A numerical analysis of phytoextraction processes

Une analyse numérique des processus de phyto-extraction

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ABSTRACT: Phytoextraction is an in situ remediation technique involving the uptake of contaminants by plant roots and their subsequent accumulation in plant tissues. Despite its many advantages, phytoextraction is not widely used because of difficulties in estimating its efficiency and the required remediation time. The objective of our research was to numerically evaluate the effectiveness of phytoremediation of Pb^{2+} and Zn^{2+} using a previously calibrated Hydrus-1D software package. The simulations considered soil and climatological data representative of the coastal lowlands of the municipality of Rio de Janeiro in Brazil and were organized in three steps: pre-contamination (analysis of the hydrological conditions), contamination (analysis of the contamination plume before planting) and remediation. Several conditions were tested, including different root depth and irrigation schemes. Although the results are specific for the assumed scenarios, it was possible to identify several trends in the simulations. While more elaborate calibrations may be needed using long-term field data, the numerical analysis provided useful insight into the phytoextraction process important for the design of future experiments.

RÉSUMÉ : La phyto-extraction est une technique de dépollution in situ basée sur l'absorption de contaminants par les racines des plantes puis de leur accumulation dans les tissus végétaux. Malgré ses nombreux avantages, la phyto-extraction est peu utilisée en raison de la difficulté à estimer son efficacité et la durée de traitement qu'elle implique. L'objectif de notre étude était d'évaluer numériquement l'efficacité de la phyto-extraction du Pb^{2+} et du Zn^{2+} à l'aide d'un logiciel préalablement étalonné Hydrus-1D. Les simulations ont pris en compte pour le sol et la climatologie des données représentatives de la plaine côtière de la municipalité de Rio de Janeiro au Brésil et ont été organisées en trois étapes : la pré-contamination (analyse des conditions hydrologiques), la contamination (analyse du panache de contamination avant le semis) et la dépollution. Plusieurs conditions ont été testées, en particulier diverses profondeurs des racines et différents systèmes d'irrigation. Bien que les résultats soient spécifiques aux scénarios pris en compte, il a été possible d'identifier plusieurs tendances dans les prédictions. Si des étalonnages plus élaborés peuvent être nécessaires en utilisant des données de terrain à long terme, l'analyse numérique fourni des indications utiles sur le processus de phyto-extraction qui sont importantes à prendre en compte pour la conception des expériences futures.

KEYWORDS: contaminant transport, plant solute uptake, irrigation, root density.

1 INTRODUCTION

Phyto-extraction is a remediation technique based on contaminant uptake by plant roots. Pollutants are generally accumulated in plant tissues. Plant based remediation processes are currently used for many classes of contaminants, including hydrocarbons, pesticides, explosives, metals, radionuclides, chlorinated solvents, and waste landfill leachate. These techniques can be complementary or alternative to chemical and mechanical treatments. Their applicability depends basically on the resistance of the plant to contaminants. In addition, the efficiency of the process depends strongly on the site characteristics such as soil, climate, hydrology and soil-contaminant interactions. Due to this variability, it is difficult to estimate the cost and the time necessary for a phytoremediation project. Some studies (ITRC, 2009; Truong et al., 2010) show that the costs due to installation, instruments and labor can be significantly lower compared to other techniques.

The present research was focused on numerical modeling of soil-plant-atmosphere continuum, proposing a method for the calculation of:

1. time required for remediation (according to Brazilian Law),
2. efficiency, defined as the ratio between contaminant mass withdrawn from the soil and contaminant mass previously leached into the soil.

The software Hydrus-1D (Šimůnek et al., 2009) was applied to scenarios of contamination by Pb^{2+} and Zn^{2+} chosen for their different reactivity with the soil solid phase. The remediation was carried by Vetiver grass (*Chrysopogon zizanioides*). Soil and climate data were relative to an industrial area of the municipality of Rio de Janeiro. The model parameters, relative to the crop, were determined and calibrated in a previous study, based on greenhouse experiment (Lugli et al., 2011).

2 MATERIALS AND METHODS

2.1 *Numerical Model*

The *Hydrus-1D* code uses linear finite element method of *Galerkin* type for spatial discretization and finite difference method for time discretization of the Richards equation (variably saturated flows). For solute transport, *Hydrus-1D* is based on the resolution of the advection-dispersion equation by finite elements (Šimůnek et al., 2009).

The main hypotheses of this study were:

1. one-dimensional approach,
2. absence of preferential flow paths,
3. invariance of the potential root contaminant uptake,
4. remediation process based only on direct extraction of the contaminant,
5. absence of growth, senescence, intoxication phenomena,
6. contaminants are considered separately.

2.1.1 *Water uptake model*

Water uptake was calculated by *Hydrus-1D*, through a macroscopic approach determining the sink term in *Richards equation* (Feddes et al., 1978; Vogel, 1988). In this study water stress was considered according to Feddes' formulation (Feddes et al., 1978).

The root water uptake was calculated directly by *Hydrus* code, through a macroscopic approach determining the sink term in the Richards equation. This term, s [T^{-1}], was calculated from the equation

$$s(h,h_\phi,x,t) = \alpha(h,h_\phi,x,t)\, b(x,t)\, T_p(t) \qquad (1)$$

where $T_p(t)$ [LT^{-1}] was the normalized root distribution [L^{-1}], a function of space and time (in the case of root growth). The function α [-] represented the response to plant stress ($0 \le \alpha \le 1$), by varying the hydraulic and osmotic head.

2.1.2 *Contaminant uptake model*

Roots contaminant uptake, when present, was calculated with models defined as passive and active. The first assume that the solute uptake is locally proportional to root water uptake and the concentration of the solute dissolved in water:

$$p(x,t) = s(x,t)\, c(x,t) \qquad (2)$$

The active root solute uptake $a(x,t)$ [$ML^{-3}T^{-1}$] was calculated using *Michaelis-Ment*en kinetics (Jungk, 2002). The theoretical maximum uptake value was called as potential active solute uptake $A_p(t)$ [$ML^{-2}T^{-1}$], characteristic of the pair plant-solute and function of time (Šimůnek and Hopmans, 2009).

$$a(x,t) = \frac{c(x,t)}{K_m + c(x,t)} b(x,t) A_p(t) \qquad (3)$$

K_m was defined as *Michaelis-Menten constant* [ML^{-3}]. Applied values were K_m = 1,32 μg/cm^3 and A_p = 0,4757 μg·cm^{-2}/day for Pb^{2+}.

2.1.3 *Soil*

The soil analyzed is a *Halpic Gleysol*. In the simulations only the unsaturated zone was modeled. The water table was assumed to have a fixed depth (90 cm). Two horizons were considered: *A*, clay and *C*, sandy clay loam. The parameters of *van Genuchten - Mualem hydraulic model* (van Genuchten, 1980) were estimated for each horizon using pedotransfert functions proposed by Tomasella et al. (2003).

Table 1. Hydraulic parameters of the *van Genuchten - Mualem model* (van Genuchten, 1980) relative to Halpic Gleysol

horizon	θ_r [cm^3/cm^3]	θ_s [cm^3/cm^3]	α [cm^{-1}]	n [-]	K_s [cm/day]
A	0.1555	0.5688	0.0654	1.1910	61.66
C	0.0900	0.4265	0.0450	1.3154	68.02

2.1.4 *Boundary conditions*

The top boundary conditions were imposed using daily values of precipitation, potential evaporation and transpiration. The reference evapotranspiration was determined using the equation of *Penman-Monteith* (Allen et al., 1989; Allen et al., 1998).

Pressure head h was considered constant and equal to zero at the bottom of the profile.

2.1.5 *Soil-contaminant interaction*

Ion sorption in soil solid phase was considered using a linear model for both horizons. The distribution coefficients (K_d) were inferred from a study (Soares, 2004) about tropical soils with similar characteristics, using 1500 cm^3/g and 70 cm^3/g, respectively, for Pb^{2+} and Zn^{2+}. Standard values for the diffusion coefficients in free water were applied (Shackelford and Daniel, 1991).

2.1.6 *Simulation phases*

The numerical simulations were organized in three phases: pre-contamination, contamination and remediation. The first phase (one year) was necessary to fix average pressure head profile. The presence of shrubby vegetation was included in the top *BC*.

During the contamination phase, the presence of containers, leaching metal ions in presence of rain, was simulated. It was also estimated that the vegetation suffered degradation due to toxicity of the contaminants. Therefore, transpiration values were considered equivalent to 20% of the reference. In this phase, no contaminant uptake was considered. The simulated period was of five years.

For remediating the soil, original vegetation was substituted by *Chrysopogon zizanioides*. According to the experimental study by Tavares (2009), this variety doesn't suffer any toxicity effect at considered concentrations. The *Feddes´* parameters where estimated by analogy with similar plants from *Poaceae* family (Wesseling, 1991). The solute uptake model selection and the determination of the relative parameters were performed in Lugli (2011). An active model was used for Pb^{2+} and a passive model for Zn^{2+}. The process was considered complete when the soil concentration of each contaminants would be punctually lower than the Brazilian standard values for industrial areas (CONAMA, 2009) respectively 900 mg/kg and 2000 mg/kg for Pb^{2+} and Zn^{2+} .

2.2 *Previous studies*

Lugli and Mahler (2012) showed that, by increasing the fraction of contaminant sorbed on the solid phase, the phyto-extraction process became less effective. No relevant consequences were observed in the remediation of Pb^{2+}. For contaminants characterized by low retardation factors (e.g. Zn^{2+}), the remediation process resulted more efficient.

Moreover, water stress partially inhibited contaminant uptake, but prevented plume migration towards water table. The results also showed that phyto-extraction process becomes more efficient by increasing the amount of transpiration at the expense of the portion of evaporation (e.g. increased crop density).

In the present study, some results form Lugli and Mahler (2012) were revisited analyzing the influence of root depth. The focus was to study if an engineered choice of plant species in terms of root distribution could promote (or not) an improvement in remediation process. For both Pb^{2+} and Zn^{2+} three different root models were analyzed and compared with the reference (root depth = 40 cm). All of them where static and linear interpolated with the lowest value corresponding to zero; the depth was determined multiplying the plume depth for each contaminant by 2/3, 1 and 1.5.

3 RESULTS AND DISCUSSION

3.1 *Influence of root distribution*

3.1.1 *Lead Ion*

In the case of lead ion (high retardation factor) it is known that the remediation process is not efficient (Lugli and Mahler, 2012).

Modified roots caused the remediation time to exceed 120 months (test 2, 3 and 4 in Table 2). This happens because the plume is substantially blocked due to the hydraulic conditions (Figure 1). According to the Brazilian Law, this result is not favorable. Despite of this, root modification implied an increase in the amount of contaminant extracted in comparison with the reference (test 1 in Table 2), This, together with the smaller mobilization of the plume, can be evaluated as an improvement from the environmental point of view. It could be identified that the most favorable configuration corresponded to a root depth of 3.5 cm: this value is less than the initial plume depth (5 cm).

Table 2. Transport and Pb^{2+} uptake with different root distributions

test	Ion	Root max depth	remediation time [months]	contaminant extracted/initial	plume depth [cm]
1	Pb^{2+}	40	90	1.68%	12.23
2	Pb^{2+}	7	>120	1.74%	6.34
3	Pb^{2+}	5	>120	6.43%	7.04
4	Pb^{2+}	3.5	>120	6.95%	7.16

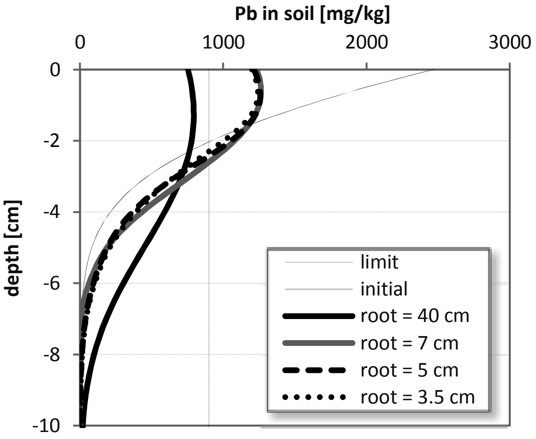

Figure 1: Pb^{2+} plumes: initial and after 10 years of remediation with different root depth

3.1.2 *Zinc Ion*

The same improvement observed in the previous paragraph for lead ion was present also for a more mobile ion such as zinc (Table 3). In this case all the indicators of remediation process register a favorable trend: remediation time, amount of contaminant extracted and plume depth. Differently from the previous case, the reduction of the concentration values took place in all the rizosphere (Figure 2). The most favorable configuration, also for Zn^{2+}, corresponded to a root depth lower than the initial plume depth (23 cm).

Table 3. Transport and Zn^{2+} uptake with different root distributions

test	Ion	Root max depth	remediation time [months]	contaminant extracted/initial	plume depth [cm]
5	Zn^{2+}	40	48	41.6%	35.87
6	Zn^{2+}	34,5	48	42.7%	36.09
7	Zn^{2+}	23	46	42.7%	35.76
8	Zn^{2+}	15	42	46.6%	35.65

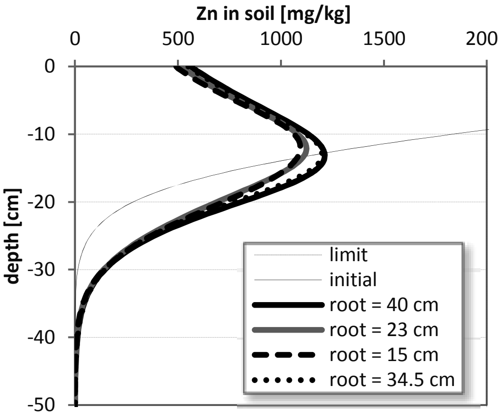

Figure 2: Zn^{2+} plumes: initial and after 10 years of remediation with different root depth

3.2 *Influence of water balance*

The object of this paragraph was to verify if the effects due to the addition of irrigation (Lugli and Mahler, 2012), persisted in the case of the optimized root depth. These effects were mainly:

- enhanced contaminant extraction,
- displacement of the contaminant plume downwards.

In Table 4 and Figure 3 it could be notice that both effects are present also in the case of the reduction of root depth.

Table 4. Transport and Zn^{2+} uptake with different root distributions and presence of irrigation

test	Ion	irrigation	Root max depth	remediation time [months]	contaminant extracted/initial	plume depth [cm]
5	Zn^{2+}	0	40	48	41.6%	35.87
8	Zn^{2+}	0	15	42	46.6%	35.65
9	Zn^{2+}	330 mm/year	40	42	42.8%	36.60
10	Zn^{2+}	330 mm/year	15	36	48.2%	38.29

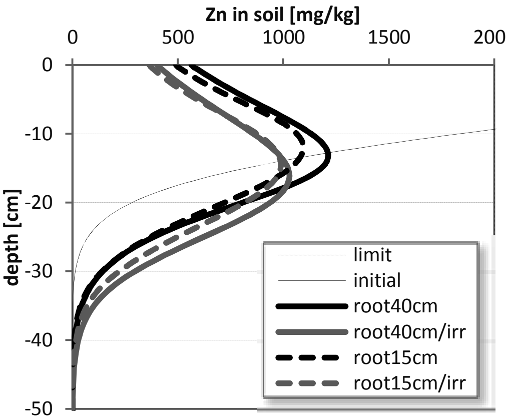

Figure 3: Zn^{2+} plumes: initial and after 10 years of remediation with different root depth and presence of irrigation

4 CONCLUSION

The present study examined an example of optimization of a phyto-extraction process in the presence of metal ions, based on numerical modeling. According to the assumptions related to the model and the analyzed scenarios, it was highlighted that, by modifying root depth and introducing irrigation, the phyto-extraction process could be optimized for contaminants characterized by low (e.g. Zn^{2+}), and high (e.g. Pb^{2+}) retardation factors. Moreover, both cases studied evinced better performances for root distribution shallower than plume contamination.

As a general consideration, the proposed methodology provided important data for the design and evaluation of a phyto-extraction process.

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