MODELING MOBILIZATION OF HEAVY METALS BY CHELATIG AGENTS IN UNSATURATED SOILS

DIPARTIMENTO DI INGEGNERIA
CIVILE, EDILE E AMBIENTALE

SAPIENZA
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The problem

Soil contamination by heavy metals
as lead needs remediation technologies.
Soil flushing , soil washing, phytodepuration are widely used.

The chelating agents (EDTA, EDDS ..) increase the extraction of metals. During the reaction, composite molecules are formed. The complex is transported in liquid form into the soil, collected and finally extracted.

This work

The aim of this work is to present a mathematical model applied to a not saturated soil in non-stationary conditions with chemical kinetics related to the mineralogical composition of soil

Richards's equation is used for the study of the motion in the vadose zone

$$\frac{\partial\theta}{\partial t}=\frac{\partial}{\partial z}\left[K(\theta)\frac{\partial\psi}{\partial z}\right]-\frac{\partial K(\theta)}{\partial z}$$

θ _based

$$\frac{\partial\theta}{\partial t}=\frac{\partial}{\partial z}\left[D(\theta)\frac{\partial\theta}{\partial z}\right]-\frac{\partial K(\theta)}{\partial z}$$

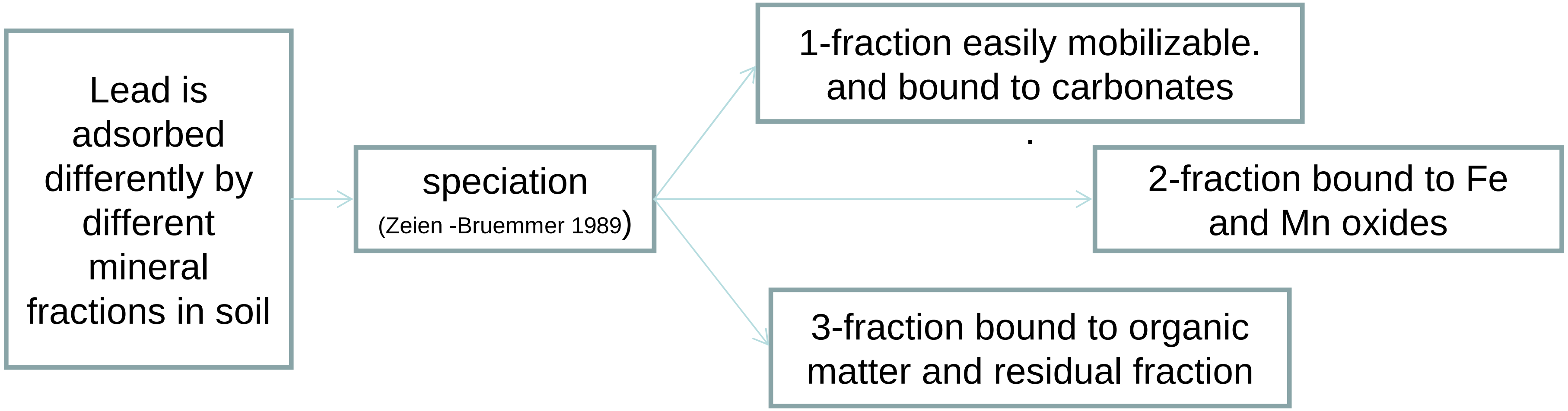
The transport and diffusion equation, resolved coupled to the motion one, describes the transport and dispersion of the pollutant in the soil.

$$\frac{\partial(\theta C)}{\partial t}=\frac{\partial}{\partial z}\left[D\theta\frac{\partial C}{\partial z}-wC\right]$$

The equations are solved by numerical integration (finite differences method) with appropriate initial and boundary conditions.

Parameters ψ,C,K,D, are determined by means of Brooks and Corey model.

Lead into the soil



Lead is adsorbed differently by different mineral fractions in soil

speciation
(Zeien -Bruemmer 1989)

1-fraction easily mobilizable. and bound to carbonates

.

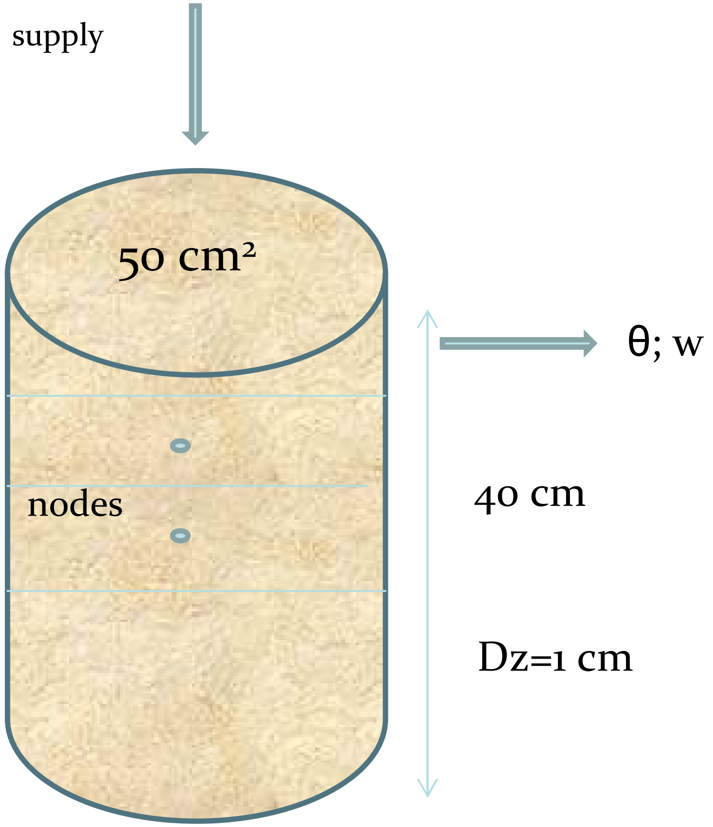
2-fraction bound to Fe and Mn oxides

3-fraction bound to organic matter and residual fraction

For each fraction we assume a two-phase desorption model, called "fast“ and "slow" (Yip 2009)

Desorption and chelation process are time dependent and affected by the fraction stated above. In an unsaturated soils transport process is typically unsteady and this influences the chemical kinetics.

Model construction



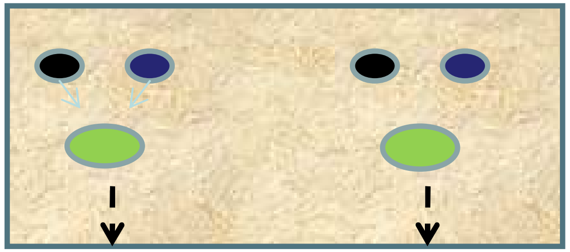
The soil is modeled as a discretized column. The number of nodes depends on stability conditions required for the numerical solution of model equations

The feeding in the calibration phase (saturated soil) is equal to the field capacity of the soil. In the simulation tests it is gradually reduced to simulate further conditions of not saturated soil

Model construction

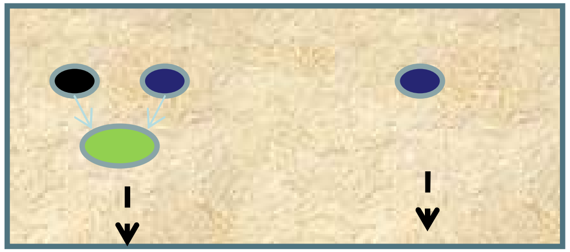
Mechanism of formation of Pb - EDTA complex

Pb = EDTA



Complex Complex

Pb < EDTA

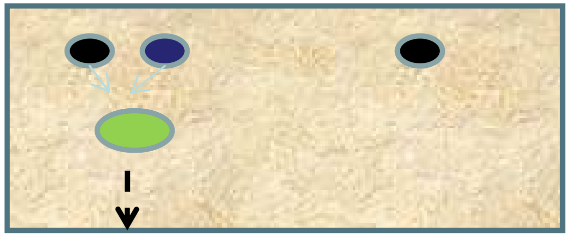


Complex Residual EDTA

complex mass equal to that of the lead

The EDTA has the property of reacting in a molar ratio 1:1 with the lead.

Pb > EDTA



Complex Residual lead

complex mass equal to that of the EDTA

Model Equation

In the model three fractions of lead linked to as many mineralogical components of the basic constituents of the ground, are considered. So we have a system consisting of 6 equations, three for the fast and three for the slow phases .

Fast reaction

$$\frac{\partial C_i^{'}}{\partial t} = -k_i^{'} f_i C_i$$

Slow reaction

$$\frac{\partial C_i^{''}}{\partial t} = -k_i^{''}(1 - f_i) C_i$$

C 'and C" are the concentrations of lead in the two phases, k' and k" constants of reaction [T^{-1}] and f a dimensionless factor of proportionality.

(i=1,2 or 3)

When the chelating agent reacts with the lead, the six reactions start simultaneously but the amount of elements that react depends on the time that the chelating agent takes to pass through the soil with respect to time of which every reaction requires to develop. The adsorbed lead into the ground will participate in a complete or incomplete way to the reaction depending on the relationship between the two times stated above.

Model Equation

The equation for the transport and diffusion is modified with the addition of a term representing the complexation

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z}\left[D \cdot \theta \cdot \frac{\partial C}{\partial z} - q \cdot C\right] \pm R$$

- residual EDTA

+ EDTA – Pb complex

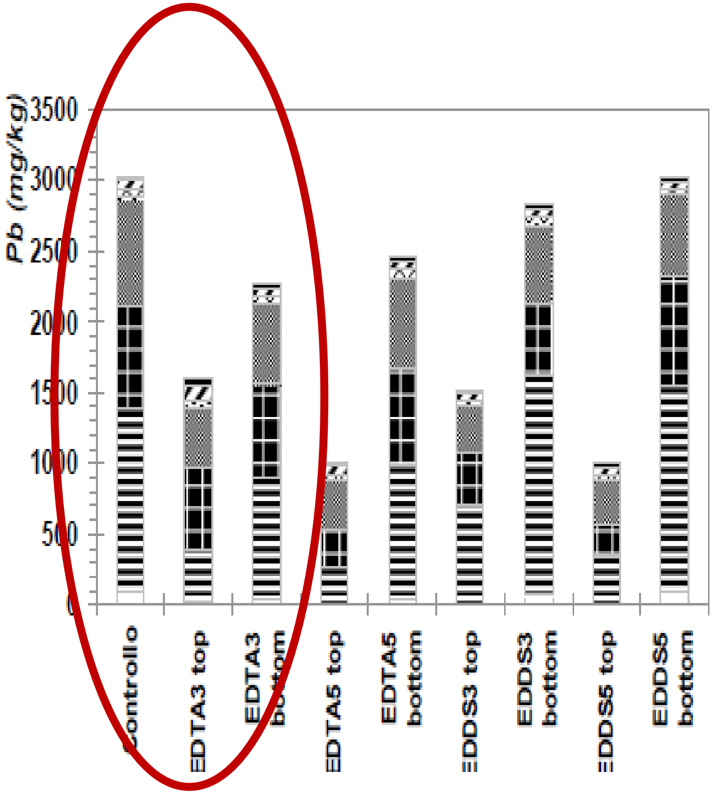
$R' = M_i' k'_i f_i$ $\qquad R'' = M_i'' k''_i (1 - f_i)$ $\qquad R = R_i' + R_i''$ $\quad (i=1,2,3)$

M 'and M" represent the amount of lead which participates in any reaction calculated by multiplying the initial concentration of absorbed lead with the ratio between the time that the chelating agent takes to pass through the layer of soil in question and the time required for the fully development of the reaction.

In an unsaturated soil the velocity of the solution is not constant and consequently also the contact time of the chelating agent with lead , in the various nodes in which the column is divided ,depends on the time.

Calibration and validation

- Comparison with experimental data



For model calibration and validation, were used experimental values □□obtained from the University of Catania (M.Bruno, 2010).

Values of the initial and residual concentration of lead at 5 and 35 cm deep , for the different fractions of Pb into the soil determined with a process of sequential extraction, are known□□.

It was taken into account the case of 0.003 mol / kg soil EDTA concentration.

Calibration

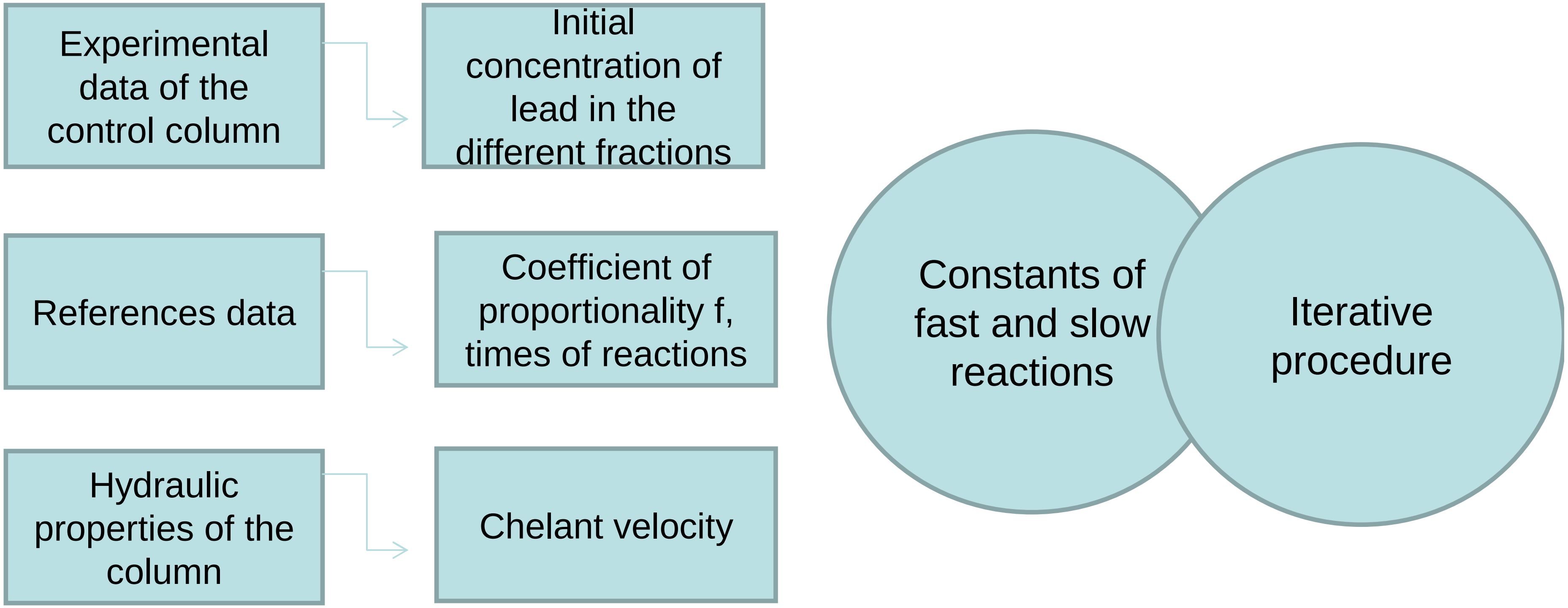
$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z}\left[D\cdot\theta\cdot\frac{\partial C}{\partial z} - q\cdot C\right] \pm R$$

- residual EDTA

+ EDTA – Pb complex

$R' = M_i' k'_i f_i$ $\quad R'' = M_i'' k''_i (1-f_i)$ $\quad R = R_i' + R_i''$ $\quad (i=1,2,3)$

The equations can be solved if some data are known



Experimental data of the control column

Initial concentration of lead in the different fractions

References data

Coefficient of proportionality f, times of reactions

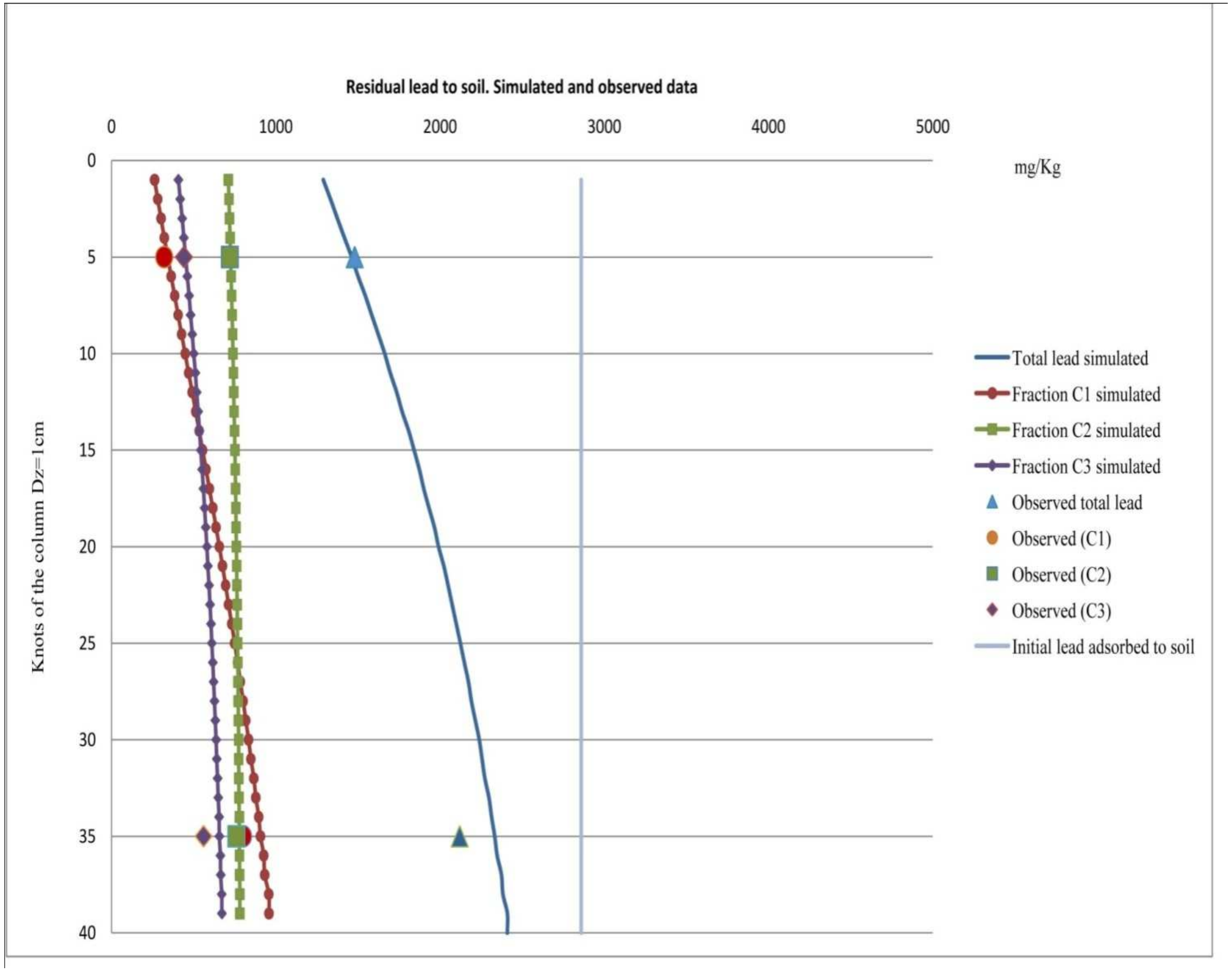
Hydraulic properties of the column

Chelant velocity

Constants of fast and slow reactions

Iterative procedure

Results



The curves represent the residual lead into the soil and are obtained by the simulation model; the points represent the experimental data. We observe a good agreement between experimental and simulated data

Further developments

The model can be used for evaluate the best remediation strategy

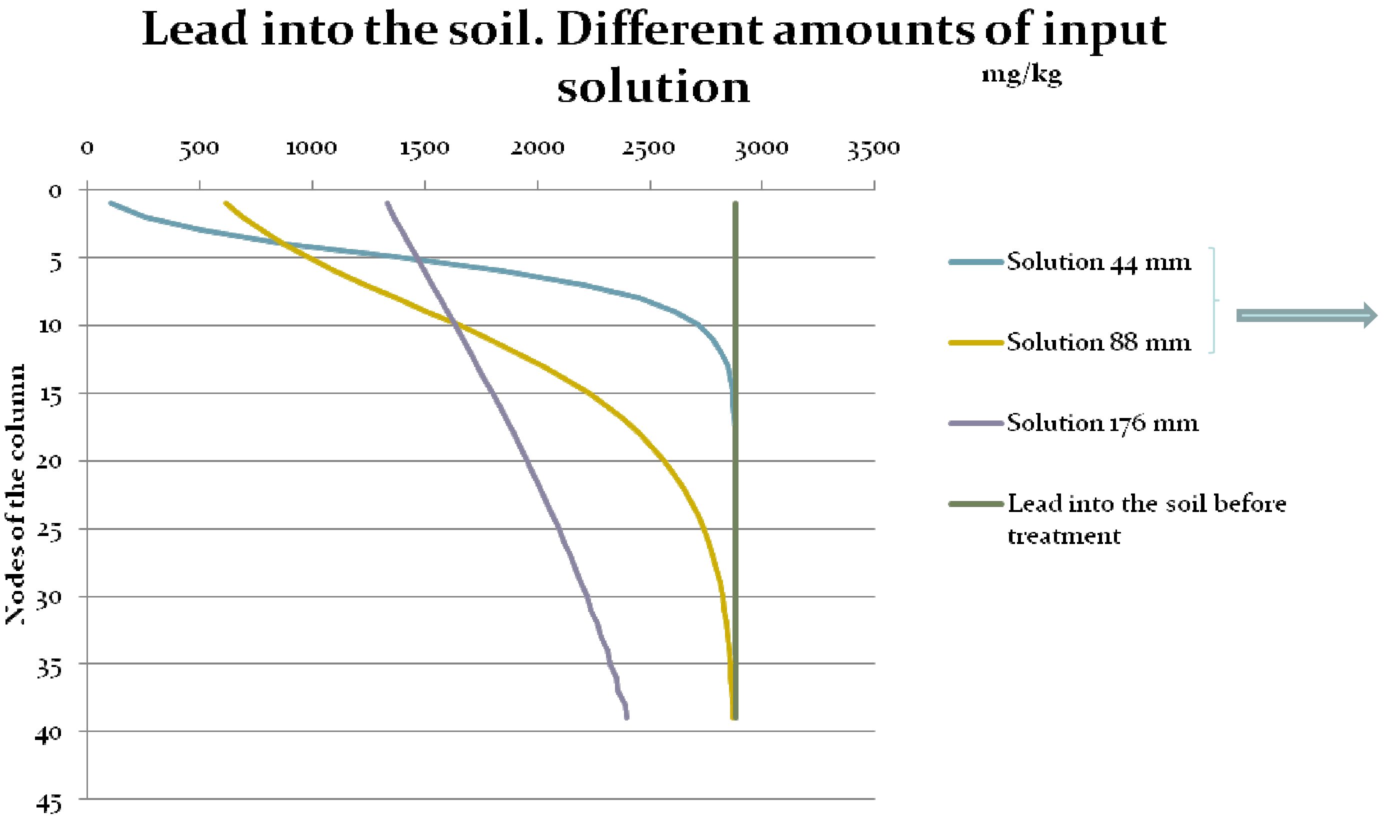
Different feed, same chelant concentration

Different feed, different chelant concentration

Sequential feed

Further developments

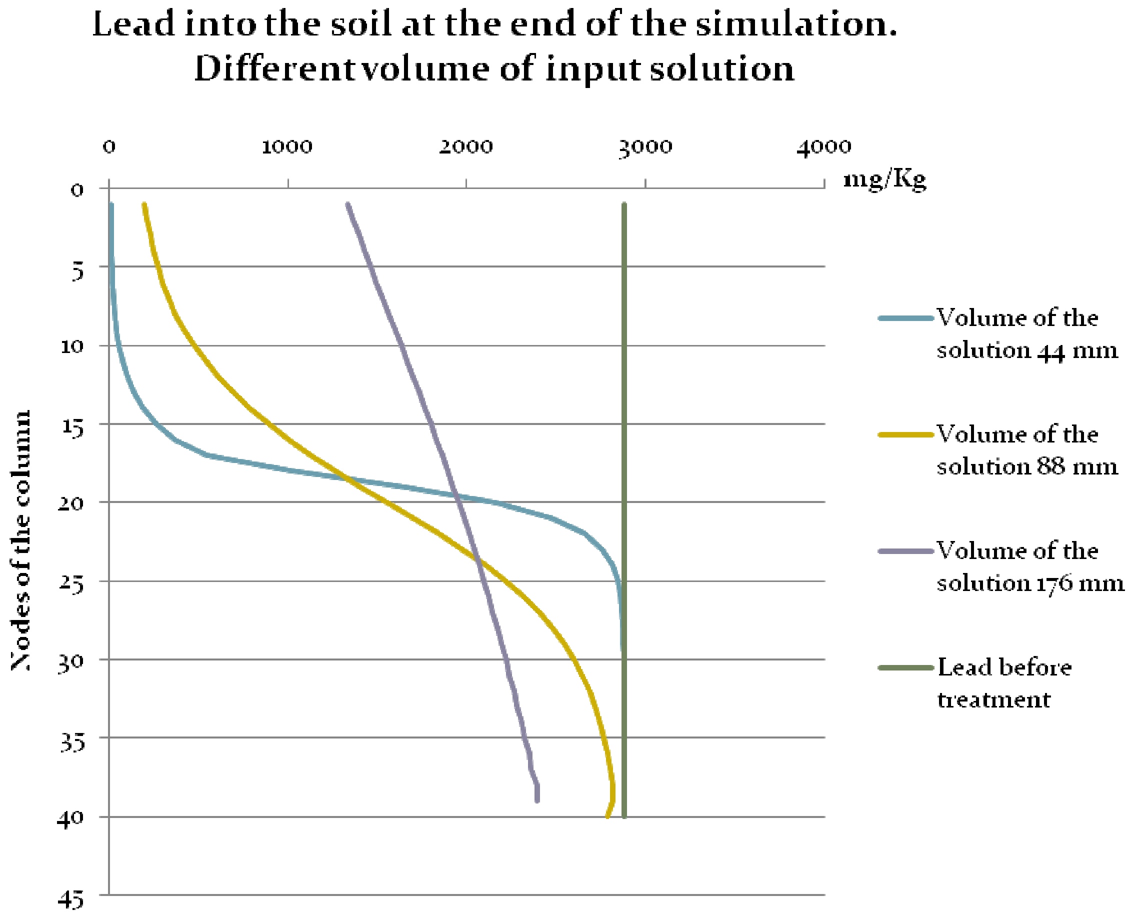
Case 1. Different feed, same chelant concentration



The soil is unsaturated and the chelator passes through the soil less quickly. The lead is mainly eliminated from the top of the column

Further developments

Case 2.Different feed, different chelant concentration

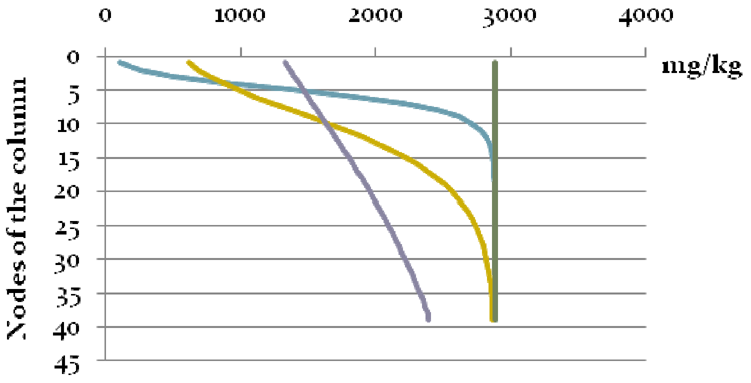


We observe that the more effective removal is obtained for a particular combination of concentration and volume of the solution.

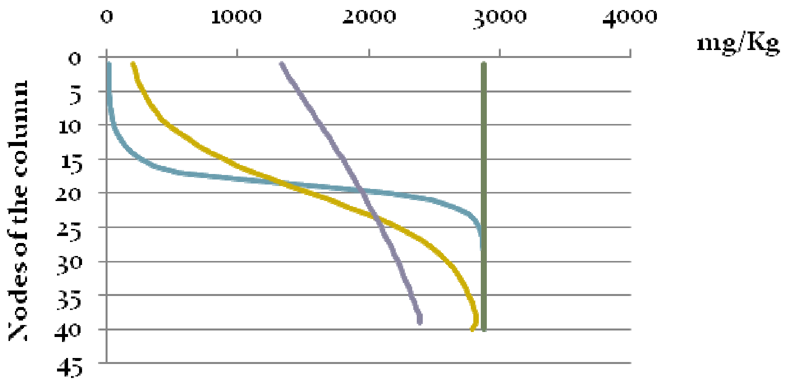
Further developments

Extraction efficiency

Case 1	**Feed 44 mm**	**Feed 88 mm**	**Feed 176 mm**
Initial lead mg	8353	8353	8353
Residual lead mg	7338	6451	5533
Extraction efficiency %	12.23	22.76	33.76



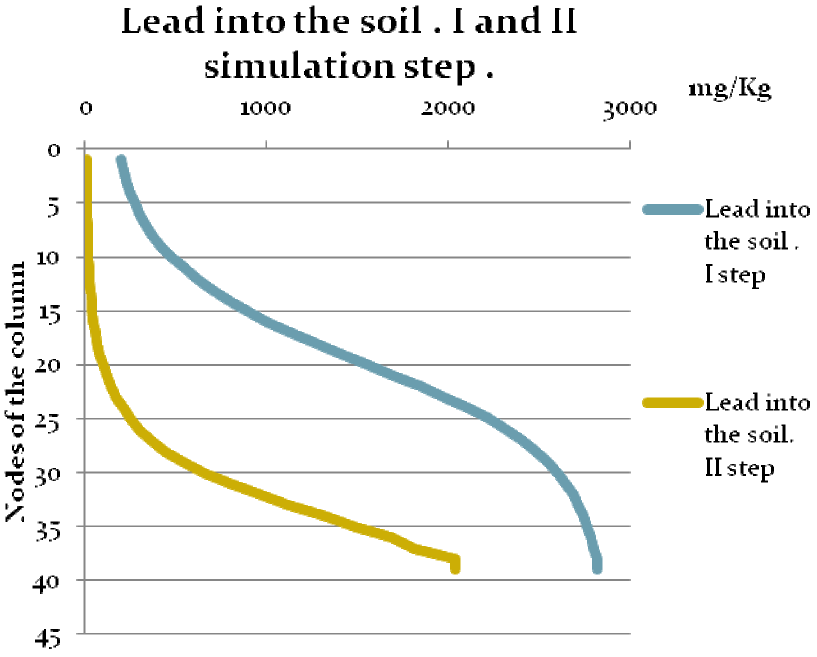
Case 2	**Feed 44 mm**	**Feed 88 mm**	**Feed 176 mm**
Inial lead mg	8353	8353	8353
Residual lead mg	4601	4548	5533
Extraction efficiency %	44,92	45,56	33.76



Further developments

Sequential feed

The EDTA acts more effectively in the upper portion of the column. Repeated application of the chelator may therefore entail a gradual elimination of the pollutant with increasing removal efficiencies. Since EDTA can cause the dissolution of the soil, for example due to the interaction with the calcium ion, it would be necessary to take into account the eventual permeability reduction of the column. This will be the next step of our work



Extraction efficiency Feed 88 mm			
	Initial lead mg	Residual lead mg	Extraction efficiency %
I step	8535	4548	45,56
II step	4548	1353	70,25

References

- Bruno M. (2010), Verifica sperimentale di un’applicazione in “modalità batch” di soil flushing con chelanti, per la bonifica di terreni ad elevata contaminazione da Piombo. *Università di Catania. Dottorato di Ricerca in Ingegneria Idraulica XXIII ciclo*.
- Fangueiro D., Bermond A., Santos E., Carpuça H., Duarte A. (2005) Kinetic approach to heavy metal mobilization assessment in sediments: choose of kinetic equations and models to achieve maximum information. *Talanta* **66**, pp 844-857
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Thanks for your attention