Numerical approach to modelling pulse-mode soil flushing on a Pb-contaminated soil

Antonella Luciano · Paolo Viotti · Vincenzo Torretta · Giuseppe Mancini

Abstract

Purpose Soil flushing can represent a suitable technology in remediation of soils, sediments and sludge contaminated by persistent species (e.g. toxic metal). This paper presents a model specifically developed to evaluate the feasibility of chelating agent-enhanced flushing. The model, here applied to the remediation of real Pb-contaminated soils, was conceived also to simulate an innovative pulse-mode soil flushing technique.

Materials and methods The soil flushing application was firstly carried out through columns laboratory experiments. Columns were filled with a real Pb-contaminated soil (3,000 mg kg^{-1} of dry soil) and flushing was operated in a pulse mode with different chelating agent dosages (3 and 4.3 mmol kg^{-1}soil). Experimental results were used to calibrate and validate the developed reactive transport model that accounts for transport of ethylenediamine tetraacetic acid (EDTA) and EDTA–Pb chelate complexes, Pb residual concentration on soil and the reduction in permeability by soil dissolution. Determination of hydrodynamic and hydrodispersive parameters was carried out through a numerical approach incorporating the use of neural network as interpolating function of breakthrough data obtained by a tracer test.

Results and discussion The EDTA dosage strongly influenced the efficiency in Pb extraction and soil permeability. Cumulative extractions of Pb were found to be 20 and 29 % for the EDTA concentrations of 3 and 4.3 mmol/kg of dry soil, respectively. The soil dissolution caused a significant flow rate decrease, as a consequence of the increase in chelating agent concentration. Therefore the recovery phase duration increased from 738 to 2,080 h. The ability of the model in simulating all the examined phenomena is confirmed by a good fit with experimental results in terms of (a) soil permeability reduction, (b) eluted Pb and (c) residual Pb in the soil.

Conclusions Results highlighted as the model, supported by a preliminary and careful characterization of the soil, can be useful to assess the feasibility of the flushing treatment (avoiding soil clogging) and to address the choice of the operating parameters (flow rate, chelating agent dosage and application method). On the basis of the present research results, a protocol is suggested for in situ soil pulse–flushing application.

Keywords Chelating agents · Lead · Neural network · Numerical model · Soil flushing

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1 Introduction

Soil contamination by toxic metals has become a major environmental concern worldwide due to the rapid industrialization, increased urbanization, intensive agricultural practices and inappropriate waste disposal methods. As a consequence, the need for soil remediation is growing and the development of low-cost, efficient and environmentally friendly remediation technologies has become a key research issue (Lestan et al. 2008)

Soil flushing is an in situ soil washing technique applicable to sandy soil or sediment with middle to high hydraulic conductivity. Hydraulic conductivity should ideally be greater than 1.0×10^{-3} cm/s to allow flushing solutions to pass through the geologic matrix in a reasonable period of time. Less permeable materials, with hydraulic conductivities ranging from 10^{-5} to 10^{-3} cm/s may also be considered for in situ flushing but with increased difficulties in full-scale application. Soil flushing is particularly suitable when the contaminated area is located on top of a low-permeability layer; in such case, the soil thickness can be used as a reactor in which the motion of the chelant solution is mainly mono-dimensional. These factors allow the process to be operated in safety conditions (i.e. pump-and-treat technology; Khan et al. 2004).

Chelating agents such as ethylenediamine tetraacetic acid (EDTA), nitriloacetic acid, diethylenetriamine pentaacetic acid and S,S-ethylene-diaminedisuccinic acid have been extensively investigated in their ability to increase metal extraction through the formation of strong metal–ligand complexes (Norvell et al. 1984; Elliott and Brown 1989; Kim and Ong 1999). EDTA is so far the most studied chelating agent because of its high extraction efficiency and the high stability of the formed metal complexes (Zou at al. 2009). However, because EDTA is recalcitrant to biodegradation and, therefore, characterized by high environmental persistence (Nowack 2002; Oviedo and Rodríguez 2003), evaluating its dynamic in the soil columns can be crucial to minimize potential environmental adverse effects. The high cost of the EDTA also moved several studies in focusing on the recovery of the flushing solution and EDTA recycling (Ager and Marshal 2003; Di Palma et al. 2003; Zeng et al. 2005; Di Palma et al. 2005; Weihua Zhang et al. 2007).

Some researches (Kedziorek et al. 2000; Sun et al. 2001; Mancini et al. 2011) also highlighted important soil minerals and organic matter dissolution effects during EDTA-enhanced flushing that can dramatically alter both physical structure and chemical properties of the soils. The dosage and application terms of chelating agent are thus fundamental factors for an effective remediation with minimal soil damages (Tsang et al. 2007). As a result, a simulation of the overall effects should be carefully carried out, before full-scale application, in order to avoid or reduce the discussed issues.

Soil flushing has been simulated using semi-empirical approaches (Šváb et al. 2008) or numerical models (Samani et al. 1998; Kedziorek et al. 1998). Models include the classic one-dimensional advective–convective equation (ADE) modified by including a sink or a source term to take into account metal solubilization. The ADE equation must be solved through numerical methods and the most applied integration method is represented by finite-difference techniques (FDT).

However, the numerical diffusion generated by the convective term, during the integration process (Bella and Dobbins 1968; Bella and Grenney 1970; Fried 1975; Gresho and Lee

1979), remains a key issue to be controlled and different methods can be applied such as: (1) the use of a pseudo-dispersion coefficient (Schweich and Sardin 1981; Noorishad et al. 1992), (2) the choice of time and space steps in order to create a numerical diffusion which fits the physical one (Jauzein et al. 1989), (3) the use of particle tracking for the convective terms or, (4) in the case of a 1D approximation, the use of a multi-step approach, where convective and dispersive terms are sequentially solved (Siegel et al. 1997).

This paper proposes a 1D numerical model to assess the chelant-enhanced flushing process and predict the fate and transport of involved chemicals (EDTA–Pb complex and free EDTA) through the porous media. A first-order kinetic law was used to describe the extraction reaction. The model was implemented and validated using laboratory-scale column experiments. The advective–dispersive transport equation of involved chemicals was solved with a multi-step finite-difference technique. Hydrodynamic parameters were evaluated through the use of a neural network interpolating breakthrough curves data obtained by a tracer test (Chotpantarata et al. 2011).

2 Materials and methods

2.1 Materials

The contaminated soil utilized for the experiments was obtained by mixing three different soils, including a highly (54,000 mg kg^{-1}) Pb-contaminated soil (5 %) from an abandoned industrial site located in the area around Enna (Italy), a sandy soil (66.5 %) from a sandpit and a silty clay (28.5 %) collected from the 100–150-cm top layer in an agricultural area. The field-contaminated soil had been exposed to natural ageing conditions for several years after the contamination event. The other two mixture constituents were added to obtain a lower Pb concentration (about 3,000 mg kg^{-1}) and a final soil hydraulic conductivity suitable for application of the flushing process. Prior to mixing, each soil was oven-dried at 105 ± 5 °C to constant weight and crushed to pass to a 2-mm sieve. The resulting soil mixture was then characterized: electrical conductivity (EC) and pH were measured on the soil slurry obtained by contacting the soil with deionised water at liquid-to-solid (L/S) ratios of 10 and 5 L kg^{-1}, through an EC-meter and a pH-meter, respectively. The total metal content in the leachate was determined by ICP-OES (Perkin–Elmer Optima 4300DV) analysis of the liquid solutions (1:3 v/v concentrated HNO$_3$/HCl solution) obtained from acid digestion of the samples (ETOS D Milestone).

Pb contents of each 1,000-mg dry soil sample were extracted using nitric acid–hydrochloric acid (1:3 v/v concentrated HNO$_3$+HCl solution) digestion (ETOS D Milestone):

The digested solutions were filtered through Whatman no.42 filter paper and then diluted with deionized water to a volume of 50 ml in a flask. Pb concentration of filtered digestates was quantified using ICP-OES (Perkin–Elmer Optima 4300DV) and expressed as milligrammes of Pb per gramme dry weight of soil. This analytical system had a 98 % recovery efficiency and detection limit of 5 ppb PB.

Organic matter content was indirectly measured through the measurement of total organic carbon (TOC). Both TOC in the soil and dissolved organic carbon (DOC) in the leachates were measured using a Shimadzu Model TOC-V CSH/CSN analyser with 8-Port Sampler OCT-1, calibrated with a potassium hydrogen phthalate standard ($C_8H_5O_4K$) solution containing 150, 375, 750, 1,500 and 2,500 mg Cl^{-1}. For each sample, a minimum of triplicate measurements was made. The results from the soil mixture characterization are reported in Table 1.

2.2 Column experiments

The soil flushing experiments lasted more than 200 days and were carried out on three laboratory-scale polyethylene columns (8.0-cm inner diameter, 50-cm height), using either deionised water or chelating agent as flushing solutions. Each column was filled (from bottom to top) with: (1) 1 cm of acid-washed gravel (<5 mm); (2) 2 cm of acid-washed sand (<1 mm); and (3) 40 cm of dry soil (2,900 g). Care was taken in compacting the soil layers obtaining a final bulk density of 1.4 $g\,cm^{-3}$.

The flushing solution was fed into the column from the top layer, while the effluent solution was recovered from the bottom. Feeding was gravity controlled by an approximately constant head (10 cm). The soil columns were exposed to room temperatures (T=20–26 °C) during the operation. Each experiment was run on a single replicate.

A pre-saturation phase was carried by continuously flushing the columns (from the top) with water, under a constant head (10 cm), for a total of 10 pore volumes. The application of water from the top (although with a constant water head) does not assure that any of the interconnected pore spaces are filled with water. Usual soil column lab experiments are carried out by saturating the columns from the bottom to avoid bubbles entrapping. However, saturation method applied in the present experiments was considered much more closer to what can happen in field application of the technique (rather than in traditional lab experiments) where the soil is subjected to a constant water head (or chelate solution) application from the top.

One of the three columns (column 1) was flushed only with deionised water and used as a control section; the same column was also utilized to obtain hydrodynamic and hydrodispersive parameters through a tracer test. The conservative and non-reactive tracer (chloride) was applied in a step way (concentration of 500 mg/l of Cl^-) for one pore volume.

The other two columns were operated to simulate the pulse-mode flushing treatment with different chelating agent dosages. The disodium EDTA salt dihydrate ($C_{10}H_{12}N_2Na_2O_8\ 2H_2O$) was used at concentrations of 3 and 4.3 mmol kg^{-1} of soil, for columns 2 and 3, respectively. Ideally, the minimum EDTA molar amount needed to extract lead from contaminated soil should be the same as the molar amount of lead in the soil. However, EDTA is a nonspecific chelating agent and it reacts with other metals present in soil. In some soils, the molar amount of metals such as ferric and calcium ions may be larger than that of lead resulting in the formation of metal–EDTA complexes rather than Pb–EDTA complexes. Therefore, in most studies, EDTA molar concentrations higher than the molar concentration of lead in soil are used to achieve maximum lead extraction from lead-contaminated soils.

Doses in the present research were selected on the basis of some preliminary batch experiments (not reported) and are comparable with those reported in similar research experiences that are reported in bibliography (Chen et al. 2004).

The sequence of experimental phases was:

- Phase 0: soil saturation through flushing with deionised water (soil pre-saturation phase);
- Phase 1: pulse-mode (one pore volume) application of chelating agent (EDTA application phase)
- Phase 2: flux interruption to allow a contact time of 48 h (equilibrium phase);

Table 1 Soil chemical and physical characteristics (dry weight basis)

Parameter	Value	Elemental composition	Concentration
pH	7	Pb (mg kg^{-1})	2,880
Electric conductivity (mS cm^{-1})	2,760	Cd (mg kg^{-1})	1.0
Bulk density (g cm^{-3})	1.41	Cu (mg kg^{-1})	21.0
TOC (%)	1.81	Fe (mg kg^{-1})	8,790
Particle size distribution (%)		Ni (mg kg^{-1})	9.0
Sand (Φ>0.05 mm)	70	Zn (mg kg^{-1})	28.0
Silt (0.01≤Φ≤0.05 mm)	18		
Clay (Φ<0.01 mm)	12		
Hydraulic conductivity (cm/s)	2.21×10^{-4}		

– Phase 3: continuous flushing with deionised water to allow lead and chelates removal from the soil (flushing and recovery phase).

The experimental setup characteristics and operating conditions are reported in Table 2.

Considering the expected different reduction of permeability of the two columns it was assumed to use a constant head boundary condition to be able to compare the two flux behaviours. Besides, it is expected to be easier to control the head in a full-scale application. The water head was considered easily applicable and able to determine suitable flux velocity and related remediation times both in the experiments and full-scale applications for soil of similar conductivity.

It was assumed that all the leached Pb in the filtered sample is in the form of EDTA–metal complex (EDTA–Pb). Residual Pb values on the soil, after the treatment, were obtained by sampling 25 g of the soil by operating two holes in the columns at two different depths in each column (5 cm from the surface and 5 cm from the bottom respectively). It was assumed that residual Pb concentration (Pb per gramme dry weight of soil) is the Pb in dry soil only because residual solution was all flushed away during the third phase. Analysis of the Pb concentration in the lecheates and residual Pb in the treated soil samples were carried out as described in Section 2.1.

3 Model and theory

3.1 Model development: mathematical formulation and numerical resolution

The model is based on a 1D flow approximation that was considered acceptable for an EDTA application to superficially contaminated soils where the flow is predominantly in the vertical direction. The model was developed in order to simulate:

(a) the EDTA transport (advection–dispersion equation—ADE);
(b) the solubilisation caused by EDTA complexation of metals bound to the soil;
(c) the transport of EDTA–metal complexes in solution (ADE);
(d) the residual lead in the soil.

For both the free EDTA and EDTA as metal complex, the 1D reactive transport equation can be written:

$$\frac{\partial C_{EDTA}}{\partial t} = D\frac{\partial^2 C_{EDTA}}{\partial z^2} - v\frac{\partial C_{EDTA}}{\partial z} - R \qquad (1)$$

$$\frac{\partial C_{EDTA-Pb}}{\partial t} = D\frac{\partial^2 C_{EDTA-Pb}}{\partial z^2} - v\frac{\partial C_{EDTA-Pb}}{\partial z} + R \qquad (2)$$

Where:

v (cm s^{-1})	is the mean pore velocity
D (cm^2 s^{-1})	is the hydrodynamic dispersion coefficient
C_{EDTA} (mg L^{-1})	is the EDTA concentration
C_{EDTA}-Pb (mg L^{-1})	is the concentration of chelated Pb

R is the dissolution rate of Pb complexed by EDTA:

$$R = -\frac{dC_{Pb.ads-extr}}{dt} = \frac{dC_{EDTA-Pb}}{dt} \qquad (3)$$

Where $C_{Pb-ads-extr}$ is the concentration of potentially extractable Pb and $C_{EDTA-Pb}$ is the deriving EDTA complex.

The dissolution rate may be described through a first-order kinetic reaction (Amacher 1991; Ruby et al. 1992):

$$R = \frac{dC_{EDTA-Pb}}{dt} = K_{eq}\left(C_{EDTA-Pb.eq} - C_{EDTA-Pb}\right) \qquad (4)$$

Where: K_{eq} (s^{-1}) is the kinetic coefficient of solubilisation and $C_{EDTA-Pb\ eq.}$ (mol L^{-1}) is the equilibrium solubility concentration.

Since the chelating reaction ratio of metal to EDTA is 1:1, the concentration of the complex EDTA-Pb at the equilibrium ($C_{EDTA-Pb.eq}$) is assumed to be: (a) the concentration of free EDTA available for the extraction if the desorbable Pb is the reaction limiting factor, or (b) the initial concentration of Pb adsorbed onto soil if it is the free EDTA to be the reaction limiting factor.

The numerical integration of (1) and (2) was carried by FDT in the explicit formulation. To avoid numerical diffusivity and, at the same time, to assure the algorithm stability, the ADE equation was spitted in two terms (convective and dispersive) that were solved separately (Siegel et al. 1997). The time step for the convective term (Δt_{conv}) was suitably chosen in order to eliminate the numerical diffusivity. The time step for the diffusive term was consequently assumed

Table 2 Characteristics of the experimental setup

Run name	Flushing solution (type)	Flushing solution (EDTA dosage)	Pore volume (ml)
Column 1 (control)	deionized water	–	799
Column 2 (EDTA 3)	EDTA	3 mmol kg^{-1} soil	879
Column 3 (EDTA 4.3)	EDTA	4.3 mmol kg^{-1} soil	867

as a fraction ($1/k$) of the previous one in order to also guarantee stability. The algorithm solves firstly the dispersive term and calculates it for k dispersive time steps until the convective time step is reached and the corresponding convective term can be calculated as well.

3.2 Hydrodynamic parameters assessment

Hydrodynamic and hydrodispersive parameters n_{eff} and α (effective porosity and dispersivity, respectively) are needed for the resolution of the ADE equation in saturated soils. The estimation of such parameters is generally carried out through different deductive approach often causing approximation errors. In the present case, the two parameters were estimated through a best-fitting algorithm applied to results from the experimental breakthrough curve of a conservative tracer (chloride) and the corresponding simulation values provided by the model.

Concentrations of the tracer was measured by EC measurements in the leachate, later converted to chlorides concentrations (through a calibration curve) to be used in the model.

For the application of this optimization algorithm, experimental (C_{si}) and simulated (C_{Mi}) concentrations had to be referred to the same time step. Since discretization time step is limited by numerical constrains, an artificial neural network (ANN) was implemented, as interpolating method of the experimental data, to provide the concentration value at any time.

The overall procedure included the following steps:

- experimental tracer test to obtain the breakthrough concentration curve (BTC (pore volume));
- application of the neural network algorithm as interpolating function to provide concentrations as a function of time (BTC (t));
- application of the model to simulate breakthrough concentration curves;
- application of the best-fitting algorithm between experimental BTC, as rebuilt by ANN, and simulation results.

The neural network was implemented as a multi-layer feed forward perceptron, with a back propagation algorithm (Werbos 1988; Hornik et al. 1989; Hines 1997; Viotti et al. 2002). The network consisted of three layers processing elements (one hidden). The network was operated in two directions: (1) in the forward way, the first layer was fed with the measured concentrations values at the different times. (2) During the training phase, in the backward way, the network output was compared with the experimental concentration (C (t)), continuously correcting the weights of the neurons in the hidden layer in order to minimize the residuals. The result at the end of the training phase was a unction able to give back the concentration value corresponding at a desired time t^*.

The transport of the conservative tracer was simulated through Eq. (4) deprived of the reactive term.

The best-fitting algorithm finally operated in the way of minimizing the following objective function (O.F.):

$$O.F.(v, D) = \sum_{i=1}^{n} w_i [C_{SNi}(t) - C_{Mi}(t, v, D)]^2 \qquad (5)$$

Where

|	
n	is the number of compared data
w_i	is the weight associated to each data
C_{SNi} (mg L^{-1})	is the experimental concentration value derived from the function 'rebuilded' using neural network
C_{Mi} (mg L^{-1})	is the simulated concentration value.

4 Results

4.1 Column test results

The modality of EDTA application was significant in determining the Pb leaching behaviour as already observed by Wu et al. (2004) and Finzgar and Lestan (2007). As reported in previous studies (Zhang et al. 2010), EDTA can enhance the metal mobilisation by two mechanisms: a fast thermodynamically favourable complexation between some cationic metals and EDTA, as well as a slow EDTA-promoted dissolution. The former can directly break down some weak bonds between metals and soils, while the latter can indirectly mobilise metals that are bound to oxides and organic matter through partially disrupting the soil.

The effects of EDTA addition in terms of Pb and DOC concentrations in the column effluents are shown in Fig. 1 as a function of the flushed volumes. For the two EDTA-flushed columns, Pb mobilisation peaked at a level strictly depending on the applied concentration of the EDTA. In the case of the control column, flushed only with deionised water, the Pb extraction was negligible as also confirmed from the Pb cumulative release (see Fig. 1a). The pH versus time varied, in the eluates, in a relatively narrow range (8.0–8.6) for all the columns (see Fig. 1d). DOC concentration in the eluates during the soil pre-saturation were comparable, for all the three columns, (concentrations below 50 mg L^{-1}), indicating a limited contribution from the original organic matter of the soil. Upon application of the chelating agents, DOC in the eluates was found to increase until a peak (plateau) value was reached. The observed DOC peak concentrations were 1,645 mg L^{-1} (EDTA 3), 2,220 mg L^{-1} (EDTA 4.3), respectively. The DOC level was thus basically associated to EDTA concentration as evident from the comparison with the very low pre-application levels. In addition,
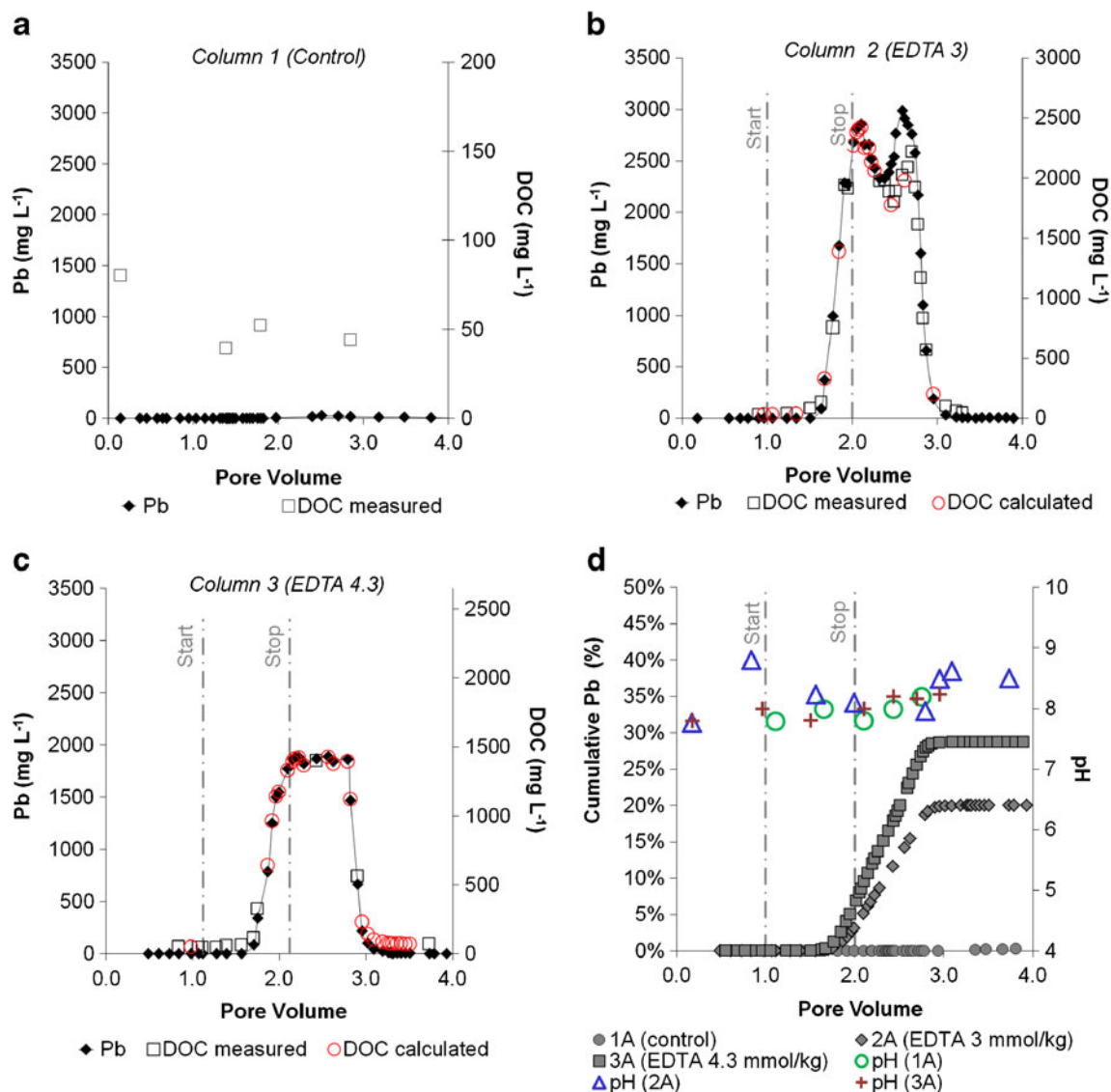
Fig. 1 Pb and DOC mobilisation during the flushing treatment: **a** control, **b** column 2 (3 mmol kg^{-1} EDTA solution), **c** column 3 (4.3 mmol kg^{-1} EDTA solution), and **d** cumulative amount of extracted Pb

correlation between Pb and DOC concentrations in all the eluates were found to be very high (R^2=0.9956), confirming the strict relation EDTA–DOC–Pb. Based on this correlation other DOC values (not measured during the experiments) were calculated, as a linear function of Pb concentration, and plotted in Fig. 1c.

The cumulative amount of DOC eluted from each column was then calculated as the integral of the corresponding eluates curve and compared with the total DOC amount associated with the chelating agent solution. The difference between the two values was found to be lower than ~8.5 %, confirming that DOC can represent an adequate measure of EDTA concentrations.

A similar heavy metals leaching behaviour, as a result of applying EDTA (5.0 mmolkg^{-1} of dry soil) to the surface of an artificial contaminated soil was observed by Chen et al. (2004) using short soil leaching columns (9.0-cm diameter, 20-cm
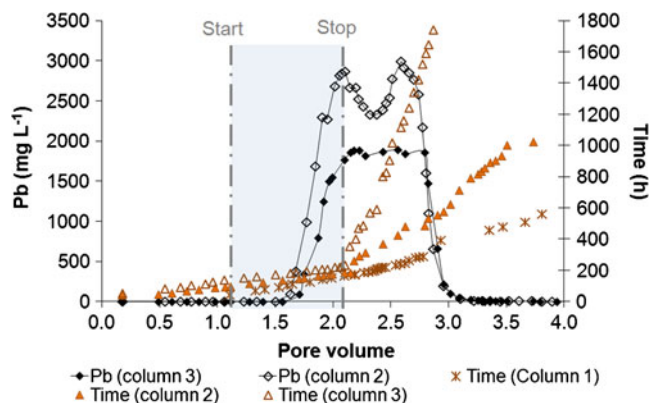
Fig. 2 Pb mobilisation and flushing time for column 2 (3 mmol kg^{-1} EDTA solution) and column 3 (4.3 mmol kg^{-1} EDTA solution)

height). In the leachates from the soil columns where EDTA had not been applied, the concentrations of DOC ranged from 15 to 50 mgCl^{-1}. After the EDTA treatment, the TOC in the leachates increased rapidly at the beginning of the leaching experiment. The highest TOC concentrations reached 2,640 and 2,280 mgCl^{-1} in the leachates; thereafter, the concentrations of TOC in the leachate solution declined and remained at a fairly low level (about 20 mgCl^{-1}). The authors observed as concentrations of dissolved Pb closely followed the pattern of DOC.

As indicated in Fig. 2, different hydraulic behaviours were observed, for the three columns, during the flushing process. The hydraulic conductivities of the three columns in the first limb of the curves (soil pre-saturation with deionized water— phase 0) were substantially equal as it can be observed by comparing the hydraulic behaviours (time vs pore volume) of all the columns before chelate addition. The EDTA application (phase 1 and 2) caused a rapid and drastic reduction in the flow velocity more evident at the higher chelating agent concentration. As a consequence of the permeability reduction, the time required to leach 1 pore volume of extracting solution increased from 86 (before the chelating agent application) to 695 h (after the chelating agent application) for the column 2, and from 89 to 1,160 h for the column 3, respectively . The average flow rate decreased in the columns, according to the increase in chelating agent concentration (phase 3), from 10 cm^3 h^{-1} before EDTA injection to 1.26 cm^3 h^{-1} for column 2 and to 0.75 cm^3 h^{-1} for column 3, respectively.

Kedziorek and Bourg (2000) in laboratory soil columns, flushed with EDTA, found similar results. At high EDTA concentration 10^{-2} M., elution of Pb was very efficient for one pore volume, after which it decreased to almost zero due to depletion of available Pb and to competition with Ca and Fe slowly solubilized during the passage of the EDTA front. Clogging occurred after the end of the EDTA plateau. At lower EDTA concentrations 10^{-3} and 10^{-4} M, elution was less efficient, but extraction decreased little with the volume percolated.

The reduction in soil permeability has been reported in other studies (Heil et al. 1999; Di Palma and Ferrantelli 2005) and can be attributed to different phenomena: the soil dispersion (Hauser et al. 2005; Yip et al. 2010) due to the solubilization of soil minerals (Al, Fe and Mn oxides), the Ca^{2+} dissolution, responsible for the soil aggregate stability (Sun et al. 2001; Kay and Angers 2002) or the reverse of coagulation (Kedziorek et al. 2000). Clogging represents a major problem in view of the application of chelant-enhanced flushing and can potentially limit the future use of the treated soils. For this reason the proposed numerical model for simulating soil flushing, by taking into account the reduction in soil permeability, represents an useful tool: (1) to assess the feasibility of a flushing treatment and (2) to optimize the operating parameters (flow rate and EDTA dosage) for achieving an efficient treatment compatible with acceptable soil final characteristics.
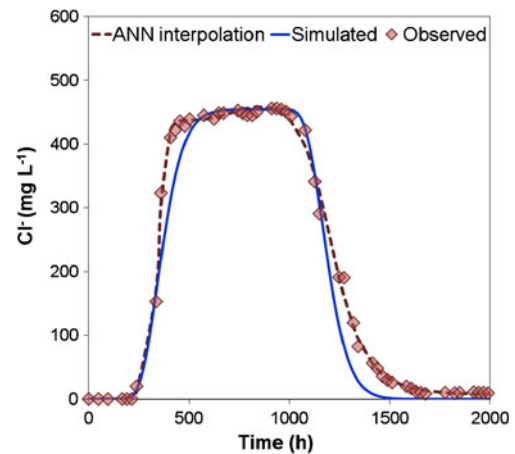

Fig. 3 Chloride breakthrough curves (observed, interpolated by ANN and simulated values)

4.2 Hydrodynamic and hydrodispersive parameters

Figure 3 shows the experimental chloride BTC together with its ANNs interpolation and the related model simulation. Under saturated steady state-flow conditions, the BTCs of chloride were symmetrical, indicating ideal transport behaviour in the homogeneous soil columns (Chotpantarata et al. 2011). Soil flushing technology is most effectively applied when geologic materials exhibit moderate to high hydraulic conductivity, and are also relatively homogeneous. Non-homogeneous conditions could cause channelling and uneven treatment that could preclude use, or render implementation of in situ flushing complex. For these reasons, dual porosity mechanisms were not considered in the present experiments and the model as well. As reported in Section 3.2, the interactive comparison of the curves allowed obtaining the required hydrodynamic and hydrodispersive parameters that are reported in (Table 3). The ANN forecast resulted as excellent with a root mean square error (RMSE) lower than 2 %, while the RMSE of the ADE model was 26 %.

4.3 Simulation of pulse chelate-assisted flushing

Once the hydrodynamic and hydrodispersive parameters were obtained for the test column, the model was used to simulate the EDTA pulse–flushing sequence as carried out

Table 3 Hydrodynamic and hydrodispersive parameters

	Hydrodynamic/hydrodispersive parameters	
u_{eff}	Effective velocity (cm s^{-1})	0.000029
D	Dispersion coefficient (cm^2 s^{-1})	0.000032
α	Dispersivity (cm)	1.08
n_{eff}	Effective porosity (–)	0.20

Table 4 Simulation input parameter

Parameters	Phase 1		Phase 2		Phase 3	
	Col 2	Col 3	Col 2	Col 3	Col 2	Col 3
Number of nodes	998	998	998	998	998	998
Column length (cm)	40	40	40	40	40	40
Column diameter (cm)	8	8	8	8	8	8
Effective porosity (−)	0.2	0.2	0.2	0.2	0.2	0.2
Phase simulation time (h)	86	95	48	48	1,944	2,500
Cumulative simulation time (h)	86	95	134	143	2,078	2,643
Water field capacity (cm^3)	879	867	0	0	0	0
Effective velocity (cm s^{-1})	2.78E−04	2.51E−04	0	0	b	b
Dispersion coefficient (cm^2 s^{-1})	3.00E−04	2.71E−04	0	0	c	c
Intrinsic dispersion coefficient (cm)	1.08	1.08			1.15	1.29
Pb initial concentration in soil (mg kg^{-1})	2,900	2,900	a	a	a	a
Reaction kinetic constant (s^{-1})	1.2E−05	1.2E−05	1.2E−05	1.2E−05	1.2E−05	1.2E−05
EDTA input concentration (mg L^{-1})	3,647.95	5,360.26	0	0	0	0
Pulse (chelant/water) time step (h)	86	95	0	0	1,944	2,500

[a] Output of the previous phase

[b] Time-dependent value calculated through Eq. 6

[c] Velocity-related value

in the laboratory experiments. The flux reduction after EDTA injection and reaction (Phase 1 and 2), was modelled through the following equation:

$$v_{POST} = \left(\frac{v_0}{C_{EDTA}}\right)^{\gamma} - R_{EDTA}t \qquad (6)$$

Where:

v_{POST} (cm s^{-1}) is the flow velocity

$(v_0/C_{EDTA})^{\gamma}$ (cm s^{-1})) is the velocity after the EDTA injection, sharply reduced by soil dissolution and depending on chelate dosage (Wu et al. 2004) and contact time (flow velocity

during the chelate application) (Mayes et al. 2000; Zhang et al. 2010). Gamma (γ) is an empirical parameter. Its value was obtained minimizing the scat between observed and simulated velocities for both the two columns.

R_{EDTA} is an empirical coefficient accounting for the slight decrease observed in flow velocity from the start ($t=0$) of the recovery phase.
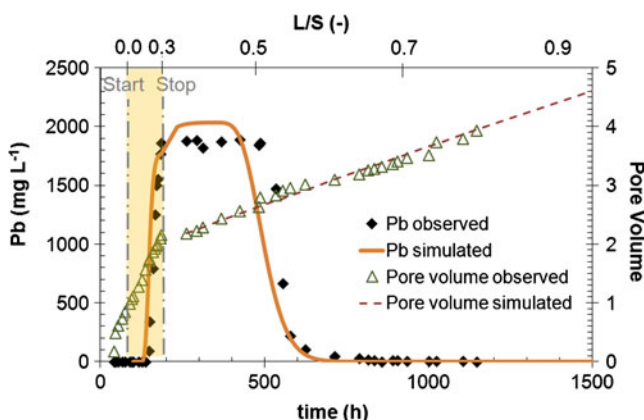
Fig. 4 Pb concentrations in the eluates and flushed pore volumes (observed and simulated) for column 2 (3 mmol kg^{-1} EDTA solution)
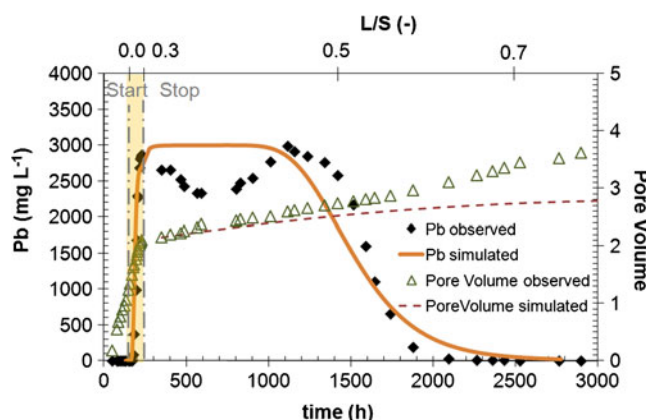
Fig. 5 Pb concentrations in the eluates and flushed pore volumes (observed and simulated) for column 3 (4.3 mmol kg^{-1} EDTA solution)
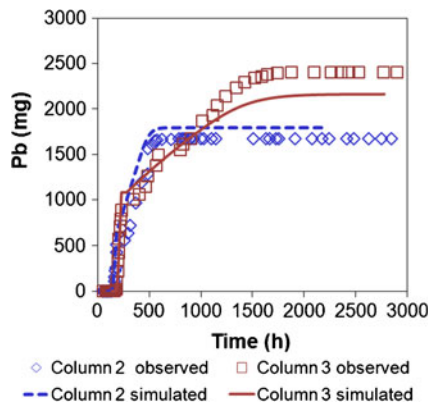
Fig. 6 Cumulated Pb in the eluates and related simulated values

A single kinetic constant value was used for all the three treatment phases and the two EDTA concentrations. This choice was considered acceptable because of the slight variation of the kinetic constant with the EDTA concentration as also observed in other researches (Kedziorek et al. 1998). The kinetic constant K_{eq} (Eq. (4)) value (1.2×10^{-5} s^{-1}), defined through a calibration process with the experimental results, was similar to the one obtained by Kedziorek et al. (1998).

The model input parameters, for the three different flushing steps are reported in Table 4 for columns 2 and 3, respectively. Figures 4 and 5 report observed and simulated Pb concentrations in the eluates and related pore volumes, for columns 2 and 3, respectively. The rising limb of the Pb curves corresponds to the chelant immission phase (phase 1) and the no flux phase (phase 2) whereas the constant and decreasing limbs correspond to the chelant and metal recovery phase (phase 3).

The recovery phase duration depends on flow velocity and it is significantly influenced by permeability reduction due to soil dissolution. Column 3 (4.3 mmol kg^{-1} EDTA solution), characterized by a higher chelating agent concentration (and consequent high permeability reduction), showed a significantly slower recovery phase (2,080 h) if compared with column 2 (3 mmol kg^{-1} EDTA solution) (738 h). The availability of such information can be particularly important when scheduling the different treatments phases of the flushing process.

Results show a good agreement of simulation outputs with experimental data (see Figs. 4 and 5), confirming the validity of the model assumptions on metals solubilization kinetics.

The efficiency of the model was evaluated through the concurring following results:

1. The congruence of measured and simulated Pb concentrations in the leachates from the columns as reported in Figs. 4 and 5 (for both the columns).
2. The congruence (Fig. 6) of simulated and observed residual Pb concentrations in the soil, after the treatment, at the two investigated depths (for both the columns).
3. The congruence of the total residual Pb as simulated from the model and as calculated from the total Pb columns content by subtracting the measured Pb-eluted amounts (for both the columns).

Table 5 highlights these results. The cumulative extractions of Pb were experimentally found to be 20 % (1,674 mg) and 29 % (2,500 mg) for the EDTA concentrations of 3 and 4.3 mmol/kg of soil, respectively. The model returned a cumulative Pb extraction of 20.6 % (1,720 mg) and 25.9 % (2,160 mg) for the corresponding EDTA concentration, respectively. The total residual Pb was experimentally found to be 80 % (6,678 mg) and 70 % (5,852 mg) for the EDTA concentrations of 3 and 4.3 (mmol/kg of soil) respectively. The model returned a total residual Pb of 79 % (6,612 mg) and 70 % (5,882 mg) for the corresponding EDTA concentration, respectively.

Figures 7, 8 and 9 report the concentration trends of free EDTA, EDTA–Pb complexes and the residual Pb over the columns depth, at the end of each treatment phase.

Figure 7 shows as, by the end of Phase 1, the EDTA progressively reacts, during the percolation, losing its extraction capability with the depth. As a consequence, the metal extraction was more effective in the upper layers. When the higher EDTA dose was used (column 3) an increased extraction capability was observed in the first 30 cm. This was also ascribed to the consequent high reduction in soil permeability that caused higher contact times and improved chelation efficiency in the upper layers.

**Table 5** Comparison between experimental and simulation results for both the two columns

|	Total Pb eluted (mg)		Local residual Pb (mg/kg)				Total residual Pb (mg)	
	Observed	Simulated	Observed		Simulated		Observed	Simulated
			Top	Bottom	Top	Bottom		
Column 2 (EDTA 3)	1,674 (20 %)	1,720 (20.6 %)	1,597 (56 %)	2,274 (79 %)	1,870 (65 %)	2,594 (90 %)	6,678 (80 %)	6,612 (79 %)
Column 3 (EDTA 4.3)	2,500 (29 %)	2,160 (25.9 %)	1,005 (35 %)	2,461 (85 %)	1,306 (45 %)	2,587 (90 %)	5,852 (70 %)	5,822 (70 %)
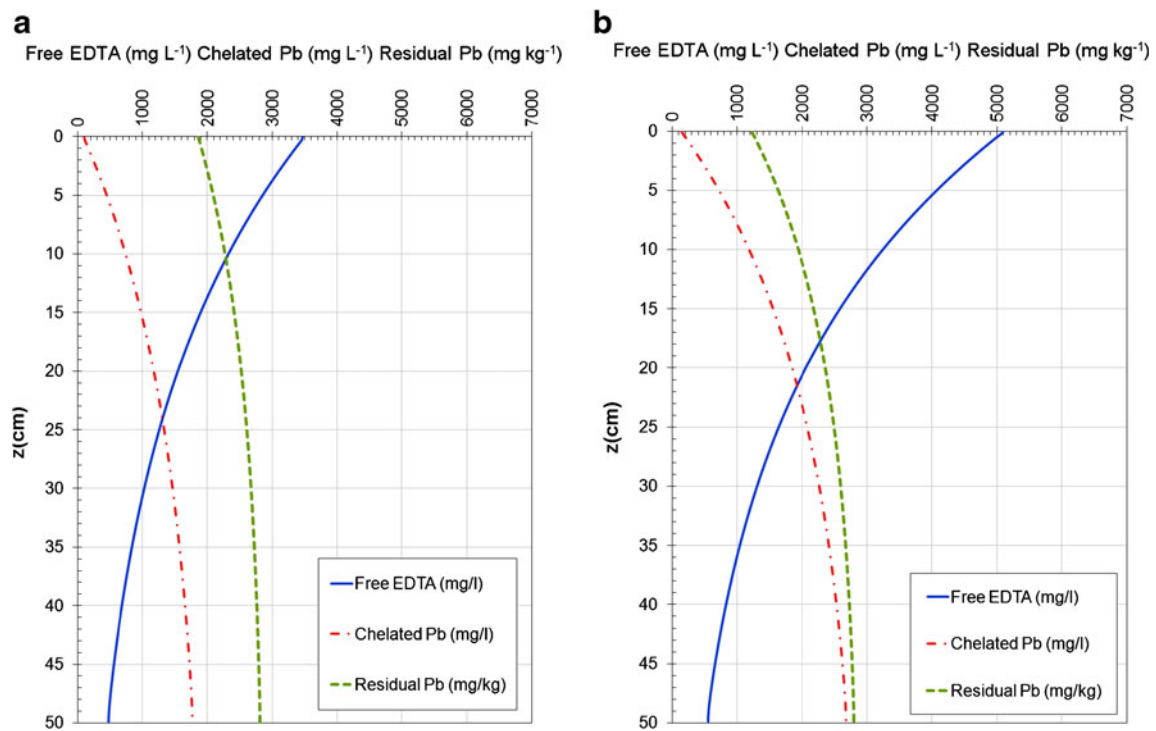
Fig. 7 Result from simulations: free EDTA (milligrammes per litre), chelated Pb (milligrammes per litre) and residual Pb (milligrammes per kilogramme of soil) over the depth by the end of phase 1 (stop of EDTA application) for columns 2 (**a**) and 3 (**b**)

In the second phase, the no-flux condition ensured the chemical equilibrium in all the layers where free EDTA was still available (see Fig. 8).

From the analysis of the residual Pb, over the column depth (end of phase 3, see Fig. 9), the effects in terms of extraction capacity of the chelant pulsed application are
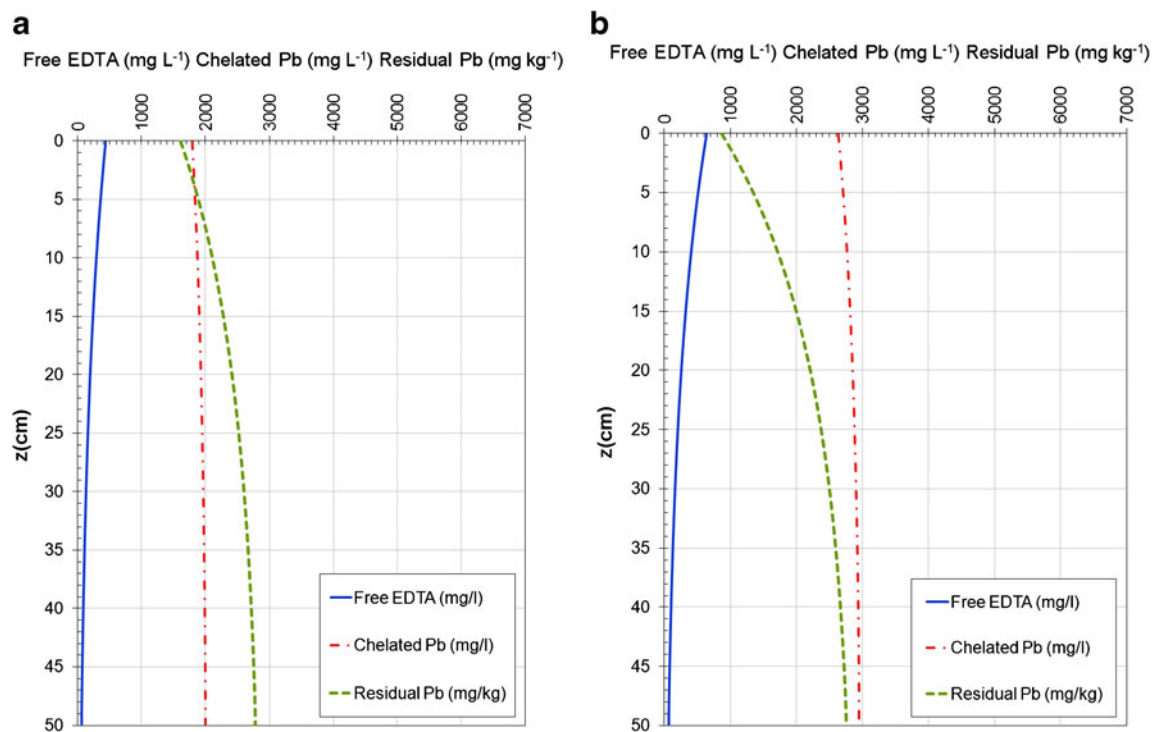
Fig. 8 Result from simulation: free EDTA (milligrammes per litre), chelated Pb (milligrammes per litre) and residual Pb (milligrammes per kilogramme of soil) over the depth by the end of phase 2 (no flux condition) for columns 2 (**a**) and 3 (**b**)
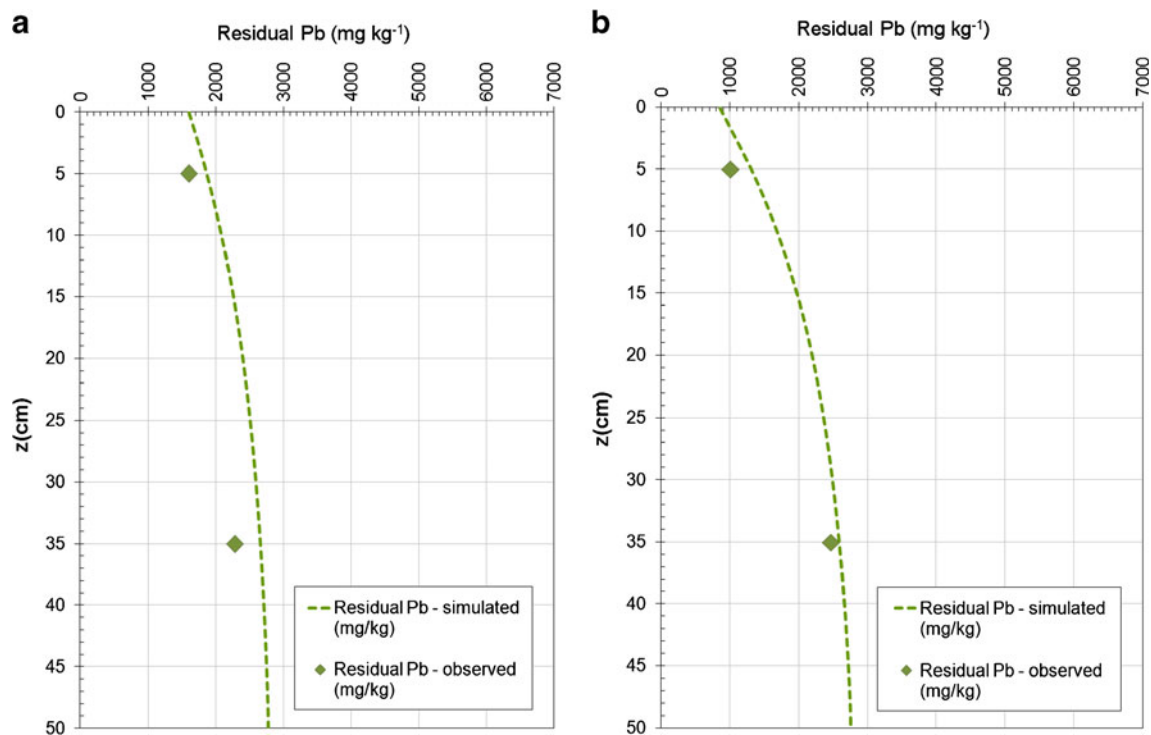
Fig. 9 Result from simulation: free EDTA (milligrammes per litre), chelated Pb (milligrammes per litre) and residual Pb (milligrammes per kilogramme of soil) over the depth by the end of phase 3 (recovery) for columns 2 (**a**) and 3 (**b**)

evident. Specifically the important reduction in extraction ability with depth, also reported by other authors (Hauser et al. 2005; Xia at al. 2009) can be explained with the progressive saturation of EDTA that form complexes with Pb and other metals so becoming less able to extract the remaining Pb as it proceeds towards the lower layers of the soil columns. As a consequence, also the effects of the higher EDTA concentration were noticeable only in the upper layers (25 cm) while residual Pb levels in the depth layers were substantially comparable at the two applied EDTA dosages. If not properly designed, the effect of an increase of chelating agent concentration can thus only improve the treatment effectiveness in the upper layer leaving only slightly modified the contamination in the lower ones.

As a final consideration, it should also be noted as abiotic (ageing) processes change the availability/mobility of residual labile heavy metal species in all leaching treatments and should thus be considered in final remediation effectivity evaluation (Udovic and Lestan 2009).

5 Conclusions

A reactive transport model, accounting for reaction and transport of EDTA, EDTA–Pb chelates and soil permeability reduction, was implemented to simulate a soil pulse–flushing remediation technology. The model uses an artificial neural network for hydrodynamic and hydrodispersive parameters determination while a FDT, applied in combinations with a multi-step numerical integration method, allows to prevent numerical diffusion effects on the solution.

The simulation results show a good fit with the experimental Pb concentration in the eluates and the residual Pb values, over the column depth, confirming the validity of the assumptions (specifically the Pb solubilization kinetics). The assumption of a first-order kinetic and the use of a unique kinetic constant for all the experiments phases, independent from the EDTA concentration, seem to well-approximate EDTA–Pb complexation phenomena.

The variation of the soil physical and chemical properties, after the treatment, may potentially limit the subsequent use of the treated soil. For this reason, the proposed numerical model, taking into account the reduction in soil permeability by dissolution, can be useful to assess the feasibility of the flushing treatment (avoiding soil clogging) and to address the choice of the operating parameters (flow rate, chelating agent dosage and application method). The model, supported by preliminary and careful soil characterization and calibration, could thus represent an effective tool for flushing unit design and planning of in situ or ex situ remediation activities.

On the basis of the present research results, the following protocol is suggested for in situ soil pulse–flushing application:

– field sampling of undisturbed soil columns for laboratory tests, soil characterization and field water capacity determination;

– laboratory tracer test for the determination of hydrodynamic and hydrodispersive parameters;

– laboratory column tests for model calibration and validation

– application of the model to determine the optimal field procedures (chelating agent dosage, duration of each phase and number and frequency of pulsed application);

– field application including: pre-saturation with water, EDTA application (with 5 to 10 cm of head of an EDTA solution) with a volume equal to the soil water field capacity),

– flushing with water and wells (or deep drains) recovery of the flushing solution;

– groundwater and soil continuous monitoring.

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