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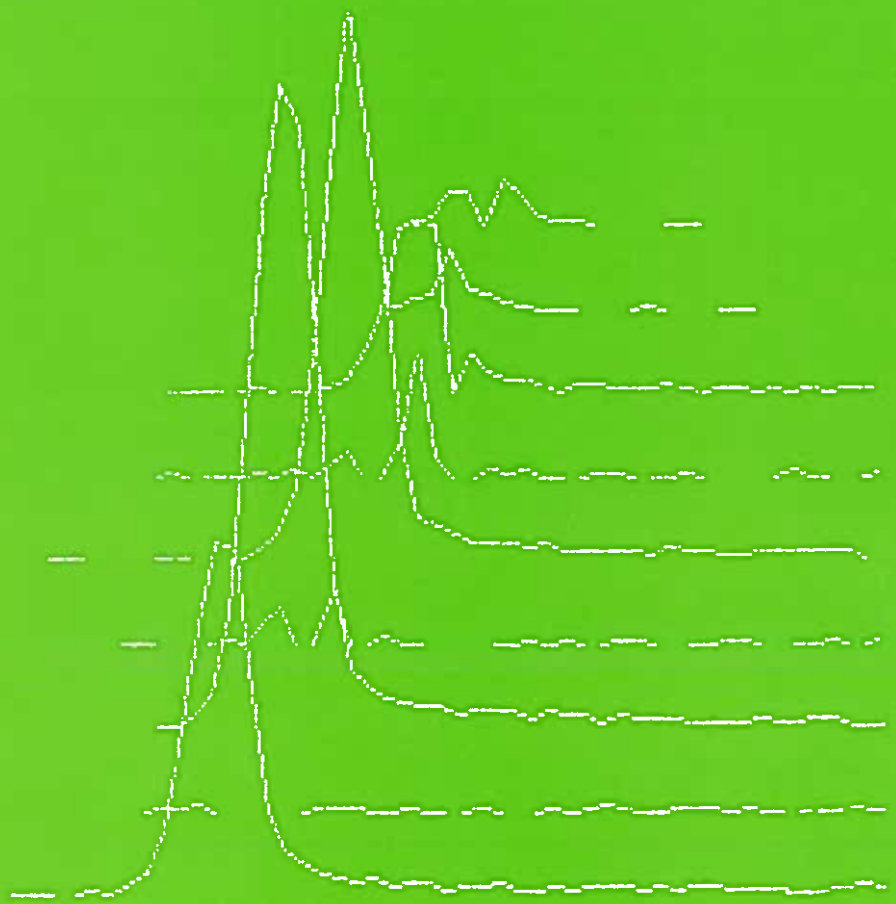

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Transport and Distribution in Complex Systems

Influence of Chemical and Physicochemical Reactions on the Migration of Cobalt in the Saturated Zone

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Data sheet

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Summary

The fate of pollutants in the terrestrial environment may be strongly affected by the operation of chemical as well as physico-chemical reactions such as sorption/desorption, precipitation/dissolution, redox equilibria, complex- or colloid formation. The report addresses the importance of chemical and physico-chemical processes in the migration of pollutants, cobalt being used as an illustrative example. The processes involved in the study include dispersion, convection with the movement of interstitial water, retention by sorption in or on the solid phase and homogeneous chemical reactions of 1st and higher order in the aqueous phase. The report demonstrates the influence of chemical and physico-chemical reactions on the migration behavior of selected species including cobalt and naturally occurring organics such as fulvic acids as well as the influence of non-equilibrium sorption and sorption kinetics.

Resumé

Skæbnen af forurenende stoffer i det terrestriske miljø vil være afhængigt af kemiske og fysisk-kemiske reaktioner som sorption/desorption, udfældning/opløsning, redox ligevægte, komplex- og/eller kolloiddannelse. Rapporten behandler betydningen af kemiske og fysisk-kemiske processer på spredningen af forurenende stoffer, med cobolt som et illustrativt eksempel. Processerne, der er inddraget i denne undersøgelse er dispersion, konvektion i det interstitielle vand, retention via sorption i eller på den faste fase og homogene kemiske reaktioner af 1ste og højere orden i den vandige fase. Rapporten demonstrerer betydningen af kemiske og fysisk-kemiske reaktioner på spredningen af udvalgte forbindelser som cobolt og naturligt forekommende organisk materiale som fulvussyrer samt betydningen af ikke-ligevægtssorption og sorptionskinetik.

1 Introduction

Transport and distribution in the terrestrial environment are crucial parameters in relation to a risk evaluation of pollutants due to their close relationship to the availability of the compounds (*Vermeire et al., 1997*). Following both deliberate and accidental application of pollutants, inorganic or organic to soil surfaces as either diffuse or point sources, the underlying soil column will typically be the only barrier protecting the ground water from impact by these compounds through leaching caused by infiltration of rain water.

Humic substances

Complexation

It is well known that humic substances interact with polyvalent metal ions and organic pollutants thereby altering the migration and sorption properties of the ions and pollutants (*Carlsen, 1989, 1992; Randall et al., 1994; 1996*). Thus, many studies have investigated the complexation of metals (*e.g. Buffle, 1980; Buffle et al., 1980; Sposito et al., 1979, Dharmavaniz and van den Berg, 1983; Carlsen et al., 1992; Warwick et al., 1988*) and actinides (*Nelson et al., 1986; Nash et al., 1981; Kim, 1986; Maes et al., 1991; Moulin et al., 1991; Czerwinski et al., 1996*) with these humic material and field studies (*Champ and Robertson, 1986*) have shown that these pollutants have migrated further distances from the source of pollution than can be explained by considering the inorganic speciation of the metals alone.

Mineral surfaces

Also the interaction between humic substances and mineral surfaces may play a crucial role in determining the fate of pollutants in e.g. the soil/ground water system due to significant changes in surface characteristics as a consequence of the surface coating with organic material (*Haas and Horowitz, 1986; Keoleian and Curl, 1989; Takahashi et al., 1996; Kretzschmar et al., 1997*).

Effective dispersion

Pollutants in the terrestrial environment are typically subject to a variety of physico-chemical reactions, such as sorption/desorption and precipitation/-dissolution (*Carlsen, 1985; 1992; Carlsen et al., 1986; 1987*). These parameters are typically characterized by a single 'effective' dispersion coefficient in studies modeling transport behaviour (*Carlsen et al., 1987; 1989*). However, other processes such as chemical and microbial degradation, formation of micelles and/or associates as well as complexation reaction involving naturally occurring organic matter may significantly influence and eventually control the transport and distribution of xenobiotics in the terrestrial environment (*Carlsen, 1989; 1992; Carlsen et al., 1997*). Furthermore, sorption as well as dissolution kinetics can be expected to play a crucial role. The combined effect of these processes can be rationalized as 'chemical dispersion' which will appear as an additional term in the transport equation (*vide infra*) (*Carlsen et al., 1987*).

The present study aims at elucidating the above using the migration of cobalt in the saturated zone in the presence of humic material as an illustrative example. For this purpose a laboratory column system (*Higgo et al., 1993a*) was selected. The migration of cobalt are modelled using the COLUMN3 computer code (*Bo and Carlsen, unpub*).

The COLUMN3 computer code is a completely rewritten version (for Macintosh computers and PC) of the original COLUMN program (*Nielsen et al., 1985*) using a combination of LabView for the user interface and C++ for solving the transport equation. The COLUMN code is developed to model and predict transport, distribution and transformation of chemical compounds in saturated, porous media taking both sorption as well as chemical and physico-chemical reactions into account. Thus, in contrast to most transport codes, the COLUMN code is designed to handle not only dispersion and convection with the movement of interstitial water, retention phenomena by sorption in or on to the solid phase but also ***any combination of homogeneous chemical reactions of 1st and higher order***. Further the code is capable of handling non-equilibrium sorption processes by inclusion of sorption kinetics for the single species, thus offering an extended possibility theoretically to elucidate the possible influence of 'chemical dispersion' on the transport and distribution of complex mixtures. The model is well developed including a theoretically founded sorption and reaction description. It represents an effective way of testing hypotheses regarding possible sorption and/or process oriented phenomena as the effects of complex mixtures on the transport and distribution of chemical substances in the environment, the eventual aim being to derive Predicted Environmental Concentrations (PEC).

Chemical reactions

PEC

2 The model

COLUMN3 solves the one dimensional transport equation

Migration equation

$$\partial c_i / \partial t = (D_i / R_f(i))\partial^2 c_i / \partial x^2 - (V / R_f(i))\partial c_i / \partial x + F(c_i, t) \qquad (1)$$

where c_i, D_i and $R_f(i)$ are the concentration, the dispersion coefficient and the retention factor of component i, respectively, and V is the water velocity. D_i is estimated based on a conservative tracer (cf. sect. 4). Thus, the two first segments of eqn 1 account for dispersion and convection processes, respectively. Through the term $F(c_i,t)$ possible chemical and physico-chemical reactions can be taken into account.

The chemistry term

$$F(c_i, t) = \frac{\sum_r (k_r n_{i,r} \cdot \prod_i c_i^{n_{i,r}})}{R_f(i)} \qquad (2)$$

where k_i is the rate constant of the ith reaction of reactant r, $n_{i,r}$ the stoichiometric coefficient. The retention factor $R_f(i)$ is related to the dimensionless distribution coefficient $K_D(i)$ through eqn. 3, ε being the porosity of the column.

Retention

$$R_f(i) = 1 + \frac{1-\varepsilon}{\varepsilon} K_D(i) \qquad (3)$$

In addition to the above mentioned parameters such as initial concentrations, dispersion coefficients, retention factors and water velocities for the single species, as well as the rate constants for the involved chemical reactions serve as input parameters for the calculations.

For the calculations, the system is divided into three sub-sections, i.e. repository, column and receiving volume. It is possible to add components in the repository part as well as in the column part in order to simulate the possible concentrations of reactive species at specific locations within the transport route.

Output parameters

The output parameters are time- and space-resolved concentration profiles for the single components within the column and in the receiving volume. Thus, the modelling will elucidate and rationalize the experimentally obtained concentration and elution profiles. The single species may be composed of various components, e.g. they may be in a complexed and non-complexed form, different oxidation states etc. The output facilities of the program enable the user to define overall concentrations of the various species as well as concentrations of the single components both in solution and on the solid phase. This facility is of importance in relation to studies of toxicity, availability, biocon-centration factors (BCF) etc.

Previous versions of the COLUMN code have successfully been applied in studies of the migration behaviour of radionuclides in certain studies on nuclear waste management (*Carlsen et al., 1986; 1987; 1989*).

Saturated zone

The present study serves as part of the validation of the COLUMN3 code for transport studies in the saturated zone. Unsaturated zone water transport phenomena have not been included in the present study. However, it should be possible, without much effort, to modify the COLUMN3 code applying existing knowledge and well established modelling concepts about unsaturated zone water transport to take the latter into account as well.

3 The column experiment

Column experiments were run using the procedure described by *Higgo et al. (1993a)*. A column of length 6.3 cm and diameter 1 cm was packed with sand taken from a glacial sand aquifer and equilibrated with ground water from the same aquifer at a flow rate of 0.063 m/min. To determine the column conditions 2.35 ml of Cl-36 spiked ground water was injected without interrupting the flow. The eluate fractions were collected and counted to determine the elution curve of Cl-36, which was regarded as a conservative, i.e. non-retarded solute.

The migration behaviour of the combined fulvic acid - cobalt complex system was disclosed by injection of a 2.35 ml sample of groundwater containing 32 mg/L fulvic acid which had been spiked with Co-57 and allowed to equilibrate for 24 hr. The fulvic acid had previously been extracted from groundwater and fully characterized (*Higgo et al., 1993b*). The actual concentration of Co-57 was approximately 10^{-7} molar. The eluate was fraction collected, the concentrations of Co-57 in the single fractions being determined by γ-counting. The eluate concentration of fulvic acid was continuously monitored by UV detection. After 5 days of elution with ground water the column was eventually sectioned and the concentration profile of total Co-57 within the column was determined by γ-counting of the single sections.

4 Results and discussion

Dispersion coefficient

As the first step the experimental data for the migration of Cl-36 through the column was used to determine the dispersion coefficient in the column. Thus, the COLUMN3 program was set up to calculate the migration of one non-retained component ($R_f = 1$), the calculated eluate concentration being fitted to the experimental data applying the dispersion coefficient as fitting parameter (Fig. 1). The dispersion coefficient D_{Cl} was 0.02 cm^2min^{-1}, which was applied as dispersion coefficient for all further calculations.

Ground water velocity

R_f(Co)

For the following simulations it was assumed that all components migrating through the column, except Co-57, could be regarded as a dissolved fraction and a sorbed fraction. Thus, the dissolved fraction was assumed to be transported with the interstitial ground water ($v = 0.22$ cm/min), without retention. On the other hand, components that are fixed relative to the column, to simulate sorption sites and sorbed components, are given velocity and dispersion equal to zero. Co-57 is regarded as either a retarded species the retention factor being 3600 (*vide infra*), or as a cobalt-fulvic acid complex.

Sorption

Turning to the elution curve for fulvic acid (cf. Fig. 2), the arrival time of the fulvics in the eluate combined with the rather broad elution curve were strongly indicative of the operation of slow sorption/desorption, since simple equilibrium sorption (retention) of a single component will lead to a much narrower elution curve at the experimental elution time. Furthermore, the recovery of the fulvic acid is only 60% indicating the operation of a simultaneous irreversible sorption.

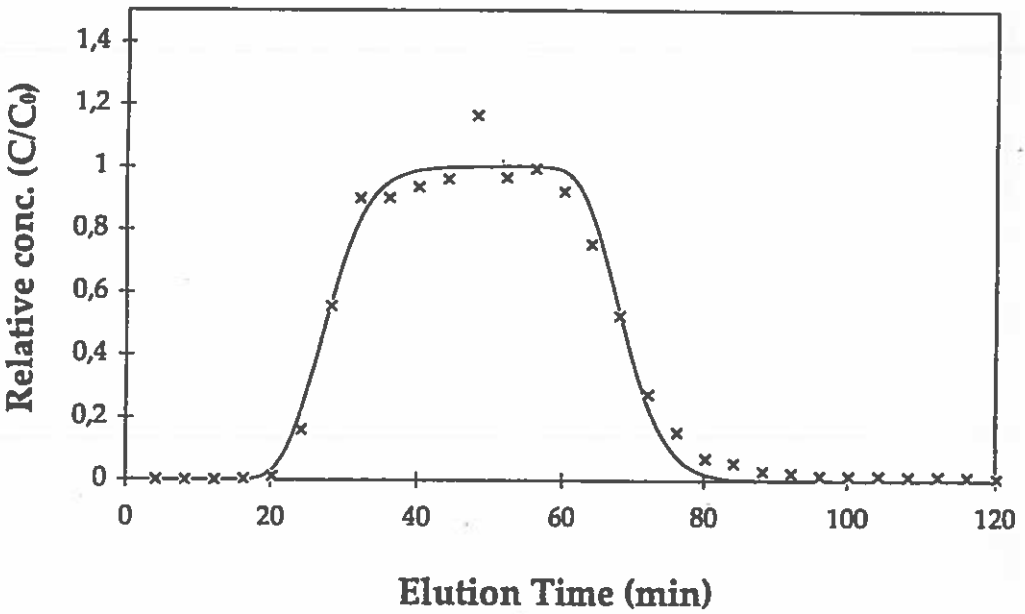

Figure 1. Experimentally (x) derived and COLUMN3 modelled elution curves for Cl-36 (Concentrations given relative to the input concentration C0)

Sorbing sites

To simulate the observed transport of fulvic acid (FA) through the column a reaction scheme involving 5 components and 3 reactions was set up in COLUMN3 with sorbing sites (SolidSite and FixedSite) and sorbed components (FASolidSite and FAFixedSite) fixed with respect to the column (v = 0) (cf. Scheme 1). The interaction between FA and SolidSite are reversible, whereas the reaction of FA with FixedSite leads to an irreversible sorption of the fulvic acid (cf. Scheme 2). The resulting simulation of the migration of fulvic acid through the column is visualized in Fig. 2.

Scheme 1. Compounds fixed relative to the column

SolidSite
FASolidSite
CoFASolidSite
XFASolidSite

FixedSite
FAFixedSite

Competition

Introducing Co-57 to the simulation it became evident that in order to simulate the experimental Co-57 eluate curve, the latter being as broad as the FA curve, the cobalt - fulvic acid complexation constant, i.e. the ratio of the two rate constants (cf. Scheme 2), must be large resulting in a much larger recovery than experimentally observed (1.3%). This suggest that multivalent metal ions in the ground water, in agreement with the ground water analyses (*Higgo et al., 1993b*), compete with the cobalt for the fulvic acid. Thus, the coelution of cobalt and fulvic acid as well as the observed recoveries are a combined result of a comparatively high complexation of cobalt with fulvic and competition for available sites in the fulvics from multivalent metal ions in the ground water (X).

In Scheme 1 the various components in the combined reaction setup that are fixed to the column, i.e. exhibiting velocity and dispersion equal to zero, are shown.

In Scheme 2 the reactions involved in the migration of the cobalt-fulvic acid system through the column are displayed.

Scheme 2. Chemical reactions used in simulation of column experiment[1]

Cobalt - Fulvic acid complex formation

[Co] + [FA] -> [CoFA]; $k_1 = 50.0$
[CoFA] -> [Co] + [FA]; $k_{-1} = 0.05$

Competing complexformation with metal ions in the ground water

[X] + [FA] -> [XFA]; $k_2 = 50.0$
[XFA] -> [X] + [FA]; $k_{-2} = 0.1$

Slow sorption/desorption processes

[FA] + [SolidSite] -> [FASolidSite]; $k_3 = 0.003$
[FASolidSite] -> [FA] + [SolidSite]; $k_{-3} = 0.175$

[CoFA] + [SolidSite] -> [CoFASolidSite]; $k_4 = 0.003$
[CoFASolidSite] -> [CoFA] + [SolidSite]; $k_{-4} = 0.175$

[XFA] + [SolidSite] -> [XFASolidSite]; $k_5 = 0.003$
[XFASolidSite] -> [XFA] + [SolidSite]; $k_{-5} = 0.175$

Irreversible sorption of major FA-containing compounds

[FA] + [FixedSite] -> [FAFixedSite]; $k_6 = 0.025$
[XFA] + [FixedSite] -> [FAFixedSite] + [X]; $k_7 = 0.025$

[1] 1st order rate constants in min^{-1}
2nd order rate constants in mL min^{-1} $relmol^{-1}$

Scheme 3. Relative molar concentrations used

FA	1	total in injected sample
Co-57	0.01	total in injected sample
X	20	in flowing ground water
SolidSite	100	originally in column
Fixed Site	1	originally in column
		Not mentioned concentrations are initially set equal to 0 throughout the column

The calculations are carried out using relative molar concentrations (relmol) for the single species involved. In Scheme 3 the relative molar concentrations corresponding to the initial state of the system are given.

In Figure 2 the experimentally derived elution curves for fulvic acid and for Co-57 are depicted together with the COLUMN3 simulated curves, applying the above given reaction setup.

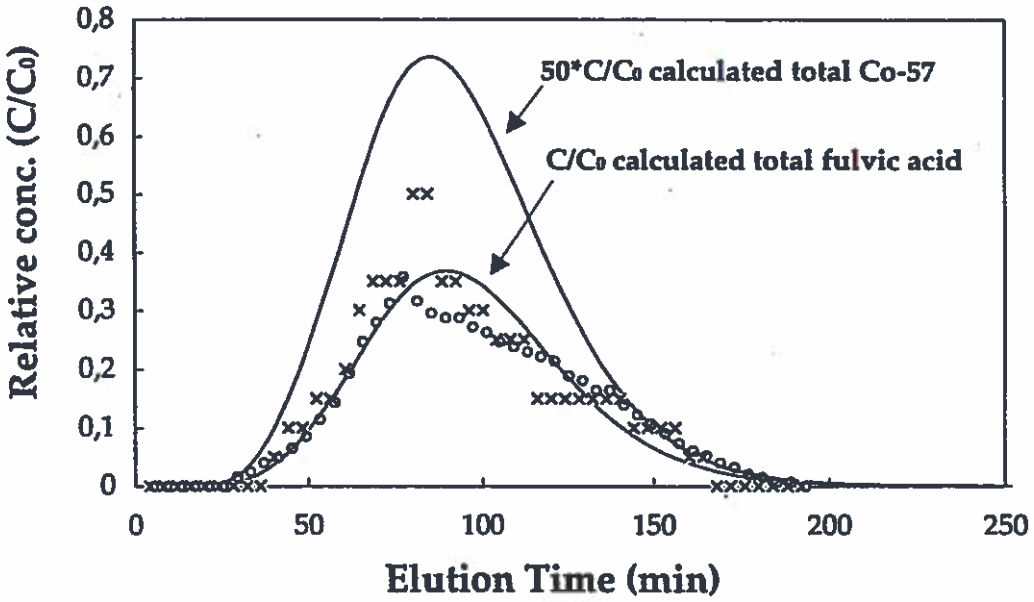

Figure 2. Experimentally derived and COLUMN3 modelled elution curves for fulvic acid (x) and Co-57 (o). (Concentrations given relative to the input concentration C0)

Fulvic acid elution

Cobalt elution

Whereas an almost perfect simulation of the fulvic acid elution can be noted, some deviation between the experimentally derived and the modelled elution of Co-57 can be noted. It should be possible to optimize the fit by adjusting the single rate constants in the reaction scheme. However, at the present time this seems not justified. It is emphasized that the rate constants applied are suggested values and apparently it make little sense to adjust these values only to make a perfect fit. Further it should be emphasized that the recovery of the Co-57 is only 1.3% and as such most probably somewhat inacurate. Thus, the above figure unambiguously demonstrates that the suggested reaction scheme (Scheme 2) may explain the migration behaviour of the cobalt - fulvic acid system through the column, the actual magnitude of the single rate constants being of lesser importance. Further studies would probably lead to a significantly enhanced accuracy in estimating correct rate constants.

The concentration profile obtained through the eventual sectioning of the column was used to determine an approximate retention factor for Co-57 to be used in the complete simulation of the column experiment. Based on the COLUMN3 simulation the retention factor was estimated to be ca. 3600. The simulation of the Co-57 concentration profile is visualized in Fig. 3.

Cobalt elution

It is immediate noted that the calculated Co-57 concentration profile in the column is not very accurately determined. Two reasons for this apparent discrepancy have to be considered.

1: When the retention is so high that the effective convective velocity (= v/ R_f(Co)) is smaller or comparable to the spreading by dispersion (D_{Co}) the normal column boundary condition at the column entrance is not fulfilled. This applies to both calculated and experimental data.

2: When the retention is as high as with Co-57 the simple numeric solution used in COLUMN3 is stable but inaccurate. In practice this is observed during the calculation process as it is noted that the calculated total amounts of Co-57 vary during the calculations by as much as a factor of 2 or in certain cases even more.

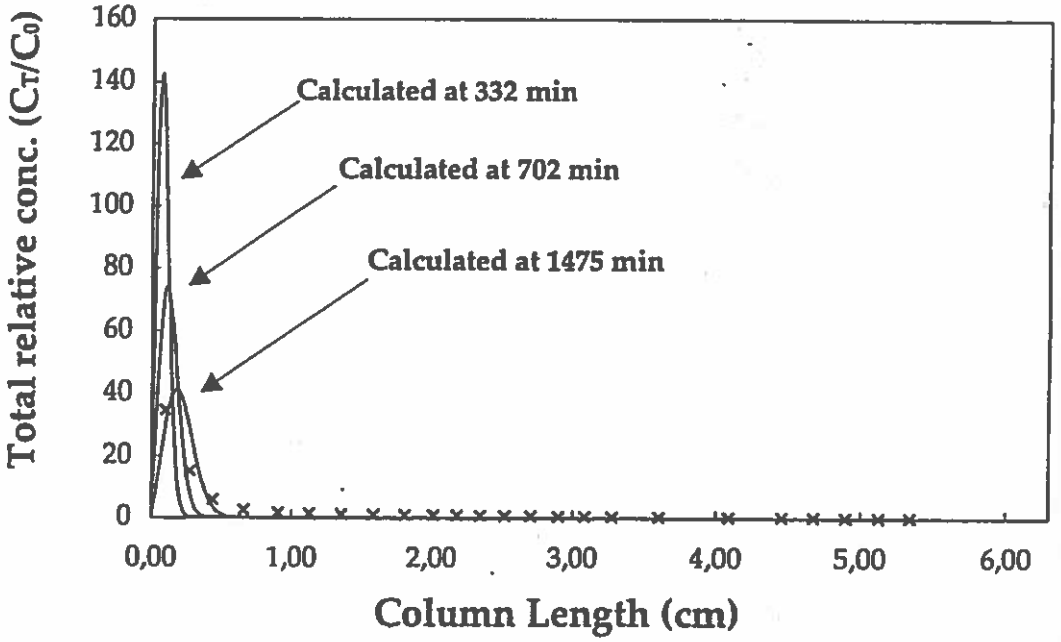

Figure 3. Experimentally derived (x) and COLUMN3 modelled concentration profile of total Co-57 in the column. Experimental values after 7200 min.s of elution. (Concentrations given relative to the input concentration C0)

Cobalt retention

Although the correct Co-57 retention is probably 2 to 3 times higher than the value used in the present study, the calculated total relative Co-57 concentration profiles show the order of magnitude of the penetration into the column and the effect of the initial passage of fulvic acid as the distance that cobalt actually has moved during the first 332 minutes is comparatively larger than the distance moved within the time period from 332 to 705 minutes (Fig. 3). Future work will include introduction of an option to choose advanced numerical methods in order to handle situations with large retention factors and large reaction constants more accurately.

5 Conclusions

The applicability of the COLUMN3 code to the modelling of column experiments studying the transport of cobalt in the presence of fulvic acid has been elucidated. Thus, it has been demonstrated that COLUMN3 satisfactorily models the transport and distribution of cobalt in a complex system taking into account 1° equilibrium and non-equilibrium sorption/-desorption as well as irreversible sorption, 2° chemical reactions of 1st and higher orders in the present case complex formation and competition. Further the study has disclosed the capability to elucidate possible reaction mechanisms controlling the migration behaviour of pollutants.

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