A Generalized Trace Element Mass Balance Model for Cropland Soils: Arsenic and Cadmium

Final Report Submitted to
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by

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Executive Summary

A mass balance model is developed to assess trace element transformations in the root zone of irrigated cropland soils that receive routine phosphorus (P) fertilizer and micronutrient applications. A schematic diagram of the trace element mass balance model is depicted as follows:

\[
\frac{\partial Q}{\partial t} = -\frac{\partial F}{\partial z} - CR - U + R + I \quad [1]
\]

The schematic diagram assumes that the trace elements present in the root zone are distributed in the soil solution and four solid phases, namely, the inorganic mineral phase (CR), the surface adsorbed phase (Ad), the organic phase, which is represented in the diagram by “other solid phases” (R), and the residual phase, which is not depicted in the diagram. The residual phase is assumed to be constant and does not participate in the transformation reactions. The inorganic mineral phase (CR), surface adsorbed phase (Ad), and organic phase (R) are in dynamic equilibrium with the trace elements in the solution phase, which is expressed by the volumetric water content of soil, \( \theta \), multiplied by the soil solution concentration, \( \mathcal{C} \). The trace elements in the solution phase may be absorbed by plants (U) and are subject to leaching (F). The mass balance of trace elements in this soil layer may be expressed mathematically in terms of the above described components, such that:
where $Q$ is the trace element in the labile fraction (mmol cm$^{-3}$ soil), $t$ is time, represented in hours or years (time), $F$ is the flux of the trace element mass movement per unit surface area (mmol cm$^{-2}$ time$^{-1}$) along the soil depth and represents the leaching of trace elements out of the soil layer under consideration, $z$ is the depth of the soil layer (cm), $CR$ is the net precipitation-dissolution (mmol cm$^{-3}$ soil time$^{-1}$), $U$ is the plant uptake from the soil (mmol cm$^{-3}$ soil time$^{-1}$), $R$ is the reaction term describing the mineralization of trace elements in organic forms (mmol cm$^{-3}$ soil time$^{-1}$), and $I$ represents the sum of inputs from external sources (mmol cm$^{-3}$ soil time$^{-1}$). Each mass balance term in this equation is defined mathematically by parameters characterizing the biogeochemical processes represented. A PC-based algorithm is developed to solve the equation and the mass balances of arsenic (As) and cadmium (Cd) in California cropland soils are simulated for 100 years using this model.

Cropland soils in California typically contain 7.7 and 0.22 mg kg$^{-1}$ of As and Cd and receive 30 and 13 g ha$^{-1}$yr$^{-1}$, respectively, of As and Cd inputs through the application of P fertilizers and irrigation water. It appears that the cropping practices do not have significant effects on the total As content of the soils. However, the total Cd content of cropland soils may rise steadily over the 100-year simulation period. Results show that the total As and Cd content of the cropland soils will change from 7.7 to 7.6 and 0.22 to 0.35 mg kg$^{-1}$, respectively, over the 100-year simulation period. Factors that govern trace element transformations between the solid phases in the soils and plant uptake of trace elements may affect the resulting total trace element content of soils. There may be large uncertainties in the model estimations due to uncertainties in defining the values of model parameters. The uncertainties of the model estimates are characterized by Monte Carlo simulations. The mean and 95% confidence interval of the estimated total As and Cd contents of the soils are illustrated as follows:

From these two diagrams, it is obvious that the long-term arsenic and cadmium accumulations in the cropland soils may vary considerably depending on the assignments of the reaction rate constants and initial parameters that defining the soil characteristics. While the arsenic content of typical cropland soils (7.7 mg kg$^{-1}$) might not have changed significantly over 100 years, the 95% confidence interval showed that this value could vary from 7.2 to 8.2 mg kg$^{-1}$. While the typical cadmium content of the cropland soils might have rise from 0.22 to 0.35 mg kg$^{-1}$ over 100 years, the 95% confidence interval...
showed that this value could vary from 0.25 to 0.5 mg kg$^{-1}$. The ranges of changes estimated are rather small. They are not likely to cause adverse impacts on the plant absorption of arsenic and cadmium from cropland soils.
Introduction

Trace elements such as arsenic (As), cadmium (Cd), and lead (Pb) are ubiquitous in the natural environment. Trace elements indigenous in soils are derived from the weathering of minerals in parent material. Their concentrations in soils are several orders of magnitude lower in comparison to the major elements such as calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K). The distributions of trace elements in soils are influenced by soil forming processes. Factors such as climate, vegetation, topography, organic matter, microorganisms, and pH may affect their presence, chemical forms, and transformations in the soils. Mineral extractions and manufacturing processes often concentrate the broadly dispersed trace elements, which end up in industrial products and consumer goods. Thus, anthropogenic activities often redistribute the extracted trace elements near and around human habitats when the wastes from mining, manufacturing and consuming are disposed. Trace elements are potentially harmful to humans and other biota that are exposed to them, even in rather small quantities.

In crop production, trace elements may be introduced into soils through a variety of environmental exposure pathways that include applications of fertilizers and micronutrients, irrigation, pesticide uses, land application of organic wastes, re-incorporation of crop residues, and atmospheric fallouts (Chang and Page, 2000). The fate and transport of trace elements are governed by biogeochemical processes that include all of the physical, chemical and biological reactions taking place in the soil. Depending on their chemical nature and concentration, trace elements in the soil may transform to other chemical forms, accumulate in soils, leach into deeper soil strata, be carried away by surface runoffs, become airborne, and/or be absorbed by growing plants.

Reactions that control the fate and transport of the introduced trace elements in soils are numerous and complex. Through food chain transfers, trace elements that are deposited in soils, in turn may adversely affect human health. In a field-based study on plant uptake of metals from fertilizers, the Washington State Department of Agriculture (2001) demonstrated that the uptake of As, Cd, and Pb by vegetable plants may be significantly enhanced by these non-nutritive trace elements that are present in the applied fertilizers. Plants absorb water, nutrients, and toxic substances from the soil solution. Consequently, the plant uptake of trace elements is a function of their concentrations in the soil solution. In soils, the introduced trace elements tend to be chemically stable and form solid phases with minerals in the soil. Therefore, they must undergo the dissolution process before they may be absorbed by plants. Trace element concentrations in the soil solution, however, are controlled by the kinetics of chemical equilibrium between those in solution and those in the solid phases. In the solution phase, trace elements in the soil may be absorbed by growing plants and are subject to leaching. To characterize the environmental fate and transport of soil-borne trace elements, it is imperative to employ a mass balance computation that accounts for the interactive nature of processes governing the reactions of trace elements in soils.

Chang and Page (2000) assessed the trace element inputs and outputs of cropland soils in the Central Valley of California, and they observed that trace elements may be
introduced through various sources and accumulate in cropland soils. The extent of the buildup, however, is dependent on the frequency of applications and the quantity applied. Among the exposure pathways, fertilizer and micronutrient applications are by far the most consistent inputs for cropland soils. In a single application, the magnitude of such an input is rather small and its transformations in soils may not be readily detectable by routine soil sampling in the field. Over time, however, the concentrations of As, Cd, and Pb in cropland soils may slowly become elevated. The margins of safety for As, Cd, and Pb are rather narrow, and the onset of trace element-induced environmental calamity is ambiguous. It is vital that the long-term trends of trace elements’ fates and transformations in cropland soils are properly assessed.

The mass balance approach may be used to examine the flow of trace elements as influenced by the interactive processes in soils. The outcomes of the mass balance computation are useful to identify the primary trace element sources and sinks and the key reactive processes. Moreover, the model allows for assessments over a long-term time horizon and puts into perspectives the issues one must focus on when the impacts of trace elements in soils are evaluated.

Several trace element mass balance models have been developed (Van der Zee et al., 1990; Boekhold, 1990; Moolenaar and Lexmond, 1998; Keller et al., 2001, Meeüs et al., 2002). They all adhere to the same basic principle that the net change in metal contents of a soil layer is the balance of inputs at the soil surface and the outputs resulting from being leached out of a defined soil layer, removed by harvested products, and carried away by surface runoffs. Each of the input and output terms in this mass balance equation is governed by a set of physical, chemical and biological processes that are interactive and concurrent. For quantification, each reactive process that is included is represented by a mathematical equation, and the equations must be solved simultaneously. The differences among the mass balance computation models are based on the types and extent of the reactive processes included and the mathematical terms employed to describe them.

While the computation capability of the mass balance models has not been a limitation, realistic solutions may only be obtained when the parameters in the mathematical equations are properly defined. It is also possible that trace elements’ transformations in the soil should or can be linked with a solute transport model that tracks the downward movement of trace elements in a soil profile (Jacques et al., 2003). In model development, one often needs to weigh the representativeness of the mathematical expressions and the practicality of quantifying the parameters. The existing models, plant uptake and leaching are frequently empirically determined from the total trace element contents or soil solution concentrations through linear partition coefficients. Generally, a great deal of data is needed to assess the parameters and to calibrate the models. Seldom, the mass balance models for trace elements are generalized for and applicable to all trace elements.
Objectives

The purpose of this investigation is to develop a generalized trace element mass balance mathematical model for evaluation of long-term fate and transport of trace elements in cropland soils. The model will consider the processes that govern trace element precipitation-dissolution in the mineral phase, leaching in the soil profile, uptake by plants, and re-incorporation of crop residues and mineralization of trace elements in organic forms. Specific objectives are as follows:

- Evaluate the long-term impacts of arsenic and cadmium additions on the accumulation of these two elements in cropland soils.
- Evaluate the effects of mineral precipitation and dissolution processes on the distribution of arsenic and cadmium deposited in soils.
- Evaluate the effects of surface adsorption process on the distribution of arsenic and cadmium deposited in soils.
- Evaluate the effects of plant uptake processes on the distribution of arsenic and cadmium deposited in soils.

Model Development

The interactive processes that determine the concentrations of trace elements (i.e. As or Cd) in soils may be generalized with a set of reactions described by the schematic diagram in Figure 1.

![Schematic Depiction of a Generalized Trace Element Mass Balance Model](image)

Figure 1. Schematic Depiction of a Generalized Trace Element Mass Balance Model
The change of the labile trace element pool in soil ($Q$) with respect to time in a uniform and completely mixed soil layer is mathematically expressed in the following continuity equation:

$$\frac{\partial Q}{\partial t} = -\frac{\partial F}{\partial z} - CR - U + R + I$$  \[1\]

where $Q$ is the trace element in the labile fraction (mmol cm$^{-3}$ soil), $t$ is time, represented in hours or years (time), $F$ is the flux of the trace element mass movement per unit surface area (mmol cm$^{-2}$ time$^{-1}$) along the soil depth and represents the leaching of trace elements out of the soil layer under consideration, $z$ is the depth of the soil layer (cm), $CR$ is the net precipitation-dissolution (mmol cm$^{-3}$ soil time$^{-1}$), $U$ is the plant uptake from the soil (mmol cm$^{-3}$ soil time$^{-1}$), $R$ is the reaction term describing the mineralization of trace elements in organic forms (mmol cm$^{-3}$ soil time$^{-1}$), and $I$ represents the sum of inputs from external sources (mmol cm$^{-3}$ soil time$^{-1}$). Each mass balance term in this equation is defined mathematically by parameters characterizing the biogeochemical processes represented.

The trace elements in the labile phase, $Q$, are the sum of those in the adsorbed phase and solution phase and may be mathematically expressed as:

$$Q = Ad + \theta \times C$$  \[2a\]

where

$$Ad = K_d \times C$$  \[2b\]

where $K_d$ is the linear adsorption distribution constant (l soil solution l$^{-1}$ soil) and $C$ is the concentration of trace element in soil solution (mmol l$^{-1}$), and $\theta$ is the volumetric water content of the soil (l l$^{-1}$ soil).

The flux term, $F$, in equation [1] represents the rate of downward movement (i.e. leaching) and is mathematically expressed as (Tinker and Nye, 2000):

$$D_p \times \frac{dC}{dz} + \nu \times \theta \times C$$  \[3a\]

where $D_p$ is the diffusion coefficient of trace elements in the soil solution (cm$^2$ h$^{-1}$), $\nu$ is the velocity of pore water (cm h$^{-1}$), and $\nu \times \theta$ represents the water flux per unit surface area. The first and second term at the right hand side of equation [3a] represent trace elements transported by diffusion in and convection of water. Assuming that the moisture content of the soil profile is uniform, $C$ and $\theta$ will be constants throughout the soil layer. Therefore, the diffusive transport, $D_p \times dC/dz$, is zero as $dC/dz = 0$. The pore water
velocity \((v)\) equals the hydraulic conductivity of the soil \(K_{hf}\) when \(d\theta/dz = 0\). Equation [3a] may then be simplified into the following form:

\[ F = v \times \theta \times C = K_{hf} \times \theta \times C \]  \[3b\]

where \(K_{hf}\) is the field hydraulic conductivity \((\text{cm h}^{-1})\).

The CR in equation [1] is the net result of precipitation-dissolution reactions of the trace elements in the mineral phase \((\text{mmol cm}^{-3}\text{ soil h}^{-1})\), which are described as (Enfield et al., 1981):

\[ CR = K_{CR} (C - C_{eq}) \]  \[4\]

where \(K_{CR}\) \((\text{cm}^3 \text{ solution cm}^{-3} \text{ soil h}^{-1})\) is the net dissolution-precipitation rate constant, and \(C_{eq}\) is the equilibrium concentration that equals the solubility of the mineral phase in the soil.

The U in equation [1] is the plant uptake \((\text{mmol cm}^{-3}\text{ soil h}^{-1})\) that is described by:

\[ U = R_d \times J/z \]  \[5a\]

where \(R_d\) is root density \((\text{cm root cm}^{-2} \text{ soil})\) in the soil layer of depth \(z\) \((\text{cm})\), \(J\) \((\text{mmol cm}^{-1} \text{ root h}^{-1})\) is the flux of trace element uptake by roots, which is described by the Michaelis-Menten kinetics equation:

\[ J = J_{max} \times C/(K_M + C) \]  \[5b\]

where \(J_{max}\) is the maximum \(J\), \(K_M\) is the root permeability coefficient \((\text{mM})\).

In this manner, each term in equation [1] is expressed in terms of the trace element concentration in the soil solution, \(C\).

The R in equation [1] is the optional reaction term that may be used to include reactions that are not considered in the standard model components specified above. The term may be used to describe the oxidation, reduction, and organic mineralization reactions that involve trace elements in soils, and the reactions are described by the first order reaction model:

\[ R_{TE(O)} = k_0 \times C_{TE(R)} - k_f \times C_{TE(O)} \]  \[6a\]

\[ R_{TE(R)} = k_r \times C_{TE(O)} - k_0 \times C_{TE(R)} + k_m \times C_{OTE} - k_{im} \times C_{TE(R)} \]  \[6b\]

\[ R_{OTE} = k_{im} \times C_{TE(R)} - k_m \times C_{OTE} \]  \[6c\]

The \(R_{TE(O)}\), \(R_{TE(R)}\), and \(R_{OTE}\) are the trace elements of soils that are in oxidized, reduced, and organic forms \((\text{mmol cm}^{-3} \text{ hr}^{-1})\), respectively and \(C_{TE(O)}\), \(C_{TE(R)}\), and \(C_{OTE}\) are the
concentrations of trace elements in oxidized, reduced, and organic forms, respectively. Reaction rate constants in equations [6] are defined, such that $k_o$ is the trace element oxidation rate constant (hr$^{-1}$), $k_r$ is the trace element reduction rate constant (hr$^{-1}$), $k_m$ is the mineralization rate constant of trace elements in organic form (hr$^{-1}$), and $k_{im}$ is the rate constant for trace element immobilization (hr$^{-1}$). The inclusion of this term will require the definition of considerably more initial conditions for trace elements in soils and reaction rate parameters that are not readily available.

For example, the first order reaction kinetics that are used to describe the transformations of As species of different oxidation status are given by:

\[
R_{As(V)} = k_o \times C_{As(III)} - k_r \times C_{As(V)} \quad [7a]
\]
\[
R_{As(III)} = k_r \times C_{As(V)} - k_o \times C_{As(III)} + k_m \times C_{OAs} - k_{im} \times C_{As(III)} \quad [7b]
\]
\[
R_{OAs} = k_{im} \times C_{As(III)} - k_m \times C_{OAs} \quad [7c]
\]

where $R_{As(V)}$, $R_{As(III)}$, and $R_{OAs}$ are soil arsenic in As(V), As(III), and organic forms (mmol cm$^{-3}$ hr$^{-1}$), respectively, and $C_{As(V)}$, $C_{As(III)}$, and $C_{OAs}$ are concentrations of As(V), As(III), and organic As, respectively. Reaction rate constants in equations [6] are defined, such that $k_o$ is the As(III) oxidation rate constant (hr$^{-1}$), $k_r$ is the As(V) reduction rate constant (hr$^{-1}$), $k_m$ is the mineralization rate constant of organic As (hr$^{-1}$), and $k_{im}$ is the rate constant for As(III) immobilization (hr$^{-1}$).

The same set of equations may be applied to Cd. As the Cd in soils does not involve oxidation and reduction reactions, this trace element in oxidized and reduced forms, $C_{TE(O)}$ and $C_{TE(R)}$, may be lumped together and the rate constants $k_o$ and $k_r$ are equal to zero. In this manner, equations [6a], [6b], and [6c] may be reduced to simply the equation [6c] that defines the mineralization and immobilization of Cd in organic form to account for the re-incorporation of crop residues.

The source term I (mmol cm$^{-3}$ hr$^{-1}$) in equation [1] specifies the input flux of trace element additions to the soil that comprise the trace elements found in P fertilizers, irrigation water, atmospheric deposition and other sources. In the computation, it may be considered as a discrete point source input at a given time, such as fertilizer application, irrigation, and re-incorporation of crop residues, or as a continuous input, such as atmospheric fallout, or both.

**Definition of Model Parameters**

The mass balance model presented in the previous section is generic in nature as the distribution of any trace element in soils may be divided into the same pools outlined in the above-presented mathematical expressions and the transformations between pools may be characterized by the same set of reaction equations. 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 the efficacy of the model, it is used to evaluate the mass balance of arsenic and cadmium as they are affected by various soil properties and plant trace element uptake factors. Data in the literature were used to define the initial conditions and the reaction rate constants needed for the computations.

**Trace Element Distribution in Soils**

In the mass balance computation, the initial concentrations and distributions of As and Cd in soils must be known. We reviewed the published literature and determined the As and Cd concentrations of soils that are representative of cropland soils and define the initial conditions accordingly.

**Total As and Cd Contents of Soils.** The baseline trace element contents of soils in the U.S. have been reported extensively. The concentrations vary considerably across the country and are dependent on the mineral compositions of parent material and the influences of the soil forming processes. Shacklette et al. (1974) reported that total As concentrations of sandy, loamy/clay, and forest soils in the conterminous United States were <0.1 to 30, 1.7 to 27, and <0.1 to 93, respectively. Kabata-Pendias and Pendias (2001) summarized data from various sources and tabulated the descriptive statistics on trace elements in soils in the U.S. Table 1 illustrates the ranges and means of As and Cd contents of the uncontaminated soils in the U.S.

**Table 1. Total As and Cd of Soils in the U.S.**
(Kabata-Pendias and Pendias, 2001)

<table>
<thead>
<tr>
<th>Category</th>
<th>Arsenic (mg kg⁻¹)</th>
<th>Cadmium (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range</td>
<td>Mean</td>
</tr>
<tr>
<td>Podzols and sandy soils</td>
<td>&lt; 0.1 to 30</td>
<td>5.1</td>
</tr>
<tr>
<td>Loamy and clayey soils</td>
<td>1.7 to 27</td>
<td>7.7</td>
</tr>
<tr>
<td>Chemozems</td>
<td>1.9 to 23</td>
<td>8.8</td>
</tr>
<tr>
<td>Forest soils</td>
<td>&lt; 0.1 to 93</td>
<td>7</td>
</tr>
<tr>
<td>Cropland soils</td>
<td>&lt; 1 to 93</td>
<td>7</td>
</tr>
</tbody>
</table>

*Summary of 3202 samples in a comprehensive national survey (Holmgren et al., 1993)*

Bradford et al. (1996) sampled and determined the concentrations of the major and minor elements of 50 benchmark soils in California that were representative of the baseline levels of major soil types in the state. In 2001, the soils at these locations were again sampled. The As and Cd concentrations of the benchmark soils in California are summarized in Table 2 (Krag, 2002).
Table 2. Descriptive Statistics of As and Cd Concentrations of 50 Benchmark Soils in California, Sampled in 2001 (Krage, 2002).

<table>
<thead>
<tr>
<th>Element</th>
<th>Range (mg kg(^{-1}))</th>
<th>Median (mg kg(^{-1}))</th>
<th>Mean (mg kg(^{-1}))</th>
<th>S.D.(^{+}) (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>1.8 to 16.6</td>
<td>6.5</td>
<td>7.6</td>
<td>3.9</td>
</tr>
<tr>
<td>Cd</td>
<td>0.07 to 0.53</td>
<td>0.19</td>
<td>0.22</td>
<td>0.11</td>
</tr>
</tbody>
</table>

+S.D. denotes standard deviation

Concentrations of As and Cd in Soil Solutions. The trace element concentrations of soil solutions are expected to be very low. There were very limited data regarding trace element concentrations of soil solutions in the published literature, as procedures of obtaining soil solutions were time consuming and methods of measurement were cumbersome (Gooddy et al., 1995). Kalbitz and Wennrich (1998) reported that the median As concentration in soil solution is 6 µg l\(^{-1}\) with a range from the below detection level to 28µg l\(^{-1}\) for clay soils and a median of 4.5 µg l\(^{-1}\) with a range from the below detection level to 23 µg l\(^{-1}\) for sandy soils. Itoh and Yumura (1979) reported similar As concentrations in soils, ranging from 4 to 12 µg l\(^{-1}\).

Mullins and Sommers (1986) characterized the Cd concentrations in the soil solutions of biosolids-treated soils. They found the Cd concentrations in soil solution varied from 2 µg l\(^{-1}\) in uncontaminated soils to 15 µg l\(^{-1}\) in biosolids-treated soils and greater than 85% of the Cd in the soil solution was present as the free ion form. Kabata-Pendias and Pendias (2001) reported the Cd concentrations in soil solution varied from 0.2 to 6 µg l\(^{-1}\). Ma and Lindsay (1995) determined the activities of Cd\(^{2+}\) in both contaminated and uncontaminated soils using the chelation method. The measured Cd\(^{2+}\) activities were highly pH dependent with correlation coefficients of 0.99 in the contaminated and 0.98 in the uncontaminated soils. The measured Cd\(^{2+}\) activities can be predicted using the following equations:

\[
\log (Cd^{2+}) = (7.64 \pm 0.27) - 2 \times pH, \text{ for contaminated soil} \quad \text{[Eq. 8a]}
\]
\[
\log (Cd^{2+}) = (6.22 \pm 0.18) - 2 \times pH, \text{ for uncontaminated soils} \quad \text{[Eq. 8b]}
\]

where (Cd\(^{2+}\)) denotes the activity of Cd ions. El-Falaky et al. (1991) and Workman and Lindsay (1990) reported similar relationships between Cd concentrations in soil solutions and soil pH.

As and Cd Distributions in Soils. In the mass balance model, the total trace elements in soils are divided into four major dynamic pools, namely the labile pool (Q) that includes trace elements in soil solution (θ x C), the surface-adsorbed trace element pool (Ad) that is linked to those in the solution phase by a solid-solution linear partitioning (Ad = b x C), the mineral pool (CR) that is linked to the trace elements in the soil solution phase through dissolution and precipitation processes of the mineral phases, other solid phases (R, such as the organic forms) that may be degraded and contribute to the labile pool, and a fifth pool, an occluded trace element pool that does not change with
time and has no significant impact on the four other, dynamic pools. The fifth pool is not represented in Fig. 1, the schematic diagram of the trace element mass balance model.

Sequential extraction procedures may be a reasonable approach to fractionating the soil’s trace elements into their respective pools. Based on the results of sequential extractions, McLaren et al. (1998) reported the distribution of As in soils: 3.9% of total soil As was present as the free exchangeable arsenic, 9.3% was non-exchangeable but readily labile in association with soil mineral surfaces, 44.7% was held more strongly by chemisorption to Fe and Al components of the soil surface, 14.2% was held at the internal surfaces of soil aggregates, 6.9% was Ca-associated As, and 21.1% was residual As. The distributions of Cd in soils have been investigated extensively (Soon and Bates, 1982; Ahnstrom and Parker, 1999; Nakhone and Young, 1993; Asami et al., 1995; Sanchez et al., 1999). Soon and Bates (1982) found that 17% of total soil Cd was water soluble and easily exchangeable fractionation, 36% was complexed or adsorbed Cd, and 47% was occluded by or co-precipitated with metal oxides, carbonates or phosphates and other secondary minerals. Ahnstrom and Parker (1999) showed that 11% of soil Cd was in the soluble-exchangeable fraction, 32% was in the sorbed-carbonated fraction, 40% was in the oxidizable fraction, 8% was in the reducible fraction and 6% was in the residual fraction. Nakhone (1993) reported labile Cd accounted on average for 48% of total Cd in 33 soils. Asami (1995) examined 38 surface soils and found that most soil-borne Cd was in exchangeable form (45%) and the exchangeable fraction of unpolluted soils was usually smaller than that of polluted soils. Sanchez (1999) showed that the sum of the Cd in exchangeable and carbonate forms in polluted mining soils is close to 50% of total Cd.

Soil is a complex chemical system consisting of fragments and weathering products of primary minerals, organic matter, microorganism, water, and gases. Trace elements are expected to be partitioned among these phases. As the above-described components are mixed and present at the same time, reactions involving these components are dynamic and simultaneous. It is imperative that the trace elements in these solid phases are identified and their dissolution-precipitation characteristics be quantified.

**Initial Conditions.** Based on the above summarized review and discussion, the initial conditions for As and Cd in cropland (loamy) soils are generalized in Table 3.

<table>
<thead>
<tr>
<th>Category</th>
<th>Arsenic</th>
<th>Cadmium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Soil Concentration</td>
<td>7.7</td>
<td>0.22</td>
</tr>
<tr>
<td>Soil Solution Concentration</td>
<td>0.08</td>
<td>0.005</td>
</tr>
<tr>
<td>Mineral Phase Pool</td>
<td>5.0</td>
<td>0.07</td>
</tr>
<tr>
<td>Organic Pool</td>
<td>0.5</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Mineral Phases of As and Cd in Soils

Arsenic Mineral Phases in Soils. Sadiq et al. (1983) outlined the As minerals of soils based on the possible reactions of As with other constituents in soils. Arsenate, the As in +5 valence, may form stable minerals with many trace metal elements that are possibly present in soils (Table 4). They concluded that Ca$_3$(AsO$_4$)$_2$ and Mn$_3$(AsO$_4$)$_2$ were the most likely As (V) controlling minerals in soils, as trace metals are most likely present in other stable solid phases. In well-oxidized and alkaline soils, Ca$_3$(AsO$_4$)$_2$ was the most abundant and stable As(V) mineral and was followed by Mn$_3$(AsO$_4$)$_2$. In acidic conditions, Ca$_3$(AsO$_4$)$_2$ became unstable in soils. On the other hand, Mn$_3$(AsO$_4$)$_2$ was stable in a wide range of soil pH spanning from acidic to alkaline. For irrigated cropland soils in California, Ca$_3$(AsO$_4$)$_2$, Mn$_3$(AsO$_4$)$_2$, and FeAsO$_4$ are the most likely forms of As mineral phases. Assuming Ca$_3$(AsO$_4$)$_2$ is the controlling As(V) mineral, the soil pH = 7.5, and Ca$^{2+}$ activity is 0.01 M, the equilibrium As(V) concentration of the soil solution will be 3.55 mM HAsO$_4^{2-}$. If Mn$_3$(AsO$_4$)$_2$ is the controlling As(V) mineral and, Mn$^{2+}$ activity is $10^{-5}$ M, the equilibrium concentration of As in the soil solution will be $5.5 \times 10^{-4}$ and $5.5 \times 10^{-5}$ M for pH = 6.5 and 7.5, respectively.

Table 4. Arsenic minerals, dissolution reactions, and equilibrium constants ($K_0$)

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Log $K_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ca$_3$(AsO$_4$)$_2$ +2H$^+$ $\leftrightarrow$ 3Ca$^{2+}$ + 2HAsO$_4^{2-}$</td>
<td>-1.91</td>
</tr>
<tr>
<td>2. Mn$_3$(AsO$_4$)$_2$ +2H$^+$ $\leftrightarrow$ 3Mn$^{2+}$ + 2HAsO$_4^{2-}$</td>
<td>-8.51</td>
</tr>
<tr>
<td>3. Cd$_3$(AsO$_4$)$_2$ +2H$^+$ $\leftrightarrow$ 3Cd$^{2+}$ + 2HAsO$_4^{2-}$</td>
<td>-8.97</td>
</tr>
<tr>
<td>4. Cu$_3$(AsO$_4$)$_2$ +2H$^+$ $\leftrightarrow$ 3Cu$^{2+}$ + 2HAsO$_4^{2-}$</td>
<td>-14.97</td>
</tr>
<tr>
<td>5. Ni$_3$(AsO$_4$)$_2$ +2H$^+$ $\leftrightarrow$ 3Ni$^{2+}$ + 2HAsO$_4^{2-}$</td>
<td>-2.21</td>
</tr>
<tr>
<td>6. Pb$_3$(AsO$_4$)$_2$ +2H$^+$ $\leftrightarrow$ 3Pb$^{2+}$ + 2HAsO$_4^{2-}$</td>
<td>-9.07</td>
</tr>
<tr>
<td>7. Zn$_3$(AsO$_4$)$_2$ +2H$^+$ $\leftrightarrow$ 3Zn$^{2+}$ + 2HAsO$_4^{2-}$</td>
<td>-8.20</td>
</tr>
<tr>
<td>8. FeAsO$_4$ + H$^+$ $\leftrightarrow$ Fe$^{3+}$ + HAsO$_4^{2-}$</td>
<td>-8.59</td>
</tr>
<tr>
<td>9. AlAsO$_4$ +H$^+$ $\leftrightarrow$ Al$^{3+}$ + HAsO$_4^{2-}$</td>
<td>-4.70</td>
</tr>
<tr>
<td>10. AsS(realger) + 8H$_2$O $\leftrightarrow$ HAsO$_4^{2-}$ + SO$_4^{2-}$ + 15H$^+$ + 11e</td>
<td>-83.13</td>
</tr>
<tr>
<td>11. As$_2$S$_2$(Orpiment) + 16H$_2$O $\leftrightarrow$ 2HAsO$_4^{2-}$ + 2SO$_4^{2-}$ + 23H$^+$ + 22e</td>
<td>-180.42</td>
</tr>
<tr>
<td>12. As$_2$S$_2$ + 20H$_2$O $\leftrightarrow$ 2HAsO$_4^{2-}$ + 3SO$_4^{2-}$ + 38H$^+$ + 30e</td>
<td>-219.14</td>
</tr>
</tbody>
</table>
Cadmium Mineral Phases in Soils. Commonly found Cd minerals and their dissolution reactions are summarized in Table 5. Except for CdS, which is present in a reduced environment, most Cd minerals are rather soluble and not likely to be in the solid phase in soils that control the soil solution concentration (Table 6). Street et al (1977 and 1978) found that Cd$^{2+}$ activities in acidified soils were undersaturated with respect to all known Cd minerals. For soils with pH > 7.25, the Cd concentration in the soil solution was controlled by the solubility of CdCO$_3$. Santillan-Medrano (1975) found that, at high Cd concentrations, the precipitation of CdCO$_3$ or Cd$_3$(PO$_4$)$_2$ regulated Cd solubility in soils and, at low Cd concentration, the equilibrium solution was undersaturated with regard to both minerals. Workman and Lindsay (1990) found that the measured Cd$^{2+}$ activities in alkaline soils were approximately two orders of magnitude lower than the activities of Cd$^{2+}$ in equilibrium with CdCO$_3$ and atmospheric CO$_2$. El-Falaky et al. (1991) constructed solubility diagrams for various Cd minerals using thermodynamic data selected from the literature. The diagrams suggest that CdFe$_2$O$_4$ was a likely solid phase mineral controlling Cd$^{2+}$ activities in their samples and the Cd$^{2+}$ activities reported were one or two orders of magnitude supersaturated with respect CdFe$_2$O$_4$- soil Fe.

Table 5. Cadmium minerals, dissolution reactions, and equilibrium constants ($K_0$)

<table>
<thead>
<tr>
<th>Minerals and Reactions</th>
<th>Log $K_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdO (monteponite) $+$2H$^+$ $\rightleftharpoons$ Cd$^{2+}$ $+$ H$_2$O</td>
<td>15.14</td>
</tr>
<tr>
<td>$\beta$-Cd(OH)$_2$ $+$2H$^+$ $\rightleftharpoons$ Cd$^{2+}$ $+$ 2H$_2$O</td>
<td>13.65</td>
</tr>
<tr>
<td>CdCO$_3$ (octavite) $+$2H$^+$ $\rightleftharpoons$ Cd$^{2+}$ $+$ CO$_2$ (g) $+$H$_2$O</td>
<td>6.16</td>
</tr>
<tr>
<td>CdSiO$_3$ $+$2H$^+$ $+$H$_2$O $\rightleftharpoons$ Cd$^{2+}$ $+$ H$_4$SiO$_4$</td>
<td>7.63</td>
</tr>
<tr>
<td>Cd$_3$(PO$_4$)$_2$ $+$2H$^+$ $\rightleftharpoons$ 3Cd$^{2+}$ $+$ 2H$_2$PO$_4^-$</td>
<td>1.00</td>
</tr>
<tr>
<td>CdS (greennokite) $\rightleftharpoons$ Cd$^{2+}$ $+$ S$^{2-}$</td>
<td>-27.07</td>
</tr>
<tr>
<td>CdSO$_4$ $\rightleftharpoons$ Cd$^{2+}$ $+$ SO$_4^{2-}$</td>
<td>-0.04</td>
</tr>
<tr>
<td>CdSO$_4$.H$_2$O $\rightleftharpoons$ Cd$^{2+}$ $+$ SO$_4^{2-}$ $+$ H$_2$O</td>
<td>-1.59</td>
</tr>
<tr>
<td>CdSO$_4$.2Cd(OH)$_2$ $+$ 4 H$^+$ $\rightleftharpoons$ 3Cd$^{2+}$ $+$ SO$_4^{2-}$ $+$4H$_2$O</td>
<td>22.65</td>
</tr>
<tr>
<td>2CdSO$_4$.Cd(OH)$_2$ $+$ 2 H$^+$ $\rightleftharpoons$ 3Cd$^{2+}$ $+$ SO$_4^{2-}$ $+$2H$_2$O</td>
<td>6.73</td>
</tr>
</tbody>
</table>
Table 6. Equilibrium concentration (C_{eq}) of selected cadmium minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Equilibrium Concentration of Cd (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH = 5.5</td>
</tr>
<tr>
<td>CdO</td>
<td>10^{-1.14}</td>
</tr>
<tr>
<td>Cd(OH)<em>{2} (PCO</em>{2}@ 0.003 atm)</td>
<td>10^{-2.65}</td>
</tr>
<tr>
<td>CdCO_{3} (PCO_{2} @ 0.05 atm)</td>
<td>10^{-2.52}</td>
</tr>
<tr>
<td>CdSiO_{3}</td>
<td>10^{-3.54}</td>
</tr>
<tr>
<td>CdS</td>
<td>+</td>
</tr>
<tr>
<td>CdS(OH)<em>{2} (SO</em>{4}^{2-} = 0.01M)</td>
<td>10^{-1.96}</td>
</tr>
<tr>
<td>CdS(OH)<em>{2}·H</em>{2}O (SO_{4}^{2-} = 0.01M)</td>
<td>10^{-0.41}</td>
</tr>
<tr>
<td>CdS(OH)<em>{2}·Cd(OH)</em>{2} (SO_{4}^{2-} = 0.01M)</td>
<td>10^{-0.88}</td>
</tr>
<tr>
<td>2CdS(OH)<em>{2}·Cd(OH)</em>{2} (SO_{4}^{2-} = 0.01M)</td>
<td>10^{-0.76}</td>
</tr>
</tbody>
</table>

*Mineral present under reduced environment

In summary, the solubility data of As and Cd minerals found in the literature do not present a clear picture regarding the nature of their inorganic mineral solid phases in soils, which underscores the need to determine the soil-specific solubility and kinetic factors of their inorganic solid phases.

For the purpose of simulations, we choose to generalize from data reported in the literature. For the solid phase As mineral, Mn_{3} (AsO_{4})_{2}, the As solubility will be 5.5 x 10^{-5} M at pH = 6.5 and Mn^{2+} = 10^{-5} M. For the solid phase As mineral, Ca_{3} (AsO_{4})_{2}, the As solubility will be 3.5 x 10^{-6} M at pH = 7.5 and Ca^{2+} activity = 0.01 x 10^{-6} M. However, As present in the soil solution frequently is undersaturated with respect to Ca_{3} (AsO_{4})_{2} which is indicative of the presence of more stable mineral phases. In such cases, we choose to reduce C_{eq} for As minerals to 0.1 x 10^{-6} M. For the solid phase Cd mineral, CdFe_{2}O_{4}, the Cd solubility will be 0.01 x 10^{-6} M. As the soil solution concentration of Cd again is often undersaturated with respect to CdFe_{2}O_{4}, we scale down the C_{eq} for Cd to 0.001 x 10^{-6} M.

The dissolution-recitation kinetics factor, K_{CR} has the units of cm^{3} soil solution cm^{-3} soil h^{-1}. In a heterogeneous system, the solid phases of trace elements are most likely formed as mixed solids with other more prominent minerals in the soils. Their rates of dissolution will be considerably slower than pure minerals. We were unable to locate in the literature, kinetics rate factors for trace minerals in soils and arbitrarily selected 10^{-5} cm^{3} soil solution cm^{-3} soil h^{-1} as the rate constant for both elements. It yields a precipitation rate of approximately 1 x 10^{-7} moles cm^{-3} soil month^{-1}.

**Surface-Adsorbed Arsenic and Cadmium**

**Surface Adsorption of Soil As.** Most investigators reported that As adsorption by soils might be described by either a Langmuir or a Freundlich adsorption isotherm model. The studies focused primarily on reactions with As(V) compounds and the upper range of the equilibrium concentrations invariably exceeded the concentrations...
normally found in soils. In natural or agricultural soils, the total As and soil solution As concentrations and their inputs are expected to be considerably lower than the range commonly covered in laboratory experiments and, under natural or agricultural soil conditions, the adsorption isotherms may be reduced to a linear model, such that, $A_d = K_d \times C$ (i.e. Equation 2b). The linear partitioning constant, $K_d$, varied considerably by soils (Table 7). The soil texture, pH, organic matter, clay content and Fe and Al hydroxide contents of soils might all affect the outcomes.

Table 7. Linear Adsorption Constants of Arsenic in Soils

<table>
<thead>
<tr>
<th>Soil</th>
<th>Total As (mg kg$^{-1}$)</th>
<th>Linear Adsorption Constant (1 kg$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>As(V)</td>
<td>As(III)</td>
</tr>
<tr>
<td>Wasco (California)</td>
<td>10.1</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>Fallbrook (California)</td>
<td>49.5</td>
<td>28.4</td>
<td></td>
</tr>
<tr>
<td>Wyo (California)</td>
<td>165.1</td>
<td>83.7</td>
<td></td>
</tr>
<tr>
<td>Plainfield sand (Wisconsin)</td>
<td>0.8</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>Waupun silty clay loam (Wisconsin)</td>
<td>3.7</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>Superior clay loam (Wisconsin)</td>
<td>3.4</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>Madison River Valley soils (Non-irrigated)</td>
<td>20</td>
<td>17.4</td>
<td></td>
</tr>
<tr>
<td>Madison River Valley soils (Irrigated)</td>
<td>14.9</td>
<td>14.7</td>
<td></td>
</tr>
<tr>
<td>Australian soils</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alfisol</td>
<td>0.6</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Oxisol</td>
<td>0.59</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>Alfisol</td>
<td>0.67</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Oxisol</td>
<td>1.94</td>
<td>46</td>
<td></td>
</tr>
</tbody>
</table>

A number of studies have focused on As adsorption by Fe oxides due to their high adsorptive affinity for As(V). These studies indicate that the HAsO$_4^{2-}$ anion forms inner-sphere Fe-As$^{5+}$ surface complexes (Sun and Doner 1996; Waychunas et al., 1993; Lumsdon et al., 1984). Attempts have been made to correlate As sorption with the Fe oxide contents of soils. When the data from one single study were analyzed, the adsorption constants increased linearly in proportion to the Fe oxide contents of the soils studied. However, the other soil mineral components also have been shown to play an important role in the adsorption of As, such as Al hydroxide and phyllosilicate minerals (i.e. clay). When soils from several studies are pooled, $K_d$ is no longer related to the Fe oxide contents of soils, as illustrated in Figure 2.

Generally speaking, the linear adsorption constants of As in soils may vary by two orders of magnitude from less than 10 to more than one hundred.
Surface Adsorption of Soil Cd. The soil solution is the central focus in characterizing the nature of Cd in natural and agricultural soils; from which plants absorb the element. The soil solution interacts with Cd associated with solid phases in soils. The amounts of Cd adsorbed per unit soil mass customarily may be quantitatively linked to those in the solution phase by the Langmuir or Frenlich adsorption isotherm. From those in solution phase, Cd can combine with dissolved organic and inorganic ligands to form complex ions. The formation of solution complexes can have a significant effect on the mobility and surface sorption of trace metals in soil. For example, the chloro-complex (e.g., CdCl\(^{+}\)) is weakly sorbed and thus likely to be more susceptible to leaching and plant uptake. The adsorption is represented by the equilibrium of those in solution and solid phases. While the Cd in different dissolved forms may exhibit different adsorption affinity and bioavailability, they are generally considered as a single chemical species in terms of reactive processes in soils.

Once introduced into the soil, Cd will quickly reach a dynamic equilibrium with the soil components and become distributed between the solution and solid phases, according to the adsorption isotherm. Generally, the chemical conditions of soils are in favor of adsorption, therefore immobilization of Cd by soils is the norm. The binding mechanisms for Cd in soils are manifold and vary with the composition of soils and their physical properties. Generally, the predominant sorption mechanism is surface complexation. When the density of surface complexes increases, surface precipitation may occur. Surface complexes can be weakly held as outer sphere complexes or more
tightly held as inner sphere complexes to the soil. Outer sphere complexation is usually a reversible process, whereas inner sphere complexation is often not reversible. Thus, the trace elements that tend to be the most mobile and bioavailable are either those that form weak outer sphere complexes with organic or inorganic (clay, metal oxides) soil components, or those that complex with ligands in solution and are not sorbed. Conversely, trace metals that form inner-sphere complexes are much less likely to desorb, and thus are less mobile and bioavailable. The results from sequential extractions of soils revealed that Cd tends to be in the mobile fraction (exchangeable fraction and adsorbed fraction), thus having high potential bioavailability.

**Arsenic and Cadmium Input Sources**

Trace elements may be added to cropland soils by applications of irrigation water, fertilizers, micronutrients, municipal biosolids, animal manure and other soil amendments such as lime and composts. In addition, all soils may receive aerial deposition through atmospheric fallout. Kabata-Pendias and Pendias (2001) summarized the data in the published literature and concluded that, on a global scale, the concentrations of trace elements in commonly used soil amendments vary considerably (Table 8) and the quantities applied are also extremely variable. As a result, the trace element inputs to cropland soils are difficult to generalize.

**Table 8. Concentrations of As and Cd in Commonly Used Soil Amendments.**

<table>
<thead>
<tr>
<th>Element</th>
<th>Biosolids (mg kg(^{-1}))</th>
<th>P Fertilizer (mg kg(^{-1}))</th>
<th>N Fertilizer (mg kg(^{-1}))</th>
<th>Manure (mg kg(^{-1}))</th>
<th>Limestone (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>2 to 26</td>
<td>2 to 1,200</td>
<td>2 to 120</td>
<td>3 to 25</td>
<td>0.1 - 24</td>
</tr>
<tr>
<td>Cd</td>
<td>2 to 1,500</td>
<td>0.1 – 170</td>
<td>0.05 to 8.5</td>
<td>0.3 to 0.8</td>
<td>0.04 - 0.1</td>
</tr>
</tbody>
</table>

(Based on data in Kabata-Pendias and Pendias, 2001).

Chang and Page (2000) computed, based on realistic local data, the trace element mass balances for field crop production operations in the Central Valley of California (Table 9). The outcomes illustrate the potential, relative contributions from various input sources. While the inputs resulting from applications of municipal biosolids and reclaimed wastewater may be considerable, only limited cropland soils routinely receive these amendments. The input from irrigation was based on the trace element contents of water in the lower reach of the San Joaquin River in the Central Valley, clearly a worst-case scenario estimate. Under ordinary situations when groundwater is used, the inputs from irrigation would be one to two orders of magnitude less than those shown in Table 9 (except for As). Fertilizers and micronutrients are routinely used in crop production. They are by far the most consistent inputs and over time may be the most significant sources of As and Cd in cropland soils. Because of low input rates, As and Cd may accumulate in soils through fertilizer and micronutrient applications for a long time before they reach levels that are detectable by routine soil sampling and chemical analysis.
### Table 9. Estimated Trace Element Inputs and Outputs of Agricultural Soils in California.

<table>
<thead>
<tr>
<th>Element</th>
<th>Irrigation</th>
<th>Wastewater</th>
<th>Biosolids</th>
<th>Fertilizer</th>
<th>Manure</th>
<th>Weathering</th>
<th>Fallouts</th>
<th>Drainage</th>
<th>Runoff</th>
<th>Harvests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>25</td>
<td>30</td>
<td>120</td>
<td>4</td>
<td>8</td>
<td>0.4</td>
<td>5</td>
<td>-</td>
<td>--</td>
<td>6</td>
</tr>
<tr>
<td>Boron</td>
<td>4,200</td>
<td>6,000</td>
<td>500</td>
<td>30</td>
<td>250</td>
<td>20</td>
<td>40</td>
<td>-</td>
<td>--</td>
<td>30</td>
</tr>
<tr>
<td>Cadmium</td>
<td>2</td>
<td>30</td>
<td>64</td>
<td>6</td>
<td>4</td>
<td>0.03</td>
<td>5</td>
<td>3</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Chromium</td>
<td>144</td>
<td>12</td>
<td>1,030</td>
<td>20</td>
<td>150</td>
<td>3</td>
<td>100</td>
<td>15</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>Copper</td>
<td>22</td>
<td>240</td>
<td>5,060</td>
<td>4</td>
<td>130</td>
<td>13</td>
<td>50</td>
<td>25</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>Lead</td>
<td>56</td>
<td>60</td>
<td>1,110</td>
<td>125</td>
<td>40</td>
<td>4</td>
<td>100</td>
<td>6</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Mercury</td>
<td>-</td>
<td>24</td>
<td>21</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>2</td>
<td>1</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>38</td>
<td>60</td>
<td>15</td>
<td>90</td>
<td>300</td>
<td>5</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>12</td>
</tr>
<tr>
<td>Nickel</td>
<td>28</td>
<td>120</td>
<td>570</td>
<td>5</td>
<td>200</td>
<td>22</td>
<td>50</td>
<td>12</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Selenium</td>
<td>18</td>
<td>20</td>
<td>57</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Zinc</td>
<td>89</td>
<td>480</td>
<td>8,300</td>
<td>40</td>
<td>200</td>
<td>20</td>
<td>200</td>
<td>30</td>
<td>5</td>
<td>100</td>
</tr>
</tbody>
</table>

*Table 3 in Chang and Page (2000)*
Environmental risk assessment has become a commonly used procedure to establish numerical limits for contaminants in fertilizers. (TFI, 2000; USEPA, 2000; AAPFCO, 2002). In 1997, the California Department of Food and Agriculture (CDFA) conducted a risk-based analysis that developed limits for As, Cd, and Pb in fertilizer products considered to be safe for use on cropland. 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). Subsequently, Washington, California, and Oregon took regulatory actions to set numerical limits on As, Cd, and Pb in the fertilizers and micronutrients marketed in their respective states (Table 10). The fertilizer regulatory agencies in California, Oregon, and Washington now track and publish online, via the Internet, the levels of non-nutrient substances in micro and micronutrient fertilizers registered for sale in their states.

Table 10. Numerical Limits for As, Cd, and Pb in P Fertilizers.

<table>
<thead>
<tr>
<th>State</th>
<th>Arsenic</th>
<th>Cadmium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washington† (March 1998)</td>
<td>0.33 kg ha⁻¹ yr⁻¹</td>
<td>0.089 kg ha⁻¹ yr⁻¹</td>
</tr>
<tr>
<td>California‡ (January 2002)</td>
<td>4 ppm, each percent P₂O₅</td>
<td>6 ppm, each percent P₂O₅</td>
</tr>
<tr>
<td>Oregon (January 2003)</td>
<td>9 ppm, each percent P₂O₅</td>
<td>7.5 ppm each percent P₂O₅</td>
</tr>
</tbody>
</table>

†Based on Canadian standards that 45 year cumulative loading limits are 15 and 4 kg ha⁻¹ for As and Cd, respectively.
‡Stepwise decrease to 2 and 4 ppm for As and Cd, respectively.

The European Union (EU) proposed limits of 60 mg Cd kg⁻¹ P₂O₅ by 2006, 40 mg Cd kg⁻¹ P₂O₅ by 2010 and 20 mg Cd kg⁻¹ P₂O₅ by 2015 (Oosterhuis, 2000). The following tabulation shows some existing regulatory limits of Cd in fertilizers in selected EU countries (Table 11).

Table 11. Regulatory Limits of Cd in Phosphate Fertilizer in Some EU Countries

<table>
<thead>
<tr>
<th>Country</th>
<th>Maximum Permissible Concentration (mg Cd kg⁻¹ P₂O₅)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria</td>
<td>75</td>
</tr>
<tr>
<td>Belgium</td>
<td>90</td>
</tr>
<tr>
<td>Denmark</td>
<td>47</td>
</tr>
<tr>
<td>Finland</td>
<td>21.5</td>
</tr>
<tr>
<td>Germany</td>
<td>40 – 90</td>
</tr>
<tr>
<td>Sweden</td>
<td>43</td>
</tr>
<tr>
<td>Portugal</td>
<td>40 – 70</td>
</tr>
</tbody>
</table>

The commonly used phosphate fertilizers: di-ammonium phosphate (DAP) contains 46% P₂O₅, mono ammonium phosphate (MAP) contains 52% P₂O₅, and triple superphosphate (TSP) contains 45% P₂O₅. Assuming an average of 50% P₂O₅ in phosphate fertilizers, then California’s regulation for Cd in fertilizers, which is 4 ppm Cd per 1% P₂O₅ in 2004 (Table 10) converts to equal 200 mg Cd kg⁻¹ P₂O₅. It is significantly higher than the thresholds being considered by the EU. The Cd concentrations of P
fertilizers being marketed in California are considerably lower than these regulatory limits. For the mass balance computations, the As and Cd inputs must be entered. Three input sources are considered and the input values are further elaborated as follows:

**Fertilizers and Micronutrients.** Kongshaug et al. (1992) reported that the average As and Cd concentrations in P fertilizers were 71 mg kg\(^{-1}\) P and 165 mg kg\(^{-1}\) P, respectively. At an application rate of 50 kg P ha\(^{-1}\) yr\(^{-1}\), the input from P fertilizer amounts to approximately 3.5 g ha\(^{-1}\) yr\(^{-1}\) for As and 5 g ha\(^{-1}\) yr for Cd.

**Irrigation.** According to the National Primary Drinking Water Regulations (CFR Title 40 Part 141), the maximum contaminant level (MCL) of As in drinking water was 50 µg l\(^{-1}\) and has recently been reduced to 10 µg l\(^{-1}\) in light of new evidence from the As chronic poisoning investigations in Bangladesh and other parts of the world. The MCL for Cd is 5 µg l\(^{-1}\). The concentrations of As and Cd in natural waters are expected to be significantly lower than the above-referenced levels. Assuming irrigation water contains 2 µg l\(^{-1}\) As and 0.2 µg l\(^{-1}\) Cd and is applied at the rate of 1 m per year, the inputs from irrigation are 20 g ha\(^{-1}\) yr\(^{-1}\) for As and 2 g ha\(^{-1}\) yr\(^{-1}\) for Cd.

**Atmospheric Deposition.** The inputs to soils from atmosphere deposition may vary from 2.6 - 19 g Cd ha\(^{-1}\) yr\(^{-1}\) in rural areas in Australia (McLaughlin, 1999). Alloway (1995) reported the atmospheric deposition of 3.9 - 9.6 g Cd ha\(^{-1}\) yr\(^{-1}\) in urban areas. Chang and Page (2000) estimated the atmospheric deposition of trace elements on agricultural soils in California based on the air quality monitoring data of the Central Valley. They reported the atmospheric fallout rates of 5 g As ha\(^{-1}\) yr\(^{-1}\) and 5 g Cd ha\(^{-1}\) yr\(^{-1}\). The values of Chang and Page (2000) are adopted.

The default As and Cd inputs for cropland soils are the sum of inputs from the three above-referenced sources, and they amount to approximately 30 g As ha\(^{-1}\) yr\(^{-1}\) and 13 g Cd ha\(^{-1}\) yr\(^{-1}\).

**Soil Property Parameters**

In the mass balance model, the soils are categorized in terms of their volumetric water content, \(\theta_r\), and hydraulic conductivity, \(K_h\). In the Handbook of Soil Science, the volumetric water contents are generalized in terms of soil texture (Table 9). Based on the van Genuchten equation, the hydraulic conductivity of soil, \(K(\theta)\), varies with the soil’s volumetric water contents, \(\theta_r\) and may be estimated in the following manner, such that:

\[
K(\theta) = K_s \times \Theta^{1/2} \times \left[1-(1-\Theta^{1/m})^m\right]^2
\]

[Eq. 9]

in which \(\Theta = (\theta_f - \theta_r)/(\theta_s - \theta_r)\) and \(m = (1 - 1/n)\). The \(\theta_s\) and \(K_s\) are the saturated volumetric water content and its corresponding hydraulic conductivity, respectively. The \(\theta_f\) represents the volumetric water contents of the soil at field capacity. \(\theta_r\) represents the residual water content. Generally, the \(n\) value varies between 2 (clay soil) to \(> 4\) (sand soil). Assuming \(n = 4\) for sand and sandy loam soil and \(n = 2\) for all the other soil, the
hydraulic conductivity for soils at field moisture content may be obtained, based on data from the Handbook of Soil Science and Eq. 9. (Table 12).

Table 12. Estimated hydraulic conductivity of soils at field moisture content

<table>
<thead>
<tr>
<th>Soil</th>
<th>$\theta_f$ (cm$^3$ cm$^{-3}$)</th>
<th>$\theta_r$ (cm$^3$ cm$^{-3}$)</th>
<th>$\theta_s$ (cm$^3$ cm$^{-3}$)</th>
<th>$K_s$ (cm hr$^{-1}$)</th>
<th>$K(\theta)$ (cm hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>0.143</td>
<td>0.035</td>
<td>0.31</td>
<td>21.00</td>
<td>0.66</td>
</tr>
<tr>
<td>Sandy loam</td>
<td>0.164</td>
<td>0.055</td>
<td>0.35</td>
<td>2.59</td>
<td>0.067</td>
</tr>
<tr>
<td>Loam</td>
<td>0.236</td>
<td>0.08</td>
<td>0.43</td>
<td>1.32</td>
<td>0.0097</td>
</tr>
<tr>
<td>Silt loam</td>
<td>0.314</td>
<td>0.1</td>
<td>0.46</td>
<td>0.68</td>
<td>0.020</td>
</tr>
<tr>
<td>Clay loam</td>
<td>0.343</td>
<td>0.15</td>
<td>0.5</td>
<td>0.23</td>
<td>0.0047</td>
</tr>
<tr>
<td>Clay</td>
<td>0.371</td>
<td>0.2</td>
<td>0.6</td>
<td>0.06</td>
<td>0.00036</td>
</tr>
</tbody>
</table>

Based on data in Table 9, we select, as inputs, field volumetric moisture content of 0.25 cm$^3$ cm$^{-3}$ and the hydraulic conductivity of 0.01 cm hr$^{-1}$ (for loamy soil).

**Plant Uptake Parameters**

Absorption of As and Cd by plants is influenced by many factors including plant species, the concentration of As and Cd in the soil solution, soil properties, such as pH and clay content, and the presence of other ions. However, the absorption rates may be normalized in terms of the As and Cd concentrations in the soil solution, $C$, representing soil-related factors; root density, $R$, representing plant growth-related factors; and the plant uptake rate parameter, $J$, representing plant species-related factors. The plant uptake factor, $J$, in turn may be expressed in terms of Michalis-Menton kinetics parameters for plant nutrient absorption, $J_{\text{max}}$ and $K_m$. Tables 13 and 14 summarize data available from the literature for plant absorption of As and Cd in hydroponic solutions.

Table 13. Plant Uptake Kinetics Parameters for Arsenic (Hydroponic Solutions)

<table>
<thead>
<tr>
<th>Species</th>
<th>$J_{\text{max}}$ (nmol g$^{-1}$ root FW h$^{-1}$)</th>
<th>$K_m$ (µM)</th>
<th>$J_{\text{max}}^+$ (µmol cm$^{-1}$ h$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H. lanatus (non tolerant)</td>
<td>284.8±21.8</td>
<td>30±4</td>
<td>8.9e-05</td>
<td>Meharg and Machair. (1992)</td>
</tr>
<tr>
<td>H. lanatus (Tolerant)</td>
<td>449.6±34.9</td>
<td>37±4</td>
<td>1.4e-04</td>
<td>Abedin et al. (2002)</td>
</tr>
<tr>
<td>Rice (Aman)</td>
<td>132.9±13.4</td>
<td>5.9±1.2</td>
<td>4.2 e-05</td>
<td></td>
</tr>
<tr>
<td>Rice (Boro)</td>
<td>97.0±10.3</td>
<td>6.3±2.6</td>
<td>3.0 e-05</td>
<td></td>
</tr>
<tr>
<td>P. Vittata (control-P)</td>
<td>129.6±19.7</td>
<td>0.52±0.21</td>
<td>4.1 e-05</td>
<td>et al. (2002)</td>
</tr>
<tr>
<td>P. Vittata (P-deficient)</td>
<td>318.6±25.8</td>
<td>0.97±0.37</td>
<td>1.0 e-04</td>
<td></td>
</tr>
<tr>
<td>Species</td>
<td>$J_{\text{max}}$</td>
<td>$K_{m}$ (10^{-9} M)</td>
<td>$J_{\text{max}}^{+}$ (µmol cm^{-1} h^{-1})</td>
<td>Reference</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------------</td>
<td>---------------------</td>
<td>-------------------------------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>Corn seeding (15-22 days growth)</td>
<td>400 (pmol m^{-2} s^{-1})</td>
<td>30-100</td>
<td>9 x 10^{-6}</td>
<td>Mullins (1986)</td>
</tr>
<tr>
<td>Soybean (10 or 12 days old)</td>
<td>29 (µg g^{-1}dw h^{-1})</td>
<td>88</td>
<td>8 x 10^{-6}</td>
<td>Cataldo et al. (1983)</td>
</tr>
<tr>
<td>Grandin wheat seeding (8 days old)</td>
<td>26 ± 2 (nmol g^{-1} h^{-1})</td>
<td>20 ± 9</td>
<td>8 x 10^{-6}</td>
<td>Hart et al. (1998)</td>
</tr>
<tr>
<td>Durum wheat seeding (10 days old)</td>
<td>29 ± 2 (nmol g^{-1} h^{-1})</td>
<td>40 ± 13</td>
<td>9 x 10^{-6}</td>
<td></td>
</tr>
<tr>
<td>White Lupin (control)</td>
<td>12.99</td>
<td>42.22</td>
<td>3.6e-06</td>
<td>Costa and Morel (1993)</td>
</tr>
<tr>
<td>White Lupin (Zn^{2+} presence)</td>
<td>7.52</td>
<td>30.68</td>
<td>2.1e-06</td>
<td></td>
</tr>
<tr>
<td>White Lupin (La^{3+} presence)</td>
<td>3.66</td>
<td>18.96</td>
<td>1e-06</td>
<td></td>
</tr>
<tr>
<td>T. Caerulescens (Ganges ecotype)</td>
<td>143.2 ±6.6</td>
<td>45±7 nM</td>
<td>4.5 e-05</td>
<td>Zhao et al (2002)</td>
</tr>
</tbody>
</table>

Note: The calculation based on fresh root bulk density of 1 kg/L and fresh root radius 0.01 cm

Most uptake studies of As$^{5+}$ and Cd$^{2+}$ absorption by plants employed As$^{5+}$ and Cd$^{2+}$ concentrations that were unrealistically high with respect to concentrations in the solution phase of uncontaminated agricultural soils. In addition, adsorption 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. As a result, the experimental data tended to overestimate the value of the maximum plant uptake factor, $J_{\text{max}}$. Therefore, we chose a $J_{\text{max}}$ that is one order of magnitude smaller than those calculated from data in Tables 13 and 14.

**Results and Discussion**

**Default Simulation**

Based on the review of the literature and the information discussed above, the inputs and model parameters for the default model simulation are set (Table 15). The default conditions depict the mass balance of trace elements in a typical loamy soil that receives As and Cd inputs from annual fertilizer application and irrigation, assuming the inputs are continuous and are uniformly distributed throughout a year. Fifty percent of annual biomass harvest along with the proportional amounts of the plant-absorbed trace elements are reincorporated as a discrete input in the organic form.
Table 15. Parameter Values for the Default Simulation of As and Cd Mass Balance in Irrigated Cropland Soils

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Arsenic</th>
<th>Cadmium</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial Trace Element Pools of Soil</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Content (mg kg⁻¹)</td>
<td>7.7</td>
<td>0.22</td>
</tr>
<tr>
<td>Mineral Phase (mg kg⁻¹)</td>
<td>5.0</td>
<td>0.07</td>
</tr>
<tr>
<td>Organic Phase (mg kg⁻¹)</td>
<td>0.5</td>
<td>0.02</td>
</tr>
<tr>
<td>Soil Solution Concentration (µM)</td>
<td>0.08</td>
<td>0.005</td>
</tr>
<tr>
<td><strong>Soil Properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Profile Depth (cm)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Bulk Density (kg l⁻¹)</td>
<td>1.41</td>
<td>1.41</td>
</tr>
<tr>
<td>Hydraulic Conductivity (cm h⁻¹)</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Volumetric Water Content (l l⁻¹)</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td><strong>Plant Uptake</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Root Permeability Coefficient (µM)</td>
<td>6</td>
<td>0.1</td>
</tr>
<tr>
<td>Maximum Influx (mmol cm⁻¹ hr⁻¹)</td>
<td>0.00001</td>
<td>0.000001</td>
</tr>
<tr>
<td>Root Density (cm cm⁻²)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Biomass Return Factor (fraction of total)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>Reaction Constants</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium Concentration of Mineral (µM)</td>
<td>0.08</td>
<td>0.005</td>
</tr>
<tr>
<td>Mineral Dissolution/Precipitation Rate Constant (hr⁻¹)</td>
<td>10⁻⁵</td>
<td>10⁻⁵</td>
</tr>
<tr>
<td>Organic Phase Mineralization Rate Constant (hr⁻¹)</td>
<td>10⁻⁶</td>
<td>10⁻⁶</td>
</tr>
<tr>
<td>Adsorption Distribution Constant (l kg⁻¹)</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td><strong>Trace Element Inputs</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Continuous Input (g ha⁻¹ yr⁻¹)</td>
<td>30</td>
<td>13</td>
</tr>
<tr>
<td>Discrete Inputs (g ha⁻¹ yr⁻¹)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The mass balance was simulated for 100 years after setting the initial conditions in terms of the trace element pools in the soil, input sources, soil properties, crop uptake information and reaction transformation constants. The outputs of the model simulations illustrate the change of the trace elements pools in the soil, the pattern of plant uptake, and leaching beyond the root zone.

Total Arsenic Concentration of Soils. Under normal crop growing conditions, trace elements are expected to derive primarily from fertilizer applications and irrigation. At a typical annual input of 30 g ha⁻¹ of As, the total As content of the receiving soils changes slowly from the initial value of 7.70 mg kg⁻¹ to approximately 7.66 mg kg⁻¹ over the 100-year simulation period (Figure 3). The Y-axis of Figure 3, which depicts the total trace element concentration of the soil, is distorted and the entire Y-axis scale represents only a 0.06 mg kg⁻¹ concentration range. As a result, the graphically depicted trend is somewhat misleading. If the graph is re-plotted on a full 0 to 9 mg kg⁻¹ range (Figure 4), the changes over this period of time are not noticeable. This level of changes in total concentration is well within the range of spatial variations expected of the soils and not measurable by routine soil sampling.
Figure 3. Simulated Total As Concentration of Cropland Soil, Receiving As Inputs from Fertilizer and Irrigation (Y-axis is plotted on an expanded scale).
Soil Solution Concentration of Arsenic. The distribution of trace elements between the soil solution and solid phases is dynamically changing with respect to the reactions depicted in Figure 1, namely the mineral precipitation and dissolution and adsorption and desorption. The trace element concentration in the solution phase in turn is a deciding factor in determining plant uptake and leaching of trace elements. Over the 100-year simulation period, the As concentration in the soil solution decreases from 0.08 µM to 0.07 µM. While the absolute values are changed by 0.01 µM, it represents a steady trend of 12.5% decline from the original concentration over the 100-year simulation period (Figure 5). The plant uptake is expected to change proportionally so slightly over the same period of time. The simulated outcomes are based on the assumption that 50% of the harvested biomass and its corresponding As are reincorporated annually. Had the entire harvested biomass been reincorporated or removed, the outcomes would be different.
Figure 5. Simulated Soil Solution As Concentration of Cropland Soil Receiving P Fertilizer and Irrigation for 100 Years.

Arsenic Concentration of the Adsorbed and Organic Phases. The lack of significant changes in the total and solution concentrations of As in soil is indicative of the fact that the major As solid phase pools of the soil remained relatively constant for much of the 100-year simulation period, despite the continuous external inputs of As over time. Figure 6 shows that changes of the mineral and organic phases over the 100 years are parallel to those of the total As content of the soil. The adsorbed phase, which represents much of the plant-available elements in the soil also remains essentially unchanged over the time period.
Figure 6. Concentrations of Major As Pools in Cropland Soils Receiving Fertilizer and Irrigation for 100 Years.

Plant Uptake and Leaching of As. Plant uptake and leaching below the soil layer are the two primary sinks through which As in the soil may be lost. Their changes may be illustrated by the annual mass balance table (Table 16). At the first year of receiving 30 g ha$^{-1}$ of As, 32.30 g ha$^{-1}$ of As is absorbed by plants and 13.10 g ha$^{-1}$ of As is leached. The As in the mineral pool is not visibly changed. The resulting net loss of 15.40 g ha$^{-1}$ is divided among the losses in the organic and labile (adsorbed) pools. As the 30 cm soil layer being considered contains approximately $4 \times 10^6$ kg of soils, the changes in mass balance, in terms of concentrations, are infinitesimally small. Nevertheless, the dynamic changes of As among the pools continues.

By the 25th and 50th years, the sums of annual outputs are much closer to the sums of annual inputs. There remain however net losses that are compensated by losses in the labile and mineral pools and increases in the organic pool. By the 100th year, the annual output almost equals the inputs and net loss is merely 0.55 g ha$^{-1}$ yr$^{-1}$. At this time, the plant uptake accounts for 19.01 g ha$^{-1}$ and leaching accounts for 11.54 g ha$^{-1}$ of As. Therefore, the As added into soils under normal cropping conditions are expected over the long run to be either absorbed by plants or leached below the root zone. The total As concentration and the labile As pool of the soil are expected to remain unchanged, based on the model.
Table 16. Simulated Annual As Mass Balance of Cropland Soil After Receiving Fertilizer and Irrigation Applications for 1, 25, 50 and 100 Years.

<table>
<thead>
<tr>
<th>Year</th>
<th>Input (g ha(^{-1}) yr(^{-1}))</th>
<th>Output (g ha(^{-1}) yr(^{-1}))</th>
<th>Change in As Solid Phase (g ha(^{-1}) yr(^{-1}))^+</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Uptake</td>
<td>Leaching</td>
</tr>
<tr>
<td>1</td>
<td>30</td>
<td>32.30</td>
<td>13.10</td>
</tr>
<tr>
<td>25</td>
<td>30</td>
<td>20.05</td>
<td>12.19</td>
</tr>
<tr>
<td>50</td>
<td>30</td>
<td>19.41</td>
<td>11.79</td>
</tr>
<tr>
<td>100</td>
<td>30</td>
<td>19.01</td>
<td>11.54</td>
</tr>
</tbody>
</table>

^+Negative sign indicates reduction of the pool.

**Total Soil Cd Concentrations.** The baseline level for total Cd concentrations in soils typically is between 0.2 to 0.5 mg kg\(^{-1}\). In this simulation, we used 0.22 mg kg\(^{-1}\) as the default value for the total soil Cd concentration. Under normal cultivation conditions, the default annual Cd input from application of P fertilizer and irrigation water is 13 g ha\(^{-1}\). Unlike the As concentration of the simulated cropland soils, the total Cd concentration of the receiving soil increases from 0.22 mg kg\(^{-1}\) to approximately 0.35 mg kg\(^{-1}\) (Figure 7). While the resulting total soil Cd concentration is still well within the expected baseline range of 0.2 to 0.5 mg kg\(^{-1}\), the rise represents a >50% increase in the Cd concentration of the soil. The rising trend is steady over the 100-year simulation period, although the rate of rise decreases with time. If the cultivation practices are continuous, the Cd concentration in the soil is predicted to reach a steady state.

On an annual basis, the increases due to Cd depositions are undoubtedly not noticeable. If cultivation practices assumed by the model continue for a long time, the accumulation of Cd will become noticeable (Figure 7). It appears that the normal cropping practices of irrigated agriculture could have a significant, long-term effect on the Cd concentration of soils.
**Figure 7.** Total Cadmium Accumulation under Normal Cropping Conditions.

**Soil Solution Cd Concentration.** The Cd concentration of the soil solution reflects the dynamic interactions of the element in the solution and solid phases and its removal from the soil layer may occur by leaching and plant uptake. Over the 100-year simulation period, the Cd concentration in the soil solution rose by five-fold, from 0.005 µM to 0.025 µM (Figure 8). The higher solution concentrations invariably indicate greater potential for the element to be absorbed by plants and to be leached below the root zone. The rise in the soil solution Cd concentration appears to follow the first order reaction model in that the rate of concentration rise decreases with time.
Figure 8. Simulated Soil Solution Cd Concentration of Cropland Soil Receiving P Fertilizer and Irrigation for 100 Years.

Cadmium Concentration of the Adsorbed and Organic Phases. The accumulation of Cd as indicated by the slow but steady rise of the total Cd content of the soil and the rise of the soil solution Cd concentration over the 100-year simulation period are indications that the Cd pools of the soils have dynamically shifted over time in response to long-term inputs. Figure 9 illustrates the dynamic changes of the Cd pools in the soil. For 100 years of continuous cultivation, the Cd input through applications of P fertilizers and irrigation cause the Cd content of the soil to increase. The increase however is not distributed evenly among the solid phase pools. The inorganic mineral pool remains essentially unchanged over time. On the other hand, the Cd contents of the surface adsorbed phase and the organic phase continue to rise with time.
Figure 9. Concentrations of Major Cd Pools in Cropland Soils Receiving Fertilizer and Irrigation for 100 Years.

**Plant Uptake and Leaching of Cd.** Table 17 illustrates the Cd loss from the root zone through plant uptake and leaching below the soil layer. At the first year of receiving 13 g Cd ha$^{-1}$, 1.3 g ha$^{-1}$ of Cd is absorbed by plants and 1.9 g ha$^{-1}$ of Cd is leached. The remainder of the added Cd results in an increase of Cd in the adsorbed phase. The mineralization of organic Cd added through the recycling of crop residues has minor effect on the mass balance.

Over time, the annual Cd uptake by plants and the annual deposits of Cd into the adsorbed phase decrease and the organic phase increases. At the 25$^{th}$, 50$^{th}$, and 100$^{th}$ years, the annual Cd uptakes by plants are 3.12, 3.85, and 8.46 g ha$^{-1}$, respectively, and the annual deposits into the adsorbed and the organic phases are 4.02, 1.89, and 0.11 g ha$^{-1}$ and 2.03, 2.30, and 3.66 g ha$^{-1}$, respectively. For the first 50 years of the simulation period, the leaching loss of Cd increases in proportion to the rise of the soil solution Cd concentration. The annual Cd leaching losses are 1.87, 3.55, and 4.56 g ha$^{-1}$ for years 1, 25 and 50, respectively. Afterwards, the Cd leaching loss decreases, as plant uptake of Cd accelerates. As a result, the leaching loss at year 100 is merely 0.88 g ha$^{-1}$. 
Table 17. Simulated Annual Cd Mass Balance of Cropland Soil After Receiving Fertilizer and Irrigation Applications for 1, 25, 50 and 100 Years.

<table>
<thead>
<tr>
<th>Year</th>
<th>Input (g ha(^{-1}) yr(^{-1}))</th>
<th>Output (g ha(^{-1}) yr(^{-1}))</th>
<th>Change in Cd Solid Phase (g ha(^{-1}) yr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Uptake</td>
<td>Leaching</td>
</tr>
<tr>
<td>1</td>
<td>13</td>
<td>1.30</td>
<td>1.87</td>
</tr>
<tr>
<td>25</td>
<td>13</td>
<td>3.12</td>
<td>3.55</td>
</tr>
<tr>
<td>50</td>
<td>13</td>
<td>3.85</td>
<td>4.56</td>
</tr>
<tr>
<td>100</td>
<td>13</td>
<td>8.46</td>
<td>0.88</td>
</tr>
</tbody>
</table>

*Negative sign indicate reduction of the pool.

Factors Affecting Trace Element Accumulation in Cropland Soils

**Biomass Reincorporation.** In common cropping practice, not all of the plant biomass is removed from the cultivated fields during harvesting. For vegetable production, only the marketable portion of the biomass is harvested and packaged. The remainder of the biomass is routinely reincorporated during the land preparation for the next cropping. Between 25 to 90% of the biomass in vegetable production may be recycled in this manner. As a result, the trace elements that are absorbed by the plants will be reintroduced into the soil.

The impact of the biomass reincorporation may be assessed by conducting mass balance simulations that account for this portion of the trace elements as inputs. We assume that (a) the amounts of trace elements reincorporated are in proportion to the fraction of biomass, (b) the trace elements are in the organic form, and (c) they are subject to mineralization before they will become labile and available for uptake by plants. At the default simulation, it is assumed that 50% of the biomass is reincorporated. Figures 10 and 11 illustrate respectively the resulting soil As and Cd contents at 0 to 75% biomass reincorporation.

The total As content of the soil is essentially unchanged for the duration of the simulation (100 years) when 50% of the biomass is reincorporated (see Figure 4). When the fraction of the biomass reincorporated is less than 50%, the total As content of the soil shows a decreasing trend, from 7.7 to 7.3 and 7.7 to 7.5 mg kg\(^{-1}\) for 0 and 25% reincorporation, respectively. When the biomass reincorporation is at the 75% level, the total As content of the soil increases from 7.7 to 7.9 mg kg\(^{-1}\) over the 100-year simulation period. While the changes in the total As contents of the soil due to biomass reincorporation are noticeable by mass balance, they represent less than a 3% change in the total As contents of the soil. It appears that biomass reincorporation does not have a significant impact on As accumulation in soils.

For Cd, the impact of biomass incorporation on its total contents in the soils is more pronounced. When the biomass reincorporation is at 50% (default simulation), the total Cd contents of the soil increases from 0.22 mg kg\(^{-1}\) to approximately 0.35 mg kg\(^{-1}\).
The increase in the total Cd contents of soils for the 25% and 75% levels of biomass reincorporation are in proportion to that of the 50% reincorporation rate. Even at 0% biomass reincorporation, the increase in the Cd contents of the soil is greater than 20%.

Figure 10.  Simulated Effects of Biomass Reincorporation (Rf) on the Total As Contents of Cropland Soils Receiving P Fertilizers and Irrigation Water for 100 Years
(Rf refers to the fraction of biomass that is reincorporated annually.)
Figure 11. Simulated Effects of Biomass Reincorporation on the Total Cd Contents of Cropland Soils Receiving P Fertilizers and Irrigation Water for 100 Years (Rf refers to the fraction of biomass that is reincorporated annually.)

Trace Element Inputs In the default simulation, we considered the inputs from the application of P fertilizers and irrigation water that contain average amounts of trace elements such as As and Cd. However, the As and Cd concentrations of the applied fertilizers may vary considerably, depending on the source of the raw material. In addition, other soil amendments may also inadvertently introduce trace elements into the soil. Thus, it is possible that the trace element inputs may be significantly higher than those considered in the default simulation.

Figure 12 summarizes the results of simulating As inputs that vary from 0 to 200 g ha$^{-1}$ yr$^{-1}$, with the default input of 30 g ha$^{-1}$ yr$^{-1}$ as the reference point. Generally, under these hypothetical conditions, the total As contents of the soil exhibit a decreasing trend over the 100-year simulation period when the As input is less than 30 g ha$^{-1}$ yr$^{-1}$. If the only As input is from atmospheric fallout (5 g ha$^{-1}$ yr$^{-1}$) and the P fertilizer and irrigation water do not contribute, the total As contents of the soil will decrease from 7.7 to 7.25 mg kg$^{-1}$ and its final outcome is essentially indistinguishable from that of a zero As input. The As additions of 60, 150, and 200 g ha$^{-1}$ yr$^{-1}$ represent the typical inputs from applications of biosolids with low, medium, and high As contents. It illustrates that
biosolids application over time will significantly increase the As level in soils. Generally, the increase in soil As contents is proportional to the inputs level (Figure 13). The As contents of the soil are sensitive to the input levels. When they are changed from the default level, the trend in As accumulation and depletion will change accordingly (Figure 14). Therefore, the components of the As mass balance in soil (i.e. plant uptake, leaching, and distribution of As in solid phase pools) are expected to change accordingly.

Figure 12.  Simulated Changes of Total As Content of Cropland Soils with As Inputs Ranging from 0 to 200 g ha\(^{-1}\) yr\(^{-1}\).
Figure 13. Total As Contents of Cropland Soils Following 100 Years of Simulated As Inputs
Figure 14. Effects of Changing As Input Levels on Total As Contents of Soils.
Figure 15 summarizes the outcomes on total Cd contents of soils when Cd inputs vary from 0 to 110 g ha\(^{-1}\) yr\(^{-1}\), with the default input of 13 g ha\(^{-1}\) yr\(^{-1}\) as the reference point. Generally, the total Cd contents of the soil exhibit a variable increasing trend, with inputs as low as 5 g ha\(^{-1}\) yr\(^{-1}\) (the atmospheric fallout rate) over the 100-year simulation period. The input rates of 43, 77, and 110 g ha\(^{-1}\) yr\(^{-1}\) again represent the Cd inputs from cropland application of biosolids with low, medium, and high Cd contents, respectively. At these rates of Cd inputs, the Cd contents of soils increase rapidly, increasing from 0.22 to 0.8, 1.1, and 1.6 mg kg\(^{-1}\) over the 100-year simulation period, respectively. Generally, the soil Cd contents increase linearly in proportion to the Cd input levels (Figure 16). Like As, the Cd contents of the soil are also sensitive to the input levels. When they are changed from the default level, the trend in Cd accumulation and depletion will change accordingly (Figure 17). Therefore, the components of the Cd mass balance in soil (i.e. plant uptake, leaching, and distribution in solid phase pools) are expected to change accordingly.

![Diagram showing the simulated changes of total Cd content of cropland soil with Cd inputs ranging from 0 to 110 g ha\(^{-1}\) yr\(^{-1}\).](image-url)

**Figure 15.** Simulated Changes of Total Cd Content of Cropland Soil with Cd Inputs Ranging from 0 to 110 g ha\(^{-1}\) yr\(^{-1}\).
Figure 16. Total Cd Contents of Cropland Soils Following 100 Years of Simulated Cd Inputs
Figure 17. Effects of Changing Cd Input Levels on Total Cd Contents of Soils.
Effects of the Inorganic Mineral Solid Phase. The inorganic trace element mineral solid phase in the soil precipitates and dissolves in response to the trace elements’ concentrations in the soil solution. In the mass balance model described in this report, the extent of the precipitation and dissolution is determined by the equilibrium concentration \( C_{eq} \) that defines the solubility of each mineral. The rate of the reaction is further controlled by the way the mineral is formed in the soil (i.e. crystalline, amorphous, co-precipitated, etc.), which is characterized by the kinetic rate constant, \( K_{CR} \). The mineral controlling this reaction may be different in soils and \( C_{eq} \) and \( K_{CR} \) will be characterized by the type of inorganic mineral and its morphological properties. In the default simulation, we define these two parameters for the As and Cd minerals that are most likely to be present, based on data reported in the literature. Under certain circumstances (such as pH and oxidation-reduction potential of soils), other minerals may be more prominent. As a result, the values of \( C_{eq} \) and \( K_{CR} \) may vary by 2 to 3 orders of magnitude. In this section, we evaluate the impacts of adding As and Cd into cropland soils having inorganic minerals of different equilibrium concentrations and precipitation/dissolution reaction kinetics.

In the default simulation, the equilibrium concentration of the As minerals in the soil is set at 0.08 \( \mu \text{M} \), based on the solubility of calcium arsenate. While most of the As minerals associated with iron (Fe) and manganese (Mn) have very low solubility (Table 3), it is also possible that As can form minerals with sodium (Na) and potassium (K) that will be much more soluble than those characterized by the default simulation. The increase in the solubility of As minerals in the soil is expected to dissolve more soilborne As and reduce the overall As content of the soil. When the As mass balance is simulated for 100 years, with the \( C_{eq} \) for As varying from 0 to 0.5 \( \mu \text{M} \) in the soil solution and the remaining conditions assumed the same as in the default, the resulting total As content of the soil changed only slightly from approximately from 7.7 mg kg\(^{-1}\) to 7.6 mg kg\(^{-1}\) (Figure 18).

There is little field-based data to define accurately the precipitation/dissolution reaction parameter of As minerals, \( K_{CR} \). Under realistic situations, the value of this parameter may vary by several orders of magnitude, even for the same mineral phase. In the default simulation, this parameter for As is set at \( 10^{-5} \) hr\(^{-1}\). When the As mass balance is simulated for 100 years, with the \( K_{CR} \) for As varying from \( 10^{-3} \) to \( 10^{-7} \) hr\(^{-1}\) and the remaining parameters being the same as in the default, the resulting total As content of the soil changed slightly (Figure 19). In Figure 19, the \( K_{CR} \) is plotted in the negative logarithm form (p\( K_{CR} \)) and a reading of p\( K_{CR} = 5 \) on the X-axis is equal to an actual reading of \( 10^{-5} \) hr\(^{-1}\). The total As content of the soil shows an increasing trend from 7.61 to 7.66 mg kg\(^{-1}\) when the rate constant decreases from \( 10^{-3} \) to \( 10^{-7} \) hr\(^{-1}\) (Figure 19). Therefore, the As mineral phase in the soil and its precipitation/dissolution reaction rate do not appear to affect the total As content of cropland soils that receive 30 g ha\(^{-1}\) yr\(^{-1}\) from P fertilizers and irrigation.
Figure 18. Effect of the As Mineral Equilibrium Concentration on the Total As Content of Soils Receiving As Inputs from P Fertilizer Applications and Irrigation for 100 Years.
In the default simulation, the equilibrium concentration of Cd minerals in the soil solution is set at 0.005 µM. Other Cd minerals have solubility higher or lower than this value (Table 5). The changes in the solubility of Cd minerals in the soil are expected to either precipitate or dissolve more soil-borne Cd and either increase or decrease the overall Cd content of the soils. We simulate the Cd mass balance for 100 years with the C_{eq} for Cd varying from 0.1 to 0.0001 µM in the soil solution and the remaining conditions assumed the same as the default (Figure 20). The results show that the total Cd content of the soil exhibits a significant decreasing trend, from >0.34 mg kg^{-1} to 0.31 mg kg^{-1} when the C_{eq} for Cd increases from 0.01 to 0.1 µM (corresponding to the X-axis of Figure 20 where pC_{eq} = 2.0 and 1.0, respectively). For C_{eq} less than 0.01 µM, the
decreasing trend continues with total Cd content of the soil decreasing from 0.31 mg kg^{-1} to 0.30 mg kg^{-1}. The reducing trend of Cd content of the soil continues with decreasing C_{eq} for Cd. This is consistent with the data shown in Figure 20.

Figure 19. Effect of the As Mineral Precipitation/Dissolution Rate Constant (K_{CR}) on the Total As Content of Soils Receiving As Inputs from P Fertilizer Applications and Irrigation for 100 Years.
solubility of Cd minerals does not have a significant effect on the total Cd content of the soil.

The precipitation/dissolution reaction parameter of Cd minerals, $K_{CR}$ is set at $10^{-5}$ hr$^{-1}$ for the default simulation. Under realistic situations, the value of this parameter may vary by several orders of magnitude, even for the same mineral phase. When the Cd mass balance is simulated for 100 years, with the $K_{CR}$ for Cd varying from $10^{-3}$ to $10^{-6}$ hr$^{-1}$ and the remaining parameters being the same as the default, the resulting total Cd content of the soil changed slightly (Figure 21). In Figure 21, the $K_{CR}$ is plotted in the negative logarithm form ($pK_{CR}$) and a reading of $pK_{CR} = 5$ on the X-axis is equal to an actual reading of $10^{-5}$ hr$^{-1}$. The total Cd content of the soil shows an increasing trend from 0.34 to 0.44 mg kg$^{-1}$ when the rate constant decreases from $10^{-3}$ to $10^{-6}$ hr$^{-1}$ (Figure 21). Therefore, the Cd mineral phase in the soil and its precipitation/dissolution reaction rate appear to affect the total Cd content of cropland soils that receive 13 g ha$^{-1}$ yr$^{-1}$ from P fertilizers and irrigation.
Effects of Surface Adsorbed Trace Elements. In addition to the inorganic mineral phases, the trace elements in the soil may also be adsorbed and desorbed by other soil solids. In the mass balance model, this reaction is assumed to be instantaneous and amounts adsorbed are in equilibrium with those in the solution phase, as expressed by a linear distribution coefficient, $K_d$ (see equation 2b). In different soils, the $K_d$ for the same trace element may be different. Other soil factors, such as the texture, organic matter content, and pH, will also affect the outcome of $K_d$. Therefore, $K_d$ is a parameter that reflects the impact soil properties may have on the trace element accumulations in the soil. Ideally, this parameter is empirically determined for a given situation.

In the default simulation, the Kd is set at 100 l hr$^{-1}$ for As and at 50 l hr$^{-1}$ for Cd. To test the effect of this parameter on the final outcomes of the total As and Cd contents of the soils, the mass balances of As and Cd are simulated for 100 years with $K_d$ varying from 30 to 150 l hr$^{-1}$ for As and 10 to 100 l hr$^{-1}$ for Cd, and the remaining conditions are held the same as the default. These ranges for Kd represent the upper and lower limits for the commonly reported $K_d$ of these two elements. The effect of Kd on the total As and Cd contents of the soils are the opposite of one another (Figures 22 and 23). The total As content of the soil is not significantly affected by the $K_d$ for As surface adsorption, because the As concentration in soil varies from 7.68 to 7.64 mg kg$^{-1}$ when $K_d$ varies
from 30 to 150 l hr\(^{-1}\) (Figure 22). The total Cd content of the soil, however, is significantly affected by the \(K_d\) that characterized the surface adsorption of Cd. The final Cd concentration of the soil varies from 0.31 to 0.39 mg kg\(^{-1}\) when the \(K_d\) varies from 10 to 100 l hr\(^{-1}\) (Figure 23).

Figure 22. Effect of As Surface Adsorption on the Simulated Total As Content of Cropland Soil Receiving P Fertilizers and Irrigation for 100 Year.
Figure 23. Effect of Cd Surface Adsorption on the Simulated Total Cd Content of Cropland Soil Receiving P Fertilizers and Irrigation for 100 Year.
Effects of the Organic As and Cd Mineralization Rates. Organic forms of the trace elements are important components of the total trace elements present in the soil. In the model simulation, we assumed that the As and Cd entering the soil through biomass reincorporation are in the organic form. This portion of the trace elements is not readily available for plant absorption and is not subject to leaching until it is mineralized from the organic to the inorganic form. The rate the organic forms of As and Cd mineralize will in turn affect the total As and Cd contents of the soils.

In the default simulations, the organic As and Cd mineralization rate constant, $K_m$, is set at $10^{-6}$ hr$^{-1}$. The actual rate of the mineralization however may vary by several orders of magnitude. To assess the impact of this parameter on the As and Cd accumulation in the soils, the mass balances of As and Cd are simulated for 100 years with $K_m$ varying 10,000-fold, from $10^{-7}$ to $10^{-3}$ hr$^{-1}$ for both As and Cd (Figures 24 and 25).

Figure 24. Effect of Organic As Mineralization on the Simulated Total As Content of Cropland Soil Receiving P Fertilizers and Irrigation for 100 Years.
Figure 25. Effect of Organic Cd Mineralization on the Simulated Total Cd Content of Cropland Soil Receiving P Fertilizers and Irrigation for 100 Years.

In Figures 24 and 25, the organic As and Cd mineralization rate constants, $K_m$, are plotted on the X-axis in negative log scale and their rates decrease with the numerical values indicated on this axis. After 100 years of receiving As inputs from applications of P fertilizers and irrigation, the total As content of the soils is expected to be less than the baseline value of 7.7 mg kg$^{-1}$ regardless of the $K_m$, if the biomass reincorporation is at 50% (Figure 24). However, the total As content of the soil decreases from approximately 7.7 to 7.2 mg kg$^{-1}$ as the organic As mineralization rate, $K_m$, increases 100-fold from $10^{-6}$ (the default value) to $10^{-4}$ hr$^{-1}$. For Cd, the resulting total Cd content of the soils is significantly higher than the Cd baseline, which is 0.22 mg kg$^{-1}$. As the organic Cd mineralization rate increases from $10^{-6}$ to $10^{-4}$ hr$^{-1}$ (corresponding to $pK_m = 6$ and 4, respectively, in Figure 25), the total Cd content of the soil decreases from 0.36 to 0.32 mg kg$^{-1}$.

The mineralization of As and Cd added into soils in the organic phases will produce more of the elements in labile forms, which are in turn absorbed by plants or are
leached below the root zone. As a result, the total As and Cd contents of the soil over time are reduced as the mineralization rates increase.

**Effects of Plant Trace Element Uptake Factors.** In the mass balance model, the plant uptake of trace elements is characterized by two parameters, namely the root density, \( R \) (cm cm\(^{-1}\)) and the Michalis-Menton based maximum per unit root length trace element influx rate, \( V_{\text{max}} \) (\( \mu \text{mol cm}\(^{-1}\) hr\(^{-1}\)). The root density is a function of growing time and characteristics of the plant species. For this version of the mass balance model, we assumed a constant average root density because the time-dependent root density functions for plant species are not available. The per unit root length trace element influx rate varies with the solution concentration of the trace element. As the solution concentration of the trace element increases, the influx rate will gradually approach the maximum, according to the Michalis-Menton kinetics model, which is a characteristic of the plant species. These two factors may be used to characterize the impact of plant species on the accumulation of As and Cd in soils.

The mass balances of As and Cd for the cropland soils receiving P fertilizer applications and irrigation are simulated for 100 years with the maximum As and Cd influx rate, \( V_{\text{max}} \), varying from \( 10^{-3} \) to \( 10^{-6} \) and \( 10^{-4} \) to \( 10^{-7} \) \( \mu \text{mol cm}\(^{-1}\) root hr\(^{-1}\), respectively and the root density, \( R \), varying from 1 to 30 cm root length cm\(^{-2}\) surface area, while the other conditions are held constant as in the default case. In general, the total As and Cd contents of the soil increase when the plant uptake of As and Cd is reduced due to the decreasing maximum influx rate of the As and Cd and/or a decrease that occurs with increasing root density (Figures 26 – 29).

The total As and Cd contents of soils increase from 7.5 to 7.9 mg kg\(^{-1}\) and 0.32 to 0.34 mg kg\(^{-1}\), respectively, when the maximum As and Cd influx rate decrease from \( 10^{-3} \) to \( 10^{-6} \) \( \mu \text{mol cm}\(^{-1}\) hr\(^{-1}\) and \( 10^{-4} \) to \( 10^{-7} \) \( \mu \text{mol cm}\(^{-1}\) hr\(^{-1}\) (Figures 26 and 28). The increases of the soil As and Cd concentrations are curvilinear with respect to the decreases in the maximum root influxes. For both As and Cd, the increases in the concentrations are much more rapid at the lower ends of the maximum root influx ranges. When the root density factor varies from 1 to 30 cm cm\(^{-2}\), the total As and Cd contents of the soils decrease from 7.8 to 7.6 mg kg\(^{-1}\) and 0.36 to 0.33 mg kg\(^{-1}\), respectively. Over the 100-year simulation period, the resulting total As and Cd contents of cropland soils receiving P fertilizers and irrigation change only slightly when the plant uptake factors vary by several orders of magnitude.
Figure 26. Effect of the Maximum As Influx Rate, $V_{\text{max}}$, on the Simulated Total As Content of Soil Receiving P Fertilizers and Irrigation for 100 Years.
Figure 27. Effect of Root Density, R, on the Simulated Total As Content of Soil Receiving P Fertilizers and Irrigation for 100 Years.
Figure 28. Effect of the Maximum Cd Influx Rate, $V_{\text{max}}$ on the Simulated Total Cd Content of Soil Receiving P Fertilizers and Irrigation for 100 Years.
Figure 29. Effect of the Root Density, $R$, on the Simulated Total Cd Content of Soil Receiving P Fertilizers and Irrigation for 100 Years.
Uncertainty Analysis

In the mass balance model, many model parameters must be defined that are associated with soil properties, plant uptake of trace elements, and reaction rates governing biogeochemical processes. Usually, insufficient information is available to define these parameters precisely. As a result, there may be considerable doubts regarding the reliability of the model calculations due to bias in defining the parameter values. The uncertainty of the measured parameter values may be characterized by statistical distribution functions in terms of the mean, standard deviation, and probability distributions and then propagated through the model calculations to give estimates of uncertainties in the outcomes of model simulations. The quantitative analysis of the uncertainties provides information about the reliability of the final results.

For the trace element mass balance model described above, we identify the following uncertain parameters:

- **Soil Properties**: field hydraulic conductivity ($K_H$) and volumetric water content ($\theta$)
- **Uptake of Trace Element by Plants**: maximum trace element influx rate ($V_{\text{max}}$) and root density ($R$)
- **Biogeochemical Processes**: surface adsorption distribution coefficient ($K_d$), precipitation/dissolution rate constant ($K_{CR}$), and organic trace element mineralization constant ($K_m$)

The means, standard deviation, and probability distribution of each parameter are defined, based on data found in the literature. Table 18 summarizes the statistical attributes of the uncertain parameters.

<table>
<thead>
<tr>
<th>Uncertain Parameter</th>
<th>Arsenic</th>
<th>Cadmium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Variance</td>
</tr>
<tr>
<td>$K_H$ (cm hr$^{-1}$)</td>
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<td>0.0001</td>
</tr>
<tr>
<td>$\theta$</td>
<td>0.25</td>
<td>0.0025</td>
</tr>
<tr>
<td>$V_{\text{max}}$</td>
<td>$10^{-5}$</td>
<td>$4 \times 10^{-10}$</td>
</tr>
<tr>
<td>$R$</td>
<td>5</td>
<td>6.25</td>
</tr>
<tr>
<td>$K_d$</td>
<td>100</td>
<td>2500</td>
</tr>
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<td>$K_{CR}$</td>
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<td>$4 \times 10^{-10}$</td>
</tr>
<tr>
<td>$K_m$</td>
<td>$10^{-6}$</td>
<td>$4 \times 10^{-12}$</td>
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</tbody>
</table>

We employ the Monte Carlo simulation technique to propagate the uncertainties of defining model parameters to provide estimates of the reliabilities of the simulated total As and Cd contents of soils receiving P fertilizers and irrigation for 100 years. To perform the Monte Carlo simulation calculations, random number generation algorithms were used to draw values for the uncertain parameters according to their probability
distribution (Table 18). Default values are used for the remainder of the model inputs. Using one set, one observation of the simulation outcome may be obtained. To get a better estimate of the uncertain quantity, more observations on the model outcomes are needed. We performed 1000 simulations in this manner and summarize the findings in Figures 30 – 35.

Figure 30. Mean and 95% Confidence Interval of the Estimated Total As Content of Soil Receiving P Fertilizers and Irrigation for 100 Years as Calculated by 1000 Monte Carlo Simulations.
Figure 31. Probability Distribution of 1000 Simulations of the Total As Content of Soil Receiving P Fertilizers and Irrigation for 100 years as Obtained by Monte Carlo Simulations.
Figure 32. Cumulative Probability Distribution Curve of 1000 Simulations of the Total As Content of Soil Receiving P Fertilizers and Irrigation for 100 Years as Obtained by Monte Carlo Simulations.
Figure 33. Mean and 95% Confidence Interval of the Estimated Total Cd Content of Soil Receiving P Fertilizers and Irrigation for 100 Years as Calculated by 1000 Monte Carlo Simulations
Figure 34. Probability Distribution of 1000 Simulations of the Total Cd Content of Soil Receiving P Fertilizers and Irrigation for 100 years as Obtained by Monte Carlo Simulations.
Figure 35. Cumulative Probability Distribution Curve of 1000 Simulations of the Total Cd Content of Soil Receiving P Fertilizers and Irrigation for 100 Years as Obtained by Monte Carlo simulations.
The average total As and Cd contents of soil estimated by 1000 Monte Carlo simulations are in good agreement with outcomes of the default simulation. Figures 30 and 33 show the mean and 95% confidence interval of the estimated total As and Cd content of the soil throughout the 100-year simulation period. At the end of the 100-year simulation period, the total As and Cd contents of soils vary from 6.6 to 8.4 mg kg$^{-1}$ and 0.19 to 0.52 mg kg$^{-1}$, respectively, due to uncertainties in the model parameters. The coefficients of variation for the estimated total As and Cd in soils are 3.3% and 13.8%, respectively. The estimated total As and Cd contents of the soils exhibit a normal probability distribution with a slight skewness toward the higher values (Figures 31 and 34).
Conclusions

1. A mass balance model is developed to assess trace element transformations in the root zone of irrigated cropland soils that receive routine P fertilizer and micronutrient applications. It assumes that the trace elements present in the root zone are distributed in the soil solution and four solid phases, namely the inorganic mineral, surface adsorbed, organic, and residual phases. A PC-based algorithm is developed to solve the equation and the mass balances of As and Cd in California cropland soils are simulated for 100 years using this model.

2. Cropland soils in California typically contain 7.7 and 0.22 mg kg$^{-1}$ of As and Cd, respectively, and receive 30 and 13 g ha$^{-1}$ yr$^{-1}$ of As and Cd inputs through application of P fertilizers and irrigation water. It appears that the cropping practices do not have significant effects on the total As content of the soils. However, the total Cd content of cropland soils may increase steadily over the 100-year simulation period. Results show that the total As and Cd contents of cropland soils will change from 7.7 to 7.6 and 0.22 to 0.35 mg kg$^{-1}$, respectively, over the 100-year simulation period.

3. Model parameters, such as the adsorption distribution coefficient ($K_d$), mineral dissolution-precipitation rate constant ($K_{CR}$), mineral equilibrium concentration ($C_{eq}$), organic trace element mineralization rate constant ($K_m$), plant uptake factors ($J_{max}$) and root density ($R$), do not affect the distribution of As in the soil pools. All of the model parameters however significantly affect the total Cd content of the soil and distribution in soil pools.

4. There may be large uncertainties in the model estimations due to uncertainties in defining the values of model parameters. The uncertainties of the model estimates are characterized by 1000 Monte Carlo simulations. The mean and 95% confidence interval of the estimated total As and Cd contents of the soils are illustrated as follows:

The ranges of variations indicated in these two diagrams do not appear to adversely affect the plant absorption of As and Cd from cropland soils.
References


The Handbook of Soil Sci. reference is moved down to “S” for editor-in-chief’s Summner’s last name.


Appendix – Description of Model

The mathematical model, as described in the previous sections, is packaged in a Windows format. A CD copy of the model may be found as an attachment to this report. When the CD is inserted into the CD drive of a Windows based PC, there will be three folders, namely Gentel (98), Gentel (XP), and Input Data. Folders Gentel (98) and Gentel (XP) are model software setup files for Windows 98 and Windows XP, respectively. The Input Data folder contains the data files for default simulations. The user shall select and open the appropriate setup file for the PC for which the software is to be installed. When the setup.exe is clicked, the user will be prompted to install the model and its default input files and to assign a name for the model.

The installed model may be opened by selecting and clicking the model name in the program file. By entering the appropriate parameter values and trace element input values, the mass balance as well as the changes of individual pools in the soil may be tracked. Using As mass balance as an example, the model operation is described.

1. The Initial Screen

The initial screen shows the title and the authors of the model software and the authors’ professional affiliations. At the right lower corner of the screen, there are three option selection buttons named [Help], [Simulation], and [Exit]. When the [Help] button is selected, it will open a PDF file which contains brief descriptions and documentations of the software package. When the [Exit] button is selected, it will close the initial screen and exit the program. When the simulation button is selected, it will lead the user to begin the simulation with the following screen:
2. Data Entry

The Simulation option will take the user to the Enter Data for Simulation screen. On this screen, there are 7 separate sections for entering different types of information. The contents of each of the seven data entry sections is briefly described as follows:

**General Information Section** is where one first specifies the simulation type to be conducted – standard, sensitivity, or uncertainty analysis. The standard analysis will perform one simulation according to the data entered; the sensitivity analysis allows the user to conduct multiple simulations by varying the value of one model parameter; and the uncertainty analysis allows the user to conduct Monte Carlo simulations according to the probability distributions of the uncertain parameters. Then, the user enters the element to be evaluated. This entry will set globally the element to be specified on all of the data summary and output files. Finally, the user selects the number of simulations to be run when uncertainty analysis is selected. The computation time is directly dependent on the number of simulations to be conducted. The data entry mode becomes inactivated when the standard analysis is selected.

At this time, the user goes to the file menu on the top left corner of the screen and selects Open Input (Ctrl+O). When this option is selected, a new screen appears to
let the user choose from the default data files or other pre-stored data files. All of the data entry boxes will immediately be filled with the selected data and the user will be ready to proceed with the simulation by a left click of the mouse arrow on the Run option button at the bottom right corner of the screen. Should any of the data in the pre-stored data file need additional modification, the user may go into each data entry box and reenter the revised data. To enter user-specified case specific values for the simulation, one selects New Input (Ctrl+N). The data entry boxes will be cleared and ready for entering the new data.

**Initial TE Pools** is where the user enters the initial values for the trace element pools of the soils. TE in this case denotes the trace element under consideration. Each entry box is self-explanatory. The boxes include concentrations in the soil solution, the inorganic mineral and organic phases, and the trace element’s total content in the soil. The amounts in the adsorbed phase are internally determined according to equation 2b in this report (page ) and the amount in the residual phase is determined to be the difference between the total and the amounts accounted for in other phases.

**Simulation Period** provides the chronological time when the simulation begins and ends. The beginning time usually is 0 and the ending time is dependent on the number of years to be simulated. The Computation Time Step specifies the number of hours included in each simulation time step. It may be set at 10 or larger. Smaller time steps may provide more accurate computation but will take a long time for the simulation and require larger computer memories. The Output Summary Time Step determines the time interval for entries in the output data table.

**Input Information** is the section to enter information about trace element inputs. The trace element inputs to the soil may be entered in Continuous Input mode, which means that the entered input is in kg ha⁻¹ yr⁻¹ and will be assumed to be uniformly distributed over each computation time step or in Point Source Input mode, which means that the inputs are entered for specific dates of each year of the simulation or are assigned to given dates of each year. For making the Point Source Input, click the data entry box and a table will appear for entering the inputs in tabulated form. The model will accept continuous inputs (i.e. atmospheric fallouts) and point source inputs (i.e. fertilizer applications and irrigation) simultaneously.

**Soil Properties.** In this section, information on the properties of the soil is provided. Profile Depth refers to the depth of soil being considered in the simulation. Usually, it is the depth of the root zone. Other parameters to be entered (Bulk Density, Field Hydraulic Conductivity, and Volumetric Water Content) are self-explanatory and correspond to the same parameters defined in the mathematical forms of the model. For the standard simulation and the sensitivity analysis, only the mean values are needed. For the uncertainty analysis,
the variance and probability distribution of the parameters also need to be specified.

**Plant Uptake Information.** In this section, the parameters that define the plant uptake of trace elements are specified. They include the Root Permeability Coefficient \( (K_m) \), Maximum Influx \( (V_{\text{max}}) \), and Root Density \( (R) \). They correspond to the parameters in the mass balance model and the symbols used in the mathematical forms are included in the parenthesis. Among them, the Maximum Influx and Root Density are uncertain parameters and their variance and probability distribution should be specified for the uncertainty analysis. In addition, the fraction of the harvested biomass that is reincorporated should also be specified. It is assumed that comparable amounts of the trace elements absorbed by plants in the previous half year will reenter the soil in the organic form.

**Constants.** In this section, reaction constants that define the transformation of trace elements between pools are entered. They are the Eq. Conc. of Mineral Phase \( (C_{eq}) \), TE Adsorption Constant \( (b) \), Mineralization Rate \( (K_m) \), and Precip/Dissol. Rate \( (K_{CR}) \)

When data entry is completed, the screen looks like the following:
Click the **Run** option at the lower right corner of the screen. An output options screen appears to prompt users to check mark the data summaries desired. They include options of **Input Summary** (summary of inputs data in tabulated form), **Data Table** (chronological tabulations of the entire output data file), **Graphs of Data** (plots of individual output parameter vs. time), **Mass Balance** (mass balance table at the end of the simulations; this option is only available for the standard simulation), and **Graphs of Distribution** (showing the probability distribution of total trace element contents; this option is available only for the uncertainty analysis). The output files will be arranged according to the selections. When the **Proceed** option button is clicked, the simulation begins and a small screen will appear to track the progress of the computation. It generally takes only a few seconds for a standard simulation to complete. The time required for the sensitivity and uncertainty analysis is dependent on the number of simulation to be run. For 1000 simulations, it may take up to 5 minutes.

### 3. Results

When the simulation completes, the result screen will automatically appear (see below).
The outputs are organized as folders in a filing cabinet and each folder may be accessed by pointing and clicking the index tabs on the top of the screen. The folder Simulation Parameters summarizes the input data used in the simulation. The folder Mass Balance shows the duration being simulated and the mass balance of the trace element over this period of time. The folder Simulation Results is further divided into eight subfolders of output data tables and plots of individual output parameters. Subfolder Data Table is the tabulation of the entire output data file in EXCEL format. The abbreviation on each data column is denoted at the bottom part of the screen. Go to the Copy Selection at the right bottom corner of the screen and by selecting the appropriate option, the data may be exported to other documents for further analysis. The tabulated data in the Simulation Parameters and Mass Balance folders may also be exported in the same manner.

The screens for the output data files for a standard mass balance are illustrated in the following pages. If the sensitivity and the uncertainty analysis option are selected, the organization of the output data files will be different but equally self-explanatory. They will not be shown in this report.

Screen Simulation Parameters – showing summary of model parameters used in the simulation.

![Screen Simulation Parameters](image-url)
Screen Mass Balance – showing the trace element mass balance for the duration indicated. Enter the beginning and ending year desired and point the cursor at Recompute and click. The mass balance will be recalculated for the duration indicated.
Screen Graph: C plotting soil solution concentration of the trace element vs. time. (Arsenic [As] is shown as an example.)
Screen: Graph TCR – plotting concentration of trace element in the inorganic mineral phase vs. time. (Arsenic [As] is shown as an example.)
Screen Graph: G – plotting the concentration of trace element in organic phase vs. time. (Arsenic [As] is shown as an example.)
Screen Graph: Q – plotting the concentration of trace element in the labile pool (Q) vs. time. (Arsenic [As] is shown as an example.)
Screen Graph: TL – plotting amount of trace element leached (g ha$^{-1}$ yr$^{-1}$) vs. time. (Arsenic [As] is shown as an example.)
Screen Graph: TU – plotting amounts of trace element uptake by plants (g ha\textsuperscript{-1} yr\textsuperscript{-1}) vs. time. (Arsenic [As] is shown as an example.)
Screen Graph: TOTAL – plotting total trace element content of soil vs. time. (Arsenic [As] is shown as an example.)