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Soil Flushing with EDTA Solutions: A Model for Channeled Flow

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ABSTRACT

A 1-D model for the flushing of metal contaminated soils with extracting aqueous solutions is presented. Previous experimental results of the flushing of carbonatic soil contaminated with lead with EDTA solutions showed the formation of channels of preferential flow as well as substantial rebounds in effluent lead concentration after periods of no pumping, indicating an important kinetic limitation for lead removal. This limitation is associated with the presence of a stagnant aqueous phase in addition to the mobile aqueous phase running through the channels. The model assumes an initial homogeneous distribution of lead in the soil, mainly present as small spheres of a solid carbonate which must dissolve. If the spheres are far from the channels, after solution the lead must diffuse through the stagnant aqueous phase until it reaches the channels and is washed out of the column. The model is able to simulate the rebound curves as well as the effluent concentration during the course of the operation. The importance of the way the channels arise is established by sensitivity studies performed for different mechanisms of the solution circulation and the formation of channels. More experimental results are needed to discriminate which of the alternatives studied is operative.

Key Words. Soil clean-up; Heavy metals; Lead; Washing-flushing; EDTA

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INTRODUCTION

Heavy metals occurrence in soil is one of the most important environmental problems due to their high toxicity and persistence. Among them, lead is one of the most significant. It reaches the soil from both nonpoint sources and deposition associated with some activities. The most important nonpoint source has been for many years, and still is in many countries, its use as tetraethyllead in gasoline formulation. For instance, in 1984 in the USA, 39,000 T were emitted to the atmosphere, 90% of which came from gasoline combustion, while the remaining 10% was produced mainly in smelters and residue incinerators (1). In 1983 about 65–85% of world lead emissions to the atmosphere arose from gasoline combustion (2).

Thus, deposition from the atmosphere is the most important source for lead soil contamination. For instance, concentrations above 500 ppm have been found in soil close to high-traffic roads (3). Levels of significance have been detected in agricultural soils (4–6), which may also come from pesticides and fertilizers. Intense lead contamination is associated with inappropriate disposal of some residuals (as automobile batteries, for instance) causing very high local concentrations, up to 76 g/kg of soil (7).

Lead, and heavy metals in general, may be mobilized from soil under certain conditions and percolate to the underlying groundwater, leading to increased environmental problems. Heavy metals are held in soil through several mechanisms, e.g., adsorption, precipitation, ion exchange, and complexation, depending on soil composition and other chemical factors such as pH or redox potential.

Soil texture is significant to *adsorption–desorption* mechanisms (8), which are also related to pH values. *Precipitation* is mainly dependent on pH values and redox potential, associated with the species of the metal, as well as on the relative concentrations of metal and/or anions present which form such insoluble species as carbonates, hydroxides, phosphates, and sulfides. *Cation exchange* is associated with the presence of clays and organic matter, and is also sensitive to pH, with increased retention at high pH values (9). The organic matter may also *complex* the metals. Some studies on the retention of metals by organic matter indicate that, for pH values close to 5, the preference is as follows (10, 11):



Thus, soil composition is a fundamental factor for any of the retention mechanisms indicated above.

Under typical soil environmental conditions, lead is generally not very mobile, unless acid conditions (12) or mobile complexing agents (13) are

present. These conditions may appear at times and mobilize this toxic substance, increasing the hazard associated with the contamination.

All these considerations prove the importance of achieving a better understanding of these complicated processes, which are not only related with the fate of heavy metals in soil, but also to the design of possible technologies that may be used to remediate the contaminated sites, as for instance soil flushing/washing (14–16) and electrokinetic and related remediation techniques (17, 18).

Due to its high capability to complex metals, ethylenediaminetetraacetic acid (EDTA) aqueous solutions have been used for the mobilization of metals from soil (14, 16), and there are some reports on the remediation of sites with lead from automobile battery disposal (15) with this reagent.

We have studied the utilization of EDTA solutions for the removal of lead from a carbonate-rich soil with no significant organic matter content, and in this paper we present a mathematical model which includes the formation of preferential flow channels which were observed during the course of the experiments.

EXPERIMENTAL BASIS OF THE MODEL

The characteristics of the soil, the experimental setup, and the results of the washing/flushing studies have been described in detail previously (19, 20). Here we only give the most significant characteristics. Speciation of lead in the contaminated soil was performed by sequential extraction (21), with the results indicated in Table 1. The soil is heavily contaminated and most of the contaminant (about 90%) is present as carbonates (cerussite). The soil was placed in a small glass column and an EDTA solution was pumped through. Elution of lead was found to be directly proportional to EDTA concentration at the beginning of the experiments, but important tailing effects, more evident at higher flow rates, were observed. The formation of channels

TABLE 1
Speciation of Lead in Carbonate-Rich Soil

Fraction	Pb ²⁺ (mg/g)	Pb ²⁺ (%)
Total	49.0	100.00
Exchangeable	3.0 ± 0.26	6.10
Carbonates	44 ± 1.16	90.60
Oxides	1.4 ± 0.06	3.10
Organic	—	—
Residual	0.05 ± 0.01	0.10

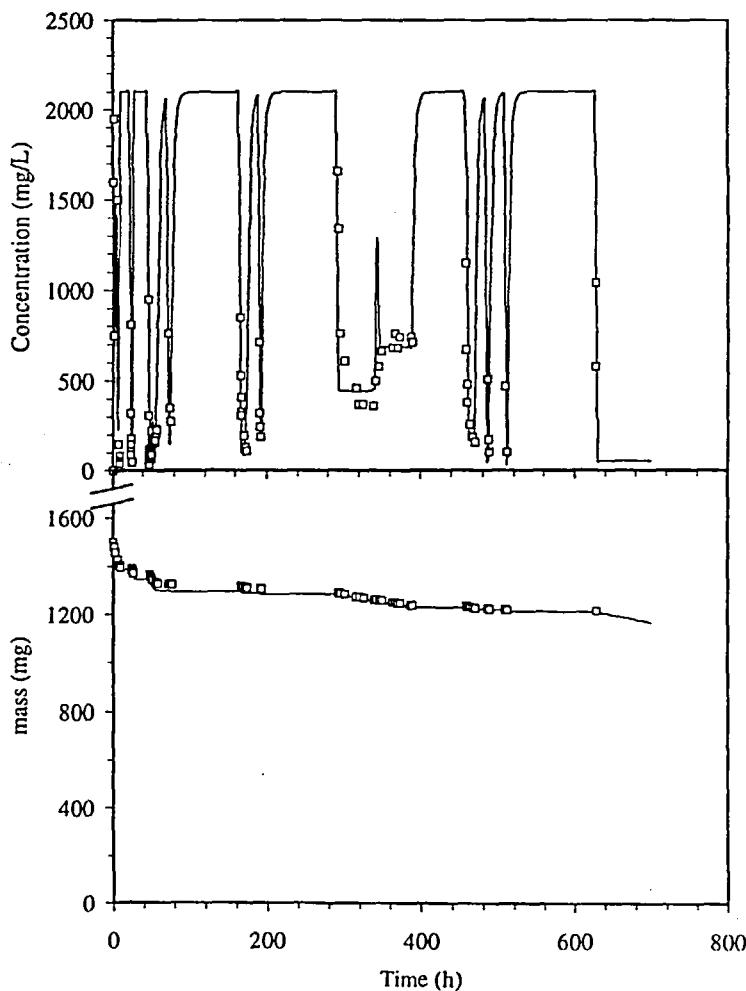


FIG. 1 Experimental and model results for a pulse experiment.

in the flow direction was visible, and pulse operation (pumping and resting consecutively) indicated important rebound effects in the effluent concentration.

Results from one of those tests are presented in Fig. 1, together with the corresponding model simulation. As can be seen, the effluent lead concentration dropped sharply from about 2000 mg/L to less than 50. Then a resting period was initiated, after which the contaminant concentration jumped again

TABLE 2
Default Model Parameters

Total volumetric flow through the column, Q	2.5 mL/h
Volumetric flow per channel, Q_i	0.5 mL/h
Column length, L	2.9 cm
Column radius, R	1.5 cm
Total porosity, θ	0.4
Porosity associated with the mobile water, ν	0.1
Number of divisions along the column length, N	10
Number of annular compartments around each channel, n_k	20
Initial contaminant concentration, C^0	77.1 g/L of soil
Effective diffusivity for the dissolved lead, D_e	2.5×10^{-10} m ² /s
Initial radius of the lead spheres, X_0	50 μ m
Effective solubility of lead in the EDTA solution, C_{sat}	2 g/L
Mass of lead per sphere volume, ρ_{Pb}	5 g/cm ³

to more than 800 mg/L. Note that the point in the figure corresponds to one sample of certain volume and thus it is not exactly the concentration at that point but rather the average concentration of the volume collected. The trend of the curve shows the same evolution every time the pulse operation is repeated. At about 300 hours the rate of pumping was decreased in order to see if the kinetic limitations are not as severe for this new lower rate. As a matter of fact, the concentration remains almost constant at values clearly higher than those observed in the later parts of the previous pumping periods, as could be expected under mass-transfer limited operation. Our model is able to reproduce the decrease of the contaminant concentration during the pumping periods, the rebound of the concentration after the resting periods (of course there are no experimental values for these periods since no samples are drawn from the column), and the stabilization at higher values when low rate pumping is performed. The parameters of the model in this run are those given in Table 2.

The model requires a substantial number of parameters, so sensitivity analysis to determine which are more significant to clean-up efficiency—high recovery yields, short operation time, and high effluent concentration—is of great interest. Those parameters which can be modified during actual operation are of particular interest.

THE MODEL

The following mathematical model is able to reproduce the most significant observations made during the lab experiments; these are extensive tailing

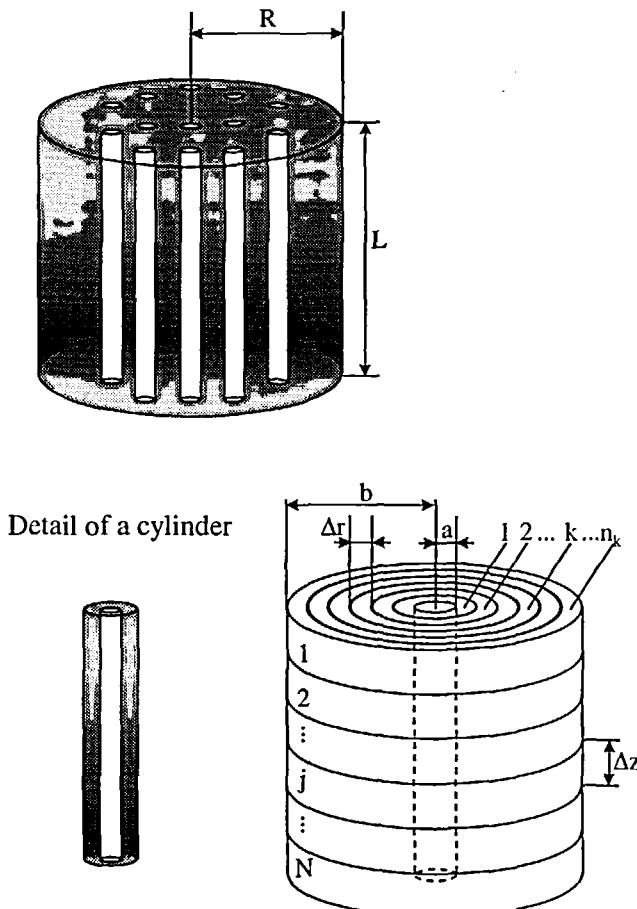


FIG. 2 Column representation for the channeled flow model.

effects during continuous operation and rebound of effluent concentration after periods without pumping.

The column is represented in Fig. 2. The model assumes that preferential flow channels are developed in the column as the EDTA solution is pumped through it, while other regions in the column are wetted by a stagnant aqueous phase. Thus, the contaminant localized in these regions of immobile aqueous phase will have to dissolve and then diffuse to the mobile aqueous phase running through the nearest channel. The contaminant which is initially present in the channels is gradually dissolved and flushed out with the aqueous stream. It is also assumed that the ratio of mobile to total water remains constant during the course of remediation.

Other simplifying assumptions are that the contaminant is initially present as small solid spheres of equal radius and homogeneously distributed in the column. The radius of the spheres will decrease during the course of the remediation, as they are gradually dissolved. All channels are assumed to be of equal radius and permeability and are placed parallel at regular distances. Around each channel there is a cylinder wetted by the stagnant aqueous phase through which the diffusion of EDTA from the flushing solution and the diffusion of the dissolved contaminant should occur. All the mass transport processes taking place in the immobile aqueous phase are assumed to be represented, using an effective diffusion coefficient, by the diffusion of the complexed metal which is considered the rate-limiting phenomena. Thus, neither the diffusion of EDTA into the channel nor the reaction kinetics between EDTA and lead are included in this first version of the model.

The number of channels, n , is given by

$$n = Q/Q_i \quad (1)$$

where Q is the volumetric flow through the column and Q_i is the volumetric flow in each channel. See Fig. 2 and Table 2 for the meaning of the model parameters.

The volume of the cylinders is associated to the total volume (V) of the column by

$$n(\pi b^2)L = V = \pi R^2 L \quad (2)$$

where b is the radius of the cylinder associated with each channel, R is the column radius, and L is the length of both the column and the channels. Thus, there are small regions of the soil out of the cylinders with a volume equal to other regions shared by two contiguous cylinders, and the model assumes that the diffusion phenomena are described with enough approximation.

The radius b can then be calculated:

$$b = \frac{R}{n^{1/2}} = R \left(\frac{Q_i}{Q} \right)^{1/2} \quad (3)$$

Thus, for a given value of the volumetric flow, Q , and an assumed value of the volumetric flow through each channel, Q_i , the number of channels and the radius of each cylinder are determined.

Let θ be the total porosity (volume of water/total volume) and ν the porosity associated with the mobile aqueous phase (volume of mobile water/total volume), so the radius of the mobile part of each cylinder (radius of the channel), a , can be calculated from

$$\pi R^2 L \nu = n \pi a^2 L \theta \quad (4)$$

Once the dimensions of the channel and the region associated with each channel are defined, for numerical integration the length of the column, L ,

is divided into N cylinders of radius b and length $\Delta z = L/N$, and each cylinder is divided into a number (n_k) of concentric annular volume elements—AVEs—of thickness Δr , so that

$$\Delta r = \frac{(b - a)}{n_k} \quad (5)$$

and the internal radius of the k th AVE will be given by

$$r_k = a + (k - 1)\Delta r \quad (6)$$

The volume (v) of the stagnant water in each AVE is

$$\Delta v_k = \pi \Delta z (r_{k+1}^2 - r_k^2) \theta = \pi \Delta z (2a\Delta r + (2k - 1)(\Delta r)^2) \theta \quad (7)$$

Let us assume that, before the EDTA solution is introduced at $t = 0$, all the lead in the soil is solid, and the mass of lead in each AVE, $m_{j,k}^0$, and in each channel, m_j^0 , can be calculated as

$$m_{j,k}^0 = C^0 \Delta v_k / \theta \quad (8)$$

$$m_j^0 = C^0 \pi a^2 \Delta z \quad (9)$$

where C^0 is the initial lead concentration in the soil (mass of lead/total volume of soil).

Now we can obtain the system evolution with time from the corresponding mass balances.

Mass Balances at the Channels

This includes advection along the channel, diffusion from the stagnant region of the cylinders, and solution of the solid phase already in the channel.

Advection Transport

$$n\pi a^2 \theta \Delta z \left(\frac{\partial C_j^M}{\partial t} \right)_{\text{ADV}} = Q(C_{j-1}^M - C_j^M) \quad (10)$$

where C_j^M is the lead concentration in the mobile aqueous phase of the j th cylinder or channel ($1 \leq j \leq N$) at time t . Note that $C_0^M = 0$ (no lead in the washing solution being fed).

Diffusion from the Innermost AVE in the Cylinder ($k = 1$) into the Channel

$$n\pi a^2 \theta \Delta z \left(\frac{\partial C_j^M}{\partial t} \right)_{\text{DIF}} = D_e n 2\pi a \Delta z \frac{(C_{j,1}^W - C_j^M)}{(\Delta r/2)} \quad (11)$$

where $C_{j,1}^W$ is the lead concentration in the immobile aqueous phase and D_e is the effective diffusivity of lead in the immobile aqueous phase.

Solution of the Solid Contaminant in the Channels

$$n\pi a^2 \theta \Delta z \left(\frac{\partial C_j^M}{\partial t} \right)_{\text{DIS}} = - \frac{dm_j}{dt} \quad (12)$$

where m_j is the mass of lead present as solid in the j th section of each channel.

Total Mass Balance in the Channels

$$\left(\frac{\partial C_j^M}{\partial t} \right) = \frac{1}{(\pi R^2 \nu \Delta z)} \left[Q(C_{j-1}^M - C_j^M) + D_e (n2\pi a \Delta z) \frac{(C_{j,1}^W - C_j^M)}{(\Delta r/2)} - \frac{dm_j}{dt} \right] \quad (13)$$

Balances for the Inner AVEs (from $k = 2$ to $k = n_k - 1$)

These balances account for diffusion between the AVEs and dissolution of the solid contaminant:

Diffusion between Inner AVEs

$$\Delta v_k \left(\frac{\partial C_{j,k}^W}{\partial t} \right)_{\text{DIF}} = D_e 2\pi n \Delta z \left[\left(\frac{r_k}{\Delta r} \right) (C_{j,k-1}^W - C_{j,k}^W) + \left(\frac{r_{k+1}}{\Delta r} \right) (C_{j,k+1}^W - C_{j,k}^W) \right] \quad (14)$$

Dissolution of Solid Contaminant

$$\Delta v_k \left(\frac{\partial C_{j,k}^W}{\partial t} \right)_{\text{DIS}} = - \frac{dm_{j,k}}{dt} \quad (15)$$

Total Mass Balance at the Inner Volume Elements

$$\left(\frac{\partial C_{j,k}^W}{\partial t} \right) = \frac{1}{\Delta v_k} \left[D_e 2\pi n \Delta z \left[\left(\frac{r_k}{\Delta r} \right) (C_{j,k-1}^W - C_{j,k}^W) + \left(\frac{r_{k+1}}{\Delta r} \right) (C_{j,k+1}^W - C_{j,k}^W) \right] - \frac{dm_{j,k}}{dt} \right] \quad (16)$$

Mass Balance for the Outermost Volume Element in the Cylinder ($k = n_k$)

This AVE is adjacent to other cylinders with the same contaminant distribution, so there is no mass transport between two cylinders. Therefore only diffusion toward the $(n_k - 1)$ AVE and solution of the solid contaminant should be considered:

$$\left(\frac{\partial C_{j,n_k}^W}{\partial t} \right) = \frac{1}{\Delta v_{n_k}} \left[D_e 2\pi n \Delta z \left[\left(\frac{r_{n_k}}{\Delta r} \right) (C_{j,n_k-1}^W - C_{j,n_k}^W) \right] - \frac{dm_{j,n_k}}{dt} \right] \quad (17)$$

Mass Balance in the Innermost AVE in the Cylinder ($k = 1$)

Here the length for the diffusion from the first AVE to the channel where advection is taking place is one-half of that between other adjacent AVEs, so the total mass balance is

$$\left(\frac{\partial C_{j,1}^W}{\partial t} \right) = \frac{1}{\Delta v_1} \left[D_e 2\pi n \Delta z \left[\left(\frac{2r_1}{\Delta r} \right) (C_j^M - C_{j,1}^W) + \left(\frac{r_2}{\Delta r} \right) (C_{j,2}^W - C_{j,1}^W) \right] - \frac{dm_{j,1}}{dt} \right] \quad (18)$$

Rate of Solution of the Solid Spheres

We use the convention that for the channels the subindex k is omitted. Then the rate of solution is given by:

$$-\frac{dm_{j,k}}{dt} = -\frac{4\pi D_e x_0 (C_{\text{sat}} - C_{j,k}^W) (m_{j,k}/m_{j,k}^0)^{1/3}}{1 - \left(\frac{x_0}{d} \right) (m_{j,k}/m_{j,k}^0)^{1/3}} \quad (19)$$

where C_{sat} is the effective lead solubility in the EDTA solution and d is the distance between spheres, which is obtained from the model input initial radius of the spheres, x_0 , and initial contaminant concentration, C^0 .

$$N_E \left(\frac{4\pi x_0^3}{3} \right) \rho_{\text{Pb}} = C^0 \Rightarrow N_E = \frac{3C^0}{\rho_{\text{Pb}}(4\pi x_0^3)} \Rightarrow d = (1/N_E)^{1/3} = \left[\frac{\rho_{\text{Pb}}(4\pi x_0^3)}{3C^0} \right]^{1/3} \quad (20)$$

where N_E is the number of spheres of contaminant per volume of soil and ρ_{Pb} (model input) is the density of lead in the spheres, this is, the mass of lead per volume of sphere.

MODEL RESULTS AND DISCUSSION

Default model parameters are listed in Table 2. Column length and radius as well as the total porosity and initial contaminant concentration are those used for our laboratory experiments, and the density of the spheres is close to that of PbCO_3 . The volumetric flow rates are within the range used in the lab experiments.

Once it was clear that mass transfer kinetic limitations can be important, we focused our attention on the way the channels arise and the possible differences in removal efficiency. Thus, sensitivity analysis of the volumetric flow rate was performed under several situations. One can control the volumetric flow over a range under field conditions but we can expect quite different results once the volumetric flow has been established, depending on the number of channels developed, the ratio between mobile and total water, the pore water velocity, and the flow rate per channel.

Obviously these variables are related, but four different extreme situations can be considered which we have explored with the model. These are as follows.

1. The number of channels does not change nor does the ratio of mobile to total water, and changes in the volumetric flow per channel are due exclusively to an increase in the velocity of water in each channel (n and v do not change while Q_i changes) (Fig. 3)
2. The volumetric flow per channel and the ratio of mobile to total water is kept constant while the number of channels and the velocity within each channel are changed (Q_i and v do not change while n changes) (Fig. 4)
3. The velocity within the channels and the number of channels are kept constant while the volumetric flow and the ratio of mobile to total porosity change (n is kept constant while Q_i and v change) (Fig. 5)
4. The volumetric flow per channel and pore velocities are kept constant while the number of channels and the ratio of mobile to total water are changed (Q_i is constant while n and v are changed) (Fig. 6)

The four curves represent results for the same set of volumetric flows, with that of minimum value corresponding to identical conditions for all of them (default values). Other values of the volumetric flow are obtained by the variations indicated for each case. In all the figures three different stages may be distinguished along the remediation: **(A)** stage of advective control, **(B)** stage of diffusive control with almost constant effluent concentration, and **(C)** stage of diffusive control with decreasing effluent concentration. The three stages give effluent concentration versus time curves with the characteristic chair-shape similar to those obtained for simulation of soil vapor extraction (22) under conditions of diffusive control.

The first stage **(A)** is characterized by a high and almost constant value of the effluent concentration, close to that of saturation. The rate of lead removal from soil is therefore almost constant, as can be seen in the corresponding curves of remaining lead mass versus time with linear regions of slope proportional to the volumetric flow rate of the flushing solution.

At the beginning of the second stage, (B), the effluent concentration shows a sharp decrease down to a value where the rates of diffusive transport to the mobile aqueous phase and advective removal are similar. Therefore, after this sharp decrease the concentration remains almost constant, with a slight decrease with time, which corresponds to a zone of slight curvature in the mass-time representation. The rate of lead removal is slower in this stage and is almost independent of the volumetric flow rate.

At the third stage of the remediation, (C), the effluent concentration decreases with time, but it is now following a linear trend, which result in a decreasing removal rate, with a logarithmic curve with a zero asymptote..

Case 1. Pore Velocity and Flow per Channel

When changes in the volumetric flow are due to changes in the pore velocity of water along the channel, calculated by Eq. (21), without affecting the number or the size of the channels, increases of the volumetric flow gives greater probability for the control of the diffusive transport of the contaminant to the mobile aqueous phase of the system (Fig. 3):

$$V_i = \left(\frac{Q}{n\pi a^2 \theta} \right) = \left(\frac{Q}{\pi R^2 v} \right) \quad (21)$$

This can be observed in Fig. 3 where increases in the volumetric flow result in a decrease in the advective control period (A). The mass-time curve corresponding to this first stage indicates that the mass of lead remaining in the column is similar for the four runs, so the advective control period may be associated with the period of time required to dissolve the contaminant within the channels rather than to diffusive transport processes.

Once this period is over the effluent concentration goes down to values which are smaller for the higher velocities, indicating control during this stage by diffusive transport from the immobile to the mobile aqueous phase. Furthermore, observation of the mass-time curve shows that the four runs have similar slopes during stage (B), or in other words, the rates of remediation are about the same during this period. Therefore, little or no advantage in the cleanup time can be achieved from higher volumetric flow rates during stage (B). This effect becomes more evident as the volumetric flow is increased, and it results in very similar cleanup times for the two runs with higher values of V_i .

At the third stage, (C), where the effluent concentration decreases following a linear trend, slopes are very similar for the four runs. (The steps of the curves are due to numerical integration, with one step for each division along the flow direction.) Again, an increase of the volumetric flow does not lead to higher removal rates during this stage.

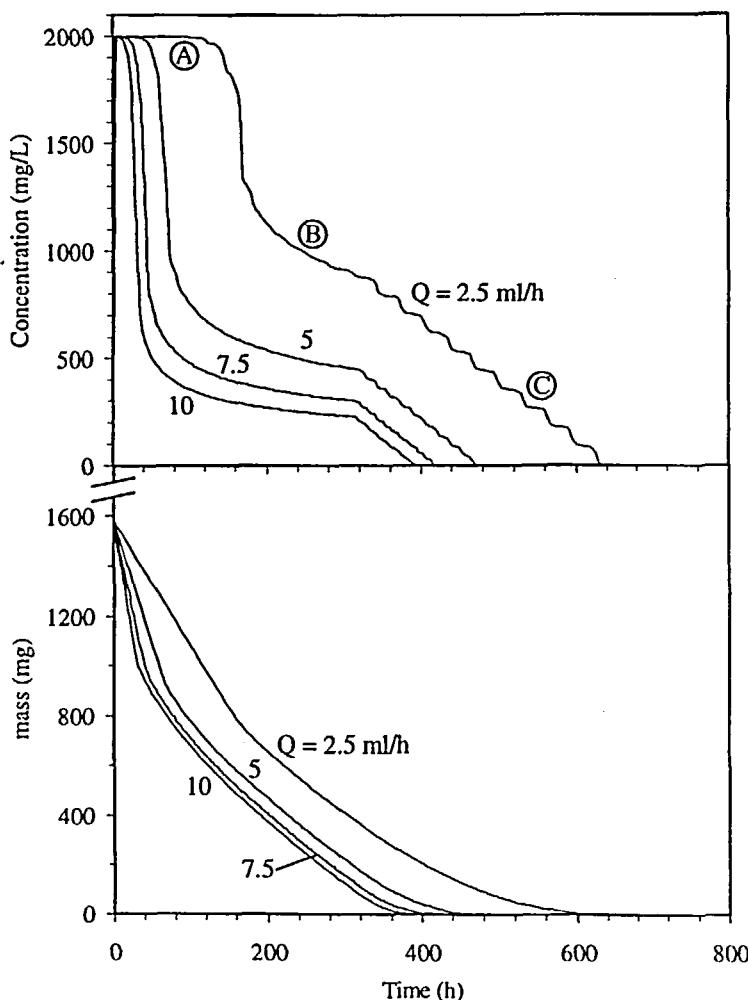


FIG. 3 Model results for different flow rates for the same number ($n = 5$) of channels and mobile-to-total-water ratio ($v/\theta = 0.25$), and different flows per channel (from left to right $Q_i = 2.0, 1.5, 1.0$, and 0.5 mL/h) and pore velocities (as obtained from Eq. 21).

Thus, if the system obeys the regime postulated for these runs (an increase in the volumetric flow results in higher velocities in each channel without increasing the number or the size of the channels), little or no advantage will be obtained from higher volumetric flow rates, and the removal rate will be controlled by the mass transfer processes.

Case 2. Number of Channels and Pore Velocity

If an increase in the volumetric flow rate results in an increase of the number of channels without changes in the mobile to total water ratio or in the volumetric flow per channel, as postulated in the runs presented in Fig. 4, a decrease in the duration of the first stage, t_{Q} , is observed, similar to that seen in Case 1, so that $Qt_{\text{Q}} = \text{constant}$, and t_{Q} can be interpreted as the time required to remove the contaminant initially present within the channels, which is the same in both cases for all the runs.

Observation of the concentration curves during stage ④ shows that the duration of this stage decreases with increases in the volumetric flow, and the effluent concentrations after this stage are very similar for all the runs, which is clearly different from our observations for Case 1. Now an increase of the volumetric flow results in increases of not only the advective but also of diffusive transport due to decreases in the distance for diffusion caused by the larger number of channels.

This increase of diffusive transport with volumetric flow rate is also observed during stage ⑤, where the concentration decreases following a linear trend but with higher negative slopes for runs with higher volumetric flow rates.

As a result, if the removal takes place under conditions similar to those postulated for Case 2, the remediation will be controlled by diffusive transport for most of the time, but the consequences of using higher volumetric flow rates are clearly more positive than for Case 1, and one can achieve the remediation requirements sooner if the volumetric flow rate is increased. Furthermore, the total volume of flushing solution (Qt) is very similar, so the average concentrations must also be similar for the four runs, which is a situation typical of local equilibrium models and not of those cases with control by diffusive transport.

Case 3. Flow per Channel and Mobile to Total Water Ratio

Here higher values of total flow rate result in proportional increases of the flow per channel without changes in the number of channels nor in the pore velocity, and they are due to wider channels (width of channels, a , is related to v and θ through Eq. 22):

$$\left(\frac{a}{R}\right)^2 = \frac{v}{n\theta} \quad (22)$$

Therefore, Case 3 postulates a decrease in the distance between channels as the flow increases, as in Case 2, but this time with a constant value for the number of channels. Results are presented in Fig. 5.

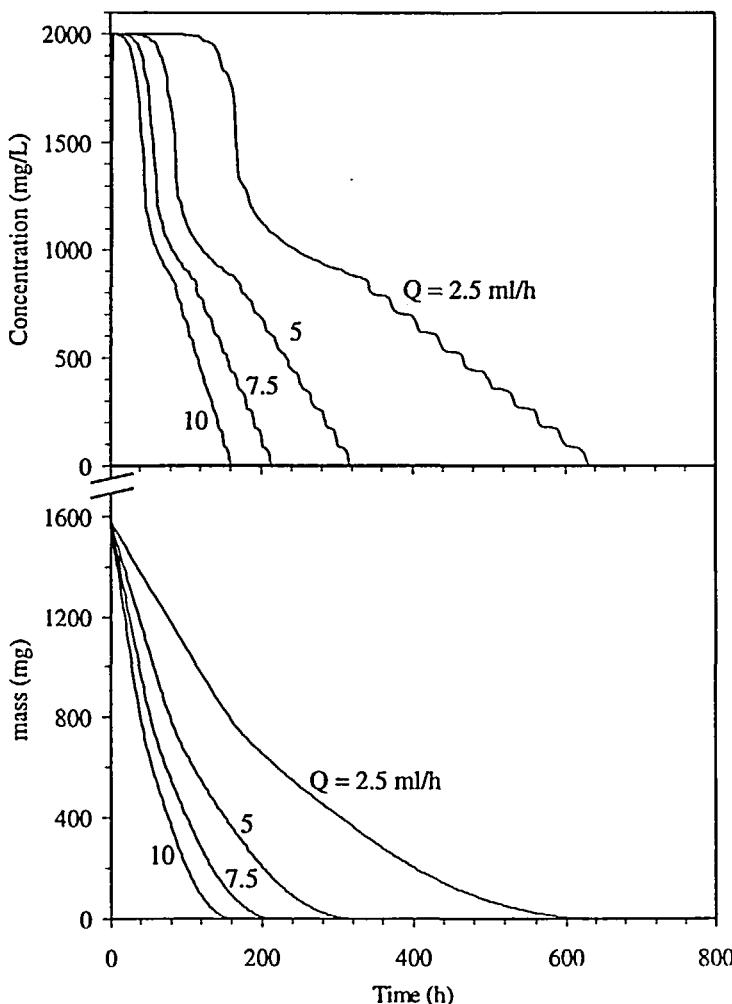


FIG. 4 Model results for different flow rates for the same flow per channel ($Q_i = 0.5 \text{ mL/h}$) and mobile-to-total-water ratio ($v/\theta = 0.25$), and different number of channels (from left to right $n = 20, 15, 10$, and 5) and pore velocities (as obtained from Eq. 21).

Since stage ④ takes place while there is contaminant in the solid phase within the channels, and the size of the channels increases now with the volumetric flow, the amount of contaminant removed during this stage is directly proportional to the flow. Of course the removal efficiency during

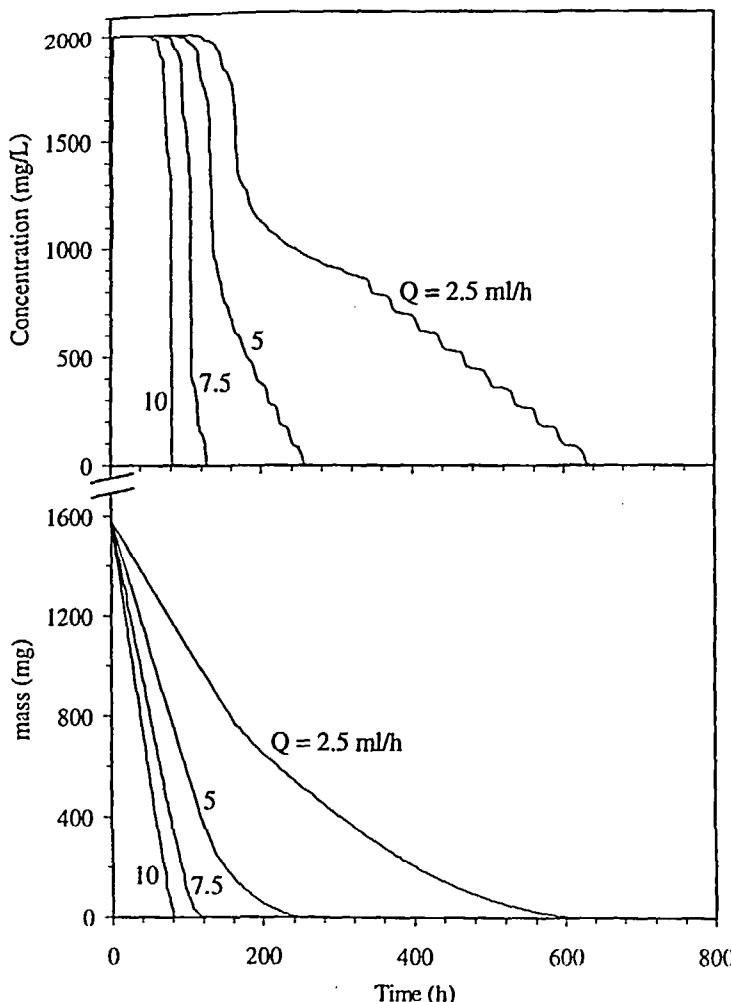


FIG. 5 Model results for different flow rates for the same number of channels ($n = 5$) and pore velocities, and different flows per channel (from left to right $Q_i = 2.0, 1.5, 1.0$, and 0.5 mL/h) and mobile-to-total-water ratios (from left to right $v/\theta = 1.0, 0.75, 0.5$, and 0.25).

this stage is optimum (concentration close to saturation conditions), so the longer it lasts, the better the overall results will be.

The relative importance of the other stages, (B) and (C), which take account of the diffusive transport limitations, diminishes as the flow rate increases, not only because there is less contaminant in the column once stage (A) is

over, but also because the distance for diffusion decreases, down to a zero value when $v = 0$, which occurs when the flow rate is increased with respect to the default values by

$$(Q)_{\max, \text{Case 3}} = \left(\frac{Q\theta}{v} \right)_{\text{default}} \quad (23)$$

For our default values all the water will be mobile for a volumetric flow of 10 mL/h, which is the highest value used in the set of four runs. Thus, for this run, stages (B) and (C) do not occur.

The results are even more optimistic than those for Case 2, for which the volume of the flushing solution and the mean value of the effluent contaminant concentration were quite similar for the four runs. If for field conditions the system approaches to the postulates of Case 3, then the higher the volumetric flow, the lower the volume of flushing solution required to reach the remediation requirements, and the higher the mean value of the effluent contaminant concentration, which is exactly opposite from the conclusion one usually obtains when dealing with a remediation technique which may be controlled by diffusive transport.

Case 4. Number of Channels and Mobile to Total Water Ratio

As in Case 3, the ratio of mobile to total water changes with the volumetric flow, but in this case, instead of a constant number of channels the size of which increases as the flow rate increases, we have postulated that the size of each channel does not change with the flow rate, but that new channels arise as the flow increases. Results are presented in Fig. 6.

The effects during stage (A) are similar to those of Case 3; that is, the amount of contaminant removed during stage (A) increases with the volumetric flow rate, and stages (B) and (C) become of minor relevance down to a value of the volumetric flow rate for which there is no immobile water. Therefore the results for the run for maximum flow rate (10 mL/h) are equal for both runs and are omitted in Fig. 6.

Nevertheless, some differences can be observed between Cases 3 and 4 if one compares the results obtained for the run corresponding to 5 mL/h (second from the right in Fig. 5 and 6). Stage (A) is the same for both cases, but stages (B) and (C) result in lower contaminant concentration for Case 3 because the length for diffusion (related to the distance between channels) is larger when the remediation is represented by wider channels than when a larger number of channels is used to represent increases of the volumetric flow. Thus, Case 4 gives the most optimistic situation among the four considered.

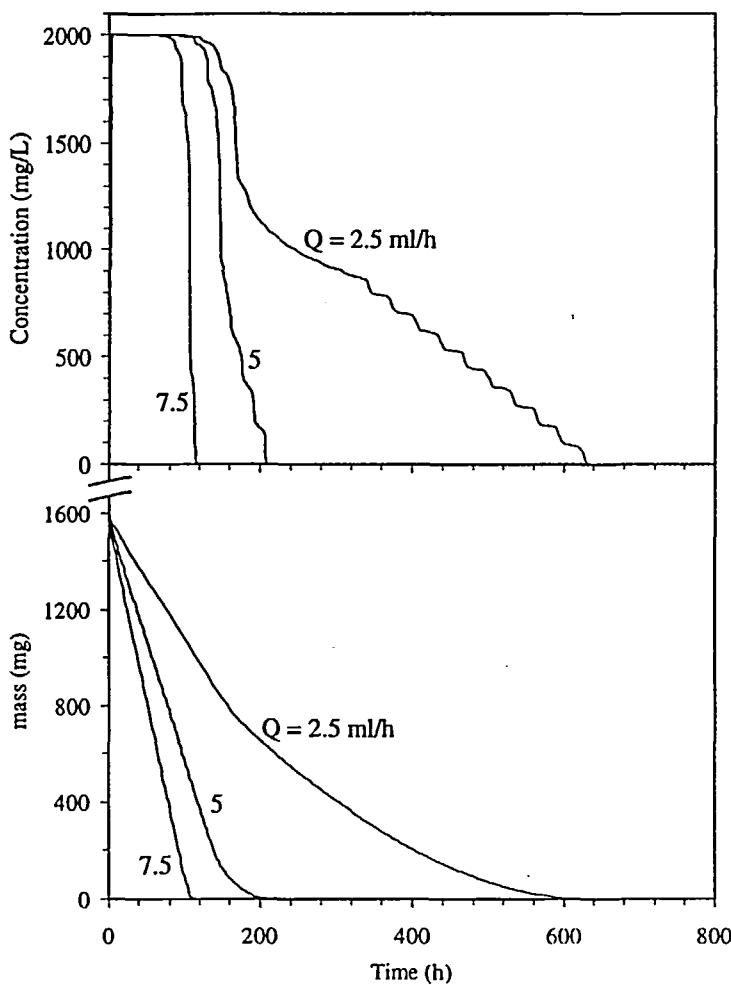


FIG. 6 Model results for different flow rates for the same velocities and volumetric flow rate per channel ($Q_i = 0.5 \text{ mL/h}$), and different numbers of channels (from left to right $n = 15, 10$, and 5) and mobile-to-total-water ratios ($v/\theta = 0.75, 0.50$, and 0.25).

CONCLUSIONS

A model is presented which is able to simulate the most significant phenomena observed during lab experiments presented in previous work. This model considers the development of channels of preferential flow surrounded by

regions with an immobile aqueous phase. These channels were observed, but there is no information on how they develop. The model, which is able to reproduce the most important phenomena observed in the experiments, is used to explore the influence of the way these channels arise over the system efficiency to determine if further experiments are needed.

Four extreme situations are considered. They represent the effects of changes in volumetric flow through the column, to see if important differences arise between these four cases. Model results show a wide range of removal efficiencies for the four cases considered, so further research to elucidate which of the four cases best represents the processes taking place, or even if new considerations (such as, for instance, changes in channel formation during operation) should be introduced, for better accuracy of the models.

Actually, our previous experiments in this direction show that different results are obtained if specific flow rate is established from the beginning of a experiment or if this value is reached slowly starting with low flow rates which are then increased up to the final flow rate.

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REFERENCES

1. C. C. Travis and S. T. Hester, "Global Chemical Pollution," *Environ. Sci. Technol.*, 25, 814-819 (1991).
2. J. O. Nriagu and J. M. Pacyna, "Quantitative Assessment of World Wide Contamination of Air, Water and Soils by Trace Metals," *Nature*, 333, 134-139 (1988).
3. J. F. Lagerwerff and A. V. Specht, "Contamination of Roadside Soil and Vegetation with Cadmium, Nickel, Lead and Zinc," *Environ. Sci. Technol.*, 4, 583 (1970).
4. M. Hutton and C. Symon "The Quantities of Cadmium, Lead, Mercury and Arsenic Entering the U.K. Environment from Human Activities" *Sci. Total Environ.*, 57, 129 (1986).
5. K. C. Jones, J. Walsh, and A. E. Johnston, "Lead in Vegetation since the Mid-1960s at a Semi-Rural Site in the U.K.," in *International Conference on Heavy Metals in the Environment, Vol. II* (J. P. Vernet, Ed.), CEP Consultants, Geneva, Switzerland, 1989, p. 497.
6. K. C. Jones and A. E. Johnston, "Significance of Atmospheric Inputs of Lead to Grassland at One Site in the United Kingdom since 1860," *Environ. Sci. Technol.*, 25(6), 1174-1178 (1991).
7. J. L. Hessling, M. P. Esposito, R. P. Traver, and R. H. Snow "Results of Bench-Scale Research Efforts to Wash Contaminated Soils at Battery-Recycling Facilities," in *Metal Speciation, Separation and Recovery, Vol. II*, Lewis Publishers, Chelsea, MI, 1990, pp. 497-514.
8. M. H. Bates, "Fate and Transport of Heavy Metals," in *Proceeding of a Seminar on Ground Water Quality*, University of Oklahoma, Norman, OK, 1980, pp. 213-229.

9. H. L. Bohn, B. L. McNeal, and G. A. O'Conner, *Soil Chemistry*, Wiley, New York, NY, 1979.
10. B. E. Reed and S. R. Cline, "Retention and Release of Lead by Very Fine Sandy Loam. 1. Isotherm Modeling," *Sep. Sci. Technol.*, 29(12) 1529–1551 (1994).
11. L. J. Evans, "Chemistry of Metal Retention by Soils," *Environ. Sci. Technol.*, 23, 1046 (1989).
12. S. S. Jorgensen and M. Willens, "The Fate of Lead in Soils: Lead Originating from Roofs of Ancient Churches," *Ambio*, 16, 16–19 (1987).
13. F. J. Stevenson and L. F. Welch, "Migration of Applied Lead in a Field Soil," *Environ. Sci. Technol.*, 13, 1255–1259 (1979).
14. W. F. Pickering, "Ore," *Geol. Rev.*, 1, 83 (1986).
15. G. A. Brown and H. A. Elliott, "Influence of Electrolysis on EDTA Extraction of Pb from Polluted Soil," *Water, Air Soil Pollut.*, 62(1–2), 157–165 (1992).
16. W. D. Ellis, T. R. Fogg, and A. N. Taturi, *12th Annual Research Symposium on Land Disposal Remedial Action. Incineration and Treatment of Hazardous Waste*, Hazardous Waste Engineering Research Laboratory, US EPA, 1986.
17. R.C. Sims, "Soil Remediation Techniques at Uncontrolled Hazardous-Waste Sites. A Critical Review," *J. Air Waste Manage. Assoc.*, 40, 704–732 (1990).
18. J. W. Assink, "Physico-Chemical Treatment Methods for Soil Remediation," in *Contaminated Soil '88*, Kluwer Academic Publishers, Dordrecht, Holland, 1988.
19. R. A. García-Delgado, F. García-Herruzo, J. M. Rodríguez-Maroto, C. Gómez-Lahoz, and C. Castellón "Lead Mobilization from a Clayey Soil in Relation to Carbonate Content," *J. Environ. Sci. Health, A31*(9), 2087–2097 (1996).
20. R. A. García-Delgado, F. García-Herruzo, J. M. Rodríguez-Maroto, and C. Vereda, "Influence of Soil Carbonates in Lead Fixation," *Ibid., A31*(9), 2099–2109 (1996).
21. A. Tessier, P. G. C. Campbell, and M. Bisson, "Sequential Extraction Procedure for the Separation of Particulate Trace Metals," *Anal. Chem.*, 51, 844 (1979).
22. C. Gómez-Lahoz, J. M. Rodríguez-Maroto, and D. J. Wilson. "Soil Cleanup by In Situ Aeration. XVII. Field Scale Model with Distributed Diffusion," *Sep. Sci. Technol.*, 29, 1367 (1994).

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