Influence of suspended sediment on the transport processes of nonlinear reactive substances in turbulent streams

By R. REVELLI AND L. RIDOLFI

Dipartimento di Idraulica, Trasporti ed Infrastrutture Civili,
Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

The fluid dynamic behaviour of a reactive chemical in a stream can be greatly influenced by the presence of sorbing suspended particles. In this case, a kinetically controlled mass transfer is established between sorbed and dissolved phases and complex interactions emerge between fluid dynamical transport processes, sorption–desorption kinetics and chemical reactions. These conditions often occur in rivers, where both suspended sediment and reactive substances are frequently present. This paper deals with the important case in which the chemical reactions are nonlinear decay phenomena that often affect chemical or biological substances. A vertical two-dimensional mathematical model is formulated to take into account advection, turbulent diffusion, particle sedimentation, exchange kinetics between sorbed and dissolved phases, and decay. The decay is modelled for the case in which two different nonlinear decay reactions affect the dissolved and sorbed phases. The main result of the work is to obtain analytically a one-dimensional differential model of the vertically averaged concentration of the dissolved phase, this being conceptually similar to the classical advection–dispersion–decay equation. However, in this case we include the effects of (i) the kinetics with the phase sorbed by suspended particles and (ii) the influence of the two different decay processes. For this purpose, the multiple-scale method of homogenization is applied to the two-dimensional model. The resultant one-dimensional differential model shows how suspended load and decay phenomena affect the pollutant transport mechanisms to a great extent in a non-intuitive way and that the links are nonlinear. Some quantitative results show that these influences are, in general, not negligible.

1. Introduction

The study of transport processes in a stream has always been an important topic in fluid mechanics, the reason being twofold. On one hand, these physical phenomena demonstrate a remarkable variety of interesting behaviour patterns and therefore lead to fascinating speculations. Some examples of these speculations are the role of coherent structures (e.g. Nezu & Nakagawa 1993; Bernard & Rovelstad 1994; Kaftori, Hetsroni & Banerjee 1995; Wang & Squires 1996; Rouson & Eaton 2001), the interaction between a current and a mobile bed (e.g. Pan & Banerjee 1996; Niño & Garcia 1996; Elliott & Brooks 1997), the effects of sorbing particles in suspension (Ng 2000a, b; Ng & Yip 2001) and the influence of the storage zones and boundary adsorption (e.g. Smith 1983, 1986; Czernuszenko & Rowinski 1997, Wörman 1998; Choi, Harvey & Conklin 2000; Forsman, Johansson & Jonsson 2002). On the other hand, there has always been a great interest in applications, because of the numerous

real phenomena that involve transport processes in streams. Geophysical applications (e.g. Fischer *et al.* 1979) or those in chemical and environmental engineering (e.g. Rathbun 2000) are but a few examples.

Because of the wealth and complexity of this subject there are still several problems that have to be solved. One of these problems, which is the subject of this work, concerns the role of suspended sediment that is able to adsorb part of the transported chemical substances which undergo decay processes. As will be shown, the interaction between sediment, stream and reactive substance induces intriguing and non-trivial fluid transport phenomena. The work considers rivers as an example. This is because both the presence of solid materials in suspension and the presence of reactive substances that interact with the suspended material are usual in rivers, if not the rule (e.g. Graf 1984; Walling & Webb 1992). Nevertheless, the example of rivers is only the most obvious and the results obtained are valid for any turbulent open channel flow in which sorbing suspension particles are present.

Let us now describe the phenomenon under examination to show why it is interesting not only from an application point of view but also from a conceptual point of view. Sediment in suspension intervenes to a great extent in transport mechanisms when the transported substance can be sorbed by the particles in suspension. When this occurs, the transported chemical separates into an aqueous phase and a sorbed phase with continuous exchanges which are regulated by the local concentration gradients between the two phases themselves. The two phases follow different fluid dynamic evolutions: the aqueous one undergoes advection, turbulent diffusion and dispersion due to shear processes while the sorbed one, being connected to the sediment, also undergoes sedimentation. It therefore follows that an interaction between three mechanisms is established: (i) the evolution of the aqueous phase, (ii) the transport of the material in suspension and (iii) the exchange kinetics between the two phases that act as a 'bridge' between their evolutions thus making one feel the presence of the other and vice versa. In this way, the problem of transport in the aqueous phase is coupled to that of the sorbed phase. If a fourth mechanism is added, that is, the reactive phenomena, the picture becomes even more interesting since an element that is able to modify the concentrations in both the aqueous and sorbed phases intervenes thus altering the exchanges between the two phases. Reactions are often present in aqueous environments, whether of physical, chemical or biological origin (e.g. Runkel *et al.* 1996; Schnoor 1996; Steefel & van Cappellen 1998; Manson & Wallis 2000; Rathbun 2000). In order to avoid introducing other elements into an already complex phenomenon, any influence of storage zones and sorbing boundaries is neglected.

The aim of this work is to start from the two-dimensional model that describes the four previously mentioned fluid dynamic and chemical mechanisms in a vertical plane to obtain the equation that describes the spatial and temporal evolution of the aqueous-phase concentration averaged vertically. In other words, the aim is to obtain a one-dimensional model like Taylor's classical one (1953, 1954) but which now includes the complex interplay among turbulent diffusion, dispersion, advection, decay and interaction with the suspended material. It is shown how the suspended material and its interaction with the decay are able to change the advective–diffusive Taylor-type model to a great extent, with important consequences for applications. The analytical approach that we have followed is that of the homogenization method (e.g. Mei, Auriault & Ng 1996; Cioranescu & Donato 1999). The coexistence of mechanisms with different typical temporal scales makes this method suitable for searching for a model to describe the entire phenomenon at greater scales.

The problem has already been dealt with by Ng and Yip in the case of passive substances, i.e. without including decay mechanisms, in three seminal works (Ng 2000a,b; Ng & Yip 2001), that have made a great contribution to the study of the influence of sorption kinetics on transport processes. They have shown how the inclusion of the suspended load introduces remarkable features. A new dispersive term arises that is added to that introduced by Taylor, and which is connected to the correlation between the vertical profile of the concentration of the suspended sediment and the vertical profile of the velocity of the stream. This additional dispersion can be of the same order of magnitude as that of Taylor and can therefore have serious repercussions on the quantitative description of the evolution of a pollutant in a stream. There is also an effect on the advection, with a reduction of the velocity of the centroid of the chemical plume. The works by Ng have dealt both with the case in which local equilibrium partitioning is assumed (Ng 2000b) and with the case in which sorption kinetics exist (Ng 2000a; Ng & Yip 2001). In addition, they also included (Ng 2000b; Ng & Yip 2001) or excluded (Ng 2000a) the presence of a longitudinal evolution of the suspended sediment concentration.

This work continues along the path of Ng and investigates the role of the decay processes, which introduce a further variety to the fluid dynamic behaviour of the transported substance. The most general and realistic case (Schnoor 1996) is considered in which the decay is (i) nonlinear, (ii) different for the aqueous phase and for the sorbed phase, and (iii) there is sorption kinetics between the two phases. It is also assumed that there are negligible longitudinal variations of the suspended sediment concentrations, that is, the open channel flow yields the same steady discharge of suspended load. The differential equation that is found shows how great the differences are in comparison to the model that would be obtained simply by adding a monophase decay term to the passive chemicals model. The interaction between the sediment and the decay instead leads to numerous nonlinear terms, some of which are able to strongly influence the chemical transport.

The work is organized as follows. The mathematical problem is presented in the next section, where the basic hypotheses are discussed and the spatial and temporal scales that are typical of each phenomenon are described. The homogenization method is applied in the third section and the differential model that governs the depth averaged concentration is deduced. This model is then discussed in the fourth section and some quantitative results are shown. Finally, some conclusions are drawn in the fifth section.

2. Statement of the problem

2.1. *Mathematical model*

Let us consider a two-dimensional, steady, uniform turbulent channel flow with a mild slope. A reference system with the x-coordinate along the channel and the z-coordinate vertical upwards is introduced (see figure 1). The stream has depth-averaged velocity U_b, depth H, time-averaged local velocity profile $u = u(z)$, and yields a steady uniform suspended load. Let us suppose that the solid particles behave like fluid particles, except that they tend to settle with a fall velocity w_f. Low sediment concentration is assumed so that sediment does not affect the flow to any extent. Consequently, sediment concentrations of about 10^{-1}–10^{-2} Kg m^{-3}, which are quite common in rivers (e.g. Graf 1984; Walling & Webb 1992), are considered. The coordinate axes are assumed to coincide with the principal directions of the tensor of turbulent diffusion (e.g. Sumer 1974; Fischer *et al.* 1979) and the longitudinal and
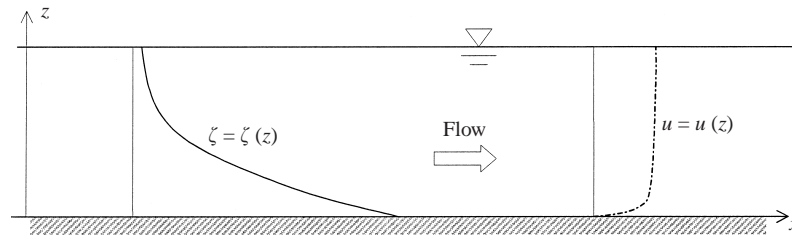
FIGURE 1. Diagram of the stream. The qualitative profiles of the suspended sediment concentration and the local averaged velocity are indicated with continuous and dot-dashed lines, respectively.

vertical eddy diffusion coefficients are denoted as E_{xx} and E_{zz}, respectively. The same longitudinal and vertical eddy diffusion coefficients are assumed for both sediment and fluid particles.

Let us hypothesize that the settling and turbulent diffusive flux of the particles are in dynamic equilibrium throughout the depth. Therefore

$$E_{zz}(z)\frac{\partial \zeta}{\partial z} + w_f \zeta = 0, \qquad (2.1)$$

where $\zeta = \zeta(z)$ is the suspended sediment concentration and w_f can be taken to be independent of ζ for the sediment concentrations considered here (Jansen 1979). Therefore, the following equilibrium vertical profile is established for the suspended sediment concentration:

$$\zeta(z) = \zeta_0 \exp\left(-\int_0^z \frac{w_f}{E_{zz}(z')}\, dz'\right), \qquad (2.2)$$

in which ζ_0 is a reference sediment concentration at the bed level $z = 0$.

Before continuing with the description of the problem, it is important to recall an aspect that is a basis of this work. The physical domain of the problem is discontinuous, as it is made up of a set of fluid and solid (porous) particles. In order to write down the differential model of the transport phenomena, a macroscopic level of description is adopted, obtained using the so-called continuum approach. This approach is the same as that used to pass from the molecular level of description of a fluid to a continuous description, or used to model the flow in a porous medium (e.g. Bear 1979; Mei *et al.* 1996; see also the hierarchical systems (Cushman 1990)). The approach consists of three steps. First, a representative elementary volume is chosen that is sufficiently large to always contain solid particles. Secondly, upscaling by one level is done in order to obtain values of concentration, in the aqueous and sorbed phases, averaged on the entire elementary volume. Thirdly, the average values are assigned to the centroid of the representative volume. In this way, macroscopic variables are obtained that are differentiable functions of the space coordinates. The balance equations that are written in this paper already refer to a second level of upscaling, which permitted us to formulate the dependent variables, namely the sediment or chemical concentrations, in terms of macroscopic variables.

Now let us consider that a reactive pollutant is present in the stream and the suspended load is able to give rise to sorption reactions. In this case several fluid dynamic and chemical (or biological) actions determine the fate of the chemical. These actions are summarized in figure 2. First of all, the chemical is partitioned into a dissolved and a sorbed phase. If local volume-averaged concentrations are considered
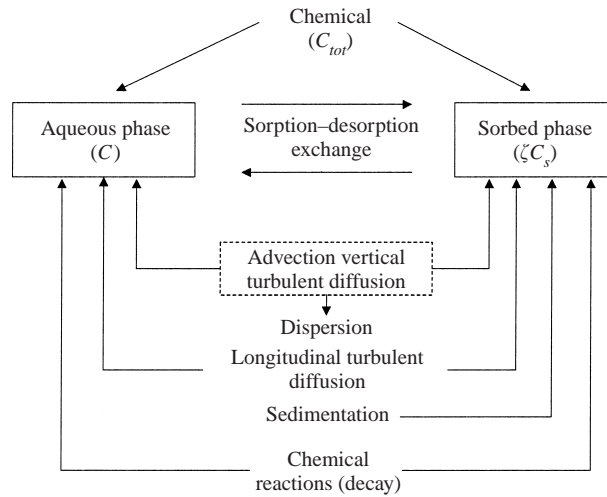
FIGURE 2. Diagram of the fluid dynamic and chemodynamic mechanisms that were taken into consideration.

(as mentioned in the previous paragraph), the total mass of the chemical per bulk volume, $C_{tot} = C_{tot}(x, z; t)$, is

$$C_{tot} = C + \zeta C_s, \tag{2.3}$$

where $C = C(x, z; t)$ is the mass of the dissolved phase per volume of water, $C_s = C_s(x, z; t)$ is the mass of the sorbed phase per mass of solid load and t is the time. The units of C are $\mathrm{Kg\,m^{-3}}$, while those of C_s are Kg (of chemical)/Kg (of sediment).

Soluble chemicals can sorb onto particulate suspended material for different reasons, including physical adsorption, chemisorption and partitioning (e.g. Schnoor 1996). Whatever its chemical origin, it is possible to define – at the isothermal dynamical equilibrium of adsorption–desorption mechanisms – a sorption partition coefficient $K_d = C_s/C$ (measured in $\mathrm{m^3\,Kg^{-1}}$) that relates the concentrations of the chemical in the sorbed and dissolved phases. This coefficient usually depends on C and C_s, but if these are not large, K_d can be assumed to be constant for fixed chemical and sediment characteristics (Karichoff, Brown & Scott 1979; O'Connor & Connolly 1980; Schweich & Sardin 1981; Schnoor 1996). This condition is hereinafter assumed.

In order to deal with the cases in which the sorbed phase plays a significant role in the transport processes, let us assume that the dissolved and sorbed concentrations at equilibrium are of the same order of magnitude, that is

$$K_d \zeta_0 = O(1), \tag{2.4}$$

where ζ_0 is a reference sediment concentration and $K_d \zeta_0$ is the bulk solid–water distribution ratio. This condition occurs in various cases (e.g. Karichoff *et al.* 1979; Rathbun 2000; Ng & Yip 2001) and, in particular, when the chemical is sufficiently hydrophobic, the sediment is fine (silt or clay), and its concentration and fractional mass of organic carbon are significant. Values of the sorption partition coefficient of about 10^1–$10^2\,\mathrm{m^3\,Kg^{-1}}$ are considered here.

The evolution of both the aqueous and sorbed phases is governed by several fluid dynamic mechanisms. In order to model these mechanisms, the following hypotheses are made: (i) the molecular diffusion is negligible compared to the turbulent diffusion,

(ii) sufficient time has passed from the chemical input and the chemical is well distributed in a vertical section, and (iii) the flux of the sorbate phase is equal to the sorbate concentration times the corresponding sediment flux. Under these hypotheses, the fluid dynamic evolution of the two phases is regulated by advection, vertical turbulent diffusion, longitudinal turbulent diffusion, and sedimentation. This last process affects only the sorbed phase (see figure 2). In figure 2 it is shown how the interaction between the vertical turbulent diffusion and the non-uniform velocity profile gives rise to the dispersion of the contaminant. This aspect is fundamental for sufficiently long times and it is important to select the scales of interest in the following subsection.

By modelling the fluid dynamic processes according to the advection–diffusion equation (Sumer 1974; Fischer *et al.* 1979), the mathematical model that governs the transport of the chemical in the domain $0 < z < H$ is

$$\frac{\partial C_{tot}}{\partial t} + u \frac{\partial C_{tot}}{\partial x} - w_f \frac{\partial C_s \zeta}{\partial z} = \frac{\partial}{\partial x} \left(E_{xx} \frac{\partial C_{tot}}{\partial x} \right) + \frac{\partial}{\partial z} \left(E_{zz} \frac{\partial C_{tot}}{\partial z} \right), \qquad (2.5)$$

which, using condition (2.1), becomes (see also Ng 2000*a, b*)

$$\frac{\partial C_{tot}}{\partial t} + u \frac{\partial C_{tot}}{\partial x} = \frac{\partial}{\partial x} \left(E_{xx} \frac{\partial C_{tot}}{\partial x} \right) + \frac{\partial}{\partial z} \left[E_{zz} \left(\frac{\partial C}{\partial z} + \zeta \frac{\partial C_s}{\partial z} \right) \right]. \qquad (2.6)$$

Apart from the sorption–desorption kinetics, let us suppose that the substance is also subjected to a decay process. Many chemical or biological processes give rise to decay which can therefore be considered one of the most common and important examples of reaction in an aqueous environment (e.g. Schnoor 1996; Rathbum 2000). The general case in which the decay is nonlinear and different for the dissolved and sorbed phases is studied (see Schnoor 1996, pp. 103–106). The corresponding reaction rates, R and R_s, can be modelled as power laws (Thibodeaux 1996; Schwarzenbach *et al.* 1993):

$$R = -\lambda C^n, \quad R_s = -\lambda_s C_s^m, \qquad (2.7)$$

where the coefficients λ and λ_s are the decay rate constants for the dissolved and sorbed phases, respectively (their units are $(\text{Kg}\,\text{m}^{-3})^{1-n}\,\text{s}^{-1}$ and s^{-1}). Values of exponents n and m greater than or equal to one are considered, in order to capture the common chemodynamic nonlinearities (Schwarzenbach *et al.* 1993; Schnoor 1996; Brezonik 1996).

Regarding the values of the coefficients λ and λ_s, it is necessary to note that the reactivity of the substances can lead to a significant interaction with other transport processes – without dominating or being negligible to other fluid dynamic mechanisms – only if the time scale of the decay is comparable to the characteristic time of the advective phenomena, which, in rivers, is usually of the order of days. Let us choose the half-life time of the chemicals, $t_{1/2}$, as the characteristic scale of decay; for the reactions modelled by equations (2.7) this is equal to

$$t_{1/2} = \frac{C_{t=0}^{1-n}(2^{n-1} - 1)}{\lambda(n - 1)}, \quad t_{1/2} = \frac{C_{s_{t=0}}^{1-m}(2^{m-1} - 1)}{\lambda_s(m - 1)}, \qquad (2.8)$$

respectively, with $C_{t=0}$ or $C_{s_{t=0}}$ being the respective initial condition. Therefore λ and λ_s have to be chosen equal to

$$\lambda = \frac{C_{t=0}^{1-n}(2^{n-1} - 1)}{t_{1/2}(n - 1)}, \quad \lambda_s = \frac{C_{s_{t=0}}^{1-m}(2^{m-1} - 1)}{t_{1/2}(m - 1)}, \qquad (2.9)$$

where $t_{1/2} = O(L/U_b)$ is of the order of 10^5 s, with L being the typical length scale of advection. Equations (2.9) show how the values of the decay rates depend to a great extent on the nonlinearity and initial conditions. In particular, λ and λ_s decrease with an increase of the nonlinearity and an increase of the initial concentration. The latter is not influential only in the case of linear decay when the rates are equal to $(\ln 2)/t_{1/2}$, from which one determines that λ and λ_s are $O(10^{-6}\,\mathrm{s}^{-1})$.

Finally, when the decay processes is included in the model (2.6), the mathematical model that governs the transport and fate of the chemical is

$$\frac{\partial C_{tot}}{\partial t} + u \frac{\partial C_{tot}}{\partial x}$$
$$= \frac{\partial}{\partial x}\left(E_{xx} \frac{\partial C_{tot}}{\partial x} \right) + \frac{\partial}{\partial z}\left[E_{zz}\left(\frac{\partial C}{\partial z} + \zeta \frac{\partial C_s}{\partial z} \right) \right] - (\lambda C^n + \zeta \lambda_s C_s^m). \quad (2.10)$$

The concentration of the sorbed phase, C_s, is controlled by (i) the kinetics of the sorption exchange with the aqueous phase and (ii) the decay reaction in the sorbed phase. Assuming linear first-order kinetics (e.g. Schweich & Sardin 1981; Cvetkovic & Dagan 1994; Schnoor 1996), the sorbate concentration evolution can be described by the following model in the domain $0 < z < H$:

$$\frac{\partial C_s}{\partial t} = k_d(K_d C - C_s) - \lambda_s C_s^m, \quad (2.11)$$

where the desorption rate constant, k_d, modulates the strength of the kinetic sorptive exchange. To make (2.11) valid, we assume that $\lambda_s d_p/D_{eff} \ll 1$, where d_p is the particle diameter and D_{eff} is the effective aggregate diffusion coefficient (Schwarzenbach *et al.* 1993).

The boundary conditions are defined by

$$E_{zz}\left(\frac{\partial C}{\partial z} + \zeta \frac{\partial C_s}{\partial z} \right) = 0 \quad \text{at} \quad z = 0, H, \quad (2.12)$$

which state that there is zero flux in the vertical direction through the free surface and through the bed. Equations (2.10)–(2.12), together with sediment profile (2.2) and the initial conditions, define the mathematical problem that describes the interaction between the advective–diffusion–decay process and the suspended load.

2.2. *Typical scales*

The multiple-scale method of homogenization is used in the following to obtain the one-dimensional model that describes the evolution of the depth-averaged chemical concentration. This method is effective when there are two or more distinct spatial or temporal scales in the phenomenon. It allows one to deduce the effective equations on the larger scale through a rational process of averaging (Mei *et al.* 1996). The first step is to assess the physical scalings of the terms that are present in the model (2.10)–(2.12) to evaluate the number of typical scales in the process. For details on the advective, diffusive and dispersive terms, reference can be made to the works by Ng (2000*b*) and Ng & Yip (2001).

Once a steady vertical profile of the suspended sediment has been assigned, five mechanisms intervene in the entire transport process: the advection, the vertical and longitudinal turbulent diffusions, the sorption kinetics and the decay. Moreover, the combined action of the non-uniform advection and the vertical turbulent diffusion gives rise to dispersion. As this paper focuses on the transport of the chemical over a

long period of time after discharge, dispersion plays a key role in the upscaling, for two reasons. First, dispersion introduces its own typical longitudinal scale L that is much longer than the spatial scale (usually the flow depth H) which is characteristic of the vertical diffusion (e.g. Fischer *et al.* 1979). Secondly, it is well known (e.g. Sumer 1974; Fischer *et al.* 1979) that over a long period of time the dispersive process is more dominant than the longitudinal turbulent diffusion in controlling the longitudinal spreading of the chemical. Consequently, the longitudinal turbulent diffusion can be neglected with respect to the dispersion.

For a steady two-dimensional turbulent open-channel flow, the following expressions are valid (Elder 1959; Fischer 1973):

$$\overline{E}_{xx} = \overline{E}_{zz} = 0.07 u_* H, \quad D = 5.86 u_* H, \tag{2.13a,b}$$

where the overbar denotes the depth average, D is the dispersion coefficient, and $u_\star$ is the friction velocity. The ratio $\epsilon \equiv \overline{E}_{zz}/D = O(10^{-2}) \ll 1$ can therefore be chosen as the perturbative parameter for the application of the homogenization method and as the reference term to evaluate the order of magnitude of the individual terms in the model (2.10)–(2.12).

From the previous relationships it follows that

$$\frac{\partial}{\partial x}\left(E_{xx}\frac{\partial C}{\partial x}\right) \Big/ \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) = O(\epsilon). \tag{2.14}$$

Recalling that Aris (1956) showed that the coefficients due to the turbulent diffusion and the turbulent dispersion are additive, (2.14) justifies the possibility of neglecting diffusion with respect to dispersion.

Let us assume that the vertical diffusion is two orders of magnitude greater than the longitudinal dispersion and one order of magnitude greater than advection (Ng & Yip 2001), that is

$$\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \Big/ \frac{\partial}{\partial z}\left(E_{zz}\frac{\partial C}{\partial z}\right) = O(\epsilon^2), \tag{2.15}$$

$$u\frac{\partial C}{\partial x} \Big/ \frac{\partial}{\partial z}\left(E_{zz}\frac{\partial C}{\partial z}\right) = O(\epsilon). \tag{2.16}$$

From relationship (2.15) and using (2.14), it follows that

$$\frac{\partial}{\partial x}\left(E_{xx}\frac{\partial C}{\partial x}\right) \Big/ \frac{\partial}{\partial z}\left(E_{zz}\frac{\partial C}{\partial z}\right) = O(\epsilon^3), \tag{2.17}$$

and, from (2.15), one obtains

$$\frac{H}{L} = O(\epsilon^{3/2}). \tag{2.18}$$

Therefore, if $\epsilon \equiv 10^{-2}$, one obtains $H/L = O(10^{-3})$, which is a reasonable ratio in a river, where H is of the order of metres and L of the order of kilometres.

Assumption (2.16) and ratio (2.18) allow one to obtain an estimate of the Péclet number, which indicates the ratio of advection to vertical diffusion. According to the previous hypotheses one obtains

$$Pe \equiv \frac{U_b H}{\overline{E}_{zz}} = O\left(\frac{U_b}{0.07 u_\star}\right) = O(\epsilon^{-1/2}). \tag{2.19}$$

The ratio of the desorption rate to the vertical diffusion is equal to the Damköhler

number $Da \equiv k_d H^2 / \overline{E}_{zz}$. By modelling the sorption kinetics as rate-limiting diffusion into a spherical particle (Wu & Gschwend 1986; Schwarzenbach *et al.* 1993; Ng 2000*a*) and by assuming the effective aggregate diffusion coefficient, D_{eff}, of the order $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ (Ng & Yip 2001), the desorption rate can be estimated as $k_d = O(10^{-4} \text{ s}^{-1})$. If the typical values $H \approx 5 \text{ m}$ and $u_* \approx 0.01 \text{ m s}^{-1}$ are used, the Damköhler number is of the order of unity.

Regarding the decay terms, let us consider the case of the dissolved phase and let us study the ratio

$$\frac{\lambda C^n}{u \partial C / \partial x} = \frac{C_{t=0}^{1-n}(2^{n-1} - 1)}{T_{1/2}(n-1)} \frac{C^n}{u \partial C / \partial x}, \tag{2.20}$$

where relationship (2.9) has been used. If the following dimensionless quantities, which are based on the previous scaling estimates, are introduced:

$$\hat{x} = \frac{x}{L}, \quad \hat{u} = \frac{u}{U_b}, \quad \hat{C} = \frac{C}{C_{t=0}}, \tag{2.21}$$

and taking into consideration that $t_{1/2} = O(L/U_b)$, one finds that ratio (2.20) is $O(\epsilon^0)$. The same result can be obtained for the concentration of the sorbed phase, C_s.

On the basis of these orders of magnitude, equations (2.10) and (2.11) give

$$\epsilon \frac{\partial C_{tot}}{\partial t} + \epsilon u \frac{\partial C_{tot}}{\partial x} = \epsilon^3 \frac{\partial}{\partial x} \left(E_{xx} \frac{\partial C_{tot}}{\partial x} \right)$$
$$+ \frac{\partial}{\partial z} \left[E_{zz} \left(\frac{\partial C}{\partial z} + \zeta \frac{\partial C_s}{\partial z} \right) \right] - \epsilon (\lambda C^n + \zeta \lambda_s C_s^m), \tag{2.22}$$

$$\epsilon \frac{\partial C_s}{\partial t} = k_d (K_d C - C_s) - \epsilon \lambda_s C_s^m, \tag{2.23}$$

where the ordering parameters are kept for the identification that is necessary in the next section.

It is important to bear in mind that the dispersion – which is 'hidden' in the interaction between the advective and vertical turbulent diffusion terms – has an ordering parameter equal to ϵ^2. As we are dealing with long time scales in which the only really dominant process in longitudinal spreading is dispersion (e.g. Sumer 1974; Fischer *et al.* 1979; Ng 2000*a*), the upscaling should be made up to the order ϵ^2.

From a temporal point of view, it is possible to observe the existence of three different time scales that are fundamental in the whole process. The first, that of the vertical diffusion, is equal to $T_0 = H^2 / \overline{E}_{zz}$. The second, which is typical of the advection and decay along the channel, is equal to $T_1 = L/U_b$, with L being the characteristic travel distance. Finally, the third one for the dispersion spreading phenomena across L, is equal to $T_2 = L^2/D$. On the basis of the previously estimated magnitudes, one obtains

$$\frac{H^2}{\overline{E}_{zz}} : \frac{L}{U_b} : \frac{L^2}{D} = T_0 : T_1 : T_2 = 1 : \frac{1}{\epsilon} : \frac{1}{\epsilon^2}. \tag{2.24}$$

These differences in the order of magnitude are of fundamental importance for this work. As we are focusing on longitudinal transport phenomena, it is possible not to take into account the variations in concentrations associated to the vertical diffusion and therefore only scales T_1 and T_2 are important in the present study. This allows the introduction of the two multiple time coordinates $t_1 = t$ and $t_2 = \epsilon t$, and then the application of the homogenization method, with respect to time, as described

in the following section. Focusing on times much longer than T_0 also justifies the possibility of modelling the transport and decay phenomena using a one-dimensional longitudinal model (e.g. Chatwin 1970; Sullivan 1971; Fischet *et al.* 1979).

3. Depth-averaged transport equation

Let us expand the dependent variables C and C_s in power series of the perturbative parameter ϵ:

$$(C, C_s) = (C_0, C_{s0}) + \epsilon(C_1, C_{s1}) + \epsilon^2(C_2, C_{s2}) + \cdots. \tag{3.1}$$

Consequently, the nonlinear decay terms in (2.22) and (2.23) can also be expanded in power series so that

$$\epsilon\lambda C^n = \epsilon\lambda(C_0 + \epsilon C_1 + \epsilon^2 C_2 + \cdots)^n \approx \epsilon\lambda C_0^n + \epsilon^2 n\lambda C_0^{n-1}C_1 + O(\epsilon^3), \tag{3.2}$$

$$\epsilon\zeta\lambda_s C_s^m = \epsilon\zeta\lambda_s(C_{s0} + \epsilon C_{s1} + \epsilon^2 C_{s2} + \cdots)^m \approx \epsilon\zeta\lambda_s C_{s0}^m + \epsilon^2 m\zeta\lambda_s C_{s0}^{m-1}C_{s1} + O(\epsilon^3), \tag{3.3}$$

$$\epsilon\lambda_s C_s^m = \epsilon\lambda_s(C_{s0} + \epsilon C_{s1} + \epsilon^2 C_{s2} + \cdots)^m \approx \epsilon\lambda_s C_{s0}^m + \epsilon^2 m\lambda_s C_{s0}^{m-1}C_{s1} + O(\epsilon^3). \tag{3.4}$$

Because of the introduction of the two time coordinates t_1 and t_2, the time derivative is transformed, using the chain rule (Nayfeh 1973), according to

$$\frac{\partial}{\partial t} \rightarrow \frac{\partial}{\partial t_1} + \epsilon\frac{\partial}{\partial t_2}. \tag{3.5}$$

The substitution of (3.1)–(3.5) into equations (2.22)–(2.23) therefore allows one to make an analysis according to the different powers of ϵ. At $O(\epsilon^0)$, the solute decay terms do not intervene and the problem is homogeneous. Equation (2.22) becomes

$$\frac{\partial}{\partial z}\left[E_{zz}\left(\frac{\partial C_0}{\partial z} + \zeta\frac{\partial C_{s0}}{\partial z}\right)\right] = 0, \quad 0 < z < H, \tag{3.6}$$

with the boundary condition

$$E_{zz}\left(\frac{\partial C_0}{\partial z} + \zeta\frac{\partial C_{s0}}{\partial z}\right) = 0, \quad z = 0, H, \tag{3.7}$$

while equation (2.23) gives

$$k_d(K_d C_0 - C_{s0}) = 0. \tag{3.8}$$

From these relationships it is possible to immediately deduce that the zeroth order of the solute concentrations is independent of z so that

$$C_{s0} = K_d C_0, \tag{3.9}$$

which gives

$$C_{tot0} = C_0 + \zeta C_{s0} = R C_0, \tag{3.10}$$

where $R(z) = (1 + K_d\zeta(z))$ is the retardation factor (Gupta & Cvetkovic 2000; Ng 2000*a*).

At $O(\epsilon)$, by substituting (3.10) and (3.9) in (2.22), one obtains

$$R\frac{\partial C_0}{\partial t_1} + Ru\frac{\partial C_0}{\partial x} = \frac{\partial}{\partial z}\left[E_{zz}\left(\frac{\partial C_1}{\partial z} + \zeta\frac{\partial C_{s1}}{\partial z}\right)\right] - \lambda C_0^n - \zeta\lambda_s K_d^m C_0^m. \tag{3.11}$$

By taking the depth average of (3.11) and using the zero-flux boundary condition,

the first-order effective transport equation is obtained:

$$\frac{\partial C_0}{\partial t_1} + u_e \frac{\partial C_0}{\partial x} + \lambda^* C_0^n + \lambda^{**} C_0^m = 0, \tag{3.12}$$

where $u_e = \overline{Ru}/\overline{R}$ is an effective advective velocity and $\lambda^* = \lambda/\overline{R}$ and $\lambda^{**} = \lambda_s K_d^m \overline{\zeta}/\overline{R}$ are two effective nonlinear decay coefficients.

At $O(\epsilon)$ one obtains from (2.23)

$$\frac{\partial C_{s0}}{\partial t_1} = k_d K_d C_1 - k C_{s1} - \lambda_s C_{s0}^m, \tag{3.13}$$

from which, with (3.9) and by differentiating with respect to z, one obtains

$$\frac{\partial C_{s1}}{\partial z} = K_d \frac{\partial C_1}{\partial z}. \tag{3.14}$$

If (3.14) is substituted into the right-hand side of (3.11) and the derivative $\partial C_0/\partial t_1$ is eliminated using (3.11) and (3.12), the following equation is also found:

$$\frac{\partial}{\partial z} \left[E_{zz} R \frac{\partial C_1}{\partial z} \right] = R(u - u_e) \frac{\partial C_0}{\partial x} + \lambda^* K_d (\overline{\zeta} - \zeta) C_0^n - \frac{\lambda^{**}}{\overline{\zeta}} (\overline{\zeta} - \zeta) C_0^m, \tag{3.15}$$

where condition (3.10) is also retained.

The structure of (3.15) suggests the substitution

$$C_1 = N(z) \frac{\partial C_0}{\partial x} + M'(z) C_0^n + M''(z) C_0^m, \tag{3.16}$$

where $N(z)$, $M'(z)$ and $M''(z)$ are governed by the following three problems:

$$\begin{cases} R(u - u_e) = \dfrac{\mathrm{d}}{\mathrm{d}z} \left[E_{zz} R \dfrac{\mathrm{d}N}{\mathrm{d}z} \right], & 0 < z < H \\[2mm] \dfrac{\mathrm{d}N}{\mathrm{d}z} = 0, & z = 0, H, \end{cases} \tag{3.17}$$

$$\begin{cases} \lambda^* K_d (\overline{\zeta} - \zeta) = \dfrac{\mathrm{d}}{\mathrm{d}z} \left[E_{zz} R \dfrac{\mathrm{d}M'}{\mathrm{d}z} \right], & 0 < z < H \\[2mm] \dfrac{\mathrm{d}M'}{\mathrm{d}z} = 0, & z = 0, H, \end{cases} \tag{3.18}$$

and

$$\begin{cases} -\lambda^{**} \dfrac{(\overline{\zeta} - \zeta)}{\overline{\zeta}} = \dfrac{\mathrm{d}}{\mathrm{d}z} \left[E_{zz} R \dfrac{\mathrm{d}M''}{\mathrm{d}z} \right], & 0 < z < H \\[2mm] \dfrac{\mathrm{d}M''}{\mathrm{d}z} = 0, & z = 0, H, \end{cases} \tag{3.19}$$

whose solutions are, respectively

$$N(z) = \int_0^z \frac{1}{RE_{zz}} \int_0^{z'} R(u - u_e) \, \mathrm{d}z'' \, \mathrm{d}z' + N(0), \tag{3.20}$$

$$M'(z) = \lambda^* K_d \int_0^z \frac{1}{RE_{zz}} \int_0^{z'} (\overline{\zeta} - \zeta) \, \mathrm{d}z'' \, \mathrm{d}z' + M'(0), \tag{3.21}$$

$$M''(z) = -\lambda^{**} \int_0^z \frac{1}{RE_{zz}} \int_0^{z'} \frac{(\overline{\zeta} - \zeta)}{\overline{\zeta}} \, \mathrm{d}z'' \, \mathrm{d}z' + M''(0). \tag{3.22}$$

Without loss of generality, we take $\overline{C_1} = 0$ in such a way that the vertical average of C is equal to C_0 with an error of no greater than $O(\epsilon^2)$. From this, using (3.16) and (3.20)–(3.22), it is possible to deduce

$$N(0) = \overline{N(0)} = -\overline{\int_0^z \frac{1}{RE_{zz}} \int_0^{z'} R(u - u_e)\,dz''\,dz'}, \qquad (3.23)$$

$$M'(0) = \overline{M'(0)} = -\lambda^* K_d \overline{\int_0^z \frac{1}{RE_{zz}} \int_0^{z'} (\overline{\zeta} - \zeta)\,dz''\,dz'} \qquad (3.24)$$

$$M''(0) = \overline{M''(0)} = -\frac{\lambda^{**}}{\lambda^* \overline{\zeta} K_d} M'(0). \qquad (3.25)$$

By taking into account relationships (3.9), (3.12) and (3.16), equation (3.13) gives

$$C_{s1} = \delta \frac{\partial C_0}{\partial x} + \gamma' C_0^n + \gamma'' C_0^m \qquad (3.26)$$

with

$$\delta = K_d \left(N + \frac{u_e}{k_d} \right), \quad \gamma' = K_d \left(M' + \frac{\lambda^*}{k_d} \right), \quad \gamma'' = K_d \left(M'' - \frac{\lambda^{**}}{k_d K_d \overline{\zeta}} \right). \quad (3.27a\text{–}c)$$

Therefore, the $O(\epsilon)$ total concentration can now be written as

$$C_{tot1} = C_1 + \zeta C_{s1} = (N + \zeta\delta)\frac{\partial C_0}{\partial x} + (M' + \zeta\gamma')C_0^n + (M'' + \zeta\gamma'')C_0^m. \qquad (3.28)$$

At $O(\epsilon^2)$, by substituting (3.10) and (3.28) in (2.22) and by averaging over the depth, the following equation is found:

$$\frac{\partial C_0}{\partial t_2} - D^* \frac{\partial^2 C_0}{\partial x^2} + u^* \frac{\partial C_0^n}{\partial x} + u^{**} \frac{\partial C_0^m}{\partial x} + \lambda' C_0^{2n-1} + \lambda'' C_0^{2m-1} + \lambda''' C_0^{n+m-1} = 0, \qquad (3.29)$$

where

$$D^* = -\frac{\overline{N(u - u_e)R}}{\overline{R}} - \frac{u_e K_d}{k_d} \frac{\overline{(u - u_e)\zeta}}{\overline{R}} \qquad (3.30)$$

is an effective dispersion coefficient, while

$$u^* = \frac{\overline{R(u - u_e)M'}}{\overline{R}} + \frac{\lambda^* K_d}{k_d \overline{R}} [k_d \overline{N(\overline{\zeta} - \zeta)} + \overline{\zeta(u - 2u_e)}], \qquad (3.31)$$

$$u^{**} = \frac{\overline{R(u - u_e)M''}}{\overline{R}} - \frac{\lambda^{**}}{\overline{\zeta} k_d \overline{R}} [k_d \overline{N(\overline{\zeta} - \zeta)} - \overline{\zeta(u - 2u_e)}] \qquad (3.32)$$

are two effective coefficients for two pseudo-advective (nonlinear) terms, and

$$\lambda' = \frac{n\lambda^* K_d}{\overline{R}} \overline{(\overline{\zeta} - \zeta)M'} - \frac{nK_d(\lambda^*)^2}{k_d \overline{R}} \overline{\zeta}, \qquad (3.33)$$

$$\lambda'' = \frac{m\lambda^{**}}{\overline{\zeta}\,\overline{R}} \overline{(\zeta - \overline{\zeta})M''} - \frac{m(\lambda^{**})^2}{\overline{\zeta} k_d K_d \overline{R}}, \qquad (3.34)$$

$$\lambda''' = \frac{\lambda^*}{\overline{R}} \overline{M''(n\overline{R} - mR)} + \frac{\lambda^{**}}{\overline{\zeta}\,\overline{R}} \overline{M'(m\zeta\overline{R} - nR\overline{\zeta})} + \frac{\lambda^* \lambda^{**}}{k_d \overline{R}} [m(\overline{R} + 1) - n\overline{\zeta} K_d] \qquad (3.35)$$

are the coefficients of three nonlinear decay terms. The two relationship (3.24) and (3.25) are necessary for the computation of the first two terms of (3.35). Only when

the substance is not reactive (Ng 2000*a*) or the decay is linear are the $N(0)$, $M'(0)$ and $M''(0)$ integration constants not influential and therefore do not need to be determined.

After some re-arrangement and by integrating by parts, it is possible to obtain

$$D^* = \frac{1}{R}\overline{\mathfrak{I}_0\mathfrak{I}_1^2} - \frac{K_d u_e}{k_d \overline{R}^2}\overline{(\zeta - \overline{\zeta})(u - U_b)}, \tag{3.36}$$

$$u^* = \frac{\lambda^* K_d}{k_d \overline{R}}\left(\overline{\zeta(u - 2u_e)} - 2k_d\overline{\mathfrak{I}_0\mathfrak{I}_1\mathfrak{I}_2}\right), \quad u^{**} = -\frac{\lambda^{**}}{\lambda^* K_d \overline{\zeta}}u^*, \tag{3.37a,b}$$

$$\lambda' = -n\frac{(\lambda^* K_d)^2}{R}\left(\overline{\mathfrak{I}_0\mathfrak{I}_2^2} + \frac{\overline{\zeta}}{k_d K_d}\right), \quad \lambda'' = \frac{m}{n}\left(\frac{\lambda^{**}}{\lambda^* K_d \overline{\zeta}}\right)^2 \lambda', \tag{3.38a,b}$$

$$\lambda''' = \frac{\lambda^*\lambda^{**}}{\overline{\zeta}R}\left[\overline{\mathfrak{I}_0\mathfrak{I}_2\mathfrak{I}_3} + K_d\overline{\mathfrak{I}_0\mathfrak{I}_2\mathfrak{I}_4} - \frac{2m\overline{\zeta}}{k_d} + (m - n)\left(\overline{\mathfrak{I}_5}(1 - K_d^2\overline{\zeta}^2) - \overline{\zeta}^2\frac{K_d}{k_d}\right)\right], \tag{3.39}$$

in which

$$\mathfrak{I}_0 = (RE_{zz})^{-1}, \quad \mathfrak{I}_1 = \int_0^z R(u - u_e)\,\mathrm{d}z', \quad \mathfrak{I}_2 = \int_0^z (\overline{\zeta} - \zeta)\,\mathrm{d}z', \tag{3.40}$$

$$\mathfrak{I}_3 = \int_0^z (n\overline{R} - mR)\,\mathrm{d}z', \quad \mathfrak{I}_4 = \int_0^z (nR\overline{\zeta} - m\zeta\overline{R})\,\mathrm{d}z', \quad \mathfrak{I}_5 = \int_0^z \mathfrak{I}_0\mathfrak{I}_2. \tag{3.41}$$

Finally, by introducing the above relationships into (3.12) and (3.29) and by recalling (3.1) and (3.5), one obtains

$$\frac{\partial C_0}{\partial t} - D^*\frac{\partial^2 C_0}{\partial x^2} + u_e\frac{\partial C_0}{\partial x} + u^*\frac{\partial C_0^n}{\partial x} + u^{**}\frac{\partial C_0^m}{\partial x}$$
$$+ \lambda^* C_0^n + \lambda^{**} C_0^m + \lambda' C_0^{2n-1} + \lambda''' C_0^{m+n-1} + \lambda'' C_0^{2m-1} = 0. \tag{3.42}$$

This one-dimensional nonlinear partial differential equation models the evolution of the depth-averaged concentration in the dissolved phase of a nonlinearly decaying chemical up to $O(\epsilon)$. Equation (3.42) clearly shows how the combined action of the presence of the suspended sediment and of the decay changes the transport mechanisms to a great extent compared to the clear fluid case. It can also be noted, recalling (3.9), that the depth-average behaviour of the sorbed phase can easily be deduced once the evolution of C_0 is defined.

4. Discussion

In order to discuss the complex links between the transport mechanisms, suspended load and decay described by model (3.42) and to understand the quantitative influence of each term, it is necessary to define the vertical profiles of velocity, $u(z)$, and suspended sediment concentration, $\zeta(z)$, to be able to explicitly evaluate coefficients (3.36)–(3.39). Several profiles of varying refinement have been proposed in the literature (e.g. Vanoni 1975; Graf 1984). The laws that have been chosen here are simple and are generally accepted as describing real conditions. They enable the analytical evaluation of the integrals in the definitions of the coefficients. It is however reasonable to consider that the conceptual aspects of the following discussion do not depend on the particular choice of the profiles.

Let us consider the following velocity distribution, as proposed by Engelund (1970), for turbulent channel flows on a rough bed:

$$\frac{u(z)}{u_\star} = \frac{1}{\kappa} \ln\left(\frac{H}{\epsilon_s}\right) + 8.5 - \frac{2.63}{\kappa} + \frac{u_\star}{E_m}\left(z - \frac{z^2}{2H}\right), \tag{4.1}$$

where ϵ_s is the bottom roughness, $\kappa = 0.4$ is the von Kármán constant and E_m is the eddy viscosity, which is assumed constant throughout the depth. The classical relationship (Fischet *et al.* 1979)

$$E_m = 0.19\kappa u_\star H \tag{4.2}$$

has been chosen for the eddy viscosity and the same constant value is also assumed for the two eddy diffusivities E_{xx} and E_{zz}. The constant profile for the vertical eddy diffusivity is in general a weak approximation; however it does not intervene in the most important decay terms (see §4.3) and has no influence on the main topic of this paper. Corresponding to condition (4.2), the suspended sediment concentration is assumed to decrease exponentially upwards according to the law (Vanoni 1975)

$$\zeta = \zeta_0 \exp\left(-\alpha\frac{z}{H}\right), \tag{4.3}$$

where $\alpha \equiv w_f H/E_z = 5.26 w_f/\kappa u_\star$ is the suspension number and $\zeta_0 = \zeta(z = 0)$, the latter being used as a reference concentration in the bulk solid–water distribution ratio, $K_d\zeta_0$. As the fall velocity of small particles of sediment usually ranges from 0.1 to $10 \, \text{mm s}^{-1}$ (Graf 1984) while $u_\star = O(0.01 \, \text{m s}^{-1})$, realistic values of α can be found in the $[10^{-1}, 10^1]$ interval. These same laws have also been used by Ng (2000a) for the vertical profiles of velocity, eddy diffusivity and sediment concentration, and these laws allow useful comparisons with the case without decay that he investigated.

The two quantities α and $K_d\zeta_0$ play a fundamental role in modulating the influence of the suspended load on the chemical dynamics. The suspension number focuses on the shape of the vertical distribution of the sediment: the higher α (e.g. heavy particle or low friction velocity), the more the vertical profile of the sediment concentration moves away from uniformity, while the opposite occurs when the suspension number is low. As the influence of the sediment on the transport phenomena depends on the non-uniformity of the sediment concentration profile (see (3.36)–(3.39) and the definition of u_e), it follows that α contributes to a great extent to regulate this influence. In the limit $\alpha \to 0$, the sediment is uniformly distributed on the vertical section and

$$(u^*, u^{**}, \lambda', \lambda'', \lambda''') \to 0, \quad u_e \to U_b, \quad D^* \to 0.82D, \tag{4.4}$$

that is, advection and dispersion of the chemical occur as in the absence of sediment whose influence in (3.42) is still included in the decay terms $\lambda^* C_0^n$ and $\lambda^{**} C_0^m$ (the numerical coefficient of D in (4.4) has no particular physical meaning and only depends on the choice of the velocity and eddy viscosity profiles).

The bulk solid–water distribution ratio indicates how the chemical is distributed between the solid and aqueous phases. The higher this ratio, the more important is the role of sediment in the chemical dispersion. On the other hand, when $K_d\zeta_0 \to 0$, the sediment transport loses influence and the transport of the pure dissolved phase is recovered.

The general model (3.42) includes the two sub-cases that correspond to passive chemicals (i.e. no decay, studied by Ng 2000a) and to linear decay. For the sake of clarity and in order to underline the role of nonlinearities, let us explain these two simpler cases separately.

4.1. *Passive chemicals*

In this case, it is sufficient to put $\lambda = \lambda_s = 0$. Consequently, $\lambda^* = \lambda^{**} = 0$ and, from (3.36)–(3.39), one can deduce $u^* = u^{**} = \lambda' = \lambda'' = \lambda''' = 0$ which, when introduced into (3.42), gives

$$\frac{\partial C_0}{\partial t} - D^* \frac{\partial^2 C_0}{\partial x^2} + u_e \frac{\partial C_0}{\partial x} = 0. \tag{4.5}$$

This model coincides with the one obtained by Ng (2000*a*) in his noteworthy analysis. This model sheds light on some fundamental aspects of the role played by suspended sediment in transport mechanisms, and these aspects persist, in the second and third terms of (3.42), even when the chemical (or biological) reactivity is taken into account. It is important to recall how both the advection velocity, u_e, and the dispersion coefficient, D^*, are greatly influenced by the sediment: the advection is retarded while the dispersion is enhanced by a new dispersion coefficient which is proportional to the covariance between the velocity and sediment concentration (see equation (3.36)). Figure (3*a*, *b*) reports an example of the links that can be found between the advection, dispersion and sediment characteristics. These figures refer to the case of $H/\epsilon_s = 1000$ and $k_d H/u_\star = 0.2$ (the same as described by Ng 2000*a*) and show how the influence of sediment is usually not negligible and becomes more evident with an increase of the suspension number and of the bulk solid–water distribution ratio: the differences for advection, compared to the clear water case, can reach 3–4%, while the dispersion coefficient, D^*, can even be 5–10 times that of the classical Taylor dispersion coefficient. One should also notice that both u_e and D^* are very sensitive to the type of profile that is chosen. Some tests (not shown here) that have been carried out with some other common velocity and diffusivity profiles (e.g. the logarithmic law and the parabolic profile for $u(z)$ and $E_{zz}(z)$, respectively (Vanoni 1975; Ng & Yip 2001)) have shown that this dependence can be of the same order of magnitude as that of $K_d \zeta_0$.

4.2. *Linear decay*

This case corresponds to placing $m = n = 1$, which leads to the model

$$\frac{\partial C_0}{\partial t} - D^* \frac{\partial^2 C_0}{\partial x^2} + (u_e + u^* + u^{**})\frac{\partial C_0}{\partial x} + (\lambda^* + \lambda^{**} + \lambda' + \lambda'' + \lambda''')C_0 = 0. \tag{4.6}$$

In real cases, u^* and u^{**} and λ', λ'' and λ''' can be neglected with respect to u_e and λ^* and λ^{**}; consequently in the case of profiles (4.1) and (4.3), the coefficient of the reaction term in (4.6) becomes

$$\lambda_e = \lambda^* + \lambda^{**} = \frac{e^\alpha \alpha + (e^\alpha - 1)\,\omega\,K_d\,\zeta_0}{e^\alpha \alpha + (e^\alpha - 1)K_d\,\zeta_0}\lambda, \tag{4.7}$$

with $\omega = \lambda_s/\lambda$. Figure 4(*a*–*c*) shows that λ_e is usually different from the decay rate for the dissolved phase λ. When $\omega < 1$, i.e. for a reaction rate constant for the sorbed phase that is greater than the corresponding value for the dissolved phase, the value of the effective reaction coefficient is greater than the decay coefficient in the case without sediment or with $\lambda = \lambda_s$. Instead, when $\omega < 1$ then $\lambda_e < \lambda$. The difference, with respect to the case without sediment, grows with $K_d \zeta_0$ and can reach a value of about ± 20–40% if the bulk solid–water distribution ratio is sufficiently high. On the other hand, the difference decreases with α.
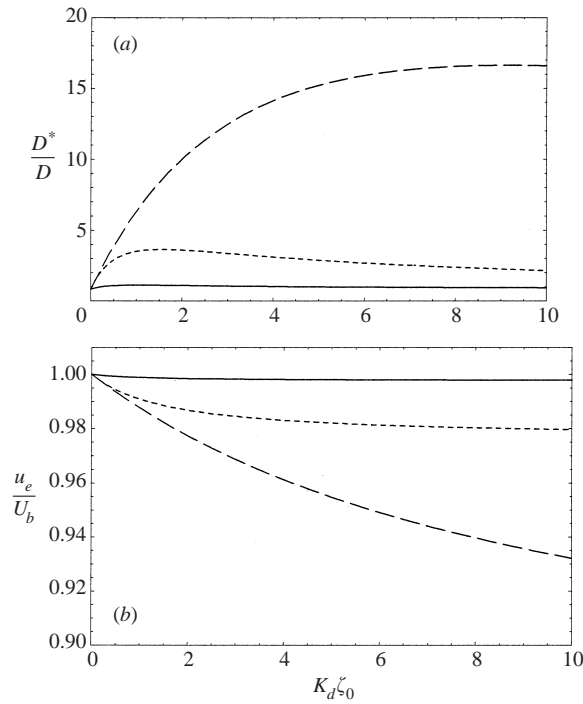
FIGURE 3. Case of passive chemicals (after Ng 2000a). Effective dispersion coefficient (a) and advection velocity (b) versus suspension number and bulk solid–water distribution ratio. $\alpha = 0.1$, continuous line; $\alpha = 1$, dotted line; $\alpha = 0.1$, dashed line.

4.3. Nonlinear decay

When the case of nonlinear decay is considered, model (3.42) shows the complexity of the links between the sorbed phase, dissolved phase and fluid dynamic mechanisms that regulate the evolution of the chemical and suspended load, and several nonlinear terms appear. These terms are important, from a conceptual point of view, as they show the variety of links between the decay and the other transport mechanisms; however if the coefficients of nonlinear terms are evaluated for realistic cases of nonlinear decay (i.e. n, $m = O(1)$) the following is encountered:

$$\left(u^* \frac{\partial C_0^n}{\partial x}, u^{**} \frac{\partial C_0^m}{\partial x} \right) \ll u_e \frac{\partial C_0}{\partial x}, \tag{4.8}$$

$$(\lambda' C_0^{2n-1}, \lambda'' C_0^{2m-1}, \lambda''' C_0^{n+m-1}) \ll (\lambda^* C_0^n, \lambda^{**} C_0^m). \tag{4.9}$$

As a consequence the fourth, fifth and the last three terms of equation (3.42) can usually be neglected for application purposes and the model can be approximated as

$$\frac{\partial C_0}{\partial t} + u_e \frac{\partial C_0}{\partial x} - D^* \frac{\partial^2 C_0}{\partial x^2} + \lambda^* C_0^n + \lambda^{**} C_0^m = 0. \tag{4.10}$$

Both the advective term and the dispersive term are the same as those that were present in the model formulated by Ng (2000a) and the same considerations that have already for the transport of passive chemicals are therefore valid. The difference concerns the decay terms. Because of the interaction between the nonlinear decay and the sorption–desorption kinetics the model, even in its approximated
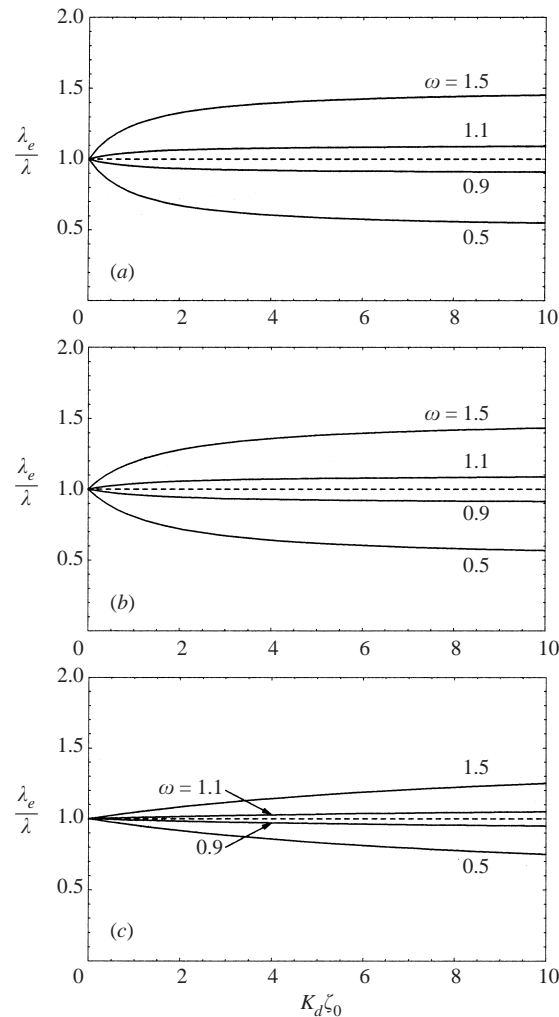
FIGURE 4. Case of linear decay. Examples of the influence of the suspension number, bulk solid–water distribution ratio and ratio between the decay rate constants on the effective decay λ_e. (*a*) $\alpha = 0.1$; (*b*) $\alpha = 1$; (*c*) $\alpha = 10$.

form (4.10), does not have a λC_0^n term, but the terms that account for decay are more complex and non-intuitive. The term $\lambda^{**} C_0^m$ makes the nonlinearity that is present in the decay in the sorbed phase appear explicitly. Only in the case in which the decay has the same degree of nonlinearity in both phases (i.e. $m = n$) does $(\lambda^* + \lambda^{**}) \to \lambda$ and, therefore, the decay terms in the model coincide with λC_0^n, that is, the decay process of the dissolved phase is not influenced by, nor does it influence, the interactions between the suspended load and the transport mechanisms. In this particular case, the decay would occur according to the same rules for the dissolved and sorbed phases and would not be able to alter the kinetics between the two phases.

For profiles (4.1) and (4.3), the coefficients λ^* and λ^{**} are given by

$$\lambda^* = \lambda \frac{e^\alpha \alpha}{e^\alpha(\alpha + K_d\zeta_0) - K_d\zeta_0}, \quad \lambda^{**} = \lambda_s \frac{(e^\alpha - 1)\zeta_0 K_d^m}{e^\alpha(\alpha + K_d\zeta_0) - K_d\zeta_0}. \tag{4.11}$$
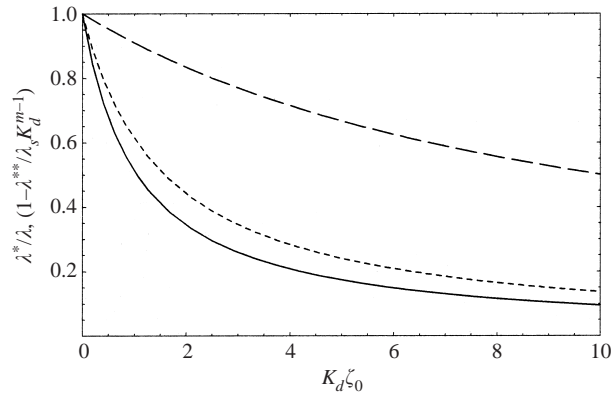
FIGURE 5. Case of nonlinear decay. Behaviour of (dimensionless) coefficients λ^* and λ^{**} as a function of the suspension number and bulk solid–water distribution ratio. $\alpha = 0.1$, continuous line; $\alpha = 1$, dotted line; $\alpha = 0.1$, dashed line.

Figure 5 reports their (dimensionless) behaviour as a function of the two key parameters α and $K_d\zeta_0$. The diagrams show how the weight of term C_0^n is always less than the weight that would occur in clear water and this difference grows with an increase of the quantity of the chemical that is transported by the sediment and with a decrease of the suspension number. The differences are large and can even be of the order of 60%–70%. The opposite behaviour is shown by coefficient λ^{**}, which, as expected, grows with an increase of the sorption partition coefficient and with a decrease of α.

It is also interesting to analyse the relative weight of the two decay terms. Using relationships (2.9) and assuming that, at the beginning of the whole transport process, $C_{s0,t=0} = K_d C_{0,t=0}$, one easily obtains

$$\frac{\lambda^{**} C_0^m}{\lambda^* C_0^n} \sim \left(\frac{C_{0,t=0}}{C_0}\right)^{n-m}. \tag{4.12}$$

As, during the evolution of the phenomenon, all the transport mechanisms lead to a diminishing of the concentration, it follows that if $n > m$ the term $\lambda^{**} C_0^m$ always becomes more important, that is, the decay in the sorbed phase always plays a more important role. The opposite occurs in the case in which $m > n$. This different behaviour can easily be interpreted if the decay laws (2.7) and equation (2.11) that describes the tendency to equilibrium between the dissolved and sorbed phases, are taken into consideration. If $n > m$, the decay is stronger in the sorbed than in the dissolved phase; therefore, as time passes (and concentration C_0 diminishes), the sorbed phase takes more and more chemical from the dissolved phase thus becoming the main decay mechanism, justifying the predominance of term $\lambda^{**} C_0^m$ in the model. It is therefore the degree of nonlinearity that determines which of the two decays in the two phases is decisive for the evolution of C_0.

Let us now study the evolution of a real cloud of pollutant in a stream to show an example of a chemical pollution governed by models (3.42) and (4.10). Introducing the moving frame $(\xi, \tau) = (x - u_e t, t)$ the models become

$$\frac{\partial C_0}{\partial \tau} - D^* \frac{\partial^2 C_0}{\partial \xi^2} + u^* \frac{\partial C_0^n}{\partial \xi} + u^{**} \frac{\partial C_0^m}{\partial \xi}$$

$$+ \lambda^* C_0^n + \lambda^{**} C_0^m + \lambda' C_0^{2n-1} + \lambda''' C_0^{m+n-1} + \lambda'' C_0^{2m-1} = 0 \tag{4.13}$$

Case	n	m	λ $((\mathrm{Kg\,m^{-3}})^{1-n}\,\mathrm{s^{-1}})$	λ_s $(\mathrm{s^{-1}})$	λ^* $((\mathrm{Kg\,m^{-3}})^{1-n}\,\mathrm{s^{-1}})$	λ^{**} $(\mathrm{s^{-1}})$
LR	1	1	6.93×10^{-6}	6.93×10^{-6}	4.25×10^{-6}	2.68×10^{-6}
NR1	1	2	6.93×10^{-6}	3.60×10^{-6}	4.25×10^{-6}	1.39×10^{-5}
NR2	2	1	3.60×10^{-5}	6.93×10^{-6}	2.20×10^{-5}	2.68×10^{-6}
NR3	2	2	3.60×10^{-5}	3.60×10^{-6}	2.20×10^{-5}	1.39×10^{-5}

TABLE 1. Values of the parameters that characterize the decay process in the dissolved and sorbed phases in the simulations.

and

$$\frac{\partial C_0}{\partial \tau} - D^* \frac{\partial^2 C_0}{\partial \xi^2} + \lambda^* C_0^n + \lambda^{**} C_0^m = 0. \tag{4.14}$$

Let us suppose that, at time $\tau = 0$, an input of unitary mass is released into the stream and is spatially distributed according to a Gaussian concentration law

$$C_{0,\tau=0}(\xi) = \frac{1}{\sqrt{4\pi D^*}} \exp\left(-\frac{\xi^2}{4D^*}\right). \tag{4.15}$$

Let us follow the evolution of this cloud over a time interval T_s, during which the concentration C_0 could be considered equal to zero outside the spatial interval $[-\xi_s, +\xi_s]$. The following initial and boundary conditions are associated with (4.13) and (4.14):

$$C_0(\xi, 0) = C_{0,\tau=0}(\xi), \quad C_0(-\xi_s, \tau) = C_0(\xi_s, \tau) = 0. \tag{4.16}$$

The above mathematical problems (4.13), (4.15), (4.16) and (4.14)–(4.16) were numerically integrated using an interpolation-collocation method based on sinc functions (Bellomo & Ridolfi 1995) that is particularly suitable for nonlinear models and to simulate wave phenomena (Revelli & Ridolfi 2002). In the present problem, a spatial discretization was used with 61 nodes and an adaptive time step varying from 0.5 s to 1500 s, and the system of ordinary differential equations that results from the spatial discretization was integrated with the Adams predictor–corrector method (Stoer & Bulirsch 1980). The numerical algorithm was tested for the case of linear decay, where a very good agreement was found with the analytical solution.

Several cases were simulated and the results of four example simulations, corresponding to the values of the parameters reported in table 1, are shown. The LR case refers to linear reactive substances, while the last three simulations refer to nonlinear reactive chemicals with different n/m and λ_s/λ ratios. All the simulations were performed for $\alpha = 1$, $K_d \zeta_0 = 1$, $\epsilon_s = 7 \times 10^3$ m and $t_{1/2} = 10^5$ s. The effective mean velocity u_e and the effective dispersion coefficient D^* were equal to $0.23\,\mathrm{m\,s^{-1}}$ and $1.03\,\mathrm{m^2\,s^{-1}}$.

Figure 6(a, b) shows the longitudinal concentration profiles after $\tau^* = 1$ day, while figures 7 and 8 compare the time evolution of the r.m.s. and the peak value, C_p. The latter is normalized to the linear case, $C_{p,l}$, to highlight the role of the nonlinearities. Some significant results clearly emerge. First, the strong influence of the nonlinear decay can be observed: the differences from the linear case are quite remarkable and, on increasing the nonlinearities in the decay, differences of up to 100% can be reached in the central portion of the plume. As expected (from laws (2.7) and recalling that $C_0 < 1$), values of greater concentrations always correspond to the nonlinear cases. Neglecting the nonlinearity in the decay always involves an approximation, to the
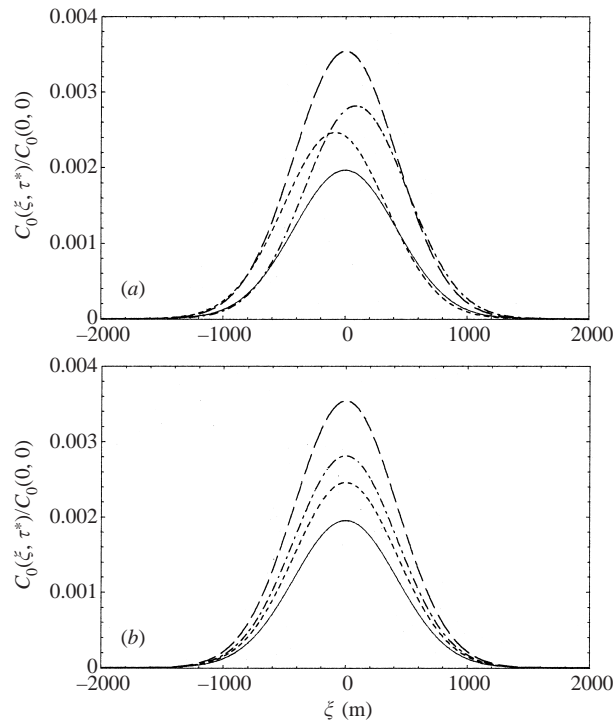
FIGURE 6. Longitudinal profiles $C_0(\xi, \tau^*)$, for the simulated cases ($\tau^* = 1$ day), according the complete model (4.13) (*a*) and the approximate model (4.14) (*b*). $m = n = 1$, continuous line; $n = 1$, $m = 2$, dotted line; $n = 2$, $m = 1$, dot-dashed line; $m = n = 2$, dashed line.
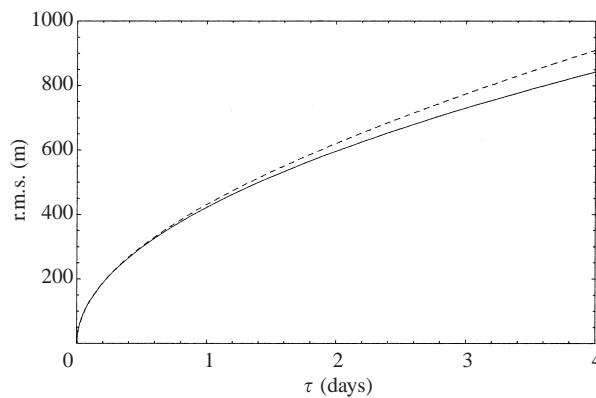

FIGURE 7. Behaviour of the r.m.s. concentration distribution for the decay cases reported in table 1. All four cases simulated with the approximated model (4.14) collapse on the continuous line, while the dashed line refers to the complete model (4.13) in the two cases with $n \neq m$.

detriment of safety, and some tests have shown that the nonlinearities in the sorbed phase have more effect than those of the dissolved phase. The effect of the nonlinear terms that were neglected in the approximate model (4.10) can also be observed. These terms contribute when the nonlinear exponents of the decay laws (2.7) differ from each other: when $n < m$ their influence determines a slowing down of the pollutant wave and the origin of a negative asymmetry (see also figure 9). The opposite occurs if
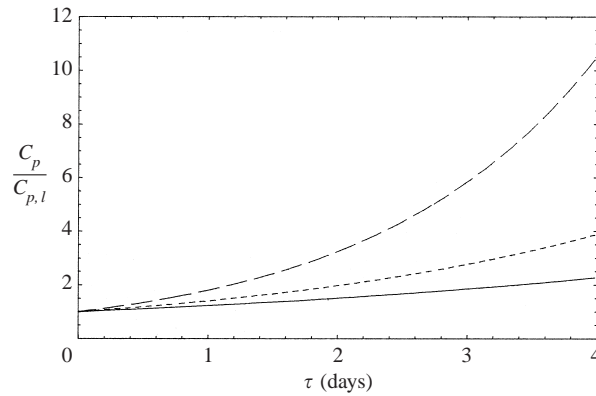
FIGURE 8. Behaviour of the peak value of the concentration C_p for the nonlinear decay cases reported in table 1 ($C_{p,l}$ refers to the linear case LR). $n = 1$, $m = 2$, continuous line; $n = 2$, $m = 1$, dotted line; $m = n = 2$, dashed line.
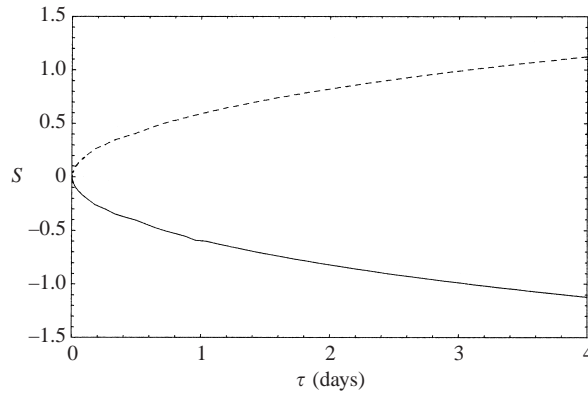

FIGURE 9. Evolution of the skewness, S, according to the complete model (4.13). ($n = 1$, $m = 2$), continuous line; ($n = 2$, $m = 1$), dotted line.

$n > m$. Regardless of the sign of the difference $(m-n)$, the neglected terms also involve an increase of the r.m.s. concentration distribution (see the dashed line in figure 7); if the r.m.s. is taken as an indication of the size of the plume, this would mean that the use of approximate model (4.14) in place of (4.13) could be detrimental to safety. Finally, kurtosis (not shown) also shows a very weak dependence on the neglected nonlinear terms even though the tails of the distribution of the concentration are never more than $3\% \pm 5\%$ different from those of the approximate model.

Apart from the effects on the r.m.s. and the asymmetry of the chemical plumes, the higher-order terms neglected in model (4.10) can be important in the case of a multi-species substance. In this case individual species may have different degrees of reactivity and the terms in model (3.42) can play an important role in separating the centroids of the concentration distributions of the species on the long time scale. An example is shown in figure 10. It refers to two species A and B – with (n, m) equal to $(1, 2)$ and $(2, 1)$ – that start with the same initial conditions. The figure describes the temporal evolution of the distance, d_{AB}, between the two centroids according to the complete model (3.42). The importance of the higher-order effects is evident: after about one day, the distance becomes similar to the size of the plumes. The approximate model (4.10) would always erroneously give $d_{AB} = 0$.
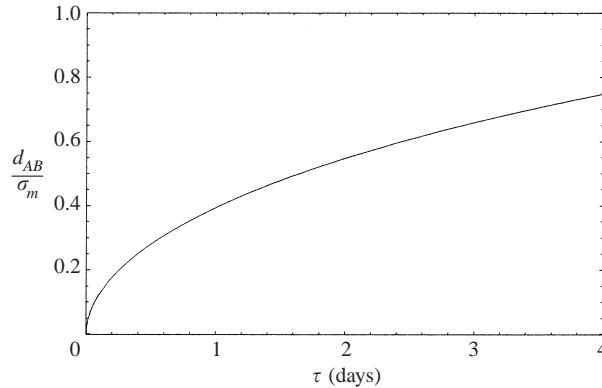
FIGURE 10. Evolution of the distance, d_{AB}, between the centroids of the concentration distributions of two species with different degrees of reactivity ($n = 2$, $m = 1$ and $n = 1$, $m = 2$). The distance is normalized to the mean, σ_m, of the r.m.s. of the two plumes.
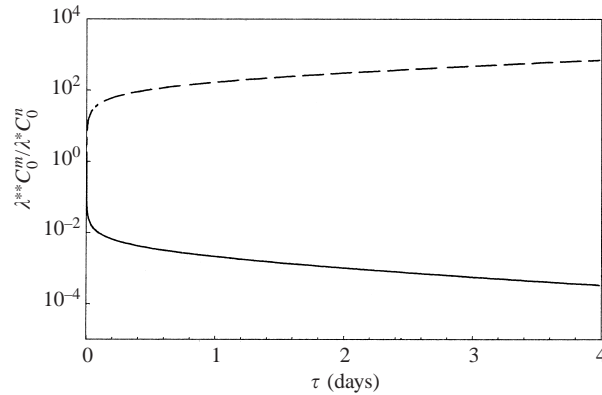

FIGURE 11. Evolution of the ratio $\lambda^{**}C_0^m/\lambda^*C_0^n$ in the cases $n = 1$, $m = 2$ (continuous line) and $n = 2$, $m = 1$ (dashed line).

Figures 7 and 8 also allow one to assess the error that would occur when, instead of using (4.14), the model

$$\frac{\partial C_0}{\partial \tau} - D^*\frac{\partial^2 C_0}{\partial \xi^2} + \lambda C_0^n = 0, \tag{4.17}$$

is used, that is the model that would result if only the decay of the dissolved phase were also to be directly applied to concentration C_0, neglecting the interaction between the decay and sorption kinetics. As an example, let us consider the case where $n = 2$ and $m = 1$. In this case, and recalling that $\lambda^* + \lambda^{**} \to \lambda$ if $m = n$, model (4.17) would give the same behaviour as that shown in figures 5 and 6 for the case where $n = m = 2$. Errors would therefore result and similar errors would also be encountered in the case of $n = 1$ and $m = 2$. This stresses the importance of the interaction between the decay and kinetic sorptive exchange.

Figure 11 reports the time behaviour of the $\lambda^{**}C_0^m/\lambda^*C_0^n$ ratio for cases NR1 and NR2. This figure confirms the previous discussion on (4.12), that is that the sign of the difference between the exponents of the laws of decay (2.7) determines which of the two decays will prevail in the evolution of C_0. It can also be observed that,

because of the rapid spreading of the chemicals, the prevalence (or not) of one term over another has a very rapid trend that develops in the first stages of the transport process.

5. Conclusions

The study of transport phenomena in an open channel flow is a fascinating subject. One interesting aspect is that of the effects of suspended particles that can adsorb chemical substances on the solute transport. The works by Ng (2000a, b) and Ng & Yip (2001) have shown how the sorption–desorption kinetics that are established between the dissolved and sorbed phases can influence the advection and dispersion of the substance to a great extent. The present paper has also investigated the added effect of decay, which often affects the fate of substances in real streams and is very important in forecasting the evolution of pollutants. Decay has been considered in both the linear and nonlinear cases and with different rates for the sorbed and dissolved phases. The main result is the deduction of a one-dimensional differential model that governs the evolution of the dissolved phase and which includes interaction with the sorbed phase. The model shows how the influence of the suspended sediment and decay alters all the transport mechanisms. In particular, even though the model only considers the fate of the dissolved phase, there are decay terms that explicitly depend on the decay in the sorbed phases. This means that the effective decay of the depth-averaged concentration of the dissolved phase can be remarkably different from the decay that would occur in the case of clear water. Some quantitative examples have confirmed the importance of the interaction between the decay and suspended sediment, which therefore should not be neglected in water quality models.

REFERENCES

ARIS, R. 1956 On the dispersion of a solute in a fluid flowing through a tube. *Proc. R. Soc. Lond.* A **235**, 67–77.

BEAR, J. 1979 *Hydraulics of Groundwater*. McGraw-Hill.

BELLOMO, N. & RIDOLFI, L. 1995 Solution of nonlinear initial-boundary value problems by sinc collocation-interpolation methods. *Comput. Math. Applics.* **29**, 15–28.

BERNARD, P. S. & ROVELSTAD, A. L. 1994 On the physical accuracy of scalar transport modeling in inhomogeneous turbulence. *Phys. Fluids* **6**, 3093–3108.

BREZONIK, P. L. 1996 *Chemical Kinetics and Process Dynamics in Aquatic Systems*. Lewis, Boca Raton, FL.

CHATWIN, P. C. 1970 The approach to normality of the concentration distribution of a solute in solvent flowing through a tube. *J. Fluid Mech.* **43**, 321–352.

CHOI, J., HARVEY, J. W. & CONKLIN, M. H. 2000 Characterizing multiple timescales of stream and storage zone interaction that affect solute fate and transport in streams. *Water Resour. Res.* **36**, 1511–1518.

CIORANESCU, D. & DONATO, P. 1999 *An Introduction to Homogenization*. Oxford University Press.

CUSHMAN, J. H. 1990 *Dynamics of Fluids in Hierarchical Porous Media*. Academic.

CVETKOVIC, V. & DAGAN, G. 1994 Transport of kinetically sorbing solute by steady random velocity in heterogeneous porous formation. *J. Fluid Mech.* **265**, 189–215.

CZERNUSZENKO, W. & ROWINSKI, P. M. 1997 Properties of the dead-zone model of longitudinal dispersion in rivers. *J. Hydraul. Res.* **35**, 491–504.

ELDER, J. W. 1959 The dispersion of marked fluid in turbulent shear flow. *J. Fluid Mech.* **5**, 544–560.

ELLIOTT, A. H. & BROOKS, N. H. 1997 Transfer of nonsorbing solutes to a streambed with bed forms: Theory. *Water Resour. Res.* **33**, 123–136.

ENGELUND, F. 1970 Instability of erodible beds. *J. Fluid Mech.* **42**, 225–244.

FISCHER, H. B. 1973 Longitudinal dispersion and turbulent mixing in open-channel flow. *Annu. Rev. Fluid Mech.* **5**, 59–78.

FISCHER, H. B., LIST, E. J., KOH, R. C. Y., IMBERGER, J. & BROOKS, N. 1979 *Mixing in Inland and Coastal Waters.* Academic.

FORSMAN, K. J., JOHANSSON, H. & JONSSON, K. 2002 The effects of partly irreversible solute exchange: comparison between conservative and sorptive transport in streams. *J. Hydrol.* **256**, 1–15.

GRAF, W. H. 1984 *Hydraulics of Sediment Transport.* McGraw-Hill.

GUPTA, A. & CVETKOVIC, V. 2000 Temporal moment analysis of tracer discharge is streams: combined effect of physicochemical mass transfer and morphology. *Water Resour. Res.* **36**, 2985–2997.

JANSEN, P. P. 1979 *Principles of River Engineering: the Non-tidal Alluvial River.* Pitman, London.

KAFTORI, D., HETSRONI, G. & BANERJEE, S. 1995 Particle behaviour in the turbulent boundary layer. II. Velocity and distribution profiles. *Phys. Fluids* **7**, 1107–1121.

KARICHOFF, S. W., BROWN, D. S. & SCOTT, T. A. 1979 Sorption of hydrophobic pollutants on natural sediments. *Water Res.* **13**, 241–348.

MANSON, J. R. & WALLIS, S. G. 2000 A conservative, semi-Lagrangian fate and transport model for fluvial systems – I. Theoretical development. *Water Resour. Res.* **34**, 3769–3777.

MEI, C. C., AURIAULT, J. L. & NG, C. O. 1996 Some applications of the homogenization theory. In *Advances in Applied Mechanics* (ed. J. W. Hutchinson & T. Y. Wu), vol. 32, pp. 277–348. Academic.

NAYFEH, A. H. 1973 *Perturbation Methods.* Wiley.

NEZU, I. & NAKAGAWA, H. 1993 *Turbulence in Open-channel Flows.* Balkema.

NIÑO, Y. & GARCIA, M. H. 1996 Experiments on particle-turbulence interactions in the near-wall region of an open channel flow: implications for sediment transport. *J. Fluid Mech.* **326**, 285–319.

NG, C. O. 2000a Dispersion in sediment-laden stream flow. *J. Engng Mech., ASCE* **126**, 779–786.

NG, C. O. 2000b Chemical transport associated with discharge of contaminated fine particles to a steady open-channel flow *Phys. Fluids* **12**, 136–144.

NG, C. O. & YIP, T. L. 2001 Effects of kinetic sorptive exchange on solute transport in open-channel flow. *J. Fluid Mech.* **446**, 321–345.

O'CONNOR, D. J. & CONNOLLY, J. P. 1989 The effect of concentration of adsorbing solids on the partition coefficient. *Water Res.* **14**, 1517–1523.

PAN, Y. & BANERJEE, S. 1996 Numerical simulation of particle interactions with wall turbulence. *Phys. Fluids* **8**, 2733–2755.

RATHBUN, R. E. 2000 Transport, behaviour, and fate of volatile organic compounds in streams. *Crit. Rev. Environ. Sci. Technol.* **30**(2), 129–295.

REVELLI, R. & RIDOLFI, L. 2002 Sinc collocation-interpolation method for the simulation of nonlinear waves. *Comput. Math. Applics.* (in press).

ROUSON, D. W. I. & EATON, J. K. 2001 On the preferential concentration of solid particles in turbulent channel flow. *J. Fluid Mech.* **428**, 149–169.

RUNKEL, R. L., BENCALA, K. E., BROSHEARS, R. E. & CHAPRA, S. C. 1996 Reactive solute transport in streams 1. Development of an equilibrium-based model. *Water Resour. Res.* **32**, 409–418.

SCHNOOR, J. L. 1996 *Environmental Modeling.* Wiley.

SCHWARZENBACH, R. P., GSCHWEND, P. M. & IMBODEN, D. M. 1993 *Environmental Organic Chemistry.* Wiley.

SCHWEICH, D. & SARDIN, M. 1981 Adsorption, partition, ion exchange and chemical reaction in batch reactors on in columns – A review. *J. Hydrol.* **50**, 1–33.

SMITH, R. 1983 Effect of boundary absorption upon longitudinal dispersion in shear flow. *J. Fluid Mech.* **134**, 161–177.

SMITH, R. 1986 Vertical drift and reaction effects upon contaminant dispersion in parallel shear flow. *J. Fluid Mech.* **165**, 425–444.

STEEFEL, C. I. & VAN CAPPELLEN, P. 1998 Reactive transport modeling of natural systems. *J. Hydrol.* **209**, 1–7.

STOER, J. & BULIRSCH, R. 1980 *Introduction to Numerical Analysis*. Springer.

SULLIVAN, P. J. 1971 Longitudinal dispersion within a two-dimensional turbulent shear flow. *J. Fluid Mech.* **49**, 551–576.

SUMER, B. M. 1974 Mean velocity and longitudinal dispersion of heavy particles in turbulent open-channel flow. *J. Fluid Mech.* **65**, 11–28.

TAYLOR, G. I. 1953 Dispersion of soluble matter in solvent flowing slowly through a tube. *Proc. R. Soc. Lond.* A **219**, 186–203.

TAYLOR, G. I. 1954 The dispersion of matter in turbulent flow through a pipe. *Proc. R. Soc. Lond.* A **223**, 446–468.

THIBODEAUX, L. J. 1996 *Environmental Chemodynamics*, 2nd edn. Wiley.

VANONI, V. A. 1975 *Sedimentation Engineering*. ASCE.

WALLING, D. E. & WEBB, B. W. 1992 Water quality: I. Physical characteristics. In *The Rivers Handbook*, pp. 48–72. Blackwell.

WANG, Q. & SQUIRES, K. D. 1996 Large eddy simulation of particle-laden turbulent channel flow. *Phys. Fluids* **8**, 1207–1223.

WÖRMAN, A. 1998 Analytical solution and timescale for transport of reacting solutes in rivers and streams. *Water Resour. Res.* **34**, 2703–2716.

WU, S. C. & GSCHWEND, P. M. 1986 Sorption kinetics of hydrophobic organic-compounds to natural sediments and soils. *Environ. Sci. Technol.* **20**, 717–725.