

Mathematical modelling of metals mobility in the soil root zone

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Technical report

Abstract

The human activity has heavily impacted the natural fields, the most prominent adverse effect being the soil and ground water contamination with metals. Among the remediation technologies of contaminated sites, the phytoremediation is increasingly used mainly due to its low economical cost. The phytoremediation involves simultaneous processes such as water flow, multicomponent solute transport, root uptake, biogeochemical processes and reactions. The increase of the computers capacity and the development of new theoretical concepts have improved our ability to model such complex phenomena. In this paper we focus on: the mass balance principle to obtain equations and the empirical relations to complete the set of equations. We will show that the integral formulation of the mass balance principle of multifluid continuum mechanics is an appropriate base not only for writing down the macroscopic equations but also for highlighting the empirical relations needed to close the model.

Contents

1	Introduction	2
2	Transport processes in soil	3
2.1	The Soil System	3
2.2	Mass balance equation	4
2.3	Richards' equation	8
2.4	Fick's model of the diffusion process	9
3	Metal Sorption	9
3.1	Empirical models	10
3.1.1	Partition coefficient	11
3.1.2	Sorption isotherm equations	11
4	Root uptake	12
4.1	Root water uptake	12

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4.2 Root metal uptake 13
 4.2.1 Root absorption factor 14
5 Conclusion **14**

1 Introduction

One of the biggest problem the civilization faces is to prevent the ground water contamination with metals. The sources of contamination are mainly situated aboveground and come from a great diversity of activities, agriculture, water waste, industrial activity, mine activity, automobile circulation, etc. The soil and the plants constitute the main natural barrier that protect ground water against the contamination with metal. In the soil the metals can be fixed in solid matter and can be extracted from the water by plants. But, also the water can dissolve the metals from the solid matter and carry them to ground water. Beside these natural processes the plants can be used to decontaminate the soil, phytoremediation.

Table 1: Classification of phytoremediation application [41]

mechanism	short description
Phytoextraction	The uptake of contaminant by plant roots and translocation within the plant
Rhizofiltration	Adsorption or precipitation onto plant roots, or absorption into the roots of contaminant that are in solution surrounding the root zone
Phytostabilization	Immobilization of a contaminant in soil through absorption and accumulation by roots, adsorption onto roots, or precipitation within the root zone of plants
Phytovolatilization	Uptake and transpiration of a contaminant by a plant, with release of the contaminant or a modified form of the contaminant to the atmosphere, from plant, through contaminant uptake, plant metabolism, and plant transpiration
Phytohydraulics	The use of plants to remove ground water through uptake and consumption in order to contain or control the migration of contaminants

In order to control the circulation of metals in soil and to design the remediation technologies it is crucial to understand the complex processes of the interaction of metals with water, soil and plant roots. The mathematical modelling is intended to help the understanding, to make prediction and to offer quantitative estimations. Up to date several mathematical models are in use, each of them covering a restricted field of application. That is because, in addition to the complexity of the problem, the fate of metals in the system soil-water-plant is metal specific, soil specific and plant specific. In this paper we focus on the basic mechanical principle of the model and the general empirical laws. As result we obtain a model that covers a large class of applications. A specific application in the class can be modeled by proper values of the parameter in the model.

In Section 2 we define the soil system and formulate the mass balance equations, (18), (19) and (20). By using the empirical Buckingham-Darcy's law and Fick's law one obtains the Richards' equation, (24), and convection diffusion equation, (29), respectively.

In Section 3 we discuss on the sorption process and we will present several empirical laws of sorption. The section 4 is devoted to root uptake.

2 Transport processes in soil

The water flow through soil, the mobility of metals and uptake of water and metals by plants are complex phenomena that need a interdisciplinary approach in order to obtain a mathematical model of them. The model combines continuum mechanical principles, chemical principles, biological laws and empirical observations.

From mathematical point of view it is very important to make a sharp distinction between principle and the empirical extrapolation. For, if one compares the prediction of the model with measurements and there exists a manifest disagreement then the sources of errors can be more easily identified. On the other hand there exists models used by the practitioners in soil sciences such that it is almost impossible to know their domain of validity.

In this section we set up the fundamental equations of the motion of the soil solution and metals in the root zone. On the base of these equations one can obtain different models by using certain empirical relations.

On this subject the readers are referred to [4], [19], [18] , [50].

2.1 The Soil System

By the soil system we understand the assembly: soil matrix, root, pores, aqueous solution, aqueous constituents and sorbed constituents. The aqueous solution and its constituents flow through the pores and roots plant extract them. Some aqueous constituents undergo sorption process. The external medium of soil system is given by the atmospheric medium, vegetation that covers the soil and the groundwater below it. The state of the soil system is known if we know: the *density of aqueous constituents*, the *density of the sorbed constituent*, the *velocity of the aqueous solution* and the *aqueous solution content*.

The main goal of the mathematical modeling it to set up a mathematical model of the soil system that allow one to determines the state of the soil system. We proceed by keeping in mind the goal.

Let Ω be a space domain in \mathbb{R}^3 occupied by the soil system. The domain Ω can be partitioned in three subdomains: the domain occupied by soil matrix, Ω_s^s , the domain occupied by the roots, Ω_s^r , and the domain occupied by the pores, Ω_v . Let us denote by Ω_s the domain occupied by solid matter, roots and soil matrix, such that

$$\begin{aligned}\Omega_s &= \Omega_s^r \cup \Omega_s^s \\ \Omega &= \Omega_s \cup \Omega_v\end{aligned}\tag{1}$$

We denote by \boldsymbol{x} the space coordinates and by t the time coordinate.

Aqueous phase.

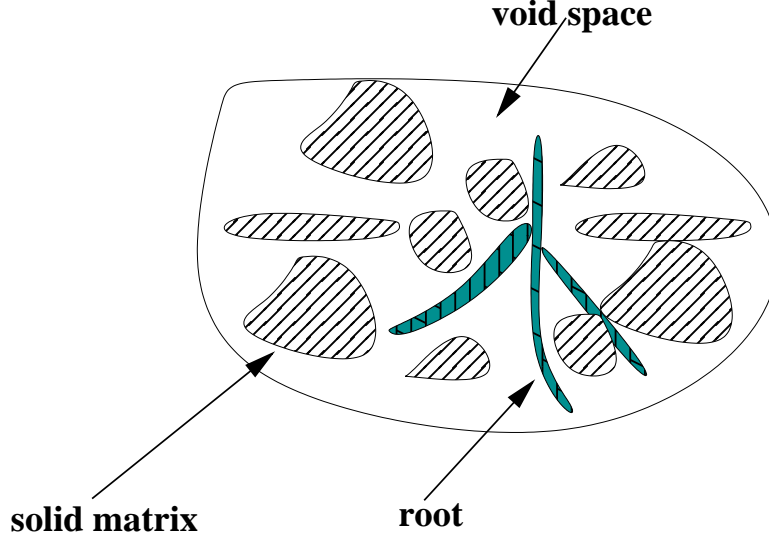


Figure 1: The components of the soil system: solid matter, pore and root. Aqueous solution can occupies only the space of the pore.

The aqueous phase is a mixture of several individual constituents that can occupy only the pores space. The mixture can be considered as a single fluid if one thinks that each position \mathbf{x} may be occupied simultaneously by several different particles \mathbf{X}_a , one for each constituent a .

The mixture and its constituents are thought as continuum medium so that for any point \mathbf{x} in Ω_v the density $\tilde{\rho}_a$ and velocity $\tilde{\mathbf{u}}_a$ of each constituent are defined as in continuum mechanics theory [32]. We assume that all processes take place at constant temperature.

The density $\tilde{\rho}$ and velocity $\tilde{\mathbf{u}}$ of the mixture are defined by:

$$\begin{aligned}\tilde{\rho} &= \sum_{a=1}^N \tilde{\rho}_a \\ \tilde{\mathbf{u}} &= \sum_{a=1}^N \frac{\tilde{\rho}_a}{\tilde{\rho}} \mathbf{u}_a\end{aligned}\tag{2}$$

respectively.

Interface solid-aqueous phase.

There exists a mass exchange between solid phase and aqueous phase, adsorption, desorption, precipitation or polymerization all named generic by sorption. All these processes take place at the interface solid matrix-aqueous phase. To take into account such phenomenon one needs to define a singular density distribution of the components of the mixture.

ρ_a^s denotes the superficial density of the a -component of the mixture that is defined on $\Gamma_{fs} = \overline{\Omega_v} \cup \overline{\Omega_s^s}$.

Solid phase.

The soil matrix is assumed to be immobile and chemical inactive.

Interface root-aqueous phase.

It is a permeable surface.

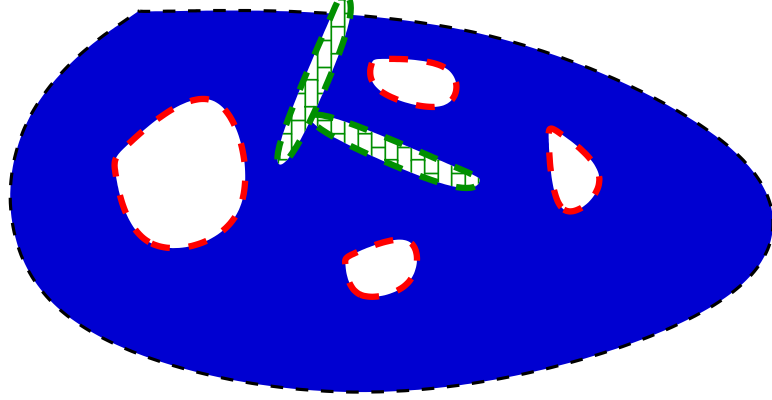


Figure 2: The soil system includes two interfaces: water-root interface and water-solid matrix interface. By desorption process the metal migrates from water-soil interface then by diffusion process it get the root surface and from here it is taken by plant.

2.2 Mass balance equation

Let ω be an arbitrary volume in Ω . The mass of an a -component which rests in ω is given by

$$m_a(t; \omega) = \int_{\omega \cap \Omega_v} \tilde{\rho}_a(t, x) dx + \int_{\omega \cap \Gamma_{fs}} \tilde{\rho}_a^s(t, x) ds. \quad (3)$$

The mass quantity $m_a(t; \omega)$ varies with time mainly dues to, see figure 3:

1. mass flux at the boundary of ω

$$\mathcal{F}_a^{ff}(t; \partial\omega) = \int_{\partial\omega \cap \Omega_v} \tilde{\rho}_a(t, x) \tilde{\mathbf{u}}_a(t, x) \cdot \mathbf{n} ds, \quad (4)$$

2. plant uptake, only for the bioavailable fraction

$$\mathcal{F}_a^{fp}(t; \omega) = \int_{\omega \cap \Gamma_{rf}} \tilde{\rho}_a(t, x) \tilde{\mathbf{u}}_a(t, x) \cdot \mathbf{n} ds, \quad (5)$$

3. supply of mass due to chemical reaction.

$$\mathcal{M}_a(t; \omega) = \int_{\omega \cap \Omega_v} \tilde{r}_a(t, x) dx. \quad (6)$$

The vector, \mathbf{n} , normal to surface points out of ω in (4) and points out of domain occupied by fluid in (5).

For an a -constituent of mixture the balance of mass asserts that

$$\frac{\partial m_a(t; \omega)}{\partial t} + \mathcal{F}_a^{ff}(t; \partial\omega) + \mathcal{F}_a^{fp}(t; \omega) = \mathcal{M}_a(t; \omega). \quad (7)$$

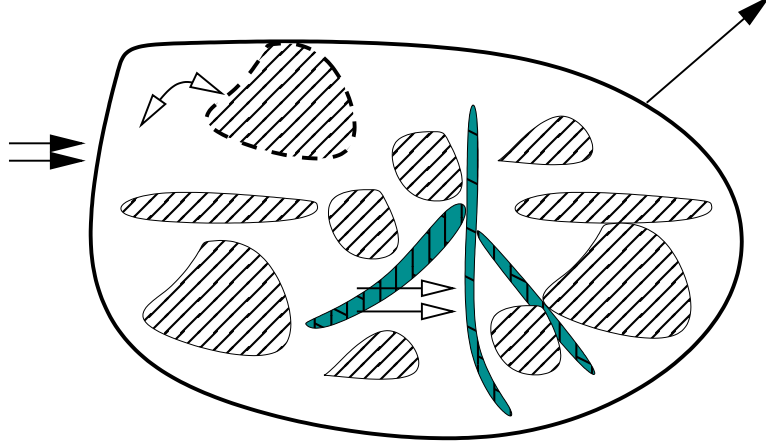


Figure 3: The mass of the fluid phase contained by a arbitrary volume ω varies due to flux of mass through boundary $\partial\omega$. The boundary includes root surface

The mass balance for the mixture as a single fluid is obtained by summing all the above equations

$$\frac{\partial m(t; \omega)}{\partial t} + \mathcal{F}^{ff}(t; \partial\omega) + \mathcal{F}^{fp}(t; \omega) = \mathcal{M}(t; \omega). \quad (8)$$

The space averaging procedure. REV method

The *representative elementary volume* (REV) method is a technique to mediate the mechanical quantities and balance equation for fluid phase (microscale, pore scale, etc.) in order to obtain balance equation for mediate quantities (macroscale).

Define the sets

$$\begin{aligned} P_\delta &= \{\mathbf{x} \in \mathbb{R}^3 \mid |x_i| < \delta, i = \overline{1, 3}\} \\ S_\delta^i &= \{\mathbf{x} \in P_\delta \mid \mathbf{x} \cdot \mathbf{e}_i = 0, i = \overline{1, 3}\} \end{aligned} \quad (9)$$

where $\{\mathbf{e}_i\}_{i=\overline{1,3}}$ are the standard base of \mathbb{R}^3 , and

$$\begin{aligned} S_\delta^i(\mathbf{x}) &= \{\mathbf{x} + S_\delta^i\} \\ P_\delta(\mathbf{x}) &= \{\mathbf{x} + P_\delta\} \end{aligned} \quad (10)$$

Definition 2.1 Using P_δ one defines the mediate variables:

$\rho_a(t, \mathbf{x})$ aqueous mass density of a -constituent

$$\rho_a(t, \mathbf{x}) = \frac{1}{\text{vol}(P_\delta)} \int_{P_\delta(\mathbf{x}) \cap \Omega_v} \tilde{\rho}_a(t, \mathbf{w}) d\mathbf{w}, \quad (11)$$

$s_a(t, \mathbf{x})$ soil mass density of a -constituent

$$s_a(t, \mathbf{x}) = \frac{1}{\text{vol}(P_\delta)} \int_{P_\delta(\mathbf{x}) \cap \Gamma_{sf}} \tilde{\rho}_a^s(t, \mathbf{y}) ds_y, \quad (12)$$

mass flux density of a -constituent

$$\rho_a \mathbf{u}_a^i(t, \mathbf{x}) = \frac{1}{\text{vol}(P_\delta)} \int_{-\delta}^{+\delta} \int_{S_\delta^i(\mathbf{x} + \eta \mathbf{e}_i) \cap \Omega_v} \tilde{\rho}_a \tilde{\mathbf{u}}_a^i(t, \mathbf{y}) \, ds_y \, d\eta, \quad (13)$$

the rate a -constituent uptake

$$q_a(t, \mathbf{x}) = \frac{1}{\text{vol}(P_\delta)} \int_{P_\delta(\mathbf{x}) \cap \Gamma_{r,f}} \tilde{\rho}_a \tilde{\mathbf{u}}_a(t, \mathbf{y}) \cdot \mathbf{n} \, ds_y, \quad (14)$$

the density of mass production due to chemical reaction

$$r_a(t, \mathbf{x}) = \frac{1}{\text{vol}(P_\delta)} \int_{P_\delta(\mathbf{x}) \cap \Omega_v} \tilde{r}_a(t, \mathbf{w}) \, d\mathbf{w}. \quad (15)$$

Note that the mediate quantities depend on the δ !

Next we give a lemma that allows us to give the local form of balance equation from the mediate field.

Lemma 2.1 *Assume that for any t and $\mathbf{x} \in \Omega$ and for any $i = \overline{1, 3}$ the function*

$$\psi(\eta) = \int_{S_\delta^i(\mathbf{x} + \eta \mathbf{e}_i) \cap \Omega_v} \tilde{\rho}_a \tilde{\mathbf{u}}_a^i(t, \mathbf{y}) \, ds_y$$

is a continuous function of η . Then $\rho_a \mathbf{u}_a(t, \mathbf{x})$ is a differentiable field and

$$\text{div} \rho_a \mathbf{u}_a(t, \mathbf{x}) = \frac{1}{\text{vol}(P_\delta)} \int_{\partial P_\delta(\mathbf{x}) \cap \Omega_v} \tilde{\rho}_a \tilde{\mathbf{u}}_a \cdot \mathbf{n} \, ds \quad (16)$$

Proof. Let us consider the $\rho_a u^1(t, \mathbf{x})$ component. One can write

$$\rho_a u^1(t, \mathbf{x}) = \frac{1}{\text{vol}(P_\delta)} \int_{x_1 - \delta}^{x_1 + \delta} \int_{S_\delta^1(\eta \mathbf{e}_1 + x_2 \mathbf{e}_2 + x_3 \mathbf{e}_3) \cap \Omega_v} \tilde{\rho}_a \tilde{u}_a^1(t, \mathbf{y}) \, ds_y \, d\eta.$$

Since ψ is a continuous function, one has

$$\frac{\partial \rho_a u^1(t, \mathbf{x})}{\partial x_1} = \frac{1}{\text{vol}(P_\delta)} \left(\int_{S_\delta^1(\mathbf{x} + \delta \mathbf{e}_1) \cap \Omega_v} \tilde{\rho}_a \tilde{u}_a^1(t, \mathbf{y}) \, ds_y - \int_{S_\delta^1(\mathbf{x} - \delta \mathbf{e}_1) \cap \Omega_v} \tilde{\rho}_a \tilde{u}_a^1(t, \mathbf{y}) \, ds_y \right)$$

This formula and similar results for remainders of the components prove lemma .

A list of the correspondence of the integral of microlocal fields and mediate field follows:

$$\begin{aligned}
 m_a(t, P_\delta(\mathbf{x})) &= \text{vol}(P_\delta) (\rho_a(t, \mathbf{x}) + s_a(t, \mathbf{x})) \\
 \mathcal{F}_a^{ff}(t; \partial P_\delta(\mathbf{x})) &= \text{vol}(P_\delta) \text{div} \rho_a \mathbf{u}_a \\
 \mathcal{F}_a^{fp}(t; P_\delta(\mathbf{x})) &= \text{vol}(P_\delta) q_a(t, \mathbf{x}) \\
 \mathcal{M}_a(t; P_\delta(\mathbf{x})) &= \text{vol}(P_\delta) r_a(t, \mathbf{x})
 \end{aligned} \tag{17}$$

By using (17) and the integral mass balance equation (8) we can assert that the mediate fields $\{\rho_a, s_a(t, \mathbf{x}), \rho_a \mathbf{u}_a(t, \mathbf{x})\}_{a=\overline{1, N}}$ satisfy:

$$\frac{\partial}{\partial t} (\rho_a(t, \mathbf{x}) + s_a(t, \mathbf{x})) + \text{div} \rho_a \mathbf{u}_a(t, \mathbf{x}) = r_a(t, \mathbf{x}) - q_a(t, \mathbf{x}). \tag{18}$$

The fields $\{\rho(t, \mathbf{x}), s(t, \mathbf{x}), \rho \mathbf{u}(t, \mathbf{x})\}$ satisfy:

$$\frac{\partial}{\partial t} (\rho(t, \mathbf{x}) + s(t, \mathbf{x})) + \text{div} \rho \mathbf{u}(t, \mathbf{x}) = r(t, \mathbf{x}) - q(t, \mathbf{x}), \tag{19}$$

where

$$r = \sum_a r_a, q_a = \sum_a q_a, s = \sum_a s_a$$

If one assumes that the aqueous solution is:

a) *inert fluid*, $r = 0$

b) *the total fraction of the constituents that undergo the sorption phenomena is a small quantity comparable with mixture density*, $s \approx 0$ then the equation (19) can be written as

$$\frac{\partial \rho(t, \mathbf{x})}{\partial t} + \text{div} \rho \mathbf{u}(t, \mathbf{x}) = -q(t, \mathbf{x}). \tag{20}$$

2.3 Richards' equation

The Richards' equation governs the motion of the mixture in the soil. It is obtained by considering an empirical relationship between pressure of the mixture and the flux of mass of mixture. This relation is an extension of the Darcy's law from saturated flow to unsaturated flow:

$$\rho \mathbf{u} = -k \nabla (p + \tilde{\rho} g z) \tag{21}$$

A more used form of this relation is given by

$$\rho \mathbf{u} = -\tilde{\rho} K \nabla (h + z) \tag{22}$$

where $h = \frac{p}{\rho g}$ is known as pressure head and $K = kg$ is hydraulic conductivity. By introducing the water content

$$\theta = \frac{\rho}{\tilde{\rho}} \tag{23}$$

one can write the Richards equation as

$$\frac{\partial \theta}{\partial t} - \text{div} K \nabla (h + z) = -j_w(t, \mathbf{x}) \tag{24}$$

The term $j_w(t, \mathbf{x})$ quantifies the water uptake by the root. Besides the equation (24) one must stipulate another relation between water content θ and pressure head h ,

$$\theta = \theta(h) \quad (25)$$

As an example of $\theta - h$ relation is the vanGenuchten model,

$$S(h) = \begin{cases} (1 + (\alpha h)^n)^{-m}, & h < 0, \\ 1, & h \geq 0, \end{cases} \quad (26)$$

$$K(S) = \begin{cases} K_s S^l \left(1 - (1 - S^{1/m})^m\right)^2, & 0 < S < 1, \\ K_s, & S \geq 1, \end{cases} \quad (27)$$

where S represents the relative water content

$$S = \frac{\theta - \theta_r}{\theta_s - \theta_r}.$$

2.4 Fick's model of the diffusion process

The Fick's diffusion law refers to the partial momentum of a constituent of the mixture. One can write

$$\rho_a \mathbf{u}_a = \rho_a (\mathbf{u}_a - \mathbf{u}) + \rho_a \mathbf{u}$$

The Fick's law is an empirical law and stipulates that

$$\rho_a (\mathbf{u}_a - \mathbf{u}) = -\theta D_a \nabla c_a \quad (28)$$

where

$$c_a = \frac{\rho_a}{\theta}.$$

By using the Fick's law one obtain the advection-diffusion reaction equation for a -component of the mixture

$$\frac{\partial}{\partial t} (\theta c_a(t, \mathbf{x}) + s_a(t, \mathbf{x})) + \text{div} (-\theta D_a \nabla c_a + c_a \theta \mathbf{u}) = r_a(t, \mathbf{x}) - q_a(t, \mathbf{x}). \quad (29)$$

The advection diffusion equation and Richards equation are the starting point to investigate the root aqueous phase interaction. The interaction is modeled by the term j_w , which quantifies the water uptake, and q_a which quantifies the root uptake of the a -constituent of the mixture.

3 Metal Sorption

The mobility of metals in soil is strongly influenced by the retention of metals in soil matrix. In soil solution metals exist as, [30]:

- a) free ions,
- b) soluble complexes with organic or inorganic ligands,
- c) associated with mobile inorganic and organic colloidal material.

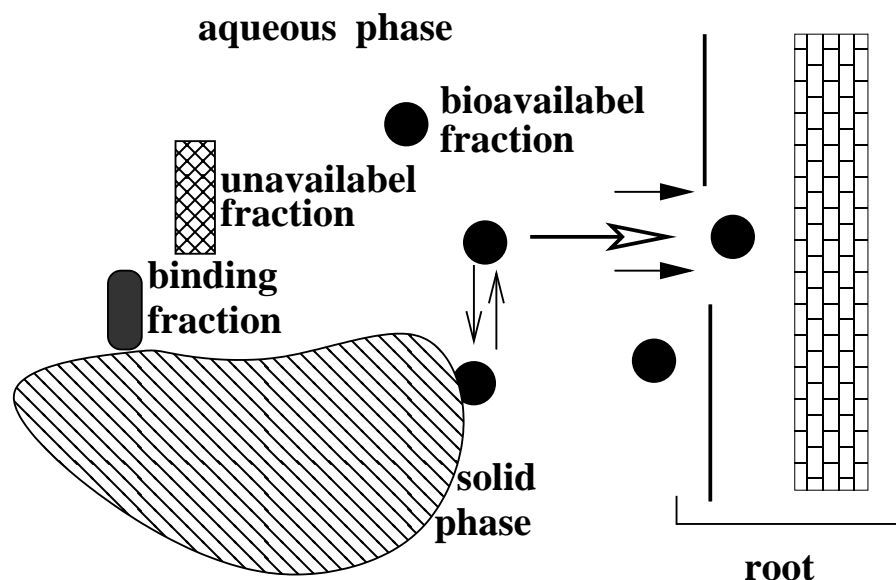


Figure 4: Sorption process and root metal uptake. Only a fraction of the metal species are available for plants.

The total concentration of a metal in soil solution is the sum of free ions concentration, the concentration of soluble organic and inorganic metal complexes, and the concentration of metals associated with mobile colloidal material.

The sorption is a generic name given to the complex processes of retention of metal at the interface soil-aqueous solution. It includes adsorption, absorption, precipitation and polymerization.

The adsorption denotes the accumulation of a substance at the interface between a solid surface and aqueous phase, the absorption is a process in which the solution is taken up into. Precipitation refers to the formation of three dimensional phase product on the solid surface.

The sorption results from either physical or chemical interaction with the surface. Physical interaction forces include van der Waals forces and electrostatic outer-sphere complexes. Chemical forces result from short-range interactions, covalent bonding and hydrogen bonding [47]. The factors affecting the sorption, [46], [30], [9], [8].

- a) Chemical properties of the solution: pH, ionic strength, complex species formation;
- b) Soil properties: pH, redox potential, soil organic matter, Fe and Mn oxides content, calcium carbonate content;
- c) Soil constituents: organic matter, clay minerals, iron and manganese oxides and hydroxides, carbonates, and amorphous aluminosilicates.
- d) Microbial activity and root exudation;

3.1 Empirical models

We restrict to the equilibrium state of the system mixture solid matrix which allows one to stipulate an algebraic relation between concentration of metal in the aqueous phase and sorbed phase. Also we consider a single chemical species of metal. Let s be the quantity of the chemical species sorbed by soil (mg metal sorbed/Kg soil) and c (mg /L) be the equilibrium solution concentration of chemical species.

3.1.1 Partition coefficient

The metal partition coefficient K_d is the ratio of sorbed metal concentration to the dissolved metal concentration [?].

$$K_d = \frac{s}{c} \quad (30)$$

A drawback of the use of partition coefficient is that it is purely empiric and can be used only in the similar conditions under which it was determined. Its advantage is that it is simple and can be applied to the system for which it is impossible to know all chemical mechanism of sorption process. The table 3.1.1 indicates values used by in EPA Risk assessment USEPA96b [?].

Table 2:

Metal	K_d (L/Kg)	
	Single value	Range
Ag	–	0.1–110
As	–	25–31
Ba	–	11–52
Be	–	23–100 000
Cd	–	15–4 300
Cr	–	1 200–4.3E06
Cr(VI)	–	14–31
Hg	1 000	–
Ni	–	16–1 900
Pb	900	–
Sb	45	–
Se	–	2.2–18
Zn	62	–

3.1.2 Sorption isotherm equations

A sorption isotherm is the relationship between the amount of metal sorbed and the equilibrium concentration of the metal in soil solution. The most used isotherm equations are, [12]:

Freundlich Adsorption Isotherm Equation. It is the oldest of the nonlinear isotherm and it is applicable to heterogeneous sites:

$$s = Kc^\beta, \quad (31)$$

where K is the an affinity parameter and β is a dimensionless heterogeneity parameter;

Langmuir Adsorption Isotherm Equation.

$$s = \frac{s_m K c}{1 + K c} \quad (32)$$

where s_m is the maximum adsorption of chemical species per unit mass of solid and K is an affinity parameter related to the bonding energy of the species to the surface.

Multisite Langmuir Adsorption Isotherm Equation.

$$s = \sum_{i=1}^n n \frac{s_{m,i} K_i c}{1 + K_i c} \quad (33)$$

where n is the number of types of surface sites.

4 Root uptake

4.1 Root water uptake

To be a live the plant needs water and the main source of water is the soil. The plant roots extracts the water from soil and delivery it to the xylem vessel. In the xylem pipes the water flows from the root to leaves. The plant mainly uses water in the photosynthesis process and to sustain the transpiration process, the transpiration process uses about 98% of the water process budget. The problem is *what kind of force extracts the water from soil* and what is its mathematical expression? In plant tissues, water moves passively along water potential gradients. The transpiration implies a negative pressure in xylem vessels, which draw water from the roots up to the aerial parts. From soil into xylem vessels of the root the water is moving by hydrostatic pressure gradient and osmotic gradient [48].

An evident fact is that the transpiration rate plays a major role in the control the water flux in the period time of transpiration. It is no clear how the two force, pressure gradient and osmotic gradient can be included in the mathematical expression of the water uptake.

To overcome such difficulties a model based on the transpiration rate is in use. There exists an external force named "transpiration water potential" that is determined by the atmospheric factors and do not depend on the state of the soil. This force impose a rate of water flux $\Pi(t, \xi)$, here ξ stands for a system of co-ordinates on the soil surface. To account for heterogeneity of the root distribution and for the unsaturated water content the rate of the water uptake is considered to be of the form, [49],[26], [28]

$$j_w = \gamma(h)\beta(\mathbf{x})\Pi(t, \xi) \quad (34)$$

where $\gamma(h)$ is water stress function and $\beta(\mathbf{x})$ is root distribution function.

4.2 Root metal uptake

The accumulation of metals by plants relies on plants working as solar "biopumps", [45]. The soil solution enters the the root and then is drawn to stem and to leaves, certain fraction of metal is absorbed by plant tissue and remainder of total metal taken by root is lost by transpiration. One

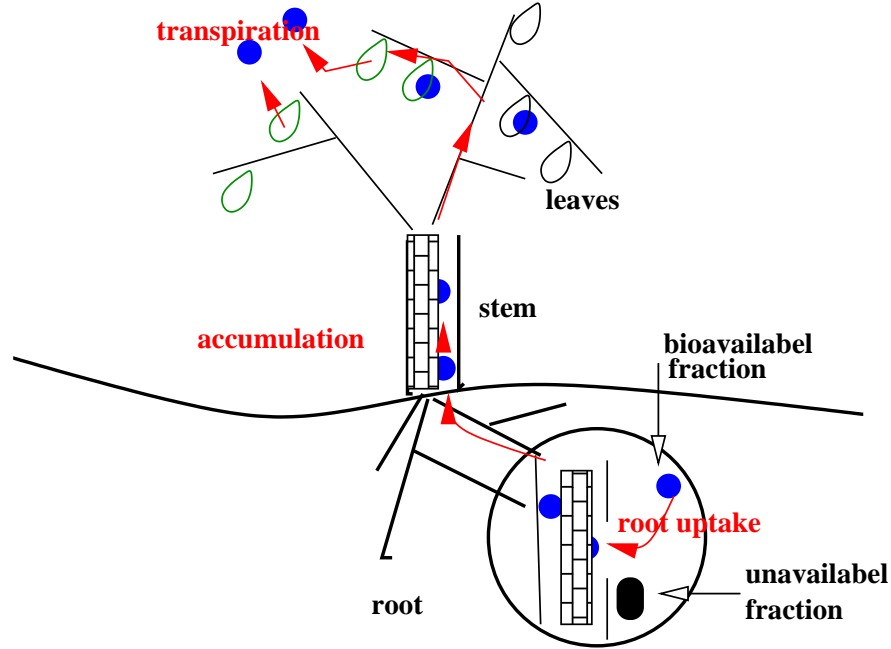


Figure 5: The pathway of metal from soil to atmosphere. A fraction of metal accumulates in plant tissue and the remainder of it is lost by transpiration

Table 3: Example of root distribution function and water stress function. One dimensional flow

$\beta(z)$	Parameters	Reference&Obs.
$\beta_0 \left(1 - \frac{z}{z_m}\right) e^{-\frac{pz}{z_m} z^*-z }$	p_z, z^*	[49] z_m maximum root depth
$\frac{1}{\delta} e^{-\frac{z}{\delta}}$	δ	[43], infinite domain
$-a^z \ln, a$	$a < 1$	[26], infinite domain
$\gamma(h)$	Parameters	Reference&Obs.
$\sqrt{H(h)\Theta(h)}$		[26] $H(h) = \frac{h - h_{pwp}}{h_{fc} - h_{pwp}},$ $\Theta(h) = \frac{\theta(h) - \theta(h_{pwp})}{\theta(h_{fc}) - \theta(h_{pwp})}$
$\begin{cases} 0, & h \in (\infty, h_4) \\ \frac{h - h_4}{h_3 - h_4}, & h \in (h_4, h_3) \\ 1, & h \in (h_3, h_2) \\ \frac{h_1 - h}{h_1 - h_2}, & h \in (h_2, h_1) \\ 0, & h \in (h_1, 0) \end{cases}$	h_4, h_3, h_2, h_1	[27],

note that only a certain fraction on metals is bioavailable to plants, the remainder is bounded to soil matrix or to organic or inorganic complexes that are unavailable to plants.

4.2.1 Root absorption factor

The root absorption factor is defined as the ratio of soluble metal concentration in root xylem to soil solution metal concentration.

$$\phi = \frac{C_r}{C} \quad (35)$$

where C_r is the soluble metal concentration (mg L^{-1}) in root xylem and C is the soluble metal concentration (mg L^{-1}) in soil solution. For many plants the factor ϕ is constant over a narrow interval of concentration C . There exists internal mechanism of plant to limit the absorption of the metal, especial for the toxic metals

$$\phi(C) = \frac{\phi_0 C_0}{C_0 + K(C - C_0)} \quad (36)$$

where ϕ_0 equals the measured root absorption factor at the soil solution concentration C_0 , and K is the decay constant.

Using the root absorption factor ϕ the rate uptake of a a -components can be written as "pasiv uptake"

$$q_a = \eta j_w(t, \mathbf{x}) c_a \phi(c_a) \quad (37)$$

where j_w is water uptake used by plant.

5 Conclusion

The Richards' equation, (24) with an empirical $\theta - h$ relation like (25) and root uptake (34) and the convection diffusion-reaction equation, (29) with one of the empirical relation for concentration of metal in sorbed phase, (30), (31), (32), 33) and root metal uptake (37) cast in the general form

$$\frac{\partial b(u)}{\partial t} - \text{div}(\kappa(u)\nabla u + \mathbf{f}(u)) = g(t, \mathbf{x}, u). \quad (38)$$

There exists a well documented literature on the mathematical setting of this type of equation both theoretically [2], [7], [10], [13], [31], [38] and numerically [11],[13],[19],[33], [35].

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Mathematical modelling of metals mobility

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