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Fast semi-analytical approach to approximate plumes of dissolved redox-reactive pollutants in heterogeneous aquifers. 1. BTEX

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ABSTRACT

Various numerical reactive transport models were developed in the last decade to simulate plumes of pollutants in heterogeneous aquifers. However, these models remain difficult to use for the non-specialist, and the computation times are often long. Users who need to fit several model parameters to match predictions with field data in heterogeneous aquifers may be discouraged by the time needed to run the simulations. The objective of this paper is to provide a set of approximations that allow performing almost instantaneous calculations for transport of redox-reactive pollutants, the most common examples being benzene, toluene, ethylbenzene and xylenes (BTEX). The approach relies on two major tools: (i) the use of flux tubes (FT), a variant of stream tubes that include dispersion, and (ii) sequential superposition of the reactions (Mixed Instantaneous and Kinetics Superposition Sequence (MIKSS)). The calculation of transport is uncoupled from the calculation of reactions. The superposition principle has been used previously for the analytical solution of a bimolecular reaction of an electron donor with an acceptor and is here extended to more than one dissolved electron acceptor reacting with more than one donor. The approach is furthermore improved by including limitations of the kinetic reactions according to the availability of the reactants and by combining kinetic and instantaneous reactions. The results computed with this approach are compared to three well known numerical models (RT3D, PHT3D, PHAST) for various test cases including uniform, slightly diverted or highly irregular flow fields and several reaction schemes for BTEX. The FT-MIKSS solution gives nearly the same results as the other models and proved to be very flexible. The major advantage of the FT-MIKSS solution is fast computation times that are generally 100 to 1000 times faster than other numerical models. This approach might be a useful tool during the long fitting procedure of field data, which may be followed by one single run of a classical numerical model using the best-fit parameters.

1. Introduction

Many reactive transport models have been developed over the last decades, and numerous codes are presently available. The major differences lie in the specialisation of the different models. In this work, we will use three different codes: RT3D [1] PHT3D [2] and PHAST [3]. RT3D is one of the most frequently used codes for organic compounds as it includes specific modules for the simulation of BTEX compounds or chlorinated solvents [1], it is based on MT3DMS [4] for the transport of species and a specific solver for the reaction network. PHT3D and PHAST both rely on PHREEQC [5] to solve chemical reactions, but PHT3D does not contain all functionalities of PHREEQC. PHREEQC is very powerful and can model almost any set of geochemical reactions. In PHT3D and RT3D the transport part is solved with MT3DMS with an operator splitting [2,6]. The same approach is used in PHAST but the transport solver is HST3D. In the literature, few sites contaminated by BTEX or chlorinated solvents were modelled and then evaluated in detail with field data [7–12], although calibrated models would be of great help for long term predictions. Modelling such sites is fairly difficult because several parameters are often unknown at the field scale: dispersivities, exact location of the source, contaminant concentrations at the source, kinetics of degradation, and spatial distribution of degrading bacteria. Chilakapati et al. [13] show that model results for chemical species are highly sensitive to most of these parameters. Facing these uncertainties and the difficult use of inversion procedures, modellers tend to solve the problem by trial-and-error approaches (e.g. [14]).

The trial-and-error approach presents two difficulties: (i) the models must run fast in order to be able to run several simulations, and (ii) the number of parameters must not be larger than the number of validation data. The first point is difficult to achieve with numerical models because reactions generally take time to be solved. The second point suggests that we may limit the number of parameters in the model, whilst reproducing the major features

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of the degradation processes. Among others, Jakobsen and Postma [15] stated that knowledge of terminal electron acceptor processes (TEAP), is needed to simulate efficiently the degradation of organic compounds. Although this is not possible with some popular models, simulating the spatial distribution of the major electron acceptors and donors would be very useful. Simulation of the distribution of electron acceptors can also be good for model validation purposes as data on electron acceptors are often available at field sites.

The Mixed Instantaneous and Kinetics Superposition Sequence (MIKSS), an extension of the superposition principle, has been previously introduced and used with an analytical solution for homogeneous domains [16,17]. This manuscript first describes improvements of the MIKSS approach which now allows applying redox reactions to more complex cases of sequential degradation of BTEX. Furthermore, a coupling of MIKSS with the flux tube calculation is introduced. The use of flux tubes (FT) allows quasi-instantaneous calculation of transport in two dimensions [18]. The FT-MIKSS combination thus permits the calculation on heterogeneous flow fields, which was not possible with the first version of MIKSS. Using several test cases of increasing complexity in terms of reactions or flow geometry, the FT-MIKSS approach is then compared to several numerical models.

Here, we show that the mixed instantaneous kinetic superposition sequence coupled to flux tubes is able to simulate efficiently and rapidly the transport and degradation of BTEX. The main objective of the approach is to have instantaneous simulations in order to estimate rapidly the major parameters, including permeability distribution, dispersivities and reaction kinetics. When these parameters are obtained, they can be used in a more refined simulation using a classical numerical model.

2. Model description

The approach considered here concerns a line source in a two-dimensional domain consisting of a heterogeneous flow field with longitudinal and transversal dispersion. Sorption is not considered here; it will be addressed in a second paper.

2.1. Tracer concentration

In our approach transport and chemical reaction are solved independently. The concentration of the non-reactive tracer is first calculated for the time of interest, and then the concentrations of all reactants are calculated from the tracer concentration. The method to calculate the transport of the tracer with flux tubes has been described in detail in [18]. It involves the same particle tracking approach as [19] but the particle trajectories are calculated differently. The flux tubes are calculated through a particle tracking algorithm that includes a dispersive part, leading to enlarged tubes that are conservative for the flux of matter. The concentrations in each flux tube are obtained by dividing the flux of matter though each tube by the cross-section of the tube.

The calculated flux tubes provide concentrations for infinite time at any curvilinear distance from the source. The travel time of each particle from the source zone is also obtained for any distance with the particle tracking algorithm. The spatial distribution of tracer concentration obtained for infinite time is $c_0\Omega_\infty$, where c_0 is the concentration at the source and Ω_∞ is the spatial term. To obtain the solution at a given time, an approximation close to the solution of [20] is used:

$$c_0\Omega_t \approx c_0 T(t)\Omega_\infty \tag{1}$$

with

$$T(t) = \frac{1}{2}\left[erfc\left(\frac{s-\upsilon t}{2\sqrt{\alpha_L \upsilon t}}\right) + \exp\left(\frac{s}{2\alpha_L}\right) erfc\left(\frac{s+\upsilon t}{2\sqrt{\alpha_L \upsilon t}}\right)\right]$$

where s is the distance along the curvilinear coordinate (m), υ is the seepage velocity (m day^{-1}), t is time and α_L is the longitudinal dispersivity (m).

The spatial distribution of the tracer $c_0\Omega_t$ is calculated for a unique line source of constant concentration c_0. This has been developed and discussed in detail in [14].

2.2. General reaction framework

Here we consider only reactions of dissolved species, which are mostly redox reactions, either instantaneous or kinetic. Solid phases are not taken under consideration as reactants. In that framework each degradation reaction involves one dissolved organic species (electron donor, ED, e.g. B, T, E, or X) and one dissolved inorganic species (electron acceptor, EA, e.g. O_2, NO_3^-, SO_4^{2-}, see Table 1).

In natural systems, redox reactions are often ordered. For instance, it is established that degradable organic matter will first react with O_2 until almost complete consumption of O_2. Then the reaction continues with NO_3^-, followed by Fe^{III}, then by SO_4^{2-} and finally by CO_2 [21]. The order of the sequence is directly related to the values of E° or ΔG° of the half redox reaction. The ΔG° values are largely different and thus all O_2 must be consumed before any NO_3^- may react. Although most reactions are mediated by bacteria, the order is respected: bacteria cannot change ΔG° values. However, it may happen that one reaction does not occur because of the absence of specific bacterial species: for instance, the system can switch directly from O_2 to Fe [22].

In such a redox system, the sequence can be subdivided in a series of independent bimolecular reactions. At first, the organic species reacts with the first inorganic species, and then, when its concentration is depleted, the remaining organic species will react with the next inorganic species. This is why bimolecular reactions are described first and then more complex sequences are treated.

2.3. Instantaneous reaction of one organic species with an inorganic species

Here we consider a source delivering continuously one organic species (an infinite source) to a groundwater bearing homogeneously only one inorganic species. As shown by Borden et al. [23], and revisited by Cirpka and Valocchi [24], the plumes resulting from instantaneous reaction can be obtained by using the superposition principle. The same approach is used in Bioscreen [25]. The considered reaction is:

$$C + M \rightarrow D + N \tag{2}$$

where C is organic or carbon species, that can be considered as the electron donor, for instance, and M the inorganic species (electron acceptor). D is the carbon-bearing product (CO_2), and N is the transformation product of M (Table 1). In order to simplify the formula, all concentrations are directly expressed in mmoles of electrons (e−): the stoichiometry coefficients are thus applied beforehand to transform moles L^{-1} or mg L^{-1} concentrations in concentrations of electron equivalents for each reaction (Table 1). For instance one mole of O_2 corresponds to 4 moles of electron equivalents when O_2 is transformed to H_2O.

If all species have the same dispersion coefficient and if there is no sorption, the sum $C + D$ can be considered as a conservative quantity that behaves as a tracer [26] and thus:

$$C + D = c_0\Omega_t = c_0 T(t)\Omega_\infty \tag{3}$$

where c_0 is the concentration in the line source and $T(t)$ the transport term defined previously.

The ambient concentration m_0 is given and, due to instantaneous reaction, the concentration of M is zero in the source zone.