



Analytical solution for solute transport resulting from instantaneous injection in streams with transient storage

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Abstract

An analytical solution is presented for solute transport in rivers including the effects of transient storage. The traditional advection–dispersion equation for transport in the main channel is linked to a first order mass exchange term between the main channel and the transient storage zones. This system of equations is solved analytically for the case of an instantaneous injection of a tracer mass in a river with constant and uniform flow. The solution enables to estimate the temporal and spatial evolution of the tracer concentration downstream of the injection point. The correctness of the solution is verified by comparison with the numerical model OTIS (USGS). The solution is programmed in MATLAB and linked to a non-linear least squares optimisation algorithm to obtain an effective and reliable method to estimate solute transport parameters from observed breakthrough curves. The procedure is successfully applied to the Chillán River, Chile, where five tracer experiments were conducted. The observed concentration profiles vs. time at the different measuring locations are well reproduced by the model. In all cases the exchange of solute between the main flow channel and transient storage zones is markedly present.

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1. Introduction

Many experimental studies have shown the effect of transient storage on solute transport in streams and small rivers (e.g. Bencala and Walters, 1983; Bencala, 1984; Harvey et al., 1996; Morrice et al., 1997; Harvey and Fuller, 1998; Czernuszenko et al., 1998;

Fernald and Landers, 2001; see also the references cited by Runkel et al., 2003). Transient storage occurs when portions of transported solute become temporarily isolated from the main channel in stagnant water zones, such as pools, dead-end side channels, and adjacent wetland areas. In addition, significant portions of the flow may move through low velocity hyporheic zones, such as coarse gravel beds or porous stream banks. The exchange of solutes between the main channel and these transient storage zones alters the transport characteristics and the magnitude

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of the solute concentration in the main stream channel. Typical effects are retardation of solute migration and asymmetrical shape of observed solute concentration profiles, characterised by steep leading edges and prolonged tails (Nordin and Troutman, 1980). This behaviour cannot be explained by a classical advection–dispersion transport equation, so that large discrepancies result between observed and calculated solute concentrations (Day, 1975; Chatwin, 1980).

Several transient storage models have been formulated for transport in the actively flowing main channel in conjunction with mass exchange in stagnant water zones. The most widespread modelling concept in this respect considers first-order mass exchange proportional to the difference in solute concentration between the main channel and a storage zone (Hays et al., 1966; Nordin and Troutman, 1980; Bencala and Walters, 1983; Bencala et al., 1990; Czernuszenko and Rowinski, 1997). Choi et al. (2000) showed that, in most streams, one lumped storage zone is sufficient to describe the effects of transient storage. However, until present no exact analytical solution has been found for this model, which severely limits applications in practice.

Other model approaches have been proposed. Lees et al. (2000) presented a lumped aggregate dead zone model. Wörman (1998) considered the exchange of solute from the main channel to a storage zone to be governed by a diffusion equation and presented an analytical solution in case dispersion in the main channel is neglected. Wörman et al. (2002) describe a modelling framework that couples longitudinal solute transport in streams with solute advection along a continuous distribution of hyporheic flow paths.

Numerical solutions for transient storage models can be found in the literature. Runkel and Chapra (1993) presented an implicit finite difference approximation for first-order mass exchange between the main channel and a storage zone. This technique was used to develop the One-dimensional Transport with Inflow and Storage (OTIS) model (Runkel and Broshears, 1991; Runkel and Chapra, 1993). This model was later extended with a parameter optimisation technique, OTIS-P (Runkel, 1998), and has been used extensively for analysing tracer experiments to estimate transient storage characteristics in rivers (e.g. Choi et al., 2000; Fernald and Landers, 2001).

Other methods are based on the analysis of the temporal moments of concentration profiles in the main channel, obtained with the Laplace transformation technique (Hays et al., 1966; Nordin and Troutman, 1980; Schmid, 1995, 2003; Runkel, 1996; Czernuszenko and Rowinski, 1997). Wörman (2000) and Lees et al. (2000) show that several models provide an identical representation up to the first three temporal moments of the solute residence time in the main channel. Some investigators have used similarity functions that have the same temporal moments as the observed concentrations in order to describe the shape of observed concentration profiles (Liu and Cheng, 1980; Chatwin, 1980; Schmid, 1995). Hart (1995) presented an alternative formulation of the storage model as a stochastic process and derived an analytical expression for the density function of a conservative solute; this was extended by Schmid (1997) to account for solute decay.

The purpose of this study is to derive an exact analytical solution for transport of solutes in streams resulting from an instantaneous injection. The solution includes the effects of exchange with transient storage zones, modelled by a first order rate equation. The solution is verified by comparison with an established numerical technique (OTIS). The practical usefulness of the solution for interpretation of physical transport characteristics is illustrated by analyses of several tracer experiments conducted in the Chillán River, Chile. Finally, the obtained transport parameters are discussed and compared to results from other studies.

2. Theory

Transport of solutes in streams with transient storage is modelled by linking the one dimensional advection–dispersion equation in the main channel to the storage equation in the dead zones using a first order mass exchange term. The transport equations are given by Bencala and Walters (1983). For a typical conservative tracer experiment the distance and time intervals are short, so that the water flow and transport parameters can be assumed constant. Consequently, the transport equations can be written as (Nordin and Troutman, 1980; 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 zone [ML^{-3}], D is the cross-sectional averaged longitudinal dispersion coefficient in the main channel [L^2T^{-1}], (v the cross-sectional averaged velocity in the main channel [LT^{-1}], α the mass exchange coefficient between the main channel and the storage zone [T^{-1}], β the ratio between the storage zone and the main channel cross-sectional area [–], x the longitudinal distance in the main stream channel [L], and t the time [T]. Note that Eq. (1a) reduces to the classical advection–dispersion transport equation when α or β become zero.

In a typical tracer injection experiment, a mass M [M] of tracer is injected at time zero and location $x=0$, well mixed over the cross-sectional area A [L^2] of the main stream channel, so that the initial conditions are given by

$$C(x, 0) = \left(\frac{M}{A}\right) \delta(x) \tag{2a}$$

where δ is a Dirac function, and because the storage zone is initially solute free

$$C_S(x, 0) = 0 \tag{2b}$$

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

$$C(\pm\infty, t) = 0 \tag{3}$$

The solution of Eqs. (1a) and (1b) subjected to conditions (2a), (2b) and (3) is derived in Appendix A, and is given by

$$C(x,t) = \int_0^t \left[\alpha + \left(\frac{x^2 - v^2\tau^2}{4D\tau^2} - \frac{1}{2\tau} - \alpha \right) J\left(\alpha\tau, \frac{\alpha(t-\tau)}{\beta}\right) - \alpha J\left(\frac{\alpha(t-\tau)}{\beta}, \alpha\tau\right) \right] C_0(x,\tau) d\tau \tag{4}$$

where $C_0(x,t)$ is the solution of the classical advection–dispersion equation subjected to the same initial and boundary conditions, well known from a number

of text-books

$$C_0(x, t) = \frac{M/A}{2\sqrt{\pi Dt}} \exp\left[-\frac{(x - vt)^2}{4Dt}\right] \tag{5}$$

The concentration distribution described by Eq. (5) at a fixed time as a function of position, x , corresponds to a normal probability density function. The J -function in Eq. (4) is defined by Goldstein (1953) as

$$J(a, b) = 1 - e^{-b} \int_0^a e^{-\lambda} I_0(2\sqrt{b\lambda}) d\lambda \tag{6}$$

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

$$J(a, b) = e^{-a-b} \sum_{n=0}^{\infty} \frac{b^n}{n!} \sum_{m=0}^n \frac{a^m}{m!} \\ = 1 - e^{-a-b} \sum_{n=1}^{\infty} \frac{a^n}{n!} \sum_{m=0}^{n-1} \frac{b^m}{m!} \tag{7}$$

The analytical expression for the density function of a conservative solute derived by Hart (1995) bears some resemblance with our analytical solution when the J -function is expanded in series form, which is no surprise because they describe the same phenomenon although based on different approaches; however these expressions are not exactly equal.

In order to illustrate and verify the analytical solution, results calculated with Eq. (4) are compared to numerical results obtained with OTIS. For this comparison, we assume an artificial situation where 1 kg of solute is instantaneously injected in the main channel of a river with a cross-section of 10 m², an average flow velocity of 1 m/s, and a dispersion coefficient of 5 m²/s. The ratio of storage zone and main channel cross-sectional area is taken as 0.2, and different values are considered for the mass transfer coefficient to verify the performance of the analytical solution. The concentrations in the main channel will be calculated at a distance of 1000 m downstream from the injection point. For the evaluation of the analytical solution, the convolution integral in Eq. (4) is calculated with the trapezium rule using 100 intervals.

For a true comparison, we should minimise possible differences that can arise because the analytical and numerical approach have different

boundary conditions. Basically, the analytical solution is obtained for an infinite system whereas the numerical solution is obtained for a finite system. In addition, the analytical solution is for an instantaneous injection, while the OTIS model considers a prescribed concentration or mass flux vs. time entering the upstream end of the modelled system. Kreft and Zuber (1978) have shown that concentration profiles can differ depending upon the boundary conditions, especially for small Peclet numbers. In order to reduce the effect of a finite length, we assume the river reach in the OTIS-model to extend from zero to 1400 m; the latter being sufficiently far away from the point, $x=1000$ m, where the concentrations will be evaluated. Actually, because we use a computational cell size of 1 m in the longitudinal direction of the river, the concentration is calculated in the cell which is centred around $x=999.5$ m. Also, the point where the concentration is evaluated is sufficiently far away from the upper boundary, such that the type of upper boundary condition has less influence. In addition, to introduce the right amount of solute and mimic the instantaneous injection as close as possible, we use a very small computational time step, $\Delta t=4$ s, and assume that all solute mass is introduced as a triangular distribution, with a peak at time 4 s and a concentration equal to $M/Q\Delta t$, where $Q=vA$ is the river discharge [L^3T^{-1}].

The concentration profiles are calculated for three values of the exchange coefficient, α , respectively, 0, 0.001 and 0.01 s^{-1} . The results are given in Fig. 1. For convenience, the numerical results obtained with OTIS are only shown for time intervals of 16 s. One can notice a very good agreement between the numerical calculations obtained with OTIS and the results of the present analytical solution. The small differences can be attributed to numerical errors and approximation of the boundary conditions. When α is zero, the analytical solution reduces to Eq. (5). However, the analytical results shown in Fig. 1 are calculated with Eq. (4). Hence, the good correspondence with the results of OTIS proves the accuracy of the numerical approximation of the convolution integral in Eq. (4). The curve calculated for $\alpha=0.001 s^{-1}$ shows the typical asymmetrical shape, which is characteristic for slow or hindered exchange of solutes between the main channel and the storage zone. Notice that the leading edge of this curve can

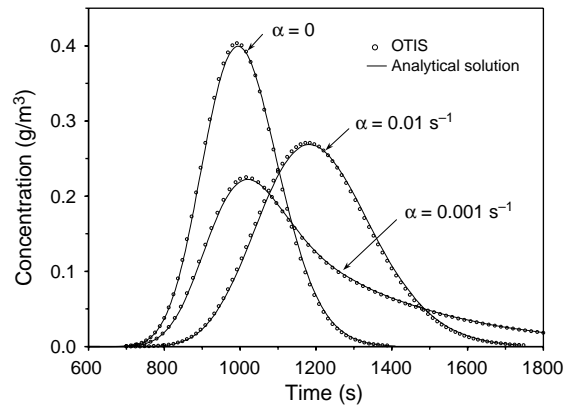


Fig. 1. Comparison of concentration profiles calculated with the analytical solution (solid lines) and the numerical results obtained with OTIS (open dots) for a hypothetical tracer experiment, considering 1 kg of solute instantaneously injected in the main channel of a river with a cross-section of 10 m², an average flow velocity of 1 m/s, a dispersion coefficient of 5 m²/s, a ratio of storage zone and main channel cross-sectional area of 0.2, and different values for the mass transfer coefficient, i.e. 0, 0.01 and 0.001 s⁻¹.

only be termed steep when compared to its tailing section, because compared to the other concentration curves, it is clearly not steeper. The concentration profile obtained for $\alpha=0.01 s^{-1}$ is characteristic for rapid exchange between the main channel and the storage zone. In this case the distinction between the main channel and storage zone largely disappears, and the concentration curve becomes more symmetrical and approaches the classical solution given by Eq. (5). Also, the overall spread of the concentration distribution is less than in the previous case, and as a consequence the maximum concentration is higher. Hence, the interpretation of concentration profiles from tracer tests will not always be simple and straightforward, because effects of exchange with transient storage zones might not be noticed, or can easily be misinterpreted. Moreover, values of flow velocities or dispersion coefficients obtained with crude estimation techniques, that ignore the effects of transient storage, might not represent the actual conditions in the river.

3. Field experiments

The usefulness of the presented analytical solution is demonstrated with a practical application involving

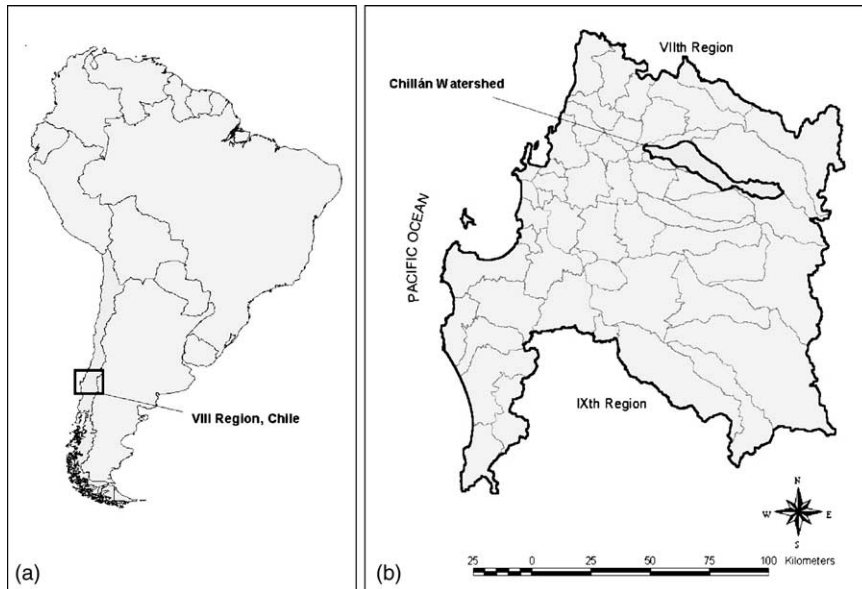


Fig. 2. Situation map: (a) location of Chile's VIIIth Region within South-America; (b) location of the Chillán Watershed within the VIIIth Region, Chile.

the analysis of tracer experiments conducted in the Chillán River, located in Chile's VIIIth Region (Fig. 2). The river emerges in the Andes Mountain Range and flows to the West to its confluence with the Ñuble River, a tributary of the Itata River, which discharges into the Pacific Ocean. The Chillán River has a drainage area of about 757 km², a total length of 105 km, and a mean discharge of 23 m³/s at its confluence with the Ñuble River (Brevis et al., 2001a). The upper part of the watershed is forested. The actual study reach of the Chillán River, shown in Fig. 3, is situated in the downstream part in the Central Valley of Chile, which is mainly agricultural. Here, the river consists of riffles and pools, generally with a cobble and gravel bed, except in some parts where the river is cut into bedrock. This section is especially interesting from the point of view of water management, because of the intensive use of river water for irrigation, and the proximity of the city of Chillán with 190,000 inhabitants, who use the river as a source of drinking water and for disposal of wastewater.

Brevis et al. (2001b) conducted five tracer-dilution experiments in the Chillán River and compared the values for the longitudinal dispersion coefficients determined with the OTIS-P model to those obtained from simple, empirical and semi-empirical equations

found in the literature. The data obtained from these experiments are used in the present study. Tracer experiments were conducted according to the general guidelines described in Hubbard et al. (1981), using a 20% Rhodamine WT solution. Dye solutions were instantaneous injected at two different river locations, denoted in Fig. 2 as injection points 1 and 2. In order to obtain good transversal mixing in the main channel, the solution was injected simultaneously at multiple points along the cross-section, leaving out dead zones and areas immediately adjacent to the stream banks. Tracer concentrations in the main river channel were measured at different sampling locations at regular time intervals using discrete samples and a calibrated fluorometer (Turner Designs Model 10, with a detection limit of 0.01 ppb). The different sampling locations are indicated in Fig. 2, and denoted by numbers from 1 to 10. At each first downstream measurement location, the transversal mixing of the solutes was verified by taking samples at different points along the cross-section. Samples were periodically checked for changes in the pH of the river water and no significant variations were observed during the duration of the experiments. Dye concentrations were measured both in the field, in order to guide the sample-taking process, and under laboratory

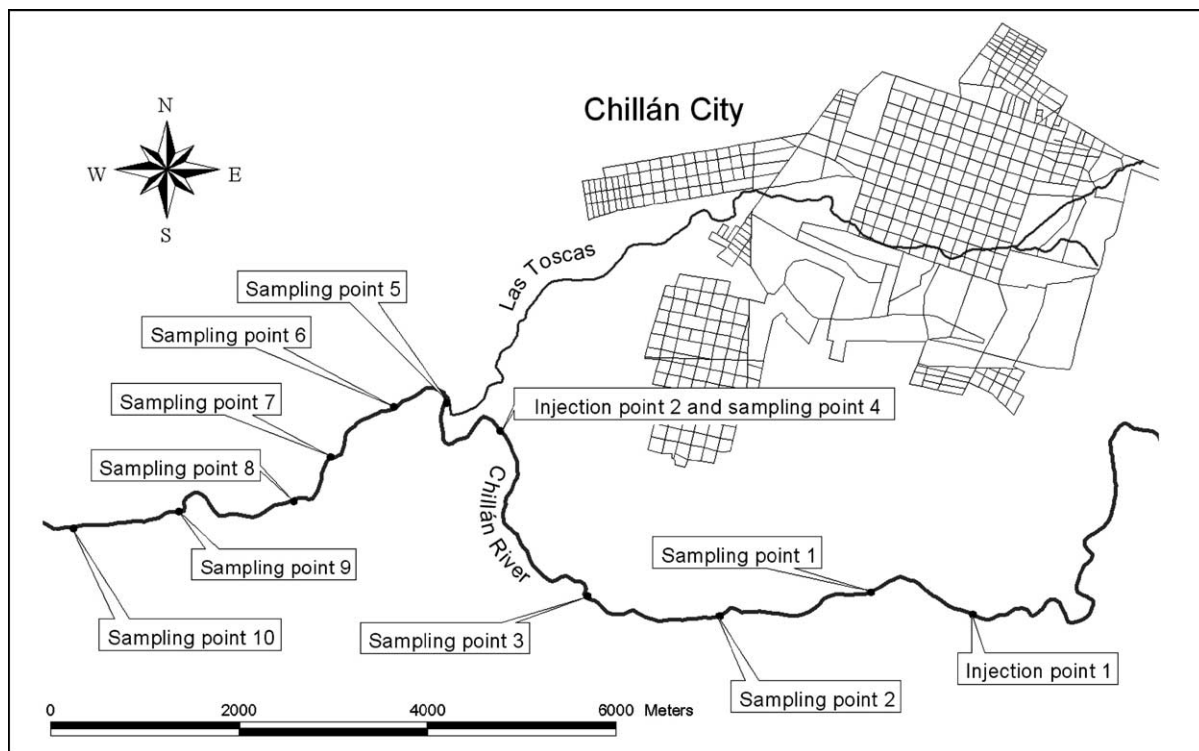


Fig. 3. Location of the tracer injection and sampling locations on the Chillán River.

conditions which yielded the final measurements used for subsequent analyses. The layout of all tracer experiments is given in Table 1, where the experiments have been labelled with Roman numbers.

Losses of mass of Rhodamine WT during tracer experiments may occur due to photodegradation and sorption (Jobson, 1997; Laenen and Bencala, 2001; Keefe et al., 2004). However, because of the short duration of the experiments, such effects are ignored in the present study and the tracer is considered as being conservative. In order to analyse the results from the tracer experiments, the present analytical solution was programmed in MATLAB and linked to a non-linear least squares optimisation algorithm, so that transport parameters that give the best match between measured and calculated concentration values can be determined. The theoretical solution, given by Eq. (4), contains five parameters that can be optimised, i.e. the main channel cross-sectional area, A , flow velocity, v , and dispersion coefficient, D , of the main flow channel, the exchange coefficient, α ,

between the main channel and the storage zones, and the ratio of storage zone and main channel cross-sectional area, β . A theoretical concentration profile can be fitted to an observed tracer breakthrough curve obtained at a certain sampling location, provided two experimental parameters are given, i.e. the injected mass, M , and the distance, x , between injection point

Table 1
Tracer experiments conducted in the Chillán River, Chile

Experiment no.	Date	Injection point	Tracer mass (g)	Observation points
I	November 18, 2000	1	157.1	3,4,9
II	February 7, 2001	1	23.8	1,2,3,4
III	February 8, 2001	2	35.7	7,10
IV	March 9, 2001	2	38.1	5,6,7
V	March 30, 2001	1	20.3	1,2

Table 2
Optimised parameter values with 95% confidence intervals for the tracer experiments conducted in the Chillán River, Chile

Exp.	x (m)	A (m ²)	v (m/s)	D (m ² /s)	β (-)	α (s ⁻¹)
I-3	4604	18.2±0.4	0.477±0.011	3.29±1.05	0.15±0.03	2.87×10 ⁻⁴ ±0.89×10 ⁻⁴
I-4	6524	21.5±0.6	0.416±0.010	2.54±1.12	0.11±0.03	1.78×10 ⁻⁴ ±0.75×10 ⁻⁴
I-9	11646	24.3±1.0	0.383±0.008	5.73±1.69	0.09±0.02	5.26×10 ⁻⁴ ±0.30×10 ⁻⁴
II-1	1100	9.0±0.4	0.188±0.009	1.61±0.52	0.22±0.05	2.20×10 ⁻⁴ ±1.23×10 ⁻⁴
II-2	2915	10.6±0.4	0.175±0.008	1.79±0.60	0.15±0.05	1.45×10 ⁻⁴ ±0.72×10 ⁻⁴
II-3	4604	11.2±0.4	0.170±0.007	4.07±0.98	0.09±0.03	3.49×10 ⁻⁵ ±3.24×10 ⁻⁵
II-4	6524	10.5±0.4	0.170±0.003	3.83±0.53	0.09±0.01	2.27×10 ⁻⁵ ±0.93×10 ⁻⁵
III-7	2969	10.5±0.3	0.174±0.004	3.02±0.66	0.18±0.02	6.81×10 ⁻⁵ ±2.10×10 ⁻⁵
III-10	6354	10.9±0.5	0.172±0.004	3.05±0.93	0.21±0.02	5.07×10 ⁻⁵ ±1.51×10 ⁻⁵
IV-5	1594	10.0±0.2	0.086±0.002	0.88±0.14	0.26±0.02	9.44×10 ⁻⁵ ±1.95×10 ⁻⁵
IV-6	1971	17.3±0.2	0.092±0.001	1.28±0.13	0.25±0.01	7.62×10 ⁻⁵ ±1.07×10 ⁻⁵
IV-7	2969	16.0±0.4	0.100±0.001	2.24±0.21	0.23±0.02	3.86×10 ⁻⁵ ±0.63×10 ⁻⁵
V-1	1100	7.5±0.2	0.132±0.004	0.52±0.21	0.32±0.04	2.70×10 ⁻⁴ ±0.66×10 ⁻⁴
V-2	2915	9.9±1.0	0.106±0.018	0.81±1.14	0.37±0.20	1.85×10 ⁻⁴ ±2.00×10 ⁻⁴

x , longitudinal distance along the main river channel between injection and sampling location; A , cross-sectional area of the main river channel; v , cross-sectional averaged velocity in the main channel; D , cross-sectional averaged longitudinal dispersion coefficient in the main channel; β , ratio between the storage zone and the main channel cross-sectional area; and α , mass exchange coefficient between the main channel and the storage zone.

and sampling location. The value for the latter was determined from a topographic map with scale 1:10.000. The results from the optimisation procedure are presented in Table 2. Each case is labelled with a code composed of a Roman number representing the experiment and an Arabic number representing the sampling location. The first column of Table 2 gives the distance between injection point and sampling location. The other columns give the optimised values for the model parameters together with their 95% confidence intervals.

4. Results and discussion

All experiments were conducted in the austral spring and summer of 2000–2001, during which the river flow became increasingly reduced. The first experiment was conducted on November 18, 2000, in order to determine the overall transport characteristics of the total study reach. A mass of 157.1 g was injected at injection point 1, well mixed over the cross-sectional area. Measurements were performed at downstream sampling locations 3, 4 and 9. The results of the model optimisation are shown in Fig. 4, depicting observed and fitted concentration profiles vs. time at the different measuring locations. Parameters A , v and β are rather accurately estimated

which is reflected by their small confidence intervals, while this is not the case for D and α (Table 2). The estimated value for the flow velocity in the main channel is fairly constant, which confirms the assumption of constant flow used in the transport equations (Eqs. (1a) and (1b)). Also, the other parameter values are rather constant except for D and α . The reason for the variation and less accurate

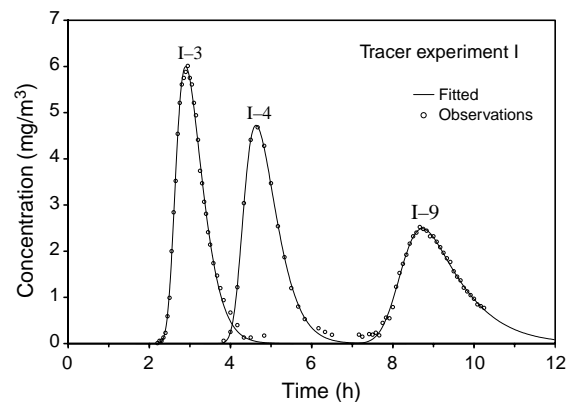


Fig. 4. Fitted and observed concentrations for the first tracer experiment conducted on November 18, 2000, in the Chillán River, Chile. Observations are shown by open dots and simulated curves by solid lines, calculated with the optimised parameter values given in Table 2. The label on the curves denotes the experiment (Roman) and sampling point (Arabic) number.

estimation of parameters D and α is probably due to the fact that transient storage exchange produces solute spreading in the main channel, which can also be explained as a conventional dispersion process; hence, parameters D and α are highly correlated. The measured and fitted concentration curves show typical shapes and trends, with peak values decreasing at consecutive sampling locations, while the solute plume is increasingly spreading out due to the effects of dispersion and transient storage. Tailing of the curves is somewhat faint, but nevertheless, distinctly noticeable. Unfortunately, the measurements at the last sampling point were interrupted too early, which explains the large uncertainty and deviating values obtained for D and α compared to the previous sampling points. Nevertheless, from the obtained results, it follows clearly that transient storage is important, and transient storage zones amount to 9–15% of the main river channel cross-sectional area.

The second experiment was conducted on February 7, 2001, in a reach of the Chillán River located upstream of the Las Toscas tributary. A tracer mass of 23.8 g was injected at injection point 1 and measurements were performed at sampling locations 1, 2, 3 and 4. This was the largest experiment conducted. Results are shown in Fig. 5. The fit between theory and field observations is very good. From the

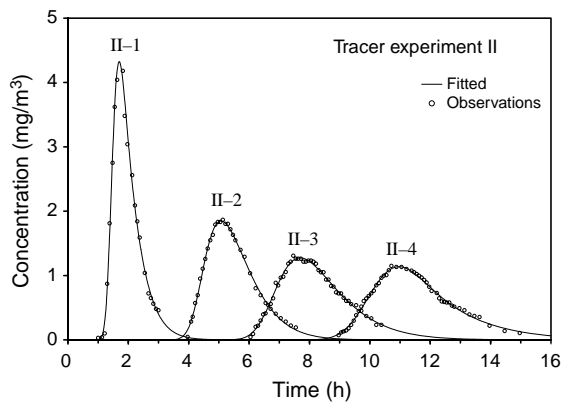


Fig. 5. Fitted and observed concentrations for the second tracer experiment conducted on February 7, 2001, in the Chillán River, Chile. Observations are shown by open dots and simulated curves by solid lines, calculated with the optimised parameter values given in Table 2. The label on the curves denotes the experiment (Roman) and sampling point (Arabic) number.

optimised parameter values presented in Table 2, one can notice that A and ν are nearly constant along the reach, but for the other parameters there is a clear difference between the first and last sampling points, with the dispersion coefficient markedly increasing, while the parameters that describe the transient storage characteristics are decreasing. In view of the fact that the optimisation procedure gives estimates of the average parameter values for the whole segment between injection and sampling point, one can conclude that in the last part of the investigated reach, containing sampling points 3 and 4, there is much less transient storage than in the upper part, containing sampling locations 1 and 2. These findings agree with conditions observed in the field: upstream of sampling point 2 the bed of the Chillán River is made up mainly of cobble and gravel, while downstream of this point the river frequently cuts through bedrock. This explains why the transient storage fraction decreases from 20 to 10% and the exchange coefficient decreases by one order of magnitude. Notice that at the same time the dispersion coefficient increases markedly. The latter has also to do with the fact that dispersion and transient storage exchange are highly correlated, and when the transient storage exchange becomes less identifiable, its effects are only seen as an increase in solute spreading, which can be explained by a conventional dispersion process.

The third experiment was conducted on February 8, 2001, downstream of the Las Toscas tributary; 35.7 g of the Rhodamine dye was injected at injection point 2 and breakthrough concentrations were measured at sampling locations 7 and 10. Results are shown in Fig. 6. Although the measurements are incomplete and appear somewhat irregular, the model fit is good and all parameters are estimated rather accurately. In addition, there is no distinctive difference of any parameter values between the two sampling locations. The results are in line with the previous experiments, i.e. there is a marked effect of transient storage exchange, with a transient storage fraction of about 20%.

Results of the fourth tracer experiment are given in Fig. 7. This experiment was conducted on March 9, 2001, in the section of the confluence of the Chillán River with the Las Toscas tributary; 38.1 g of tracer was injected at injection point 2 and breakthrough concentrations were measured at sampling locations

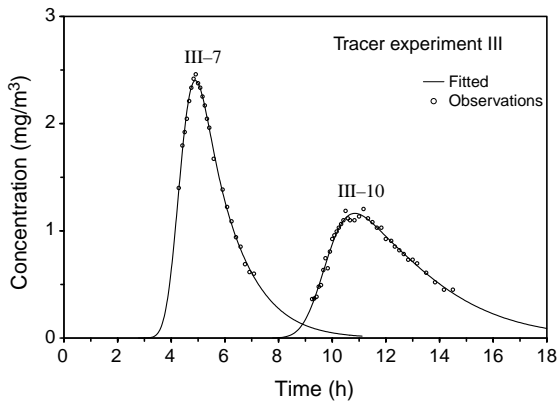


Fig. 6. Fitted and observed concentrations for the third tracer experiment conducted on February 8, 2001, in the Chillán River, Chile. Observations are shown by open dots and simulated curves by solid lines, calculated with the optimised parameter values given in Table 2. The label on the curves denote the experiment (Roman) and sampling point (Arabic) number.

5, 6 and 7. Sampling point 5 is located upstream of the confluence and the other sampling points are located downstream, far enough to ensure complete transversal mixing with the water coming from the tributary. In Fig. 7, one can see a marked decrease in concentration values between sampling point 5 and 6. This is due to a strong dilution of the dye in the river caused by its confluence with the Las Toscas tributary. In March, at the end of the austral summer (dry

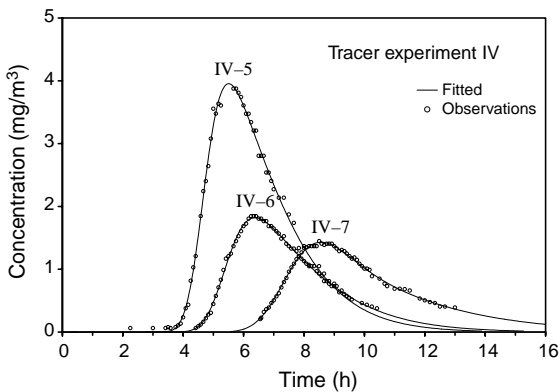


Fig. 7. Fitted and observed concentrations for the fourth tracer experiment conducted on March 9, 2001, in the Chillán River, Chile. Observations are shown by open dots and simulated curves by solid lines, calculated with the optimised parameter values given in Table 2. The label on the curves denotes the experiment (Roman) and sampling point (Arabic) number.

period), the discharge of the Chillán river River—which is already low—is further reduced by extraction of river water for irrigation purposes, while the discharge of the Las Toscas tributary is more or less maintained through the input of urban wastewater from the city of Chillán. Under these circumstances, the contribution of the Las Toscas Tributary can make up about half of the total discharge downstream of the confluence. This is also reflected in the values of the cross-sectional area of the main stream channel: the average value for each of the stream reaches between the injection point and the three sampling points increases considerably from 10 to 17 m². As the average water velocity almost remains the same, we can deduce that during the March campaign the Las Toscas tributary had a discharge of about the same order of magnitude as the discharge of the Chillán River, a conclusion that was also confirmed by field observations. The optimised values for the different parameters are similar as for the other experiments. In particular, it is found that transient storage exchange zones amount to more than 20% of the main river channel cross-sectional area in this part of the Chillán River.

The fifth experiment was conducted on March 30, 2001, at the end of the dry season. The objective was to analyse the effect of extremely low storage conditions on the behaviour of the stream reach previously studied in experiment II. A mass of 20.3 g was injected at injection point 1 and measurements were performed at sampling locations 1 and 2. The results are shown in Fig. 8. Obviously, the measurements were not that good. Some deviation between theory and observations occurs in the tail of the first breakthrough curve, and the measurements of the tail of the second breakthrough curve are incomplete. This is reflected in large confidence intervals for the estimates, especially for the second sampling point. However, the estimate of the fraction of transient storage zones for the first sampling point is rather accurate. Its value amounts to 32%, which is larger than what was obtained in the previous experiment II-1. The difference is most probably due to changes in water level and flow regime. In experiment V, the river discharge was lower than in experiment II, which is reflected in lower values of the cross-sectional area and the average flow velocity for the main river channel. Hence, in such conditions it is

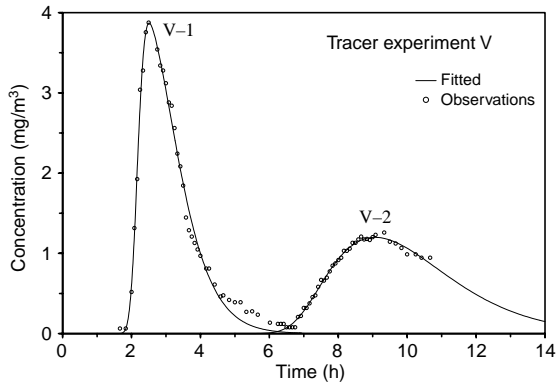


Fig. 8. Fitted and observed concentrations for the fifth tracer experiment conducted on March 30, 2001, in the Chillán River, Chile. Observations are shown by open dots and simulated curves by solid lines, calculated with the optimised parameter values given in Table 2. The label on the curves denotes the experiment (Roman) and sampling point (Arabic) number.

expected that the fraction of transient storage zones will be larger. Field observations show that the discharge occupies only a small part of the total river bed, and combined with the high irregularity of the bed topography gives rise to dead-end side channels in some reaches. As the discharge rates drop during the dry season, a braided network of several smaller channels is formed within the winter bed. Some of these channels become disconnected as discharge values continue to decrease. However, hyporheic flow may still continue through the high porosity gravel bed.

It is evident that the assumption of uniform flow and constant transport parameters cannot be expected to hold over large distances or large residence times. Nevertheless, we expect that the obtained results describe the transport behaviour in the investigated stream in an average way, and as such are representative for the prevailing conditions. This should be kept in mind when discussing the general relationships between the parameters that describe the transport of solutes subjected to transient storage and the river flow characteristics of the Chillán River. The dispersion coefficient is considered to vary in function of the friction velocity and dimensions of the river channel, as for instance expressed by the relationships of Elder (1959) and Fischer et al. (1979). This implies that the dispersion coefficient should increase with the average flow velocity and/or the water level.

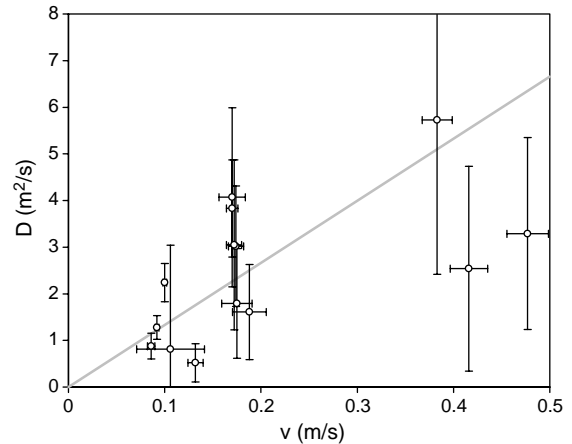


Fig. 9. Estimated values with 95% confidence intervals of the dispersion coefficient, D , vs. the average main channel flow velocity, v ; the solid line gives the best least square regression fitted line forced through the origin.

Fig. 9 depicts all combined estimated dispersion coefficients vs. flow velocities in the main channel of the Chillán River. Also shown in the figure are the 95% confidence intervals of the estimates in order to indicate the uncertainty of the estimation. No real clear unique relationship can be deduced, because there is a lot of scatter present in the data for obvious reasons, as the data originate from different locations and the dispersion coefficient could often not be estimated accurately due to interference with transient storage effects. Nevertheless, a least square regression straight-line forced through the origin fits reasonably through most of the data points. The slope of the line is 13.3 m and seems to be related to the width of the river, in accordance with Fischer's finding that transverse mixing has a great effect on longitudinal dispersion in natural channels (Rutherford, 1994). In the present case, we cannot go further into detail, because the necessary field information is lacking. However, we can conclude that although the real relationship between the dispersion coefficient and the flow velocity is not known exactly, the linear relationship shown in Fig. 9 is a fair approximation that can be useful for future studies about transport of chemicals in the Chillán River.

In the literature, no theoretical considerations can be found about the dependency of the ratio β between the storage zone and the main channel cross-sectional

area and the flow characteristics or dimensions of the flow channel. In field studies, the ratio of storage zone to main channel cross-sectional area β ranges from 0.001 to 1 (Bencala and Walters, 1983; Bencala, 1984; Harvey et al., 1996; Morrice et al., 1997; Harvey and Fuller, 1998; Czernuszenko et al., 1998; Fernald and Landers, 2001). Some authors have reported a decrease in the ratio of the transient storage zones and the main channel cross-sectional area with increasing stream flow (Harvey et al., 1996; Morrice et al., 1997). Determined values of the ratio between the storage zone and the main channel cross-sectional area vs. the main channel cross-sectional area are presented in Fig. 10, together with their 95% confidence intervals. The β -values obtained in this study vary between about 0.1 and 0.4, which is well within the range reported in literature. Again there is a lot of spreading in the data and uncertainty in the estimates, which is reflected by the large error bars. From the previous discussion, we know that the river characteristics along the different reaches can change considerably, i.e. generally, the riverbed consists of cobble and gravel, intermixed with sand, but there are also places where the river is cut into bedrock. Moreover, the amount of transient storage zones also depends upon the water level in the river and water flow velocity. Because we have insufficient information to investigate these effects we will try to only capture the overall mean characteristics. A simple

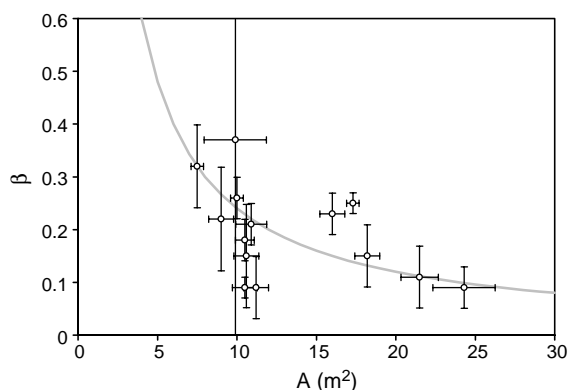


Fig. 10. Estimated values with 95% confidence intervals of the ratio between the storage zone and the main channel cross-sectional area, $\beta = A_s/A$, vs. the main channel cross-sectional area, A ; the solid curve gives the best fit relationship based on a constant value for the transient storage zone cross-sectional area, A_s .

approach is to assume a constant average cross-sectional area A_s for the transient storage zones. From the estimated values of β and A we can determine an average value for A_s of 2.40 m^2 , which yields a hyperbolic relationship between $\beta = A_s/A$ and the cross-sectional area A of the main channel, as depicted by the solid curve in Fig. 10. This curve fits the data rather well. The largest deviations occur for the reaches including sampling locations 3 and 4, where the river goes through bedrock, and for sampling points 6 and 7, which are located after the confluence with the Las Toscas tributary, where the assumption of uniform flow is violated and the obtained parameter estimates will not accurately represent the actual conditions in the field. Anyway, we conclude that an average value for A_s of 2.40 m^2 captures the main trend very well, but cannot be further verified or proved due to insufficient data.

Fig. 11 shows all estimated values of the exchange coefficient α vs. the flow velocity v in the main channel, together with their 95% confidence intervals. The α -values vary between about zero and $3 \times 10^{-4} \text{ s}^{-1}$. There is a lot of scatter present in the data and no clear dependence of α on the flow velocity v can be detected. In examples from the literature, values of the exchange coefficient α range from 10^{-5} to 10^{-3} s^{-1} (Bencala and Walters, 1983; Bencala, 1984; Harvey et al., 1996; Morrice et al., 1997; Harvey and Fuller, 1998;

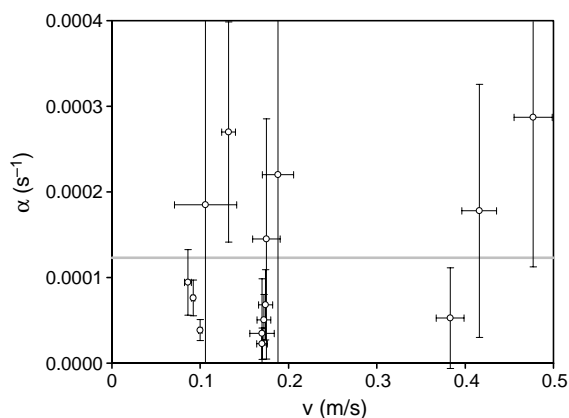


Fig. 11. Estimated values with 95% confidence intervals of the exchange coefficient, α , vs. the average main channel flow velocity, v ; the solid curve represents the un-weighted mean value of the exchange coefficient, α .

Czernuszenko et al., 1998; Fernald and Landers, 2001; Runkel, 2002). Hence, the values obtained in the present study fall between the extremes cited in the literature. Several authors have noticed an increase in the magnitude of α with increasing stream flow (Harvey et al., 1996; Morrice et al., 1997). Therefore, α might be related to the mean flow velocity in the main channel, possibly because higher flow velocities enhance the exchange between the main channel and the transient storage zones. However, such relationship is not detectable in the present results. Hence, the solid line in Fig. 11 merely represents the un-weighted average value for the exchange coefficient, which equals $1.2 \times 10^{-4} \text{ s}^{-1}$ independent of the flow velocity. This value agrees with other findings, in particular those from Fernald and Landers (2001), who used dye tracers to study transient storage in a 26 km long stretch of the Willamette River, Oregon, USA, and obtained a mean value for the exchange coefficient α of $1.6 \times 10^{-4} \text{ s}^{-1}$.

5. Conclusions

An analytical solution has been derived for the equations that describe one-dimensional transport of solutes resulting from an instantaneous injection in rivers considering the effects of transient storage. The traditional advection–dispersion equation for transport in the main channel is linked to a first order mass exchange term between the main channel and the transient storage zones. This system of equations is solved analytically for the case of an instant injection of a tracer mass in a river section with uniform flow characteristics. The solution enables to predict the temporal and spatial evolution of the tracer concentration downstream of the injection point. The correctness of the solution could be verified through comparison of the results from a sample application with those obtained using the USGS One-dimensional Transport with Inflow and Storage (OTIS) numerical model.

The solution was programmed in MATLAB and linked to a non-linear least squares optimisation algorithm, in order to obtain an effective and reliable method to estimate solute transport parameters from observed breakthrough curves. The model allows to

estimate the cross-sectional area, flow velocity and dispersion coefficient in the main flow channel, the exchange coefficient between the main channel and the storage zone, and the ratio of storage zone and main channel cross-sectional area.

The procedure was successfully applied to interpret results from tracer experiments conducted in the Chillán River, located in South–Central Chile. Five tracer experiments were conducted using Rhodamine WT, involving two different injection points and ten different sampling locations. The observed concentration profiles vs. time at the different measuring locations are always well reproduced by the model. In all cases, the exchange of solute between the main flow channel and transient storage zones is markedly present. The measured and fitted concentration curves show typical shapes and trends, with decreasing peak values and increased spreading in downstream direction, while tailing of the curves is somewhat faint, but nevertheless clearly noticeable. Also, the cross-sectional area of the main flow channel, the flow velocity in the main flow channel, and the ratio of storage zone and main channel cross-sectional area are accurately estimated, which is reflected by their small confidence intervals. On the other hand, the dispersion coefficient in the main channel and the transfer coefficient between the main channel and the transient storage zones can often not accurately be estimated, which results in large confidence intervals. The reason for the less accurate estimation is that these parameters are highly correlated, because they both describe the spreading of the solute in the main channel.

Although the scatter and uncertainty in the estimated values of the dispersion coefficient are large, the overall results indicate that the dispersion coefficient increases more or less linearly with the flow velocity in the main channel. The estimated values for the ratio of the storage zone and main channel cross-sectional area vary between 9 and 37%, which is within the range reported in literature. Analysis of the overall results obtained for the transient storage zone indicates that the mean value for the transient storage cross-sectional area is 2.40 m^2 . However, the exact nature of the transient storage zones is obscured by the lack of precise field data, and the non-uniformity of the different river reaches: in most sections the riverbed consists of cobble and gravel intermixed with sand,

but these are alternated with sections where the river bed is cut into rock. The values obtained for the solute exchange coefficient between the main flow channel and the storage zone are very variable, and rather inaccurately estimated, such that a trend or dependency on the magnitude of the flow cannot be detected. The average value for the exchange coefficient is $1.2 \times 10^{-4} \text{ s}^{-1}$, which agrees well with values cited in the literature.

We conclude that the presented analytical solution for solute transport in rivers with transient storage can be a very valuable tool for future studies, especially the analyses of tracer experiments and the estimation of transport parameters. The solution 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

The solution is obtained by means of the Laplace transform. We denote the Laplace transform of a

function $f(t)$ as

$$\bar{f}(s) = L[f(t); t \rightarrow s] = \int_0^{\infty} f(t)e^{-st} dt \quad (\text{A1})$$

Applying the Laplace transform to Eqs. (1a) and (1b) gives

$$D \frac{\partial^2 \bar{C}}{\partial x^2} - v \frac{\partial \bar{C}}{\partial x} - (s + \alpha)\bar{C} + \alpha \bar{C}_s = \left(\frac{M}{A}\right) \delta(x) \quad (\text{A2a})$$

$$\bar{C}_s = \frac{\alpha \bar{C}}{\alpha + \beta s} \quad (\text{A2b})$$

Substitution of Eq. (A2b) in Eq. (A2a) results in

$$D \frac{\partial^2 \bar{C}}{\partial x^2} - v \frac{\partial \bar{C}}{\partial x} - \left(s + \frac{\alpha \beta s}{\alpha + \beta s}\right) \bar{C} = \left(\frac{M}{A}\right) \delta(x) \quad (\text{A3})$$

When α or β is zero, Eq. (A3) reduces to the classical advection–dispersion equation, with solution $C_0(x, t)$. Hence, from Eq. (A3) it follows that

$$\bar{C}(x, s) = \bar{C}_0\left(x, s + \frac{\alpha \beta s}{\alpha + \beta s}\right) \quad (\text{A4})$$

To obtain the inverse Laplace transform of Eq. (A4), we make use of the convolution theorem of the Laplace transform (Sneddon, 1972, p. 228)

$$L\left[\int_0^t f(\tau, t - \tau) d\tau; t \rightarrow s\right] = L\{L[f(t_1, t_2); t_2 \rightarrow s]; t_1 \rightarrow s\} \quad (\text{A5})$$

Eq. (A4) is now written as

$$\bar{C}(x, s_1, s_2) = \frac{s_1}{s_2} \bar{C}_0\left(x, s_1 + \frac{\alpha \beta s_2}{\alpha + \beta s_2}\right) \quad (\text{A6})$$

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

$$L[C(x, t_1, t_2); t_2 \rightarrow s_2] = \frac{\partial}{\partial t_1} \left[\frac{1}{s_2} \exp\left(\frac{-\alpha \beta s_2}{\alpha + \beta s_2} t_1\right) C_0(x, t_1) \right] \quad (\text{A7})$$

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

$$C(x, t_1, t_2) = \frac{\partial}{\partial t_1} [J(\alpha t_1, \alpha t_2/\beta) C_0(x, t_1)] \quad (\text{A8})$$

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

$$\begin{aligned} \frac{\partial}{\partial t_1} [J(\alpha t_1, \alpha t_2/\beta)] \\ = \alpha [1 - J(\alpha t_1, \alpha t_2/\beta) - J(\alpha t_2/\beta, \alpha t_1)] \end{aligned} \quad (\text{A9})$$

which is based on properties of the J -function given by Goldstein (1953), and

$$\frac{\partial}{\partial t_1} [C_0(x, t_1)] = \left(\frac{x^2 - v^2 t_1^2}{4D t_1^2} - \frac{1}{2t_1} \right) C_0(x, t_1) \quad (\text{A10})$$

which results from Eq. (5), given in the main text. Finally, combining Eqs. (A8)–(A10), results in

$$\begin{aligned} C(x, t_1, t_2) = \left[\alpha + \left(\frac{x^2 - v^2 t_1^2}{4D t_1^2} - \frac{1}{2t_1} - \alpha \right) J \left(\alpha t_1, \frac{\alpha t_2}{\beta} \right) \right. \\ \left. - \alpha J \left(\frac{\alpha t_1}{\beta}, \alpha t_2 \right) \right] C_0(x, t_1) \end{aligned} \quad (\text{A11})$$

In view of Eqs. (A4) and (A5), Eq. (A11) yields the solution as given by Eq. (4) in the main text.

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