible mechanism of cadmium tolerance. Journal o f plant nutrition, 16:1921-1929

Darrah R. R. and S. Staunton. 2000. A mathematical model of root uptake of cations incrorporating root turnover, distribution within the plant, and recycling of absorbed species. European Journal of Soil Science, 51:643-653.

De Boo W. 1990. Cadmium in agriculture. Toxticol Environ Chem 27: 55–63.

EUROSTAT. 1995. Europe's Environment, Statistical Compendium for the Dobris Assessment, Brussels: European Commission.

Feddes, R. A., P. J. Kowalik, and H. Zaradny. 1978. Simulation of Field Water Use and Crop Yield, John Wiley & Sons, New York, NY.

Gardiner, D. T. and N. W. Christensen. 1997. A simple model for phosphorus uptake kinetics of wheat seedlings. Journal of plant nutrition, 20:271-277.

Gelhar, L. W., A. Mantoflou, C. Welty and K. R. Reyfeldt. 1985. A Review of Field Scale Physical Solute Transport Processes in Saturated and Unsaturated Porous Media. RP-2485-05, Electric Power Research Institute, Palo Alto, California.

Gooddy, D. C., P. Shand, D. G. Kinniburgh, and W. H. van Riemsdijk. 1995. Field-based Partition Coefficients for Trace Elements in Soil Solutions. European Journal of Soil Science 46(6):265-285.

Grant, C. A. and Bailey, L. D.: 1998, 'Nitrogen, phosphorus and zinc fertilizer management effects on grain and cadmium concentration in two cultivars of durum wheat', Canadian J. Plant Sci. 78, 63–70.

Gray, C. W., R. G. Mclaren, A. H. C. Roberts, and L. M. Condron. 2000. Fractionation of soil cadmium from some New Zealand soils. Commun. Soil Sci. Plant Anal. 31:1261-1273.

Guttormsen, G., Singh, B. R. and Jeng, A. S.: 1995, Cadmium concentration in vegetable crops grown in a sandy soil as affected by Cd levels in fertilizer and soil pH, Fertilizer Res. 41, 27–32.

Hanks, R. J. and R. W. Hill. 1980. Modeling crop responses to irrigation in relate to soils climate and salinity. Irrigation Information Center, IIIC, Pub. No. 6

Hart, J. J., R. M. Welch, W. A. Norvell, L. A. Sullivan1 and L. V. Kochian. 1998. Characterization of Cadmium Binding, Uptake, and Translocation in Intact Seedlings of Bread and Durum Wheat Cultivars. Plant Physiol, 116:1413–1420.

He, Q. B. and Singh, B. R.: 1994, 'Crop uptake of cadmium from phosphorus fertilizers. II. relationship with extractable soil cadmium', Water Air Soil Pollut. 74, 251–265.

Hinwood, A. L., M. R. Sim, D. Jolley, N. de Klerk, E. B. Bastone, J. Gerosmoulos, and O. H. Drummers. 2004. Exposure to inorganic arsenic in soil increases urinary inorganic arsenic concentrations of residents living in old mining areas. Environ. Geochem. Health 26:27 – 36.

Holmgren, G. G. S., M. W. Meyer, R. L. Chaney, and R. B. Daniels. 1993. Cadmium, lead, zinc, copper, and nickel in agricultural soils in the United States of America. J. Environ. Qual. 22:335-348.

Huang, B., S. Kuo, and R. Bembenek. 2004. Availability of cadmium in some phosphorus fertilizers to field-grown lettuce. Water, air, and soil pollution. 158: 37-51.

Jackson, A. P. 1990. The bioavailability of cadmium from sewage sludge amended soils. PhD. thesis, University of London, UK.

Jopony, M. and S. D. Young. 1994. The Solid-Solution Equilibria of Lead and Cadmium in Polluted Soils. European Journal of Soil Science 45(3):59-70.

Kabata-Pendias A. and G. W. Brümmer. 1991. Ecological consequences of As, Cd, Hg and Pb enrichment in European soils. In Lead, Mercury, Cadmium and Arsenic in the environment, SCOPE 32, Hutchinson, T.C. and Meema, K. Gordon, C., eds.

Kabata-Pendias A. and H. Pendias. 2001, Trace elements in soils and plants. CRC Press.

Krage, N. J. 2002. The role of fertilizers on arsenic, cadmium and lead accumulation in California cropland soil. Master dissertation of University of California, Riverside.

Krishnamurti,G. S. R., P. M. Huang, and L. M. Kozak. 1999. Desorption kinetics of cadmium from soils using M ammonium nitrate and M ammonium chloride. Commun. Soil Sci. Plant Anal. 30:2785-2800.

Kuo, S., P. E. Heilman and A. S. Baker. 1983. Distribution and forms of copper, zinc, cadmium, iron, and manganese in soils near a copper smelter. Soil-Sci., 135:101-109.

Loganathan, P., A. D. Mackay, J. Lee and M. J. Hedley. 1995. Cadmium distribution in hill pastures as influenced by 20 years of phosphate fertilizer application and sheep grazing. Australian Journal of Soil Research, 33:859-871.

Lombi E., K. L. Tearall, J. R. Howarth, F. Zhao, M. J. Hawkesford, and S. P. McGrath. 2002. Influence of Iron Status on Cadmium and Zinc Uptake by Different Ecotypes of the Hyperaccumulator Thlaspi caerulescens. Plant Physiology, 128: 1359–1367.

Lyman, Warren J., Patrick J. Reidy and Benjamin Levy. 1992. Mobility and Degradation of Organic Contaminants in Subsurface Environments. S.K. Smoley, Inc. Chelsea, Michigan.

McLaughlin, M. J. and B. R. Singh (ed.). 1999. Cadmium in soils and plants. Dordrecht: Boston: Kluwer Academic Publishers.

Meeus C. de, G. H. Eduljee and M. Hutton, 2002, *Assessment and management of risks arising from exposure to cadmium in fertilisers,* Sci. Tot. Environ. 291: 167–187.

Meharg A. A and M. R. Machair. 1992. Polymorphism and physiology of arsenate tolerance in Holcus. Lanatus L. from an uncontaminated site. Plant and Soil 146:219-225.

Meister, H. S., K. S. Mayberry, E. T. Natwick, T. A. Turini, J. L. Aguiar, K.M. Bali, and J. N. Guerrero. 2004. Guidelines to production costs and practices for Imperial County 2004-2005 vegetable crops. UC Cooperative Extension. Imperial County Circular 104-V.

Miller, W. P., and W. W. McFee. 1983. Distribution of cadmium, zinc, copper, and lead in soils of industrial northwestern Indiana under oak forest. J. Environ. Qual.12:29-33.

Millington R. J., and J. M. Quirk 1961. Permeability of porous solids. Trans. Faraday Soc.; 57:1200-1207.

Mulla, D. J., A. L. Page, and T. J. Ganji. 1980. Cadmium accumulation and bioavailability in soils from long-term phosphorus fertilization. J. Environ. Qual. 9(3):408 – 412.

Mullins G.L. 1986. Cadmium and zinc influx characteristics by intact corn (Zea mays L.) seedlings. Plant and Soil 96:153-164.

Mullins, G. L. and L .E. Sommers. 1986. Cadmium and zinc influx characteristics by intact corn (Zea mays L.) seedlings. Plant and soil, 96:153-164.

Pages, L., M. O. Jordan and D. Picard 1989. A simulation model of the three-dimensional architecture of the maize root system. Plant and Soil, 119: 147-154.

Peirjnenburg, W. J. G. M., A. C. de Groot, and R. P. M. van Veen. 2001. Experimental and Theoretical Study on Equilibrium Partitioning of Heavy Metals. Pp. 91 – 126 In: Trace Element in Soil, Bioavailability, Flux, and Transfer (I. K. Iskaandar and M. B. Kirnham, eds.). Lewis Publishers, Boca Raton. 287pp.

Raats, P. A. C. 1974. Steady flows of water and salt in uniform soil profiles with plant roots. Soil Sci. Soc. Am. Proc. 38:717–722.

Ramos, L., L. M. Hernandez, and M. J. Gonzalez. 1994. Sequential fractionation of copper, lead, cadmium and zinc in soils from or near Donana national park. J. Environ. Qual. 23:50-57.

Rao S. and S. Mahter 1994. Modeling Heavy Metal (Cadmium) Uptake by Soil-Plant Root System. J. Irrig. and Drain. Engrg. 120, 89-96.

Rasmussen, V. P. and R. J. Hanks. 1978. Spring wheat yield model for limited moisture conditions. Agron. J. 70:940-944.

Renaud, P., R. Stapel, H. Maubert, M. Bleher and E. Wirth. 1999. Comparative study of the PARK and ASTRAL post-accident decision support software. Health Physics, 76:502-509.

Rose, D. A. 1983. The description of the growth of root systems. Plant and Soil, 75:(3) 405-413.

Ruhlmann, J. 1999. Calculation of net mineralization from the decomposable soil organic matter pool. Acta Horticulturae 506, 167-173.

Sanchez, A. G., A. Moyano, and C. Munez. 1999. Forms of cadmium, lead and zinc in polluted mining soils and uptake by plants (Soria province, Spain). Commun. Soil. Sci. Plant Anal. 30:1385-1402.

Sanchez-Martin, M. J., and M. Sanchez-Camazano. 1993. Adsorption and mobility of cadmium in natural, uncultivated soils. J. Environ. Qual. 22:737-742.

Sauve, S., W. Hendershot, and H. E. Allen. 2000. Solid-solution Partitioning of Metals in Cantaminated Soils: Dependence on pH, Total Metal Burden, and Organic Matter. Environmental Science and Technology 34(7):1125-1131.

Schaap, M.G., F. J. Leij and M. Th. van Genuchten. 2001. Rosetta: a computer program for estimating soil hydraulic parameters with hierarchical pedotransfer functions. Journal of Hydrology. 251:163-176.

Schouwenaars, J. M.. 1988. Rainfall irrigation and sowing strategies in Southern Mozambique. Agric. Water Mgmt., 13:49-64.

Seuntjens R., B. Nowack and R. Schulin. 2004. Root zone modeling of heavy metal uptake and leaching in the presence of organic ligands. Plant and Soil, 265:61-73.

Šimunek, J., M. Šejna and M. Th. van Genuchten, The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably saturated media. Version 2.0, U.S. Salinity Laboratory, USDA, ARS, Riverside, California, 178 pp., 1998.

Snyder, R. L. and K. Schulbach. 1992. Central Coast Valleys evapotranspiration and crop coefficients for field crops. University of California Drought Tip 92-45.

Soon, Y. K., and T. E. Bates. 1982. Chemical pools of cadmium, nickel and zinc in polluted soils and some preliminary indications of their availability to plants. Journal of soil science. 33:477-488.

Subbaiah R. and K. A. Rao. 1993. Root growth simulation model under specified environment. Journal of Irrigation and Drainage Engineering, 119:898-904.

TFI (The Fertilizer Institute). 2000. Health Risk Evaluation of SelectMetals in Inorganic Fertilizers Post Applications. Report prepared for The Fertilizer Institite by The Weinberg Group Inc. 1220 Nineteenth St. NW, Suite 300, Washington DC 20036-2400. (http://aapfco.org/tfiRiskStd.pdf)

Tucker, W. A., and L. H. Nelken . 1982. Diffusion coefficients in air and water. In: Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt (Eds) Handbook of Chemical Property Estimation Methods. American Chemical Society, Washington, D.C. pp 17-1 to 17-25.

U.S. EPA. (U. S. Environmental Protection Agency). 1987. Process Coefficients and Models for Simulating Toxic Organics and Heavy Metals in Surface Waters. Office of Research and Development. Washington, DC: U.S. Government Printing Office (GPO).

U.S. EPA (U. S. Environmental Protection Agency). 2000. Requirements for Zinc Fertilizers Made from Recycled Hazardous Secondary Materials. Federal Register 65(229):70953-70982.

U.S. EPA. (U. S. Environmental Protection Agency). 2001. WATER9. Office of Air Quality Planning and Standards, Research Triangle Park, NC. http://www.epa.gov/ttn/chief/software/water/index.html. Accessed July 2001

van Genuchten, M. Th. 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils, Soil Sci. Soc. Am. J., 44, 892-898.

Wang, J., F. J. Zhao, A.A. Meharg, A. Raab, J. Feldmann and S.P. McGrath. 2002. Mechanisms of arsenic hyperaccumulation in *Pteris vittata*: Uptake kinetics, interactions with phosphate, and arsenic speciation. Plant-physiol, 130:1552-1561.

Wu, Q. T., J. L. Morel and A. Guckert. 1994. A mechanistic model for predicting the transfer of heavy metals in the soil-solution-plant system.

Xian X. 1989. Effect of chemical forms cadmium, zinc, and lead in polluted soils on their uptake by cabbage plants. Plant and Soil. 113:257-264.

Xian, X. 1987. Chemical partitioning of cadmium, zinc, lead, and copper in soils near smelter. J. Environ. Sci. Health Part A Environ. Sci. Eng. 22:527-54.

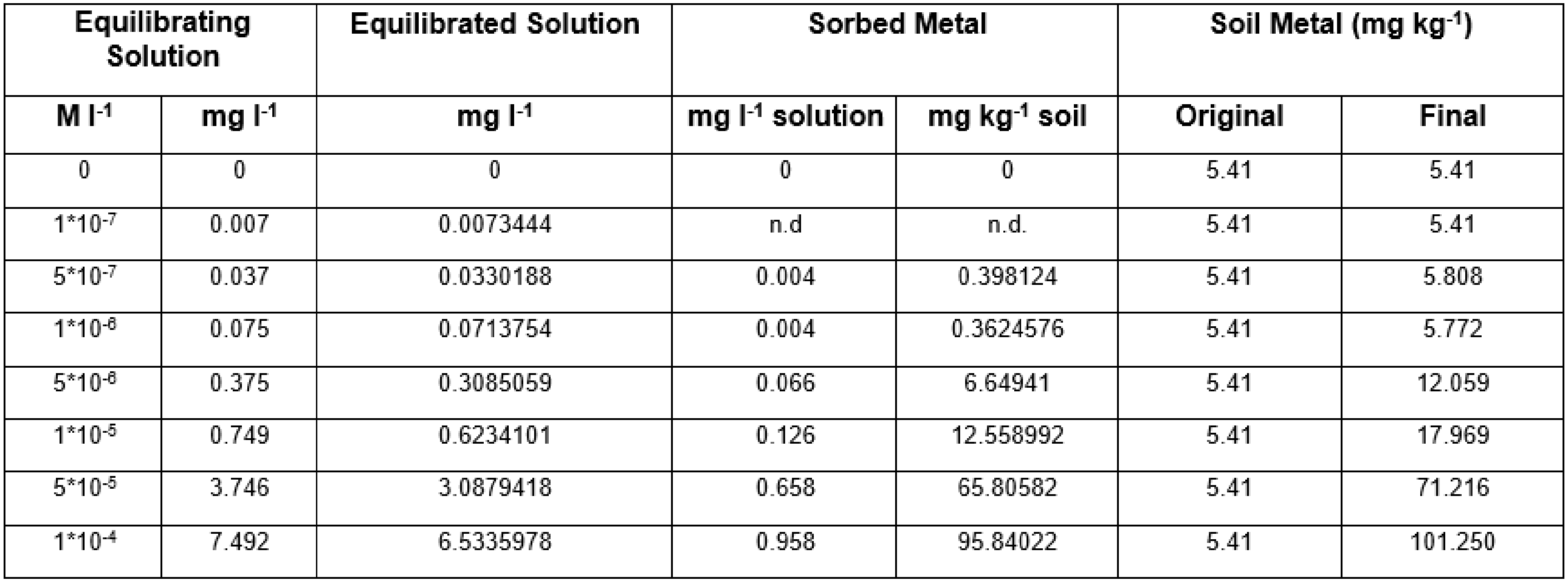
Zhao, F. J., R. E. Hamon, E. Lombi, M. J. McLaughlin and S. P. McGrath. 2002. Characteristics of cadmium uptake in two contrasting ecotypes of the hyperaccumulator *Thlaspi caerulescens*. Journal of Experimental Botany, 53:535-543.

Appendices

A. Data of the Solution-based As, Cd, and Pb Adsoprtion Experiments
B. Mass, As, Cd, Pb Inputs at Various Amendment Treatment LevelsAppendix A. Data of the Solution-based As, Cd, and Pb Adsoprtion Experiments

Adsorption Experiment - As

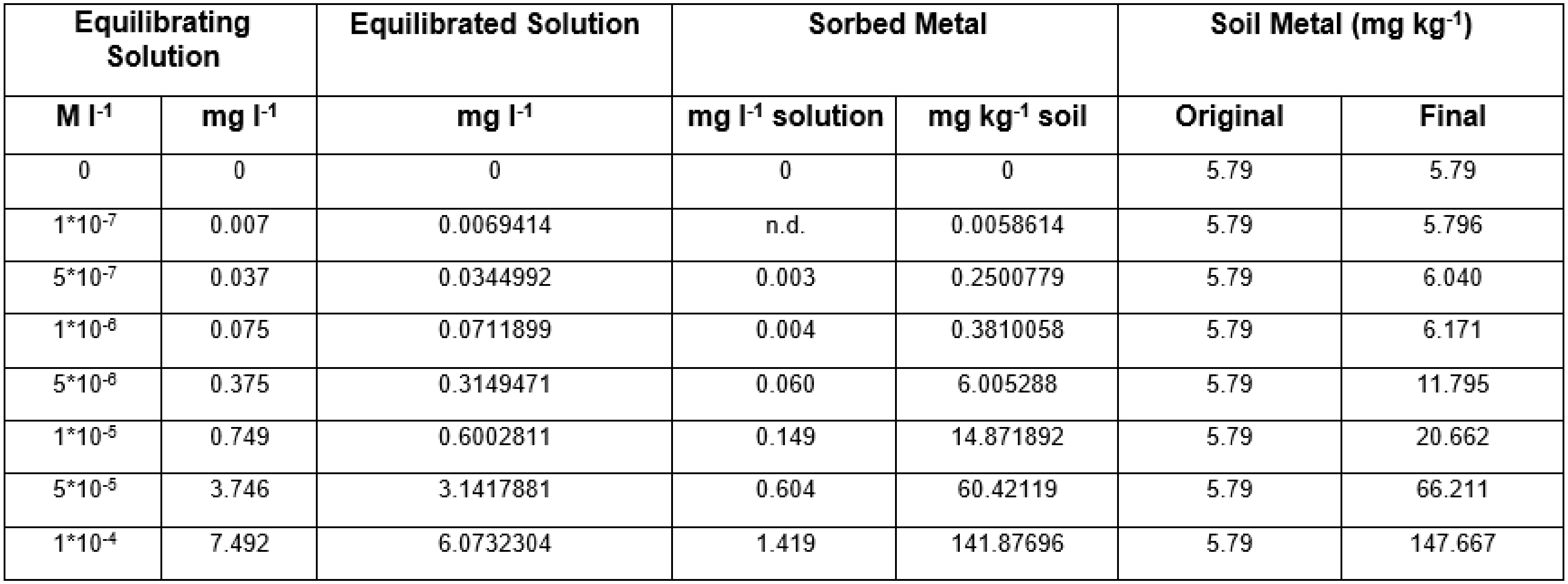
Santa Maria, RB 5



Equilibrating Solution		Equilibrated Solution	Sorbed Metal		Soil Metal (mg kg^{-1})	
M l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1} solution	mg kg^{-1} soil	Original	Final
0	0	0	0	0	5.41	5.41
$1*10^{-7}$	0.007	0.0073444	n.d	n.d.	5.41	5.41
$5*10^{-7}$	0.037	0.0330188	0.004	0.398124	5.41	5.808
$1*10^{-6}$	0.075	0.0713754	0.004	0.3624576	5.41	5.772
$5*10^{-6}$	0.375	0.3085059	0.066	6.64941	5.41	12.059
$1*10^{-5}$	0.749	0.6234101	0.126	12.558992	5.41	17.969
$5*10^{-5}$	3.746	3.0879418	0.658	65.80582	5.41	71.216
$1*10^{-4}$	7.492	6.5335978	0.958	95.84022	5.41	101.250

Adsorption Experiment - As

Santa Maria, RB 6



Equilibrating Solution		Equilibrated Solution	Sorbed Metal		Soil Metal (mg kg^{-1})	
M l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1} solution	mg kg^{-1} soil	Original	Final
0	0	0	0	0	5.79	5.79
$1*10^{-7}$	0.007	0.0069414	n.d.	0.0058614	5.79	5.796
$5*10^{-7}$	0.037	0.0344992	0.003	0.2500779	5.79	6.040
$1*10^{-6}$	0.075	0.0711899	0.004	0.3810058	5.79	6.171
$5*10^{-6}$	0.375	0.3149471	0.060	6.005288	5.79	11.795
$1*10^{-5}$	0.749	0.6002811	0.149	14.871892	5.79	20.662
$5*10^{-5}$	3.746	3.1417881	0.604	60.42119	5.79	66.211
$1*10^{-4}$	7.492	6.0732304	1.419	141.87696	5.79	147.667

Adsorption Experiment - As

Imperial Valley, VHL 3

Equilibrating Solution		Equilibrated Solution	Sorbed Metal		Soil Metal (mg kg^{-1})	
M l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1} solution	mg kg^{-1} soil	Original	Final
0	0	0	0	0	4.07	4.07
1*10^{-7}	0.007	0.0090732	n.d.	0	4.07	4.070
5*10^{-7}	0.037	0.0362009	0.001	0.0799081	4.07	4.150
1*10^{-6}	0.075	0.068141	0.007	0.6859026	4.07	4.756
5*10^{-6}	0.375	0.3155214	0.059	5.94786	4.07	10.018
1*10^{-5}	0.749	0.6325122	0.116	11.64878	4.07	15.719
5*10^{-5}	3.746	3.1266816	0.619	61.93184	4.07	66.002
1*10^{-4}	7.492	6.028313	1.464	146.3687	4.07	150.439

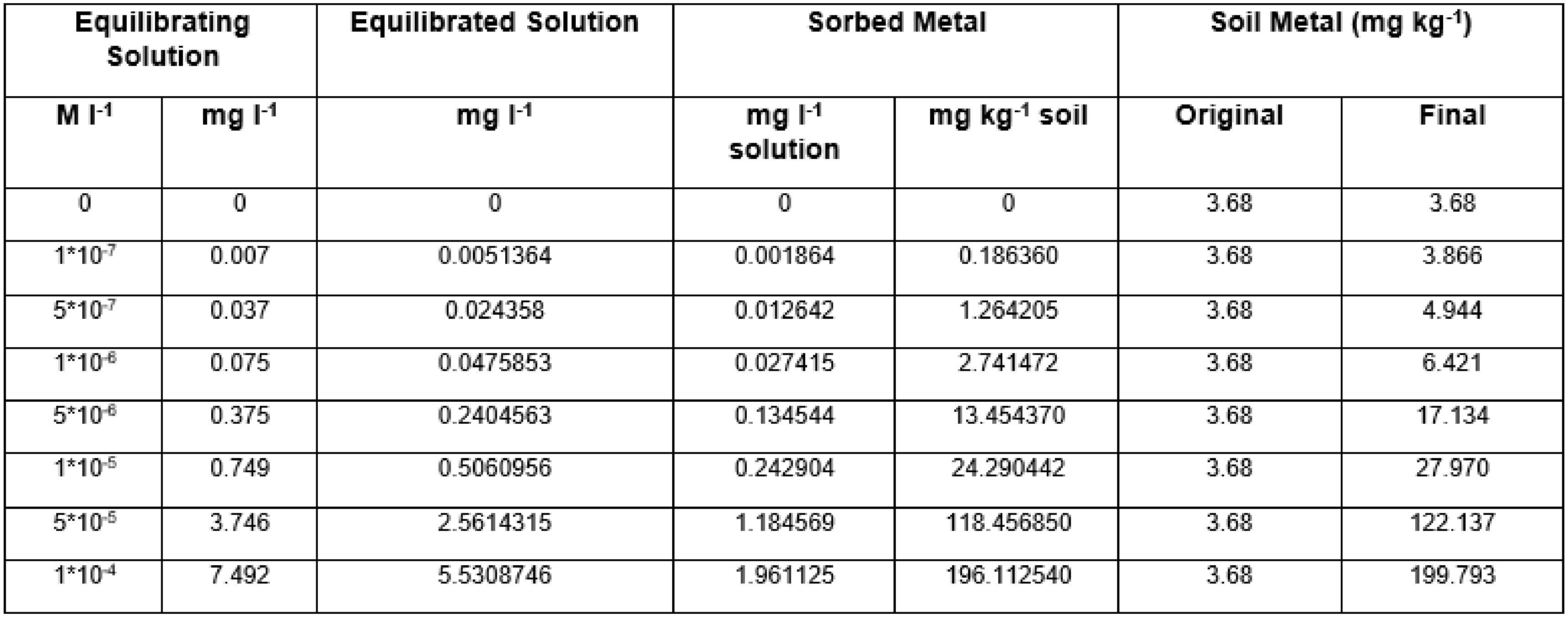
Adsorption Experiment - As

Imperial Valley, VHL 4

Equilibrating Solution		**Equilibrated Solution**	**Sorbed Metal**		**Soil Metal (mg kg^{-1})**	
M l^{-1}	**mg l^{-1}**	**mg l^{-1}**	**mg l^{-1} solution**	**mg kg^{-1} soil**	**Original**	**Final**
0	0	0	0	0	3.97	3.97
1*10^{-7}	0.007	0.0089137	n.d.	n.d.	3.97	3.970
5*10^{-7}	0.037	0.036531	0.000	0.0468997	3.97	4.017
1*10^{-6}	0.075	0.0673705	0.008	0.7629454	3.97	4.733
5*10^{-6}	0.375	0.311363	0.064	6.3637	3.97	10.334
1*10^{-5}	0.749	0.6145574	0.134	13.444258	3.97	17.414
5*10^{-5}	3.746	3.0145948	0.731	73.14052	3.97	77.111
1*10^{-4}	7.492	6.0487696	1.443	144.32304	3.97	148.293

Adsorption Experiment - As

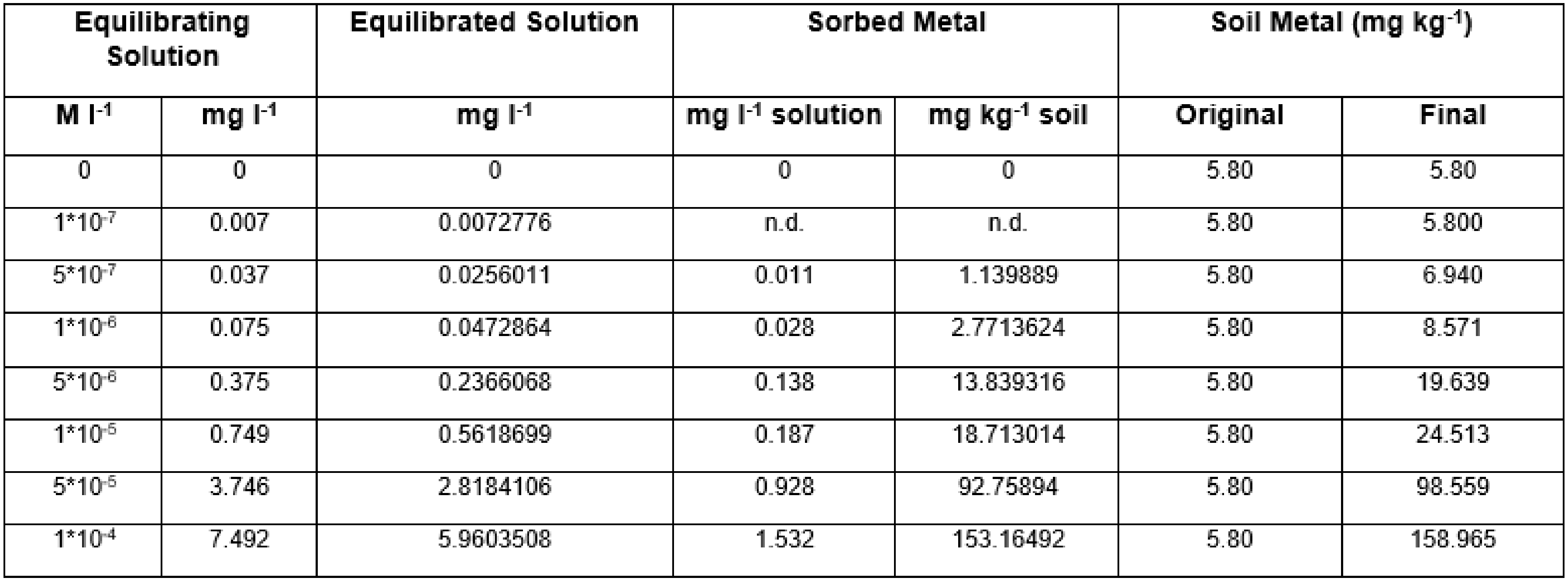
Ventura/Oxnard, B 5



Equilibrating Solution		**Equilibrated Solution**	**Sorbed Metal**		**Soil Metal (mg kg^{-1})**	
M l^{-1}	**mg l^{-1}**	**mg l^{-1}**	**mg l^{-1} solution**	**mg kg^{-1} soil**	**Original**	**Final**
0	0	0	0	0	3.68	3.68
1*10^{-7}	0.007	0.0051364	0.001864	0.186360	3.68	3.866
5*10^{-7}	0.037	0.024358	0.012642	1.264205	3.68	4.944
1*10^{-6}	0.075	0.0475853	0.027415	2.741472	3.68	6.421
5*10^{-6}	0.375	0.2404563	0.134544	13.454370	3.68	17.134
1*10^{-5}	0.749	0.5060956	0.242904	24.290442	3.68	27.970
5*10^{-5}	3.746	2.5614315	1.184569	118.456850	3.68	122.137
1*10^{-4}	7.492	5.5308746	1.961125	196.112540	3.68	199.793

Adsorption Experiment - As

Ventura/Oxnard, P 4



Equilibrating Solution		Equilibrated Solution	Sorbed Metal		Soil Metal (mg kg^{-1})	
M l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1} solution	mg kg^{-1} soil	Original	Final
0	0	0	0	0	5.80	5.80
1*10^{-7}	0.007	0.0072776	n.d.	n.d.	5.80	5.800
5*10^{-7}	0.037	0.0256011	0.011	1.139889	5.80	6.940
1*10^{-6}	0.075	0.0472864	0.028	2.7713624	5.80	8.571
5*10^{-6}	0.375	0.2366068	0.138	13.839316	5.80	19.639
1*10^{-5}	0.749	0.5618699	0.187	18.713014	5.80	24.513
5*10^{-5}	3.746	2.8184106	0.928	92.75894	5.80	98.559
1*10^{-4}	7.492	5.9603508	1.532	153.16492	5.80	158.965

Adsorption Experiment - Cd

Santa Maria, RB 5

Equilibrating Solution		**Equilibrated Solution**	**Sorbed Metal**		**Soil Metal (mg kg^{-1})**	
M l^{-1}	**mg l^{-1}**	**mg l^{-1}**	**mg l^{-1} solution**	**mg kg^{-1} soil**	**Original**	**Final**
0	0	0	0	0	0.59	0.59
1*10^{-7}	0.011	0.0003462	0.011	1.0653838	0.59	1.655
5*10^{-7}	0.056	0.0007952	0.055	5.5204767	0.59	6.110
1*10^{-6}	0.112	0.0017671	0.110	11.023291	0.59	11.613
5*10^{-6}	0.562	0.0085796	0.553	55.342042	0.59	55.932
1*10^{-5}	1.124	0.017485	1.107	110.6515	0.59	111.242
5*10^{-5}	5.620	0.1597762	5.460	546.02238	0.59	546.612
1*10^{-4}	11.24	0.524423	10.716	1071.5577	0.59	1072.148

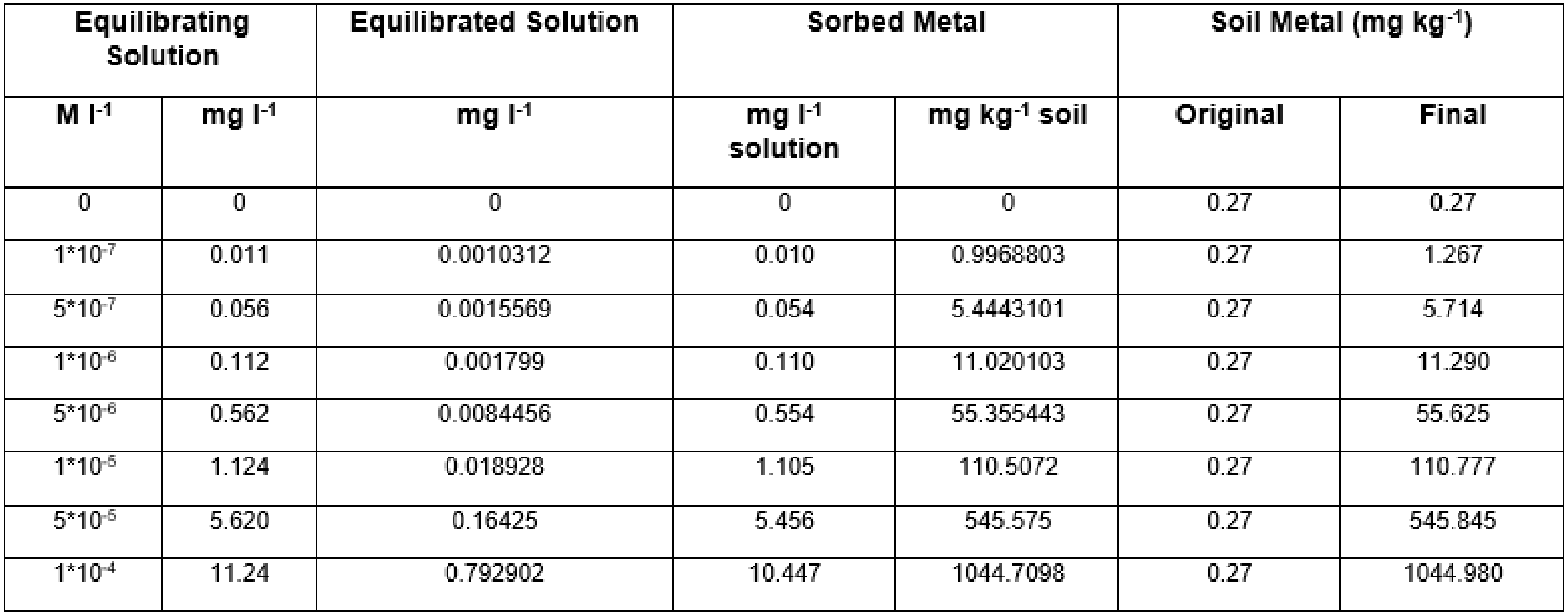
Adsorption Experiment - Cd

Santa Maria, RB 6

Equilibrating Solution		**Equilibrated Solution**	**Sorbed Metal**		**Soil Metal (mg kg^{-1})**	
M l^{-1}	**mg l^{-1}**	**mg l^{-1}**	**mg l^{-1} solution**	**mg kg^{-1} soil**	**Original**	**Final**
0	0	0	0	0	0.58	0.58
1*10^{-7}	0.011	0.0005567	0.010	1.0443304	0.58	1.624
5*10^{-7}	0.056	0.0010152	0.055	5.4984844	0.58	6.078
1*10^{-6}	0.112	0.0017662	0.110	11.023384	0.58	11.603
5*10^{-6}	0.562	0.0077798	0.554	55.422017	0.58	56.002
1*10^{-5}	1.124	0.0152832	1.109	110.87168	0.58	111.452
5*10^{-5}	5.620	0.1281966	5.492	549.18034	0.58	549.760
1*10^{-4}	11.24	0.4494594	10.791	1079.0541	0.58	1079.634

Adsorption Experiment - Cd

Imperial Valley, VHL 3



Equilibrating Solution		Equilibrated Solution	Sorbed Metal		Soil Metal (mg kg^{-1})	
M l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1} solution	mg kg^{-1} soil	Original	Final
0	0	0	0	0	0.27	0.27
1*10^{-7}	0.011	0.0010312	0.010	0.9968803	0.27	1.267
5*10^{-7}	0.056	0.0015569	0.054	5.4443101	0.27	5.714
1*10^{-6}	0.112	0.001799	0.110	11.020103	0.27	11.290
5*10^{-6}	0.562	0.0084456	0.554	55.355443	0.27	55.625
1*10^{-5}	1.124	0.018928	1.105	110.5072	0.27	110.777
5*10^{-5}	5.620	0.16425	5.456	545.575	0.27	545.845
1*10^{-4}	11.24	0.792902	10.447	1044.7098	0.27	1044.980

Adsorption Experiment - Cd

Imperial Valley, VHL 4

Equilibrating Solution		**Equilibrated Solution**	**Sorbed Metal**		**Soil Metal (mg kg^{-1})**	
M l^{-1}	**mg l^{-1}**	**mg l^{-1}**	**mg l^{-1} solution**	**mg kg^{-1} soil**	**Original**	**Final**
0	0	0	0	0	0.28	0.28
$1*10^{-7}$	0.011	0.0002496	0.011	1.0750376	0.28	1.355
$5*10^{-7}$	0.056	0.0008225	0.055	5.5177537	0.28	5.798
$1*10^{-6}$	0.112	0.0046085	0.107	10.7391455	0.28	11.019
$5*10^{-6}$	0.562	0.0079277	0.554	55.4072321	0.28	55.687
$1*10^{-5}$	1.124	0.0178762	1.106	110.612382	0.28	110.892
$5*10^{-5}$	5.620	0.1694134	5.451	545.05866	0.28	545.339
$1*10^{-4}$	11.24	0.7553075	10.485	1048.46925	0.28	1048.749

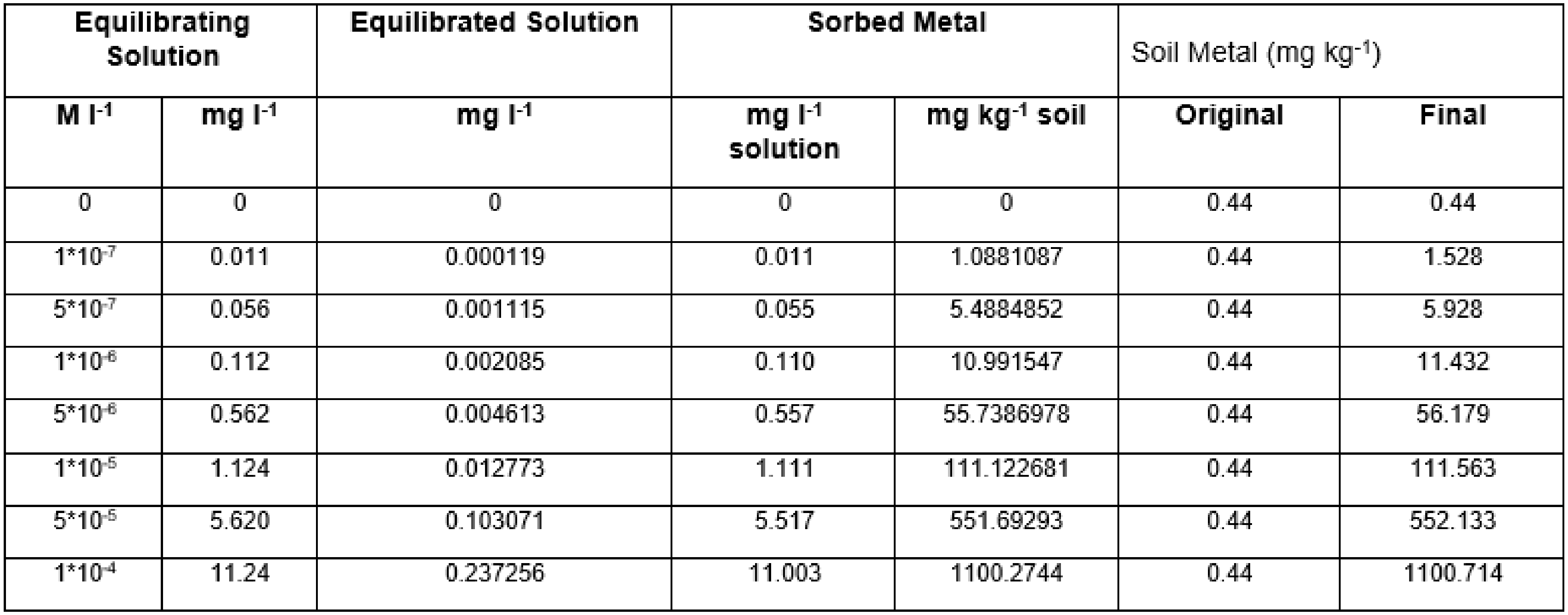
Adsorption Experiment - Cd

Ventura/Oxnard, B 5

Equilibrating Solution		**Equilibrated Solution**	**Sorbed Metal**		**Soil Metal (mg kg^{-1})**	
M l^{-1}	**mg l^{-1}**	**mg l^{-1}**	**mg l^{-1} solution**	**mg kg^{-1} soil**	**Original**	**Final**
0	0	0	0	0	0.28	0.28
$1*10^{-7}$	0.011	0.0002496	0.011	1.0750376	0.28	1.355
$5*10^{-7}$	0.056	0.0008225	0.055	5.5177537	0.28	5.798
$1*10^{-6}$	0.112	0.0046085	0.107	10.7391455	0.28	11.019
$5*10^{-6}$	0.562	0.0079277	0.554	55.4072321	0.28	55.687
$1*10^{-5}$	1.124	0.0178762	1.106	110.612382	0.28	110.892
$5*10^{-5}$	5.620	0.1694134	5.451	545.05866	0.28	545.339
$1*10^{-4}$	11.24	0.7553075	10.485	1048.46925	0.28	1048.749

Adsorption Experiment - Cd

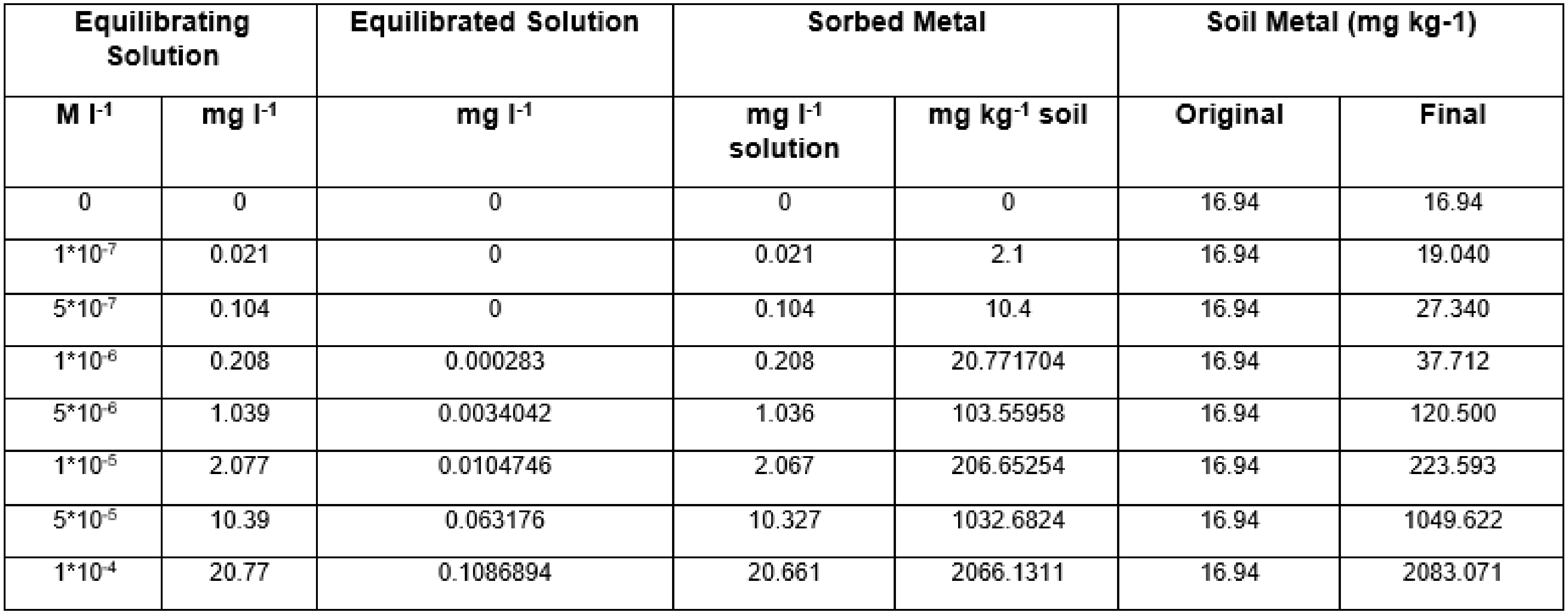
Ventura/Oxnard, P 4



Equilibrating Solution		**Equilibrated Solution**	**Sorbed Metal**		Soil Metal (mg kg^{-1})	
M l^{-1}	**mg l^{-1}**	**mg l^{-1}**	**mg l^{-1} solution**	**mg kg^{-1} soil**	**Original**	**Final**
0	0	0	0	0	0.44	0.44
1*10^{-7}	0.011	0.000119	0.011	1.0881087	0.44	1.528
5*10^{-7}	0.056	0.001115	0.055	5.4884852	0.44	5.928
1*10^{-6}	0.112	0.002085	0.110	10.991547	0.44	11.432
5*10^{-6}	0.562	0.004613	0.557	55.7386978	0.44	56.179
1*10^{-5}	1.124	0.012773	1.111	111.122681	0.44	111.563
5*10^{-5}	5.620	0.103071	5.517	551.69293	0.44	552.133
1*10^{-4}	11.24	0.237256	11.003	1100.2744	0.44	1100.714

Adsorption Experiment - Pb

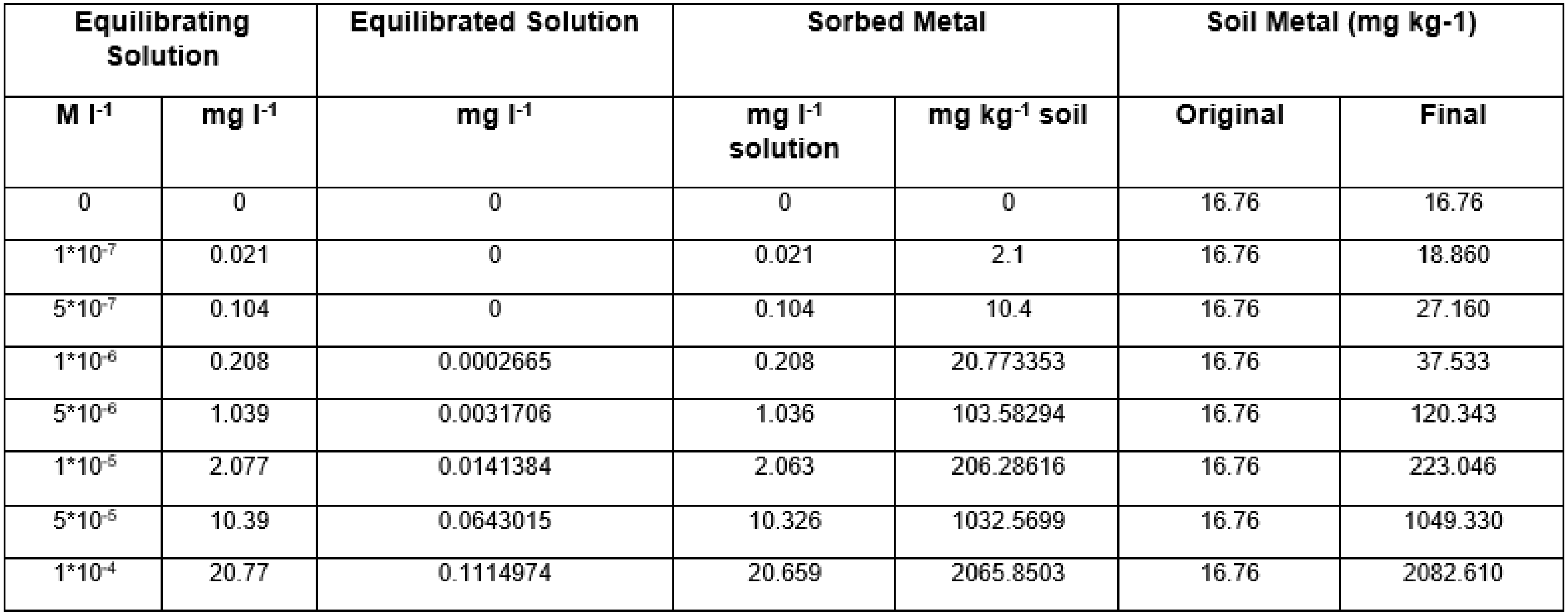
Santa Maria, RB 5



Equilibrating Solution		**Equilibrated Solution**	**Sorbed Metal**		**Soil Metal (mg kg-1)**	
M l^{-1}	**mg l^{-1}**	**mg l^{-1}**	**mg l^{-1} solution**	**mg kg^{-1} soil**	**Original**	**Final**
0	0	0	0	0	16.94	16.94
$1*10^{-7}$	0.021	0	0.021	2.1	16.94	19.040
$5*10^{-7}$	0.104	0	0.104	10.4	16.94	27.340
$1*10^{-6}$	0.208	0.000283	0.208	20.771704	16.94	37.712
$5*10^{-6}$	1.039	0.0034042	1.036	103.55958	16.94	120.500
$1*10^{-5}$	2.077	0.0104746	2.067	206.65254	16.94	223.593
$5*10^{-5}$	10.39	0.063176	10.327	1032.6824	16.94	1049.622
$1*10^{-4}$	20.77	0.1086894	20.661	2066.1311	16.94	2083.071

Adsorption Experiment - Pb

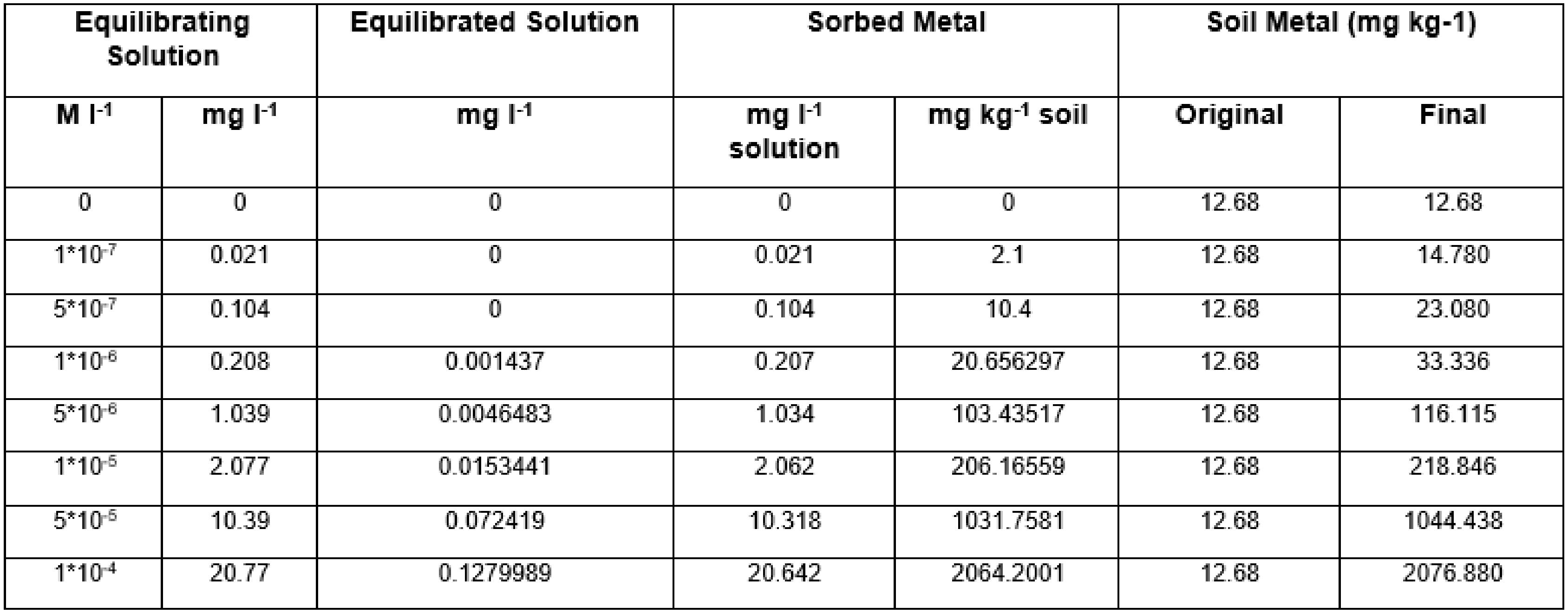
Santa Maria, RB 6



Equilibrating Solution		Equilibrated Solution	Sorbed Metal		Soil Metal (mg kg-1)	
M l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1} solution	mg kg^{-1} soil	Original	Final
0	0	0	0	0	16.76	16.76
$1*10^{-7}$	0.021	0	0.021	2.1	16.76	18.860
$5*10^{-7}$	0.104	0	0.104	10.4	16.76	27.160
$1*10^{-6}$	0.208	0.0002665	0.208	20.773353	16.76	37.533
$5*10^{-6}$	1.039	0.0031706	1.036	103.58294	16.76	120.343
$1*10^{-5}$	2.077	0.0141384	2.063	206.28616	16.76	223.046
$5*10^{-5}$	10.39	0.0643015	10.326	1032.5699	16.76	1049.330
$1*10^{-4}$	20.77	0.1114974	20.659	2065.8503	16.76	2082.610

Adsorption Experiment - Pb

Imperial Valley, VHL 3



Equilibrating Solution		**Equilibrated Solution**	**Sorbed Metal**		**Soil Metal (mg kg-1)**	
M l^{-1}	**mg l^{-1}**	**mg l^{-1}**	**mg l^{-1} solution**	**mg kg^{-1} soil**	**Original**	**Final**
0	0	0	0	0	12.68	12.68
$1*10^{-7}$	0.021	0	0.021	2.1	12.68	14.780
$5*10^{-7}$	0.104	0	0.104	10.4	12.68	23.080
$1*10^{-6}$	0.208	0.001437	0.207	20.656297	12.68	33.336
$5*10^{-6}$	1.039	0.0046483	1.034	103.43517	12.68	116.115
$1*10^{-5}$	2.077	0.0153441	2.062	206.16559	12.68	218.846
$5*10^{-5}$	10.39	0.072419	10.318	1031.7581	12.68	1044.438
$1*10^{-4}$	20.77	0.1279989	20.642	2064.2001	12.68	2076.880

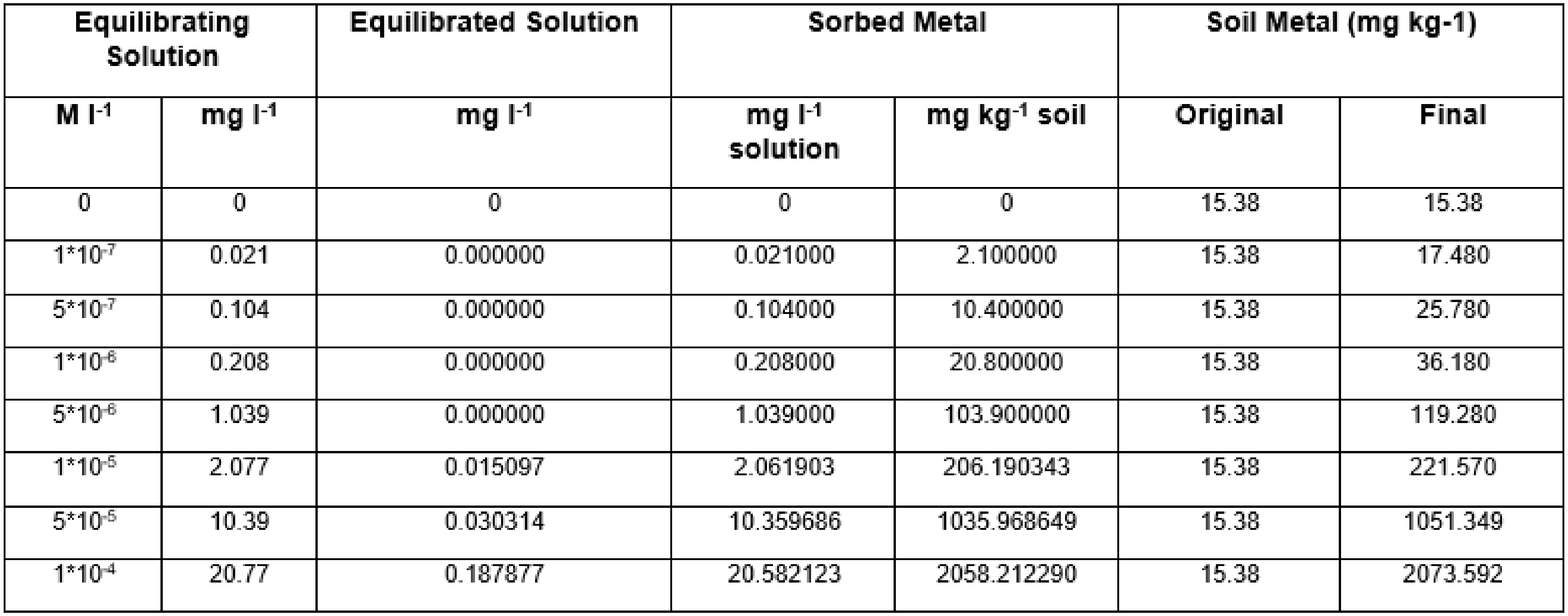
Adsorption Experiment - Pb

Imperial Valley, VHL 4

Equilibrating Solution		Equilibrated Solution	Sorbed Metal		Soil Metal (mg kg-1)	
M l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1} solution	mg kg^{-1} soil	Original	Final
0	0	0	0	0	13.24	13.24
1*10^{-7}	0.021	0	0.021	2.1	13.24	15.340
5*10^{-7}	0.104	0	0.104	10.4	13.24	23.640
1*10^{-6}	0.208	0.0006982	0.207	20.7301785	13.24	33.970
5*10^{-6}	1.039	0.0068992	1.032	103.2100793	13.24	116.450
1*10^{-5}	2.077	0.015735	2.061	206.1265033	13.24	219.367
5*10^{-5}	10.39	0.0705266	10.319	1031.94734	13.24	1045.187
1*10^{-4}	20.77	0.1578293	20.612	2061.21707	13.24	2074.457

Adsorption Experiment - Pb

Ventura/Oxnard, B 5



Equilibrating Solution		**Equilibrated Solution**	**Sorbed Metal**		**Soil Metal (mg kg-1)**	
M l^{-1}	**mg l^{-1}**	**mg l^{-1}**	**mg l^{-1} solution**	**mg kg^{-1} soil**	**Original**	**Final**
0	0	0	0	0	15.38	15.38
1*10^{-7}	0.021	0.000000	0.021000	2.100000	15.38	17.480
5*10^{-7}	0.104	0.000000	0.104000	10.400000	15.38	25.780
1*10^{-6}	0.208	0.000000	0.208000	20.800000	15.38	36.180
5*10^{-6}	1.039	0.000000	1.039000	103.900000	15.38	119.280
1*10^{-5}	2.077	0.015097	2.061903	206.190343	15.38	221.570
5*10^{-5}	10.39	0.030314	10.359686	1035.968649	15.38	1051.349
1*10^{-4}	20.77	0.187877	20.582123	2058.212290	15.38	2073.592

Adsorption Experiment - Pb

Ventura/Oxnard, P 4

Equilibrating Solution		**Equilibrated Solution**	**Sorbed Metal**		**Soil Metal (mg kg-1)**	
M l^{-1}	**mg l^{-1}**	**mg l^{-1}**	**mg l^{-1} solution**	**mg kg^{-1} soil**	**Original**	**Final**
0	0	0	0	0	15.02	15.02
$1*10^{-7}$	0.021	0.000000	0.021	2.1	15.02	17.120
$5*10^{-7}$	0.104	0.000000	0.104	10.4	15.02	25.420
$1*10^{-6}$	0.208	0.000000	0.208	20.8	15.02	35.820
$5*10^{-6}$	1.039	0.000000	1.039	103.9	15.02	118.920
$1*10^{-5}$	2.077	0.010210	2.067	206.6789763	15.02	221.699
$5*10^{-5}$	10.39	0.018480	10.372	1037.152049	15.02	1052.172
$1*10^{-4}$	20.77	0.178440	20.592	2059.155987	15.02	2074.176

Appendix B
Mass, As, Cd, Pb Inputs at Various Amendment Treatment Levels

1. P fertilizer Treatment

Treatment	Input (mg g^{-1})			
	Mass	As	Cd	Pb
1	0.5	<0.001	0.048	0.001
2	1.0	0.001	0.097	0.002
3	5	0.003	0.468	0.011
4	10	0.005	0.940	0.022
5	50	0.026	4.701	0.109
6	100	0.052	9.538	0.221

2. Zn Oxide Treatment

Treatment	Input (mg g^{-1})			
	Mass	As	Cd	Pb
1	0.2	0.004	0.004	2
2	1	0.018	0.020	11
3	2	0.036	0.041	23
4	5	0.180	0.204	113
5	22	0.792	0.896	496
6	50	1.802	2.039	1128
7	220	7.919	8.960	4956

3. Ironite Treatment

Treatment	Input (mg g^{-1})			
	Mass	As	Cd	Pb
1	0.2	0.818	0.006	0.72
2	1	4.091	0.030	3.6
3	2	8.182	0.059	7.2
4	10	40.911	0.296	36
5	20	81.734	0.591	72
6	100	408.672	2.957	361
7	200	817.345	5.914	722
8	400	1633.676	11.821	1443