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Finite mass diffusion through soil: a 1D application

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SUMMARY: A great challenge for scientists and engineers is to simulate accurate finite mass contaminant transport. This is so because most of the models used take into account an infinite mass source. Commercial software, capable of handling finite mass, are available, but can be an extra expense in a short-budget project. Analytical solutions are not always possible to obtain, nevertheless, if existent they can deliver an accurate response, but they can be time consuming and delay the project schedule. This work provides a free numerical solution to easily solve the parabolic 1D partial differential equation for reactive diffusion transport in soil. The code is based on the assumption that mass flow through the soil top surface concur to decrease the concentration in the overlying reservoir. In this case, a first-type boundary condition may be assumed on top of the soil layer while an impermeable boundary condition (second-type) is set at the bottom. The code was written in FORTRAN 90 syntax and compiled with GCC/GNU free platform for windows MINGW. It uses an FTCS numerical scheme which can be easily reproduced even in a standard personal computer. Here, the code was tested to calibrate experimental data and to evaluate its capability and was proven useful. The tests used are the result of a previous work on the diffusion transport of potassium chloride in a processed kaolin clay soil. Calibration was preceded by trial and error. Finally, a workable hypothetical problem was simulated to exemplify how the code can be used in real engineering projects or scientific investigation.

KEYWORDS: contaminant migration, diffusion, finite mass source, finite difference.

1 INTRODUCTION

Contaminant transport in soil is a key phenomenon to understand the extension and magnitude of pollution in convection dominated transport problems but, especially, in diffusion dominated problems such as contaminant migration through clay liners or back diffusion from aquitard towards the aquifer (Yang et al., 2015). A number of applications for diffusion in environmental geotechnics from a historical perspective can be found in Shackelford (2014).

Over the last decades a number of models have been proposed to assist in identifying contaminant frontas reported by Fetter (1999) and in Zheng and Bennett (2002). However, several models, even nowadays, are based on the assumption of an infinite mass source, which is rather unrealistic. Besides that, analytical solutions are scarce and, in general, present simplified boundary conditions, regular geometry and have applicability limited by the many assumptions generally needed to derive the models. In order to overcome those limitations, solutions based on numerical methods may be applied. Finite difference method (FDM) and finite element method (FEM) are the more usual numerical methods adopted in solving subsurface fluid flow and contaminant transport problems.

Rowe and Booker (1985) were pioneers by suggesting a semi-analytical solution for a finite source reactive contaminant transport, a commercial code known as POLLUTE.

Many complex analytical solutions for one-, two- and three-dimensional sources also taking into account an underlying aquifer of finite thickness were derived by Park and Zhan (2001). These researchers assumed first-type finite source boundary by a Heaviside function with regular geometry. Implementation of those solutions is complex and the range of applications is rather limited.

Bharat (2013) published the first analytical solution for 1D finite mass diffusion problems. The author showed good agreement when compared to the semi-analytical solution by Rowe and Booker (1985).

Lima et al. (2015) realized a comparison of models to obtain effective diffusion coefficients for finite mass tests. They used the solutions of Rowe and Booker (1985) and also Bharat's analytical solutions (Bharat, 2013) to analyze the results of experimental tests. The authors verified good agreement among the solutions, however, the analytical solution developed by Bharat (2013) showed itself far more complex to be applied, warranting a laborious work for every problem.

Although many researchers have published a number of models and some numerical codes that implement those models are available, there is a need yet for new codes to solve particular problems.. Sharma et al. (2014) developed and implemented a numerical code for solution of the classical advection-dispersion equation (ADE) and to evaluate their experimental work.

The present work presents a simple numerical formulation, based on finite difference method (FMD) to solve 1D reactive finite mass diffusion problems. An evaluation of its performance in comparison with the solutions provided by Bharat (2013) and POLLUTE (Rowe and Booker, 1985) is also accomplished by test calibration with data obtained from Lima et al. (2015). A workable hypothetical problem to illustrate its use is also presented.

2 METHODOLOGY

The mass flow through soil of single chemical species, dissolved in water, can be computed from (1).

$$q_c = -nD_e \frac{\partial C}{\partial x} \tag{1}$$

Where q_c is mass flow [M.T^{-1}]; D_e is effective diffusion coefficient [L^2.T^{-1}]; C is chemical species concentration [M.L^{-3}] and x is the flow direction. The effective diffusion coefficient is the product of tortuosity and diffusion coefficient for species "*i*" in infinite dilution ($D_e = \tau D_0$). The tortuosity is a constant that is used to represent the tortuous path of contaminant migration within the soil. Further information on effective diffusion coefficient can be found in Rowe et al. (1988), Shackelford (1991) and Lima et al. (2015). The general diffusion partial differential equation (PDE) is obtained by applying the mass conservation law to (1) as in (2).

$$\frac{\partial c}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \pm R_i \tag{2}$$

Where t is time and R_i encompasses all chemical reactions such as sorption/desorption, absorption, complexation, solubilization, precipitation, etc. In this model, sorption or adsorption (S) can be considered as a linear isotherm (3), a Freundlich isotherm (4) or a Langmuir isotherm (5).

$$\frac{\partial S}{\partial t} = K_d \frac{\partial C}{\partial t} \tag{3}$$

$$\frac{\partial S}{\partial t} = KC^N \tag{4}$$

$$\frac{\partial S}{\partial t} = \frac{\alpha\beta C}{1+\alpha C} \tag{5}$$

Where K_d and K are partition coefficients [$L^3.M^{-1}$]; N is a constant from Freundlich isotherm [$L^3.M^{-1}$]; α [L^3M^{-1}] and β [MM^{-1}] are constants from Langmuir isotherm and C is the equilibrium concentration in solution [$M.L^{-3}$].

Solving a 1D PDE requires at least a set of two boundary conditions (BC). To account for a finite mass contaminant source a top boundary condition must be represented as in (6).

$$C_T(x=0,t) = C_{T0} + \frac{nD_e}{H}\int_0^t \left(\frac{\partial C}{\partial x}\right)\bigg|_{x=0} dt \qquad (6)$$

where C_T is the concentration at the interface between fluid reservoir and top soil profile [$M.L^{-3}$]; C_{T0} is the initial concentration in the deposit solution above [$M.L^{-3}$]; H is the equivalent height of fluid in the deposit [L] and t is time.

This boundary condition is based on the assumption that mass flow on the top boundary is responsible for decreasing the concentration in the deposit solution. It is noticeable that the second term on the right-hand side of (6) is actually negative. The second boundary, at the bottom of the soil profile, was chosen as free drainage condition (second-type BC) like in (7).

$$\left.\frac{\partial C}{\partial x}\right|_{x=L} = 0 \qquad (7)$$

Where L is the thickness of the soil profile [L]. This boundary condition best fits the real experiments described by Lima et al. (2015) where the soil bottom is enclosed by an impermeable Plexiglas plate. Bharat (2013), for instance, admitted a height of collected fluid below soil bottom. Although this may not be relevant for short period experiments, the bottom boundary condition can be determinant for long-term diffusion tests.

The following paragraphs describe the numerical code developed in this paper and other solutions used in the paper. All solutions (numerical or analytical) presented herein are based on a number of assumptions:

1. The soil is fully saturated;
2. It is an isothermal transport model;
3. Equilibrium reactions take place immediately;
4. Sorption accounts for all possible soil-contaminant interactions;
5. No Fluid flow;
6. Fluid in the reservoir is considered an homogeneous solution as if it was permanently under shaking;
7. No convective forces are derived.

The numerical solution solves equation (2) using finite difference method (FDM) with a forward in time and centered in space (FTCS) numerical scheme (8). The numerical code was written in FORTRAN 90 and compiled with GCC/GNU free platform for windows MINGW. It was named FMCT, an anachronism for Finite Mass Contaminant Transport.

In FORTRAN syntax, discretization of soil elements was defined from 1 (top) through L (bottom) with a total of n+1 elements. The variables i and j are increments in time and space, respectively. For top boundary condition (j = 1) the previous element (j = 0) is replaced by the concentration in the reservoir for each time step i. For bottom boundary condition (j = L) the foremost point L+1 is replaced by L-1 according to the respective boundary condition as defined in (7).

$$C_j^{i+1} - C_j^i = \frac{D_e}{R_f^{i,j}}\frac{\Delta t}{(\Delta x)^2}\left(C_{j+1}^i - 2C_j^i + C_{j-1}^i\right) \qquad (8)$$

where $R_f^{i,j}$ is the retardation factor which can be derived from (3) to (5). For linear isotherm option the retardation factor is a constant in time and space, however, the other isotherm models are computed for each increment in space and time.

Solving an advection-dispersion equation ADE is always challenging because numerical stability can be lost very easily for explicit schemes. A number of attempts were necessary to guarantee code stability for the larger range of data entry. Invariably, in such explicit formulation, numerical stability relies on time increment (Smith, 1985; Abbott and Basco, 1989). This is always a limitation because, for very short time increments, the code loses its ability to record all data, and for greater increments it loses stability and convergence. After many trials, a constant ratio of time increment over space increment of 1/10 was proven capable of handling discrepancies.

For every model built with this code entries must satisfy dimensional analysis. Until now, a number of tests were conducted and all of them attained success, which ensures the feasibility of the code. Nevertheless, it is known that using implicit schemes deliver more stable models and shall be tried in future.

A simplified flowchart to illustrate FMCT steps is presented in Figure 1. Once the code is started, the user shall enter with all required data: the soil profile length, equivalent leachate height, total simulation time, chemical species coefficient of diffusion in infinite dilution, tortuosity factor, soil porosity, soil dry bulk density and the chosen isotherm parameters (equations 3 to 5). Then, the code calculates the constants obtained from deriving the PDE into a finite difference equation and computes the contaminant front for the required time. It writes out the final contaminant profile within the soil, reservoir concentration over time and the breakthrough curve.

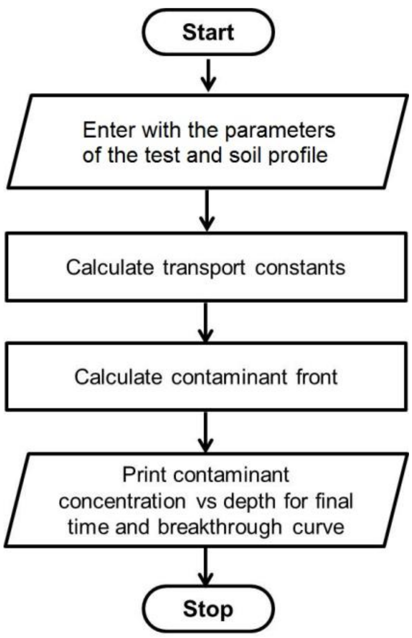

Figure 1. Flowchart for FMCT.

The code can be easily derived or manipulated by people even with low experience in programming and in finite difference method. Implementation can be readily done in any compatible compiler and the execution is fast. The ease of this code is its greater advantage.

POLLUTE software solves the 1D diffusion PDE (2) for a soil profile of finite or infinite extension, constituted of several layers. It evaluates the advection-dispersion in Laplace's domain and uses Talbot's algorithm (Talbot, 1979) to calculate the accurate numerical inverse transform (Rowe et al., 2004).

Bharat (2013) used the Cauchy theorem to solve PDE (2) similarly to what already had been used to solve a number of heat transfer equations also of parabolic nature. Bharat (2013) admits a finite mass contour over soil surface and integrates mass flow over time to achieve reservoir depletion as in (6).

Table 1 summarizes the experimental work carried out in Lima et al. (2015). In the present work only potassium diffusion transport experiment results were used although both ions, chloride and potassium, were tested. The diffusion coefficients for chloride and potassium in infinite dilution are, respectively, 20.3E-10 m²/s and 19.6E-10 m²/s (Lerman, 1979).

Table 1. Summary of the experimental setups.

Experimental setup			
Test		D 01	D 02
Time (h)		24	72
Soil thickness (cm)		5.5	4.5
ρ (g/cm³)		1.2	1.791
w (%)		43.4	43.5
n		0.64	0.516
Initial condition (mg/L)			
Soil	K^+	33	32
	Cl^-	966	525
Tank	K^+	372	438
	Cl^-	407	312

The soil used in the diffusion tests consists of processed kaolin clay. First, the soil was mixed with deionized water until a plastic homogeneous mixture was achieved. The process ended after soil saturation. Then the samples were molded into a cylindrical cell 11 cm in height and 10 cm in diameter made up of Plexiglas material.

The ratio soil thickness/equivalent solution height is 1.0 for teste D01 while for test D 02 it is 0.82. The initial concentrations of potassium and chloride in soil porewater presented in Table 1 are the measured background.

3 RESULTS AND DISCUSSION

Finite mass source is closer to reality than infinite mass source, however, as discussed previously, it is not simple to represent. To show the effect of moving boundary condition over time a few curves were plotted for the same hypothetical scenario.

For this scenario it was used an effective diffusion coefficient of 5.0x10-9 m²/s, initital concentration in solution was 100 mg/L and porewater background was zero. In Figure 2, concentration is normalized relative to initital concentration in reservoir and soil depth is normalized to soil layer thickness.

One may notice that after 1 day of diffusion transport, top concentration is about 0.85 of that of initial intake (from reservoir) while after 8 days the concentration in the same boundary is just a little higher than 0.60.

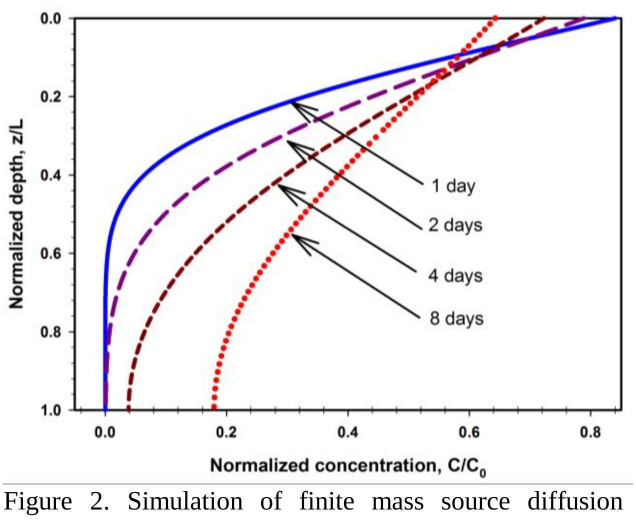

Figure 2. Simulation of finite mass source diffusion through soil for several days with FMCT.

It is certainly a more realistic way to simulate problems such like leachate dispersion through clay liners, contaminant transport in very fine-grained soil or to design barrier for impoundment.

In order to assess the validity of the numerical code FMCT, the experimental data provided by Lima et al. (2015) were used against simulated potassium transport plotted in Figure 3. Despite the possibility of some experimental errors during chemical analysis or dilution effect as discussed by Mazierri et al. (2015), there is a good agreement between numerical and experimental data in both diffusion tests (D 01 and D 02).

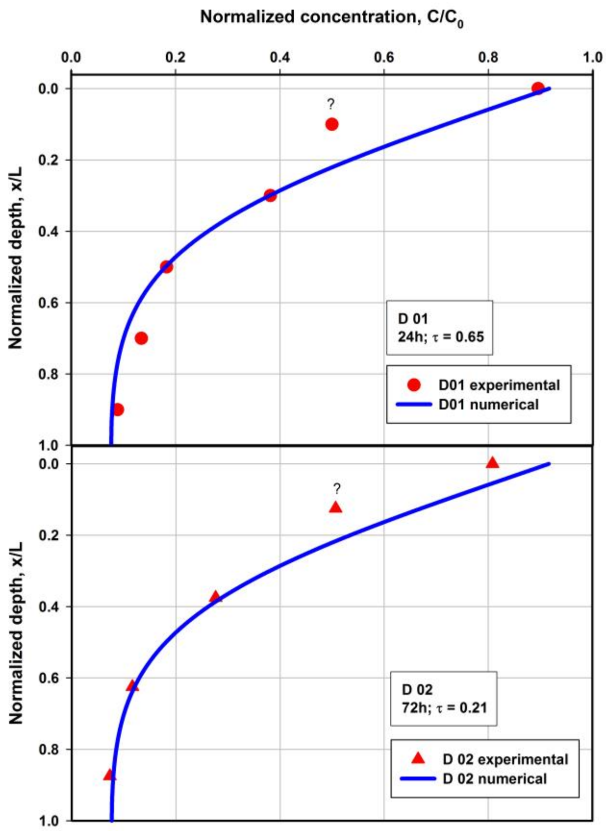

Figure 3. Results for the simulation of potassium transport by diffusion against data from tests D 01 and D 02. Concentration is normalized over initial concentration in the reservoir for each test.

The values of tortuosity are the same found by Lima et al. (2015). In that work, those values provided the best fit experimental-numerical during calibration by trial and error.

It is important to realize that experimental work was carried out with the same processed kaolin clay soil. However, soil structure is considerably different between D 01 and D 02 tests, represented by its porosity and dry bulk density in Table 1. That is possibly the cause of the similarity between the two curves although there is a difference of two days between the tests.

To perform an additional check of the numerical code, the results of simulation were evaluated against analytical solution (Bharat, 2013) and the regression curve showed a determination coefficient (R^2) of 0.9999. Lima et al. (2015) also realized a regression curve for these data simulated with POLLUTE (Rowe and Booker, 1985) and the analytical solution of Bharat (2013). The authors found the same value for the determination coefficient.

Figure 4 shows the plot of the three solutions presented here in normalized form. One may notice a line connecting the blue points. Besides that, it is possible to notice that the projection of the blue dots against x-y or x-z planes is also similar to a line, which denotes the good agreement between the solutions.

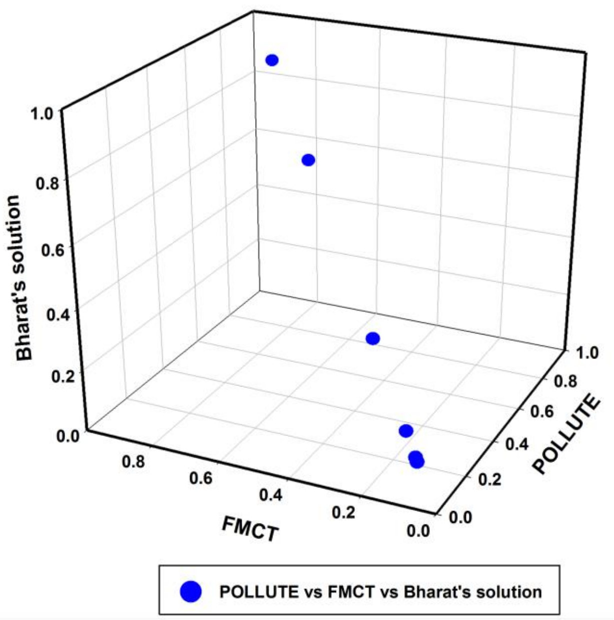

Figure 4. Three simultaneous plots from FMCT, Bharat'solution and POLLUTE for the potassium transport in D 01 in normalized base.

A common case of diffusion is that of heavy metals migration into fine-grained soil layer or engineered barriers. Suppose that a clay liner of 0.30 m as in Figure 5 is underlying an equivalent fluid height of 0.5 m with a concentration of 0.5 M $C_d(OH)_2$.

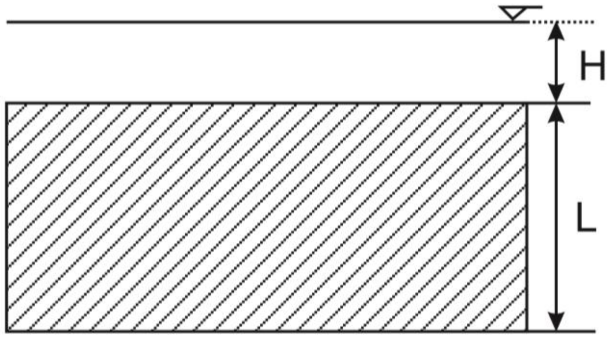

Figure 5. Scheme of soil profile with leachate height.

Figure 6 has three hypothetical isotherms to account for chemical reactions within the soil. Assuming soil profile very homogeneous composed by fine-grained soil with very small permeability, in the order of $1x10^{-9}$ cm/s, with an average porosity of 0.5, a total tortuosity of 0.3 and with a dry bulk density of 1.1 g/cm³. In this case, soil is considered impermeable for fluids. The coefficient of diffusion for cadmium in infinite dilution is $7.33x10^{-10}$ m²/s at 25°C (Lerman, 1979).

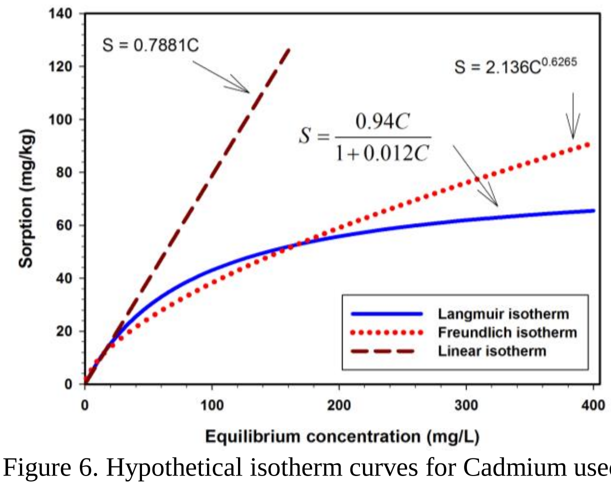

Figure 6. Hypothetical isotherm curves for Cadmium used in the problem.

The concentration curves over time for reservoir from simulations over 300 days considering no sorption and linear and Langmuir isotherms are plotted in Figure 7. The curve in blue represents no retardation effect and, in this case, the contaminant already reached the bottom of the soil profile for the simulated time. The dashed curve in dark brown accounts for Langmuir isotherm anddue to retardation the contaminant has not yet reached the bottom of the soil profile.

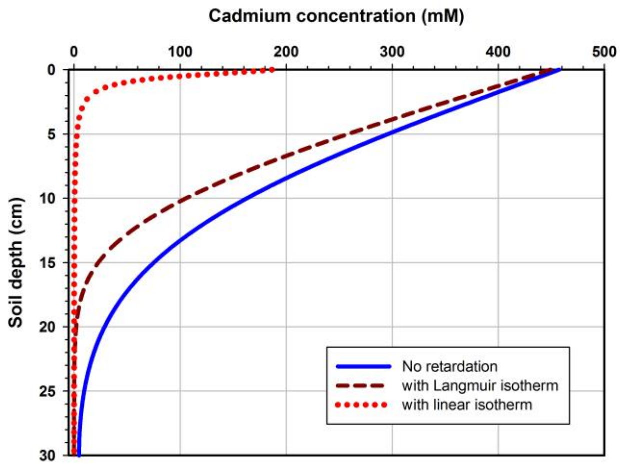

Figure 7. Simulation of cadmium migration within a soil profile over 300 days.

Finally the dotted red line represents the situation of transport with linear isotherm. Most of contaminant mass became attached to soil particles in this case and the contaminant front has reached no longer than 5 cm into soil depth after 300 days.

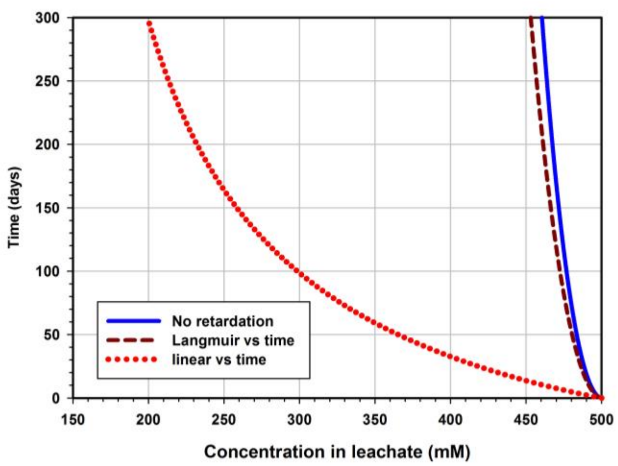

Figure 8. Cadmium concentration in the reservoir over time for 300 days period simulations.

The concentration in the reservoir diminishes over time. The results of simulations for the hypothetical example are plotted in Figure 8. The case of no retardation (blue line) and that of Langmuir isotherm (dark-brown dashed line) are very close, because the retardation effect from Langmuir isotherm has a shorter action in time than the linear isotherm (dotted red line), which represents an infinite soil sorption capacity.

One may be confused why the concentration in the reservoir diminishes so rapidly when linear isotherm is used as in Figure 8 but the answer is quite simple. Once the soil acts as a reactor because of adsorption of the incoming contaminant mass in solution, the equilibrium concentration in the pore fluid becomes very small quickly and large mass flows are derived from that due to the increase in the concentration gradient established between the reservoir and the soil. Langmuir isotherm presents a smooth shape and as discussed earlier it is asymptotic so there is a pore fluid concentration limit for adsorption.

The main reason to develop FMCT is that commercial software can be too expensive especially if it is warranted only for a few tests. The analytical solution by Bharat (2013) is far more complex to implement and for any change in tortuosity, height of fluid, soil depth and other parameters it will be necessary to rebuild the model. It is very time consuming. FMCT is not just a free source code but it can also be simulated easily and in very short time, sometimes in a few seconds.

4 CONCLUSIONS

A numerical code was written in FORTRAN 90 to simulate finite mass source contaminant transport by diffusion. The simulation of two experimental tests showed that the model can be successfully employed to simulate finite mass problems. Besides, a comparison with a well stablished semi-analytical code (POLLUTE) and an analytical solution (Bharat, 2013) proved FMCT reliable.

FMCT is particularly interesting because it can be easily implemented or compiled by personal with low programming experience and is free source. Commercial software can be expensive and the analytical solution are sometimes excessively hard to implement and might be useful to calibrate a numerical model. The versatility of FMCT was also tested in a hypothetical example as a demonstration of the use of the code in an engineering project.

In the future, an implicit scheme will be developed to ensure numerical stability and convergence for a wider range of scenarios.

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