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Analytical solutions for transport of decaying solutes in rivers with transient storage

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Summary Analytical solutions are presented for solute transport in rivers including the effects of transient storage and first order decay. The solute transport model considers an advection–dispersion equation for transport in the main channel linked to a first order mass exchange between the main channel and the transient storage zones. In case of a conservative tracer, it is shown that different analytical solutions presented in the literature are mathematically identical. For non-conservative solutes, first order decay reactions are considered with different reaction rate coefficients in the main river channel and in the dead zones. New analytical solutions are presented for different boundary conditions, i.e. instantaneous injection in an infinite river reach, and variable concentration time series input in a semi-infinite river reach. The correctness and accuracy of the analytical solutions is verified by comparison with the OTIS numerical model. The results of analytical and numerical approaches compare favourably and small differences can be attributed to the influence of boundary conditions. It is concluded that the presented analytical solutions for solute transport in rivers with transient storage and solute decay are accurate and correct, and can be usefully applied for analyses of tracer experiments and transport characteristics in rivers with mass exchange in dead zones.

Introduction

Several models have been formulated for describing solute transport in rivers with stagnant water zones, as pools, dead-end side channels, gravel beds, and adjacent wetland areas. Exchange of solutes between the main river channel and the transient storage zones can have important effects on the transport characteristics and the interpretation of tracer studies (Day, 1975; Chatwin, 1980; Nordin and Troutman, 1980; Bencala and Walters, 1983; Bencala, 1984; Harvey et al., 1996; Morrice et al., 1997; Harvey and Fuller, 1998; Czernuszenko et al., 1998; Fernald et al., 2001; see also the references cited by Runkel et al., 2003). The most widespread modelling concept to describe solute transport in such conditions considers one dimensional advective and dispersive transport in the main river channel linked to first-order mass exchange with the stagnant water zones, assumed to be proportional to the difference in solute concentration between the main channel and the storage zone (Hays et al., 1966; Nordin and Troutman, 1980; Bencala and Walters, 1983; Bencala et al., 1990; Czernuszenko and

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Nomenclature

Notation

A	cross-sectional area of the main stream [L^2]
A_s	cross-sectional area of the dead zone [L^2]
C	concentration in the main stream [$M\,L^{-3}$]
C_s	concentration in the dead zone [$M\,L^{-3}$]
D	longitudinal dispersion coefficient in the main stream [$L^2\,T^{-1}$]
I_0	modified Bessel function of first kind and order zero [–]
I_1	modified Bessel function of first kind and order one [–]
J	Goldstein J-function [–]
M	tracer mass injected in the main stream [M]
$p = \alpha\tau$	dummy variable [–]
$Q = Av$	river discharge [$L^3\,T^{-1}$]
$q = \alpha(t-\tau)/\beta$	dummy variable [–]
t	time [T]
$t_1 = \tau$	dummy time variable [T]
$t_2 = t - \tau$	dummy time variable [T]
v	mean flow velocity in the main stream [$L\,T^{-1}$]
x	longitudinal co-ordinate in the main stream [L]
α	mass transfer coefficient between main stream and dead zone [T^{-1}]
$\beta = A_s/A$	ratio of dead zone and main stream cross-sectional areas [–]
λ	first order decay coefficient in the main stream [T^{-1}]
λ_s	first order decay coefficient in the dead zone [T^{-1}]
τ	dummy time variable [T]

Rowinski, 1997). The transport equations can be written as follows (Nordin and Troutman, 1980; Bencala and Walters, 1983; Czernuszenko and Rowinski, 1997; Lees et al., 2000):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \alpha(C - C_S) \tag{1a}$$

$$\beta\frac{\partial C_S}{\partial t} = \alpha(C - C_S), \tag{1b}$$

where $C(x,t)$ and $C_S(x,t)$ are the cross-sectional averaged solute concentrations respectively in the main channel and the storage zones, D is the cross-sectional averaged longitudinal dispersion coefficient in the main channel, v the cross-sectional averaged velocity in the main channel, α the mass exchange coefficient between the main channel and the storage zone, β the ratio between the storage zone and the main channel cross-sectional area, x the longitudinal distance in the main stream channel, and t the time. For a recent overview of the state of the art and application of this so called transient storage model (TDS) see, e.g., Schmid (2004), Bencala (2005), and Ramaswami et al. (2005).

Runkel and Chapra (1993) presented a numerical solution for Eq. (1), which formed the basis for the One-dimensional Transport with Inflow and Storage (OTIS; http://co.water.usgs.gov/otis) model of Runkel and Chapra (1993), later extended by Runkel (1998) with a parameter optimisation technique. This model has been used extensively for analysing tracer experiments to estimate transient storage characteristics in rivers (e.g., Choi et al., 2000; Fernald et al., 2001).

Other approaches are based on the analysis of temporal moments of concentration profiles in the main channel, for which mathematical expressions can be obtained using the Laplace transformation of Eq. (1) (Hays et al., 1966; Nordin and Troutman, 1980; Schmid, 1995; Runkel, 1996; Czernuszenko and Rowinski, 1997; Schmid, 2003). Some investigators proposed approximate solutions using similarity functions that have the same temporal moments as the observed concentrations (Liu and Cheng, 1980; Chatwin, 1980; Schmid, 1995). Hart (1995) derived a semi analytical solution by considering the solute transport and exchange with stagnant storage zone as stochastic processes. This solution was later extended by Schmid (1997) to account for solute decay.

An analytical solution for instantaneous injection of a tracer in a infinite river reach was presented by Davis et al. (2000), but these investigators did not compare their result with other approaches. Unaware of this solution, De Smedt et al. (2005) also presented an analytical solution for the same problem that is mathematically different from Davis et al. (2000). De Smedt et al. (2005) compared their solution with the OTIS-model, and also noted some similarity with the statistically based solution of Hart (1995), which was, however, not investigated in detail.

The purpose of this study is (1) to compare the different solutions and show their equivalence, (2) extend the analytical solution to include solute decay, and (3) present analytical solutions for different boundary conditions that are useful for analysing tracer experiments.

Theory

Analytical solutions for a conservative solute

For a typical tracer experiment, a mass M of tracer is injected at time zero and location $x = 0$, well mixed over the cross-sectional area A of the main stream channel, so that the initial conditions are given by

$$C(x,0) = (M/A)\delta(x), \tag{2}$$

where δ is the Dirac function. The storage zone is considered to be initially free of solute

$$C_S(x,0) = 0. \tag{3}$$

In addition, it is assumed that there can be no tracer at infinity in the main channel

$$C(x \to \pm\infty, t) = 0. \tag{4}$$

Unaware of the solution of Davis et al. (2000), De Smedt et al. (2005), using the Laplace transformation technique, presented a solution of Eq. (1), subjected to the conditions given by Eqs. (2)–(4), as

$$C(x,t) = (M/A)\delta(x) + \int_0^t C_0(x,\tau)\left[\alpha + \left(\frac{x^2 - v^2\tau^2}{4D\tau^2} - \frac{1}{2\tau} - \alpha\right)J(p,q) - \alpha J(q,p)\right]\mathrm{d}\tau, \tag{5}$$

with $p = \alpha\tau$, and $q = \alpha(t - \tau)/\beta$, where $C_0(x, t)$ is the solution of the classical advection–dispersion equation, subjected to the same initial and boundary conditions

$$C_0(x,t) = \frac{M/A}{2\sqrt{\pi D t}}\exp\left(-\frac{(x - vt)^2}{4Dt}\right), \tag{6}$$

and $J(p, q)$ is defined by Goldstein (1953) as

$$J(p,q) = 1 - \mathrm{e}^{-q}\int_0^p \mathrm{e}^{-\lambda} I_0(2\sqrt{q\lambda})\,\mathrm{d}\lambda, \tag{7}$$

with I_0 the modified Bessel function of the first kind and order zero. The J-function can more conveniently be calculated with power series expansions given by De Smedt and Wierenga (1979)

$$J(p,q) = \mathrm{e}^{-p-q}\sum_{n=0}^{\infty}\frac{q^n}{n!}\sum_{m=0}^{n}\frac{p^m}{m!} = 1 - \mathrm{e}^{-p-q}\sum_{n=1}^{\infty}\frac{p^n}{n!}\sum_{m=0}^{n-1}\frac{q^m}{m!}. \tag{8}$$

The first term on the right hand side of Eq. (5) was omitted by the De Smedt et al. (2005), because it is zero for all practical calculations of tracer breakthrough curves at locations $x > 0$. De Smedt et al. (2005) compared their solution with the OTIS model, which yielded a good fit, and noted that the semi-analytical expression derived by Hart (1995) bears some resemblance without going into further details. They also showed that the solution, given by Eq. (5), can be written as De Smedt et al. (2005, Eq. (A8))

$$C(x,t) = (M/A)\delta(x) + \int_0^t \frac{\partial}{\partial t_1}[C_0(x,t_1)J(\alpha t_1, \alpha t_2/\beta)]\,\mathrm{d}\tau, \tag{9}$$

with $t_1 = \tau$, and $t_2 = t - \tau$. Using differential calculus this can also be written as

$$C(x,t) = C_0(x,t)J(\alpha t, 0) + \int_0^t \frac{\partial}{\partial t_2}[C_0(x,t_1)J(\alpha t_1, \alpha t_2/\beta)]\,\mathrm{d}\tau, \tag{10}$$

and with the properties of the J-function (Goldstein, 1953), this becomes

$$C(x,t) = C_0(x,t)\exp(-\alpha t) + (\alpha/\beta)\int_0^t C_0(x,\tau)\exp(-p - q)\sqrt{p/q}\,I_1(2\sqrt{pq})\,\mathrm{d}\tau, \tag{11}$$

with I_1 the modified Bessel function of the first kind and order one. Eq. (11) is the solution derived by Davis et al. (2000). The equivalence of Eqs. (5) and (11) was also proven by Huang et al. (in press). The solution given by Eq. (11) has also been obtained in case of so-called mobile-immobile zone models, which are used to simulate solute transport in groundwater (e.g., Carnahan and Remer, 1984; Goltz and Roberts, 1986; van Kooten, 1995). Moreover, if the Bessel function I_1 is expanded in series form Eq. (11) can be written as

$$C(x,t) = C_0(x,t)\exp(-\alpha t) + (\alpha/\beta)\int_0^t C_0(x,\tau) \times \exp(-p - q)\left(\sum_{n=0}^{\infty}\frac{p^{n+1}}{(n+1)!}\frac{q^n}{n!}\right)\mathrm{d}\tau. \tag{12}$$

Eq. (12) is the solution derived by Hart (1995), which was obtained by stochastic interpretation of the transport processes rather than by solving the transport equations analytically.

Hence, we have demonstrated that the solutions of Hart (1995), Davis et al. (2000), and De Smedt et al. (2005) are equivalent. There is no criterion that enables to decide which solution is best or most useful in practical applications.

Analytical solutions including decay

The solutions presented above are only valid for transport of a conservative tracer, while often in practice decay of the tracer can occur due to various chemical and biochemical processes (Jobson, 1997; Laenen and Bencala, 2001; Keefe et al., 2004). Generally first order decay processes are considered, so that the transport equations become as follows (adapted in our notation from Schmid, 1995)

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \alpha(C - C_S) - \lambda C, \tag{13a}$$

$$\beta\frac{\partial C_S}{\partial t} = \alpha(C - C_S) - \beta\lambda_S C_S, \tag{13b}$$

where λ and λ_S denote the first order decay coefficients in respectively the main stream and the dead zones. The initial and boundary conditions remain as before. The solution of Eq. (13), subjected to conditions Eqs. (2)–(4), is derived in Appendix A and is given by

$$C(x,t) = C_1(x,t)\exp(-\alpha t) + (\alpha/\beta)\int_0^t C_1(x,\tau) \times \exp\left(-p - q - \lambda_S(t - \tau)\right)\sqrt{p/q}\,I_1(2\sqrt{pq})\,\mathrm{d}\tau, \tag{14}$$

where p and q are as defined before for Eq. (5), and $C_1(x, t)$ is the solution of the classical advection–dispersion equation including decay in the main channel, subjected to the same initial and boundary conditions

$$C_1(x,t) = C_0(x,t)\exp(-\lambda t) = \frac{M/A}{2\sqrt{\pi D t}}\exp\left[-\frac{(x - vt)^2}{4Dt} - \lambda t\right]. \tag{15}$$

When λ equals λ_S, Eq. (14) reduces to the solution derived by Carnahan and Remer (1984) for mobile-immobile solute transport in porous media. Moreover, if the Bessel function I_1 is expanded in series form Eq. (14) becomes

$$C(x,t) = C_1(x,t)\exp(-\alpha t) + \frac{\alpha}{\beta}\int_0^t C_1(x,\tau) \times \exp(-p - q - \lambda_S(t - \tau))\left(\sum_{n=0}^{\infty}\frac{p^{n+1}}{(n+1)!}\frac{q^n}{n!}\right)\mathrm{d}\tau. \tag{16}$$

Eq. (16) is the solution derived by Schmid (1997), which was obtained following Hart (1995) by stochastic interpretation of the transport processes rather than by solving the transport equations analytically. Hence, we have demonstrated that the present solution given by Eq. (14) is identical to Eq. (16), originally derived by Schmid (1997).

Also, a solution similar in form as Eq. (5) using the J-function, can be obtained as shown in Appendix A

$$C(x,t) = (M/A)\delta(x)\exp(-\lambda_S t) + \int_0^t C_1(x,\tau)\exp(-\lambda_S(t-\tau)) \times \left[\alpha + \left(\frac{x^2 - v^2\tau^2}{4D\tau^2} - \frac{1}{2\tau} - \alpha - \lambda + \lambda_S\right) \times J(p,q) - \alpha J(q,p)\right] d\tau. \tag{17}$$

Again, there is no criterion that enables to decide which solution is best or most useful in practical applications.

Analytical solutions for alternative boundary conditions

Often in tracer studies, breakthrough curves are measured at different locations downstream of the injection point. Subsequently, one can analyse the different reaches separately, by using a measured upstream concentration profile as input to the following reach and the next downstream measured concentration profile as the output. In this way, different parameter values can be fitted for each of the reaches and possibly longitudinal trends be detected (e.g., Gooseff et al., 2005). Such an approach can be simulated with the transport equations by adapting the boundary conditions as follows. The measured upstream or input concentration profile $C_i(t)$ serves as upper boundary condition

$$C(0,t) = C_i(t), \tag{18}$$

while initially the main river channel and dead zones are tracer free

$$C(x,0) = C_S(x,0) = 0. \tag{19}$$

In addition, it is assumed that there will never be tracer at infinity in the main channel

$$C(x \to +\infty, t) = 0. \tag{20}$$

The solution of this transport problem is given by

$$C(x,t) = \int_0^t C_i(\tau)G(x,t-\tau)\,d\tau, \tag{21}$$

where $G(x,t)$ is the solution for a Dirac function input as upper boundary condition

$$C(0,t) = \delta(t). \tag{22}$$

The solution of Eqs. (13), subjected to conditions (19), (20), and (22), is derived in Appendix B and is given by

$$G(x,t) = C_2(x,t)\exp(-\alpha t) + (\alpha/\beta)\int_0^t C_2(x,\tau) \times \exp\left(-p - q - \lambda_S(t-\tau)\right)\sqrt{p/q}\,I_1(2\sqrt{pq})\,d\tau, \tag{23}$$

where $C_2(x,t)$ is the solution of the classical advection–dispersion equation including decay in the main channel, subjected to the same initial and boundary conditions, i.e.

$$C_2(x,t) = \frac{x}{2t\sqrt{\pi D t}}\exp\left[-\frac{(x-vt)^2}{4Dt} - \lambda t\right]. \tag{24}$$

Notice that Eq. (23) is very similar to Eq. (14), and when I_1 is expanded in series form will also yield a similar expression as Eq. (16). In addition, an alternative solution can be obtained using the J-function, by just replacing C_1 by C_2 in Eq. (17).

Theoretically the solution given by Eq. (21) requires the evaluation of two convolution integrals, one in Eq. (21) and a second one in Eq. (23). However, in practice the input concentration profile $C_i(t)$ will usually be given as a set of concentrations values $C_i(t_j)$ measured at discrete times t_j for $j = 1,\ldots,n$, so that Eq. (21) can be approximated as

$$C(x,t) = \sum_j C_i(t_j)G(x,t-t_j)(\Delta t)_j, \tag{25}$$

where the summation is over all j values for which $t_j < t$, and $(\Delta t)_j$ is the time interval corresponding to measurement $C_i(t_j)$.

Results and discussion

In order to illustrate and verify the analytical solutions, results calculated with the analytical solutions are compared to numerical results obtained with OTIS. First the solution for instantaneous injection of a tracer in an infinite river reach is investigated. Values of the different transport have been given in the literature, e.g., Bencala and Walters (1983), Bencala (1984), Harvey et al. (1996), Morrice et al. (1997), Harvey and Fuller (1998), and Fernald et al. (2001). For the present comparison, an artificial situation is assumed where 1 kg of solute is injected in the main channel of a stream with a cross-section of 10 m^2, an average flow velocity of 1 m/s, and a dispersion coefficient of 5 m^2/s. The cross-sectional area of the storage zone is taken as 2 m^2, the mass transfer coefficient between the main stream and the dead zones as 0.001 s^{-1}, and different values are considered for the first order decay coefficients to verify the performance of the analytical solution. Four cases are considered: (1) conservative tracer, i.e. no decay, (2) only decay in the main stream with a first order decay coefficient of 2 h^{-1}, (3) only decay in the dead zones with a first order decay coefficient of 10 h^{-1}, and (4) decay in the main stream and in the dead zones by combining cases (2) and (3). Different values for the decay coefficients are used in the main stream and dead zones to clearly illustrate their effect. In particular, a larger value for the decay coefficient in the dead zones is needed, because otherwise there would be little impact, as the tracer resides only partially and temporarily in the dead zone, which is also significantly smaller in size than the main stream.

The concentrations in the main channel are calculated at a distance of 1000 m downstream from the injection location. The analytical solution given by Eq. (14) is used, where the convolution integral is calculated with the trapezium rule using 10,000 intervals, and the Bessel I_1 function is approximated by polynomial expressions given by Abramowitz and Stegun (1970, page 379). The resulting breakthrough curves are presented in Fig. 1.

To compare these results with OTIS, the boundary conditions have to be approximated, because the analytical solution is obtained for an infinite river reach whereas the OTIS

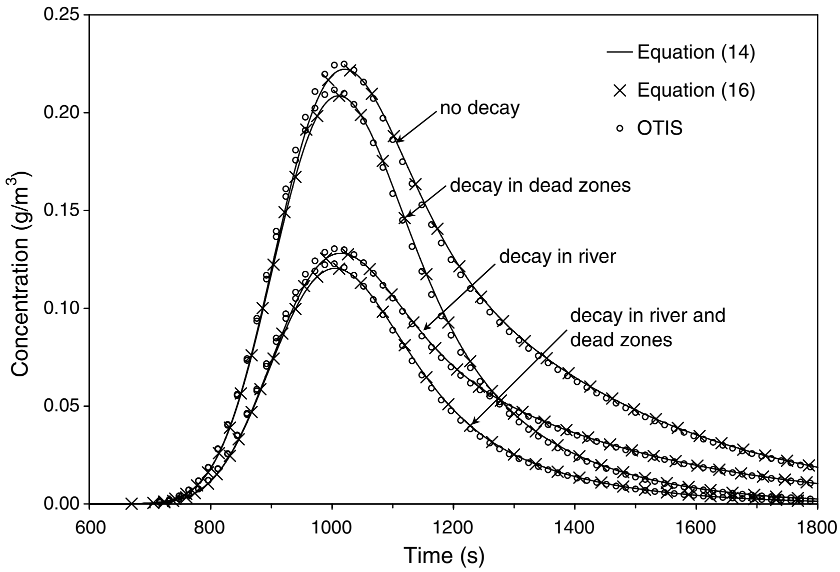

Figure 1 Comparison of concentration profiles calculated with the analytical solution given by Eq. (14) (solid lines), Eq. (16) (cross symbols) (Schmid, 2005; personal communication), and numerical results obtained with OTIS (open dots), for an instantaneously solute injection in an infinite river reach, considering: (1) no decay, (2) only decay in the main stream, (3) only decay in the dead zones, and (4) decay in the main stream and in the dead zones.

model only considers a finite river reach. In order to reduce the effect of a finite length, the river reach in the OTIS-model is assumed to extend from zero to 1400 m; the latter being sufficiently far away from the point, $x = 1000$ m, where the concentrations are evaluated. In addition, small computational time steps of $\Delta t = 4$ s are used to approximate the instantaneous injection as close as possible, and it is assumed that all solute mass is introduced as a triangular distribution, with a peak at 4 s and a concentration equal to $M/Q\Delta t$, where $Q = vA$ is the river discharge. Subsequently to compensate for the 4 s delay in the input peak, 4 s are subtracted from the time of the appearance of the breakthrough. The results are compared to the analytical solution in Fig. 1, where for convenience the numerical results obtained with the OTIS model are only shown for time intervals of 16 s.

One can notice a good agreement between the numerical calculations obtained with OTIS and the results of the analytical solution. The small differences can be attributed to numerical approximation of the boundary conditions, as will be shown further on. In particular, the somewhat higher values of the peak concentrations of the breakthrough curves are due to fact that in a finite reach no tracer can disperse upstream of the injection point.

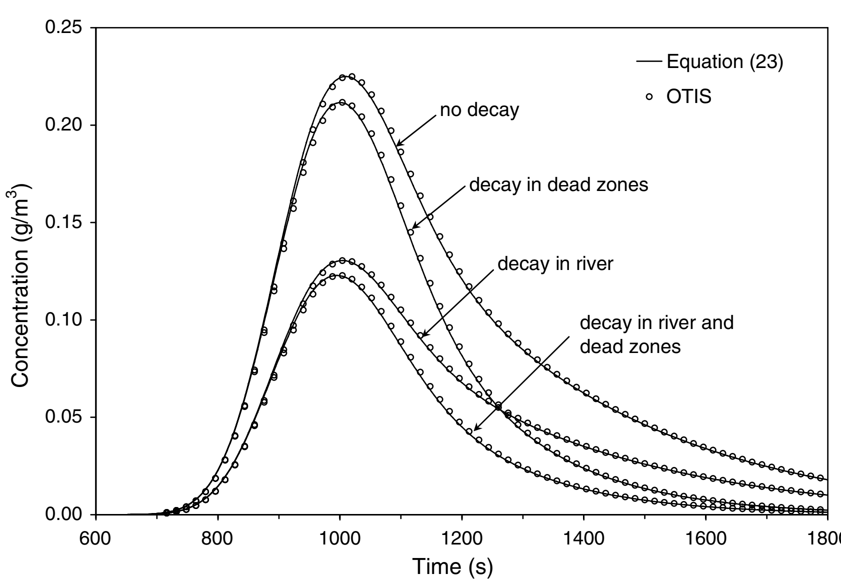

Figure 2 Comparison of concentration profiles calculated with the analytical solution given by Eq. (23) (solid lines) and numerical results obtained with OTIS (open dots) for a slug solute input in a semi-infinite river reach, considering: (1) no decay, (2) only decay in the main stream, (3) only decay in the dead zones, and (4) decay in the main stream and in the dead zones.

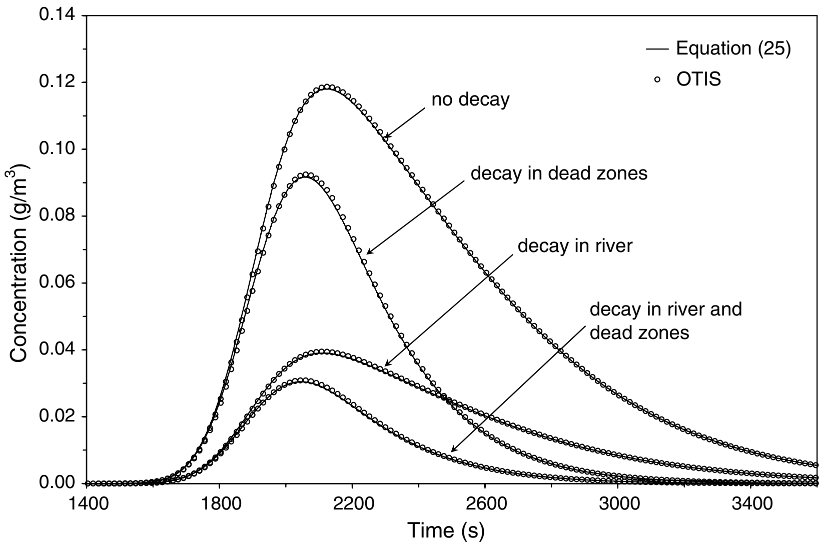

Figure 3 Comparison of concentration profiles calculated with the analytical solution given by Eq. (25) (solid lines) and numerical results obtained with OTIS (open dots) for a discrete solute time series input in a semi-infinite river reach, considering: (1) no decay, (2) only decay in the main stream, (3) only decay in the dead zones, and (4) decay in the main stream and in the dead zones.

Hence, the good correspondence with the results of OTIS demonstrates the accuracy of the numerical approximation of the convolution integral in Eq. (14). The conservative case 1 shown in Fig. 1 was also evaluated by De Smedt et al. (2005) using the analytical solution given by Eq. (5), and is indistinguishable from the present analytical results. In addition, similar results for all cases are obtained with Eq. (16) as shown in Fig. 1 (Schmid, 2005; personal communication).

In order to verify the analytical solution for semi-infinite river reach boundary conditions, previous cases are repeated but using the analytical solution given by Eqs. (21) and (23). In this case the instantaneous injection is approximated as a slug input, where the input concentration $C_i(t)$ is a Dirac peak $(M/Q)\delta(t)$, so that Eq. (21) becomes $C(x,t) = (M/Q)G(x,t)$. The convolution integral in the analytical solution is again calculated with the trapezium rule using 10,000 intervals and the Bessel I_1 function is approximated by polynomial expressions as before. The OTIS calculations also remain as before. The results are shown in Fig. 2. The correspondence between OTIS and analytical results is excellent now, because the upper boundary conditions are identical.

To prove the accuracy of the analytical solution for a semi-infinite reach in case the input is given as a discrete concentration time series, we will test Eq. (21) by considering as input to the reach the concentration profiles obtained in the first series of tests as given in Fig. 1. For the OTIS model, the input series is given by the corresponding OTIS results of the first test case (Fig. 1), in the form of a time series of concentration values with 16 s time intervals. However, the computational time step remains 4 s; hence, intermediate values of the input series are linearly interpolated, as provided in the OTIS model. For the analytical solution, the approximation given by Eq. (25) is used, were the concentration values of the input time series are taken from the analytical solution results for the first test case presented in Fig. 1, with 5 s time intervals because linear interpolation is not foreseen in Eq. (25). The results of the calculations are presented in Fig. 3. The correspondence between OTIS and analytical results is quite good. The small differences mostly at the peak of the concentration profiles are only due to the initial differences in input concentration time series. In particular, one can notice that the differences are smaller than in case of Fig. 1, because the concentration breakthrough curves are calculated further away from the location of the initial instantaneous solute injection, i.e. $(M/A)\delta(x)$ in case of the analytical solution and approximated as a slug input $(M/Q)\delta(t)$ in case of the OTIS model. The concentrations shown in Fig. 3 are actually evaluated at a distance of 2000 m from the injection point, while this was only 1000 m in case of Fig. 1. Hence, the further away from the injection location the less impact the type of boundary condition will have. Anyway, we have shown that the analytical solution for a semi-infinite reach, Eqs. (21) and (23), and the approximation given by Eq. (21) are accurate and can be usefully applied in practice.

Conclusions

Analytical solutions are derived for one-dimensional transport of solutes in a river including effects of transient storage, described by first order mass exchange, and first order solute decay, with different reaction rate coefficients in the main river channel and in the dead zone. The solution is firstly derived for the case of an instant injection of a conservative chemical in an infinite uniform river reach. It is shown that in this case the solution is identical with previous analytical expressions given by Hart (1995), Davis et al. (2000), and De Smedt et al. (2005).

Secondly, analytical solutions are presented for the case of instant injection in an infinite uniform river reach of a solute subjected to first order decay. It is shown that the obtained solution is mathematically equivalent to an expression proposed by Schmid (1997), which was derived via a stochastic interpretation of the transport processes following Hart (1995). The accuracy and correctness of the analytical solution is tested by comparison with results obtained from the numerical OTIS model. The agreement is good, as small differences are primarily due to the different type of upper boundary conditions.

Thirdly, an analytical solution is presented for a solute subjected to first order decay in case of a semi-infinite uniform river reach, with an arbitrary concentration time series input. Again, the accuracy and correctness of this solution is tested by comparison with results obtained using the OTIS numerical model. For a slug input the agreement is perfect as the upper boundary conditions are now identical. It is also shown how this solution can be used in practice to predict the transport in a river reach with an arbitrary concentration time series input. Again, the results compare favourably with the OTIS model calculations.

It can be concluded that the presented analytical solutions for solute transport in rivers with transient storage and solute decay are accurate and correct, and can be usefully applied for future studies, especially for analyses of tracer experiments and transport characteristics in rivers with mass exchange in dead zones. The solutions can also be used for the verification of other models that are developed for more complicated cases.

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Appendix A. Derivation of the analytical solution for instantaneous injection in an infinite river reach

The solution is obtained by means of the Laplace transform. We denote the Laplace transform of a function $f(t)$ as

$$\bar{f}(s) = L[f(t); t \to s] = \int_0^\infty f(t) e^{-st}\, dt. \tag{A.1}$$

Applying the Laplace transform to Eqs. (13) gives

$$D\frac{\partial^2 \overline{C}}{\partial x^2} - v\frac{\partial \overline{C}}{\partial x} - (s+\alpha+\lambda)\overline{C} + \alpha\overline{C}_S = (M/A)\delta(x) \tag{A.2a}$$

$$\overline{C}_S = \frac{\alpha\overline{C}}{\alpha+\beta(s+\lambda_S)}. \tag{A.2b}$$

Substitution of Eq. (A.2b) in (A.2a) results in

$$D\frac{\partial^2 \overline{C}}{\partial x^2} - v\frac{\partial \overline{C}}{\partial x} - \left(s+\lambda+\alpha-\frac{\alpha^2}{\alpha+\beta(s+\lambda_S)}\right)\overline{C} = (M/A)\delta(x). \tag{A.3}$$

When α or β are zero, Eq. (A.3) reduces to the classical advection–dispersion equation including decay, with solution $C_1(x,t)$. Hence, from Eq. (A.3) it follows that

$$\overline{C}(x,s) = \overline{C_1}\left(x, s+\alpha-\frac{\alpha^2}{\alpha+\beta(s+\lambda_S)}\right). \tag{A.4}$$

To obtain the inverse Laplace transform of Eq. (A.4), we make use of the convolution theorem of the Laplace transform (Sneddon, 1972, p. 228)

$$L\left[\int_0^t f(\tau, t-\tau)\, d\tau; t \to s\right] = L\{L[f(t_1,t_2); t_2 \to s]; t_1 \to s\}. \tag{A.5}$$

Eq. (A.4) is now written as

$$\overline{C}(x,s_1,s_2) = \overline{C_1}\left(x, s_1+\alpha-\frac{\alpha^2}{\alpha+\beta(s_2+\lambda_S)}\right), \tag{A.6}$$

where $s_1 = s_2 = s$, but different indexes are used to indicate that the inverse transformation is performed in two steps. The first inverse with respect to s_1 gives

$$L[C(x,t_1,t_2); t_2 \to s_2] = C_1(x,t_1)\exp(-\alpha t_1) \times \exp\left(\frac{\alpha^2 t_1}{\alpha+\beta(s_2+\lambda_S)}\right). \tag{A.7}$$

The second inverse with respect to s_2, yields

$$C(x,t_1,t_2) = C_1(x,t_1)\exp(-\alpha t_1) \times \exp(-(\alpha/\beta+\lambda_s)t_2) L^{-1}\left[\exp\left(\frac{\alpha^2 t_1}{\beta s_2}\right)\right], \tag{A.8}$$

or

$$C(x,t_1,t_2) = C_1(x,t_1)\exp(-\alpha t_1 - (\alpha/\beta+\lambda_s)t_2) \times \left[\frac{\alpha}{\beta}\sqrt{\frac{\beta t_1}{t_2}} I_1(2\alpha\sqrt{t_1 t_2/\beta}) + \delta(t_2)\right]. \tag{A.9}$$

In view of Eqs. (A.5), (A.9) yields the solution

$$C(x,t) = \int_0^t C_1(x,\tau)\exp(-\alpha\tau - (\alpha/\beta+\lambda_S)(t-\tau)) \times \left[\frac{\alpha}{\beta}\sqrt{\frac{\beta\tau}{t-\tau}} I_1\left(2\alpha\sqrt{\frac{\tau(t-\tau)}{\beta}}\right) + \delta(t-\tau)\right] d\tau, \tag{A.10}$$

which after some further small modifications leads to the solution given by Eq. (14) in the main text.

If instead Eq. (A.6) is written as

$$\overline{C}(x,s_1,s_2) = \frac{s_1+\lambda_S}{s_2+\lambda_S}\overline{C}_1\left(x, s_1+\frac{\beta(s_2+\lambda_S)}{\alpha+\beta(s_2+\lambda_S)}\right). \tag{A.11}$$

The first inverse with respect to s_1 becomes

$$L[C(x,t_1,t_2); t_2 \to s_2] = \frac{1}{s_2+\lambda_S} C_1(x,0)\delta(t_1) + \left(\frac{\partial}{\partial t_1}+\lambda_S\right) \times \left[\frac{C_1(x,t_1)}{s_2+\lambda_S}\exp\left(\frac{\beta(s_2+\lambda_S)t_1}{\alpha+\beta(s_2+\lambda_S)}\right)\right], \tag{A.12}$$

and the second inverse with respect to s_2, making use of the inverse Laplace transform of the J-function (Goldstein, 1953), yields

$$C(x,t_1,t_2) = [C_1(x,0)\delta(t_1) + (\partial/\partial t_1 + \lambda_S) \times (C_1(x,t_1) J(\alpha t_1, \alpha t_2/\beta))]\exp(-\lambda_S t_2). \tag{A.13}$$

Next, the partial derivative versus t_1 is worked out with the chain rule of differentiation, using following relationships

$$\frac{\partial}{\partial t_1}[C_1(x,t_1)] = \left(\frac{x^2 - v^2 t_1^2}{4Dt_1^2} - \frac{1}{2t_1} - \lambda\right) C_1(x,t_1), \tag{A.14}$$

and

$$\frac{\partial}{\partial t_1}[J(\alpha t_1, \alpha t_2/\beta)] = \alpha[1 - J(\alpha t_1, \alpha t_2/\beta) - J(\alpha t_2/\beta, \alpha t_1)], \tag{A.15}$$

which is based on properties of the J-function given by Goldstein (1953). When terms are combined, the following expression is obtained

$$\begin{aligned} C(x, t_1, t_2) &= C_1(x, 0)\delta(t_1)\exp(-\lambda_S t_2) + C_1(x, t_1)\exp(-\lambda_S t_2) \\ &\times \left[\alpha + \left(\frac{x^2 - v^2 t_1^2}{4Dt_1^2} - \frac{1}{2t_1} - \lambda + \lambda_S - \alpha\right)\right. \\ &\left.\times J\left(\alpha t_1, \frac{\alpha t_2}{\beta}\right) - \alpha J\left(\frac{\alpha t_2}{\beta}, \alpha t_1\right)\right]. \end{aligned} \tag{A.16}$$

In view of Eq. (A.5), (A.16) yields the solution

$$\begin{aligned} C(x, t) &= C_1(x, 0)\exp(-\lambda_S t) + \int_0^t C_1(x, \tau)\exp(-\lambda_S(t - \tau)) \\ &\times \left[\alpha + \left(\frac{x^2 - v^2\tau^2}{4D\tau^2} - \frac{1}{2\tau} - \lambda + \lambda_S - \alpha\right)\right. \\ &\left.\times J\left(\alpha\tau, \frac{\alpha(t-\tau)}{\beta}\right) - \alpha J\left(\frac{\alpha(t-\tau)}{\beta}, \alpha\tau\right)\right] d\tau, \end{aligned} \tag{A.17}$$

as given by Eq. (17) in the main text.

Appendix B. Derivation of the analytical solution for a slug input in a semi-infinite reach

Applying the Laplace transform to Eqs. (13) gives

$$D\frac{\partial^2 \overline{C}}{\partial x^2} - v\frac{\partial \overline{C}}{\partial x} - (s + \alpha + \lambda)\overline{C} + \alpha\overline{C}_S = 0 \tag{B.1a}$$

$$\overline{C}_S = \frac{\alpha\overline{C}}{\alpha + \beta(s + \lambda_S)}. \tag{B.1b}$$

Substitution of Eq. (B.1b) in (B.1a) results in

$$D\frac{\partial^2 \overline{C}}{\partial x^2} - v\frac{\partial \overline{C}}{\partial x} - \left(s + \lambda + \alpha - \frac{\alpha^2}{\alpha + \beta(s + \lambda_S)}\right)\overline{C} = 0. \tag{B.2}$$

When α or β are zero, Eq. (B.2) reduces to the classical advection–dispersion equation, with solution $C_2(x, t)$. Hence, it follows that

$$\overline{C}(x, s) = \overline{C_2}\left(x, s + \alpha - \frac{\alpha^2}{\alpha + \beta(s + \lambda_S)}\right). \tag{B.3}$$

The inverse Laplace transform of Eq. (B.3) can be obtained in a similar way as in Appendix A, yielding

$$\begin{aligned} C(x, t_1, t_2) &= C_2(x, t_1)\exp(-\alpha t_1 - (\alpha/\beta + \lambda_s)t_2) \\ &\times \left[\frac{\alpha}{\beta}\sqrt{\frac{\beta t_1}{t_2}} I_1\left(2\alpha\sqrt{t_1 t_2/\beta}\right) + \delta(t_2)\right], \end{aligned} \tag{B.4}$$

which in view of Eq. (A.5), gives the solution

$$\begin{aligned} C(x, t) &= \int_0^t C_2(x, \tau)\exp(-\alpha\tau - (\alpha/\beta + \lambda_S)(t - \tau)) \\ &\times \left[\frac{\alpha}{\beta}\sqrt{\frac{\beta\tau}{t - \tau}} I_1\left(2\alpha\sqrt{\frac{\tau(t-\tau)}{\beta}}\right) + \delta(t - \tau)\right] d\tau, \end{aligned} \tag{B.5}$$

which after some further small modifications leads to Eq. (23) in the main text. Also as in Appendix A, a solution can be obtained making use of the J-function, which yields a solution similar as Eq. (A.17), by replacing C_1 by C_2.

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