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Effects of kinetic sorptive exchange on solute transport in open-channel flow

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A theory is presented for the transport in open-channel flow of a chemical species under the influence of kinetic sorptive exchange between phases that are dissolved in water and sorbed onto suspended sediments. The asymptotic method of homogenization is followed to deduce effective transport equations for both phases. The transport coefficients for the solute are shown to be functions of the local sediment concentration and therefore vary with space and time. The three important controlling parameters are the suspension number, the bulk solid–water distribution ratio and the sorption kinetics parameter. It is illustrated with a numerical example that when values of these parameters are sufficiently high, the advection and dispersion of the solute cloud can be dominated by the sorption effects. The concentration distribution can exhibit an appreciable deviation from Gaussianity soon after discharge, which develops into a long tailing as the solute cloud gradually moves ahead of the sediment cloud.

1. Introduction

The transport of solutes in streams is affected by a suite of physical, chemical and biological processes, with the relative importance of each depending on the geo-environmental setting and properties of the solutes. For many species, chemical and biological reactions are just as influential as the physical processes of advection and dispersion in controlling their movement in an aquatic system like a stream. Rathbun (2000) has recently reviewed the characteristics of the various biogeochemical processes (namely volatilization, sorption, wet and dry deposition, microbial degradation, hydrolysis, aquatic photolysis, oxidation, bioconcentration, and so on) that can affect the fate and transport of volatile organic compounds in streams. Though chemical reactions and phase exchange mechanisms have now been incorporated into some applied transport models (e.g. Onishi 1981; Runkel et al. 1996; Wörman 1998), theoretical studies into these chemical effects on the physical transport have been very limited. There lacks, for example, a systematic understanding of the effects of sorption kinetics on the longitudinal dispersion: dispersion is conventionally considered to be affected by physical and hydrodynamic processes only.

Mass transport in streams or long open channels is typically described by a one-dimensional advection–dispersion equation, in which the longitudinal dispersion coefficient is the combination of various section-averaged hydrodynamic mixing effects. The classical work of Taylor (1953, 1954) established the fact that the primary cause of dispersion in shear flow is the combined action of lateral diffusion and differential longitudinal advection. Dispersion in two-dimensional turbulent open-channel flow was first studied by Elder (1959), whose dispersion coefficient was however found to be
too low compared with measurements. Taking account of transverse instead of vertical velocity variations, Fischer (1967) developed a more accurate expression for the coefficient of longitudinal dispersion in natural streams. McQuivey & Keefer (1974) and Liu (1977) further proposed simpler formulae for predicting dispersion in natural streams. Many others also studied the effects due to buoyancy, curvature, dead-zone, channel irregularities, and unsteady flow (see for example Fischer 1973; Fischer et al. 1979; Smith 1979a; and the references therein). Only a few works (Smith 1983, 1986) have considered effects such as boundary absorption and reaction on the longitudinal dispersion in shear flows. There exist even fewer theoretical developments in which reactive chemistry involving phase exchange of the solute is specifically taken into account.

The significance of phase exchange for solute transport in open-channel flow was recently examined by Ng (2000a,b). Ng (2000a) presented an analytical study on the transport of a chemical pollutant resulting from the discharge of polluted fine particles into a two-dimensional stream, where local equilibrium partitioning between dissolved and sorbed phases is assumed. Because of sorption, the transport of the dissolved phase is affected by that of the suspended particulates. In particular, the advection velocity and dispersion coefficient of the solute will change in space and time according to the local sediment concentration. Ng (2000b) also investigated the effects of kinetic sorptive exchange on the dispersion of a sorbing solute in a stream which is laden with a steady uniform streamwise distribution of suspended sediments. As a result, the dispersion coefficient is composed of a modified Taylor dispersion coefficient and a component due to the finite rate of mass exchange between the dissolved phase in the water column and the sorbed phase on suspended sediments. Following these works, it is the intention here to advance a more general theory for the transport of a sorbing solute under the influence of sediment transport. While essentially an extension of Ng (2000a), the present work is more general by taking into account the kinetics of sorptive exchange and a finite fall velocity of particulates, which will lead to non-trivial effects on the transport of the solute, both quantitatively and qualitatively.

The present study formulates a theory for the transport in open-channel flow of a chemical species which is partitioned between a dissolved phase in the water column and a sorbed phase onto suspended solid particles. It features original results due to the sorption kinetics, by which the advection and dispersion of the solute cloud are functions of that of the particle cloud. For non-buoyant particles such as dissolved substances, the mean advection velocity is essentially equal to the discharge velocity (Elder 1959). For heavy particles, the mean advection velocity is however the fluid velocity weighted by the particle concentration profile, which in general is smaller than the discharge velocity. Also, because of greater shear near the bed, the dispersion is enhanced by gravitational settling. Therefore, heavy particles tend to move more slowly but are subject to a larger extent of dispersion compared with non-buoyant particles. These results have been confirmed experimentally (Sayre & Chang 1968; Granata & Horne 1985), and verified by theory (Sayre 1968; Sumer 1974). It is of fundamental interest to find out how these two kinds of transport behaviour will combine to affect the transport of a sorbing chemical pollutant that has been discharged into a sediment-laden stream.

In contrast with the Aris (1956) method of moments, the method of homogenization (see its engineering applications in a recent review by Mei, Auriault & Ng 1996) is an efficient and direct method of deducing effective governing equations for the concentration distributions. The deduced advection velocity and dispersion coefficients, which can be functions of the longitudinal coordinate and time, are in general expressible in terms of some sectional averages of the flow and mixing...
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characteristics. For sufficiently simple velocity and diffusivity profiles, these coefficients
can be found analytically. The homogenization method is based on the asymptotic
technique of multiple scales, and therefore the orders of physical variables need to be
stated a priori. The advantage is that the range of validity of the deduced equations is
clearly defined. Following Ng (2000a,b), the method of homogenization is also used
in the present work.

The problem is further defined in §2. The basic assumptions and the orders
of variables are also stated in this section in order to facilitate the subsequent
perturbation analyses. The homogenization method is followed in §3 and §4, where
the effective transport equations for sediments and a chemical species are deduced,
respectively. The advection velocity and dispersion coefficients for the chemical are
shown to depend on the sediment concentration via effects of sorption partitioning
and kinetic phase exchange. A numerical example is presented in §5, where transport
of a contaminant resulting from a pulse input of contaminated sediments into a
wide stream is considered. The sorption effects become strong when the fraction
of mass in the sorbed phase is high and when the sorption exchange is slow to
attain equilibrium. Under these conditions, the sorption effects are shown to be very
influential in controlling the characteristics of the concentration distributions of the
chemical.

2. Problem formulation

To avoid excessive mathematical complication, we study a problem that is simplified
but still sufficient to reveal the physics. As in Elder (1959) and Sumer (1974), a steady
and fully developed shear flow in a wide open channel on a plane mild slope is
considered. While the dispersion coefficient is materially affected by the configuration
of the channel, the basic mechanisms that lead to dispersion remain the same.
Therefore, it suffices to consider a two-dimensional transport problem in order to
demonstrate the importance of a certain process to the dispersion. A generalized
three-dimensional theory is of course required if one needs to evaluate the effect of
the process on the dispersion coefficient for a natural stream; this is not pursued in the
present study. Also, we shall focus our attention only on one phase exchange process,
namely sorption taking place in the water column. The purpose is to develop an
analytical tool by which one can estimate the contribution of the sorptive exchange,
as a modular component among various processes, to the overall physical transport.

For the uniform flow under consideration, the normal depth is $h$ and the $(x,z)$
coordinates are such that $x$ points downstream along the channel bottom and $z$
in the upward direction. Sediments, either naturally occurring or dumped by human
activities, are fine solid particles with a constant settling or fall velocity $w_f$, and stay
in suspension in the main body of flow all the time. By this, mass exchange with the
bed is ignored; the bottom absorbency and entrainment rates are both assumed to
be zero. More general bottom conditions without these assumptions (e.g. Sayre 1968;
Smith 1986) can also be adopted, but are not considered in this work for simplicity.

The sediment particles are assumed to contain a sufficiently high content of sorbents
such as organic matter so that when a chemical pollutant is discharged into the flow,
an appreciable mass fraction of the chemical is sorbed onto the particles. The flow
characteristics are assumed to be unaffected by the presence of the dispersants. Fine
sediment particles and solutes typically have approximately equal turbulent mixing
coefficients or eddy diffusivities. A common practice (e.g. Sayre 1968), which is
adopted here, is to use exactly equal eddy diffusivities for both.
Conservation of mass gives the following transport equation for the suspended sediments:

$$\frac{\partial \zeta}{\partial t} + u \frac{\partial \zeta}{\partial x} - w_f \frac{\partial \zeta}{\partial z} = \frac{\partial}{\partial x} \left( E_x \frac{\partial \zeta}{\partial x} \right) + \frac{\partial}{\partial z} \left( E_z \frac{\partial \zeta}{\partial z} \right), \quad (2.1)$$

where \( t \) is the time, \( \zeta(x,z,t) \) is the sediment concentration (mass of suspended particles per bulk volume), \( u(z) \) is the time-smoothed fluid velocity, and \( E_x(z) \) and \( E_z(z) \) are respectively the longitudinal and vertical components of the eddy diffusivity. The net flux vanishes on the bottom and top of the channel, so the boundary conditions are

$$w_f \frac{\partial \zeta}{\partial z} + E_z \frac{\partial \zeta}{\partial z} = 0 \quad \text{at} \quad z = 0, h. \quad (2.2)$$

For the chemical species that is partitioned between an aqueous phase and a solid phase, the total mass concentration \( C_{tot}(x,z,t) \) (total mass of chemical per bulk volume) is

$$C_{tot} = C + C_s \zeta, \quad (2.3)$$

where \( C(x,z,t) \) is the solute concentration (mass of dissolved phase of chemical per bulk volume) and \( C_s(x,z,t) \) is the sorbate concentration (mass of solid phase of chemical sorbed onto unit mass of suspended sediment). The transport of the chemical is governed by

$$\frac{\partial C_{tot}}{\partial t} + u \frac{\partial C_{tot}}{\partial x} - w_f \frac{\partial C_s \zeta}{\partial z} = \frac{\partial}{\partial x} \left( E_x \frac{\partial C_{tot}}{\partial x} \right) + \frac{\partial}{\partial z} \left( E_z \frac{\partial C_{tot}}{\partial z} \right), \quad (2.4)$$

and the zero-flux boundary conditions

$$w_f C_s \zeta + E_z \frac{\partial C_{tot}}{\partial z} = 0 \quad \text{at} \quad z = 0, h. \quad (2.5)$$

Sorption is a reversible reaction between aqueous and solid phases of the chemical. As commonly assumed in transport modelling (e.g. Valocchi 1985; Bahr & Rubin 1987; Cvetkovic & Dagan 1994; Holmén 1995), the overall sorption rate can be described by a first-order linear kinetics expression

$$\frac{\partial C_s}{\partial t} = k_f C - k C_s, \quad (2.6)$$

where \( k_f \) and \( k \) are respectively the forward and reverse rate constants for the sorption reaction. When the steady state is attained or the reaction is fast compared with other processes, the two phases will be in chemical equilibrium. Then the ratio of their concentrations will be given by

$$C_s/C = k_f/k \equiv K_d, \quad (2.7)$$

where \( K_d \) is termed the sorption partition coefficient. The first-order kinetics model also assumes that the sorption isotherm is linear. The sorption coefficient \( K_d \), which can be estimated by established methods (e.g. Schwarzenbach, Gschwend & Imboden 1993), depends on the properties of both the chemical (sorbate) and the sorbing site (sorbent). On substituting (2.7) into (2.6), the first-order kinetics can be written as

$$\frac{\partial C_s}{\partial t} = k(K_d C - C_s), \quad (2.8)$$

or the rate of change of the sorbate concentration is linearly proportional to the departure from local equilibrium. The reverse rate constant \( k \) will simply be referred to as the sorption rate constant.
Three important time scales are associated with transport in a wide channel: $T_0 = h^2/E$ for vertical diffusion across the depth of flow; $T_1 = L/u$ for advection along the channel; and $T_2 = L^2/D$ for longitudinal dispersion along the channel. In these relations, $L$ is the length scale in the longitudinal direction, $h$ the flow depth, $u$ the discharge velocity, $E$ the eddy diffusivity, and $D$ the dispersion coefficient. It was first pointed out by Taylor (1953) that three-dimensional mass transport in a pipe can be modelled by a one-dimensional equation only at an asymptotic stage when the dispersion time due to advective transport is long compared with that required to remove lateral concentration variations through the action of diffusion, or in the present context $T_0 \ll T_1, T_2$. Smith (1979a) argued that a cloud needs to have been advected by a distance $O(10h)$ downstream before the dispersion can be modelled by a depth-averaged equation. Computations by Sayre (1968) revealed that for an initial plane source in a two-dimensional turbulent channel, the dispersion coefficient reaches its limiting value when $t/T_0 > 0.5$ while the skew coefficient becomes negligibly small when $t/T_0 > 3$. Many others also contributed to the analysis of the early stage of dispersion along pipes or channels (e.g. Chatwin 1970, 1972, 1976, 1977; Sullivan 1971; Barton 1976; Smith 1979b). By and large, one may conclude from these works that at a time scale much longer than $T_0$ the transport can be adequately described by a one-dimensional model. Specifically it is assumed in this study that the three time scales are distinct: $T_0 \ll T_1 \ll T_2$, and the primary scales of concern are $T_1$ and $T_2$ only. With these assumptions, the present asymptotic analysis (see §3) will recover a series expansion of the solute concentration as previously introduced by Chatwin (1970, equation 1.14). It is also shown that the terms with the third and higher derivatives of the concentration in the transport equation of Chatwin (1970, 1972) are actually subdominant if a time scale up to $O(T_2)$ is considered.

To prepare the ground for subsequent perturbation analyses, the scalings of physical variables are estimated as follows. These scaling relationships have largely been established by Ng (2000a,b), and for completeness are repeated here.

(a) The shear dispersion coefficient $D$ is expected to dominate over the eddy diffusivity $Ex$ in controlling the longitudinal spreading of the solute and sediments. Elder (1959) has evaluated that for a two-dimensional turbulent open-channel flow

$$E_x = E_z = 0.07u_*h \quad \text{and} \quad D = 5.86u_*h,$$

where the overbar denotes the depth average, and $u_*$ is the shear velocity given by

$$u_* \equiv (\tau_b/\rho)^{1/2} = (gh \sin \theta)^{1/2},$$

where $\tau_b$ is the bottom shear stress, $\rho$ is the fluid density, $g$ is the acceleration due to gravity, and $\theta$ is the channel slope. It is clear from (2.9a,b) that the dispersion coefficient $D$ is much larger than the turbulent diffusivity $E$, and the small ratio

$$E_z/D \equiv \epsilon \ll 1$$

will be used as the perturbation parameter. Accordingly, the longitudinal and vertical rates of diffusion will be scaled by $D$ and $E$ respectively.

(b) The focus is on the mass transport after a sufficiently long time from discharge. By then, the longitudinal length scale $L$ for the spread of substances will be much longer than the flow depth $h$. The length scale $L$ can be defined by assuming that the transport rate due to longitudinal dispersion is effectively two orders of magnitude
smaller than that due to the vertical diffusion, or
\[
\frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) / \frac{\partial}{\partial z} \left( E_z \frac{\partial C}{\partial z} \right) = O(\epsilon^2). \tag{2.12}
\]
The above relation, on using (2.11), gives a ratio for the two length scales:
\[
h/L = O(\epsilon^{3/2}). \tag{2.13}
\]
(c) The ratio of advection to vertical diffusion is a Péclet number, and on using (2.9a) can be estimated as follows:
\[
Pe_z \equiv \bar{u}h/E_z = O\left( \bar{u}/0.07u_* \right), \tag{2.14}
\]
where \(\bar{u}\) is the depth-averaged fluid velocity, and \(u_*\) is the shear velocity given by (2.10). Since typically \(\bar{u} \geq u_*\), the above number is much larger than unity. We specifically assume that the transport rate due to longitudinal advection is effectively one order of magnitude smaller than that due to the vertical diffusion, or
\[
\bar{u} \frac{\partial C}{\partial x} / \frac{\partial}{\partial z} \left( E_z \frac{\partial C}{\partial z} \right) = O(\epsilon). \tag{2.15}
\]
On using (2.13), the above relation gives an estimate for the Péclet number:
\[
Pe_z = O(\epsilon^{-1/2}). \tag{2.16}
\]
(d) The fall velocity \(w_f\) of a sediment particle depends on the size and shape of the particle. Grains of fine sand and silt have shape factor close to unity, and their fall velocity can be determined from the diameter \(d\) of an equivalent spherical particle. A graphical relation between the parameters \(w_f/[(\rho_s/\rho - 1)gd]^{1/2}\) and \((d/4v)((\rho_s/\rho - 1)gd)^{1/2}\), where \(\rho_s\) is the solid density, and \(v\) is the fluid kinematic viscosity, has been compiled by Madsen (1975). From this graph, one can readily determine that for fine sands with 0.1 mm nominal diameter and unity shape factor, the fall velocity is on the order of 0.01 m s\(^{-1}\). Typically, the stream velocity is on the order of 1–0.1 m s\(^{-1}\). Therefore, it is reasonable to assume that
\[
w_f/\bar{u} \leq O(\epsilon^{1/2}). \tag{2.17}
\]
This implies that, with (2.16),
\[
E_z/w_f \geq O(h), \tag{2.18}
\]
or the suspended particles fully distribute across the water column.
(e) The ratio of rate of sorption to rate of vertical diffusion is a Damköhler number, which can be written as follows:
\[
Da \equiv kh^2/E_z = O\left( kh/0.07u_* \right), \tag{2.19}
\]
where \(k\) is the first-order sorption rate constant. Given the aggregate nature of suspended solids and sediments (Johnson 1974; Zabawa 1978; Chase 1979), sorption kinetics are very often modelled with rate-limiting diffusion into a spherical particle. By virtue of this model, the sorption rate constant can be estimated by (Wu & Gschwend 1986; Schwarzenbach et al. 1993, p. 337):
\[
k \simeq 23D_e/r^2, \tag{2.20}
\]
where \(r\) is the aggregate radius, and \(D_e\) is the effective aggregate diffusion coefficient.
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\[
D_e = \frac{\phi \tau^{-1} D_w}{K_d (1 - \phi) \rho_s + \phi} \tag{2.21}
\]

in which \( D_w \) is the chemical diffusivity in pure water, \( \tau \) is the tortuosity factor of the aggregate porous structure, \( \phi \) is the aggregate porosity and \( \rho_s \) is the solid density. For a strongly hydrophobic compound, the effective aggregate diffusivity can be as low as \( D_e = O(10^{-8} \text{ cm}^2 \text{ s}^{-1}) \). Assuming an aggregate radius of \( r \approx 0.5 \text{ mm} \), the sorption rate constant from (2.20) is then \( k = O(10^{-4} \text{ s}^{-1}) \). Further, using typical values \( h \approx 5 \text{ m} \) and \( u_* \approx 0.01 \text{ m s}^{-1} \), it follows from (2.19) that the Damköhler number is of order unity:

\[
Da = O(1), \tag{2.22}
\]

or the sorption rate is comparable with the vertical turbulent diffusion rate.

(f) The fractions of chemical in the water and on the solid are assumed to be comparable with each other so that both phases are important in the resultant transport. The bulk solid–water distribution ratio, defined below, must therefore be of order unity:

\[
K_d \bar{\zeta} = O(1), \tag{2.23}
\]

where \( K_d \) is the sorption partition coefficient and \( \bar{\zeta} \) is a scale of the sediment concentration. Typically the suspended sediment concentration is in the range \( 10^{-4} - 10^{-5} \text{ kg l}^{-1} \). Even for such low concentrations, the solid–water distribution ratio can still be of order unity if the chemical is sufficiently hydrophobic and has a high value of sorption partition coefficient \( K_d \). For example, Wu & Gschwend (1986) have found that for a number of natural bed sediments the sorption partition coefficient can be as high as \( 4700 \text{ l kg}^{-1} \) where the sorbates are chlorobenzenes. Heavy metals and polychlorinated biphenyls also have very high values of \( K_d \) on the order of \( 10^4 - 10^6 \text{ l kg}^{-1} \). Schnoor (1996, p. 427) has calculated that the fraction of lead (II) adsorbed on suspended sediments can exceed 0.5 at pH 7 or above in a lake where the suspended solid concentration is only \( 10^{-6} \text{ kg l}^{-1} \). In short, it is possible for (2.23) to be realistic provided that both the sediment concentration and the sorption partition coefficient are sufficiently large.

(g) Recall the three time scales \( T_0, T_1 \) and \( T_2 \) which correspond respectively to the time scales for diffusion across the flow, longitudinal advection and longitudinal dispersion. It is now clear that these time scales are of successively higher orders:

\[
T_0/T_1 = \frac{h^2 \pi}{L \bar{E}_z} = O(\epsilon), \tag{2.24}
\]

where (2.13) and (2.16) have been used, and

\[
T_1/T_2 = \frac{D}{L \bar{u}} = O(\epsilon), \tag{2.25}
\]

where (2.11), (2.13) and (2.16) have been used. Since the focus is on the longitudinal transport, variations of concentrations over the shortest time scale \( T_0 \) associated with vertical diffusion will not be accounted for.

With the above scalings, the order of magnitude of individual terms in the governing equations and boundary conditions (2.1), (2.2), (2.4), (2.5) and (2.8) can be estimated. These equations are repeated below, with the ordering parameter \( \epsilon \) now inserted to indicate the relative order of the associated term. The sediment transport equation is

\[
\epsilon \frac{\partial \zeta}{\partial t} + \epsilon u \frac{\partial \zeta}{\partial x} - w \frac{\partial \zeta}{\partial z} = \epsilon^2 \frac{\partial}{\partial x} \left( E_x \frac{\partial \zeta}{\partial x} \right) + \frac{\partial}{\partial z} \left( E_z \frac{\partial \zeta}{\partial z} \right), \tag{2.26}
\]
with the boundary conditions
\[
wf_0 \zeta_0 + Ez_0 \zeta_0 = 0 \quad \text{at} \quad z = 0, h. \quad (2.27)
\]

The chemical transport equation is
\[
\epsilon \frac{\partial C_{tot}}{\partial t} + \epsilon u \frac{\partial C_{tot}}{\partial x} - wf \frac{\partial C_s}{\partial z} = \epsilon^2 \frac{\partial}{\partial x} \left( E_x \frac{\partial C_{tot}}{\partial x} \right) + \frac{\partial}{\partial z} \left( Ez \frac{\partial C_{tot}}{\partial z} \right), \quad (2.28)
\]
with the boundary conditions
\[
wf C_s \zeta + Ez \frac{\partial C_{tot}}{\partial z} = 0 \quad \text{at} \quad z = 0, h. \quad (2.29)
\]
The sorption kinetics equation is
\[
\epsilon \frac{\partial C_s}{\partial t} = k (K_d C - C_s). \quad (2.30)
\]

Perturbation equations are obtainable on substituting the following multiple-scale expansions into the above equations:
\[
(\zeta, C, C_s) \rightarrow (\zeta_0, C_0, C_{s0}) + \epsilon (\zeta_1, C_1, C_{s1}) + \epsilon^2 (\zeta_2, C_2, C_{s2}) + O(\epsilon^3), \quad (2.31)
\]
\[
\frac{\partial}{\partial t} \rightarrow \frac{\partial}{\partial t_1} + \epsilon \frac{\partial}{\partial t_2}. \quad (2.32)
\]
A depth-average is denoted by an overbar. For example, for any function \( F(z) \),
\[
\overline{F} = \frac{1}{h} \int_0^h F(z) dz. \quad (2.33)
\]

3. Transport of suspended sediments

The leading-order sediment concentration \( \zeta_0 \) is governed by
\[
\frac{\partial}{\partial z} \left( wf_0 \zeta_0 + E_z \frac{\partial \zeta_0}{\partial z} \right) = 0 \quad \text{in} \quad 0 < z < h, \quad (3.1)
\]
with the boundary conditions
\[
wf \zeta_0 + E_z \frac{\partial \zeta_0}{\partial z} = 0 \quad \text{at} \quad z = 0, h. \quad (3.2)
\]
Clearly, \( \zeta_0 \) satisfies \( wf \zeta_0 + E_z \zeta_0 / \partial z = 0 \) for \( 0 < z < h \), which gives
\[
\zeta_0(x, z, t) = \zeta_b(x, t)f(z), \quad (3.3)
\]
where \( \zeta_b = \zeta_0(z = 0) \) is the sediment concentration at the bed level, and \( f(z) \) is the sediment distribution factor resulting from a balance between turbulent mixing and sedimentation:
\[
f(z) = \exp \left( - \int_0^z \frac{wf}{E_z} \, dz' \right). \quad (3.4)
\]
This factor, which decreases monotonically upward with \( z \) for a positive fall velocity \( wf \), governs the distribution of the sediment concentration in the water column.

At \( O(\epsilon) \), the perturbation equation after substituting (3.3) is
\[
\frac{\partial \zeta_b}{\partial t_1} + fu \frac{\partial \zeta_b}{\partial x} = \frac{\partial}{\partial z} \left( wf \zeta_1 + E_z \frac{\partial \zeta_1}{\partial z} \right) \quad \text{in} \quad 0 < z < h, \quad (3.5)
\]
and the boundary conditions are
\[ w_f \zeta_1 + E_z \frac{\partial \zeta_1}{\partial z} = 0 \quad \text{at} \quad z = 0, h. \] (3.6)

On taking an average over the depth and using the boundary conditions, (3.5) yields the leading-order transport equation for the suspended sediments
\[ \frac{\partial \zeta_b}{\partial t_1} + u_s \frac{\partial \zeta_b}{\partial x} = 0, \] (3.7)
where \( \zeta_b(x,t) \) is the sediment concentration at the bed level, and
\[ u_s = \frac{f u}{f} \] (3.8)
is the effective advection velocity of the sediments, which is a depth-averaged velocity, weighted by the sediment distribution factor \( f \). As expected, only advection appears in this equation.

One can easily show that
\[ u - u_s = -(f - \bar{f})(u - \bar{u})/\bar{f}. \] (3.9)

Hence the difference between the velocities of discharge and sediment advection is related to the depth covariance between the sediment concentration and the fluid velocity. For heavy particles whose concentration increases monotonically towards the bottom, the covariance is negative and therefore \( u_s < \bar{u} \), or the advection speed of the sediment cloud is lower than the discharge velocity. In the limiting case of very fine particles such that the settling velocity is \( w_f h/E_z \ll 1 \), the sediment distribution factor in (3.4) can be approximated by
\[ f \sim 1 - \int_0^z \frac{w_f}{E_z} dz' \] as \( w_f h/E_z \ll 1 \). (3.10)
Then one can also show that
\[ u - u_s \sim (u - \bar{u}) \int_0^z \frac{w_f}{E_z} dz' \] as \( w_f h/E_z \ll 1 \), (3.11)
as previously obtained by Ng (2000a). On adopting a logarithmic velocity profile and a parabolic diffusivity profile, Ng further found that the right-hand side of (3.11) equals \( \pi w_f / 6 \kappa^2 \) where \( \kappa = 0.4 \) is von Kármán’s constant. Therefore, as the sediments become sufficiently fine-grained, their centre of mass is being advected more slowly than the discharge velocity by a speed of approximately ten times the fall velocity.

On eliminating the unsteady term from (3.7) and (3.5), we get
\[ f(u - u_s) \frac{\partial \zeta_b}{\partial x} = \frac{\partial}{\partial z} \left( w_f \zeta_1 + E_z \frac{\partial \zeta_1}{\partial z} \right). \] (3.12)
By linearity, it follows from (3.12) and (3.6) that the following form for the first-order sediment concentration \( \zeta_1(x,z,t) \) can be suggested:
\[ \zeta_1 = N \frac{\partial \zeta_b}{\partial X}, \] (3.13)
where \( N(z) \) is a cell function that is governed by the following boundary value problem:
\[ \frac{d}{dz} \left( w_f N + E_z \frac{dN}{dz} \right) = f(u - u_s) \quad \text{in} \quad 0 < z < h, \] \[ w_f N + E_z \frac{dN}{dz} = 0 \quad \text{at} \quad z = 0, h. \] (3.14)
The problem can be solved by the method of integrating factor, and has the solution

\[ N(z) - fN_0 = f \int_0^z \frac{dz'}{fE_z} \int_0^{z'} f(u - u_s)dz'' \quad (3.16) \]

where \( u_s \) is given by (3.8), and \( N_0 = N(0) \) is undetermined unless a uniqueness condition for \( N \) is specified. Uniqueness conditions will be specified in §4. Note that \( N(z) \) describes the vertical variation for the \( O(\epsilon) \) correction to the sediment concentration, and is a function of the fall velocity through its dependence on the distribution factor \( f \) given by (3.4).

At \( O(\epsilon^2) \), the perturbation equation is

\[ f \frac{\partial \zeta_b}{\partial t_2} + \frac{\partial \zeta_1}{\partial t_1} + u \frac{\partial \zeta_1}{\partial x} = \frac{\partial}{\partial x} \left( fE_x \frac{\partial \zeta_b}{\partial x} \right) + \frac{\partial}{\partial z} \left( w_f \frac{\partial \zeta_2}{\partial z} \right), \quad (3.17) \]

and the boundary conditions are

\[ w_f \zeta_2 + E_z \frac{\partial \zeta_2}{\partial z} = 0 \quad \text{at} \quad z = 0, h. \quad (3.18) \]

Using the boundary conditions, the depth-average of (3.17) gives

\[ f \frac{\partial \zeta_b}{\partial t_2} + \frac{\partial \zeta_1}{\partial t_1} + u \frac{\partial \zeta_1}{\partial x} = \frac{\partial}{\partial x} \left( fE_x \frac{\partial \zeta_b}{\partial x} \right). \quad (3.19) \]

Further, replacing \( \zeta_1 \) by (3.13) and \( \zeta_b/\partial t_1 \) by (3.7), we obtain an \( O(\epsilon) \) equation that describes longitudinal diffusion of sediments on the long time scale \( T_2 \):

\[ \frac{\partial \zeta_b}{\partial t_2} = D_s \frac{\partial^2 \zeta_b}{\partial x^2}, \quad (3.20) \]

where the diffusion coefficient \( D_s \) is composed of

\[ D_s = \frac{fE_x}{f}. \quad (3.21) \]

While the first component of \( D_s \) is a depth-averaged longitudinal eddy diffusivity weighted by the sediment distribution factor \( f \), the second component \( D_{T_s} \) is a dispersion coefficient, which after substituting (3.16) can be further developed as follows:

\[ D_{T_s} = -\frac{N(u - u_s)}{f} = \frac{-(N - fN_0)(u - u_s)}{f} \]

\[ = -f(u - u_s) \int_0^z \frac{dz'}{fE_z} \int_0^{z'} f(u - u_s)dz''/f \quad (3.22) \]

\[ = (fE_z)^{-1} \left[ \int_z^h f(u - u_s)dz' \right] / f, \quad (3.23) \]

where integration by parts has been used in the final step (Ellison 1960). We remark that \( D_{T_s} \) does not depend on the yet undetermined constant \( N_0 \). Being always positive, this coefficient is virtually a Taylor dispersion coefficient, where the flow quantities have been weighted by the sediment distribution factor \( f \). Smith (1996) has obtained similar weighted-square formulae for the Taylor dispersion coefficient for rising and sinking particles in wind-affected shear currents.

It is clear that the above results recover the case of dispersion of non-buoyant fluid particles when \( w_f = 0 \) or \( f = 1 \), by which (3.22) reduces to the well-known expression
for the Taylor dispersion coefficient (see for example Fischer et al. 1979):

\[ D_T = -\frac{(u - \bar{u})}{\bar{E}_z} \int_0^z \frac{dz'}{E_{z'}} \int_0^z (u - \bar{u}) dz'' . \]  

(3.24)

The integral expression (3.24) was first explicitly obtained by Elder (1959, equation 9). Elder however made a mistake on extending this expression to buoyant and heavy particles. He suggested that (3.24) could be used for such particles by simply replacing the mean fluid velocity \( \bar{u} \) by the particle advection velocity \( u_s = \bar{f}u/\bar{f} \). It is now obvious from (3.23) that Elder has omitted to take into account the distribution factor \( \bar{f} \) in several other places in the integral. This explains why Sayre (1968) and Sumer (1974) found their computed results in wide disagreement with predictions by Elder’s expression. The reason for the discrepancy seems not to have been correctly pointed out before. The issue is further discussed by Ng (2001).

To compare with Chatwin (1970), let us also find a formal expression for the \( O(\epsilon^2) \) sediment concentration \( \zeta_2 \), which can be found by eliminating \( \partial \zeta b / \partial t \) from (3.17) and (3.20):

\[ \zeta_2 = M \partial^2 \zeta_b / \partial x^2 , \]  

(3.25)

where the function \( M(z) \), which describes the vertical variation for the \( O(\epsilon^2) \) correction to the sediment concentration, satisfies the following boundary value problem:

\[ \frac{d}{dz} \left( w_f M + E_z \frac{dM}{dz} \right) = (u - u_s)N - \left( \frac{f}{\bar{f}} \right)(u - u_s)\bar{N} - fE_x + \left( \frac{f}{\bar{f}} \right)fE_x \]  

in \( 0 < z < h \),

(3.26)

and

\[ w_f M + E_z \frac{dM}{dz} = 0 \quad \text{at} \quad z = 0, h . \]  

(3.27)

Putting (3.3), (3.13) and (3.25) into (2.31), we have the following expansion series for the sediment concentration:

\[ \zeta(x,z,t) = f\zeta_b + \epsilon N \frac{\partial \zeta_b}{\partial x} + \epsilon^2 M \frac{\partial^2 \zeta_b}{\partial x^2} + O(\epsilon^3) . \]  

(3.28)

Again, considering the limiting case of non-buoyant particles, \( w_f = 0 \) or \( f = 1 \), one can easily find that the functions \( N \) and \( M \), as defined in (3.14)–(3.15) and (3.26)–(3.27), are not different from the functions \( g^{(1)} \) and \( g^{(2)} \) introduced by Chatwin (1970, equations 1.10 and 2.12). Therefore, the expansion (3.28) has the same meanings as the expansion (1.14) of Chatwin (1970), but the order of each term is now more clearly stated. It is important to realize that the effects of \( \zeta_2 \) that lead to a term proportional to \( \partial^3 \zeta_b / \partial x^3 \) (Chatwin 1970, 1972) will not show up in the depth-averaged transport equation until \( O(\epsilon^3) \). In this study, it suffices to consider a time scale no longer than \( T_2 \), and therefore the higher-order diffusion terms need not be sought.

Finally, we may combine (3.7) and (3.20) to get the effective transport equation for the sediment concentration \( \zeta_b(x,t) \), which is correct to \( O(\epsilon) \):

\[ \frac{\partial \zeta_b}{\partial t} + u_t \frac{\partial \zeta_b}{\partial x} = D_s \frac{\partial^2 \zeta_b}{\partial x^2} , \]  

(3.29)

in which \( u_t \) and \( D_s \) are constants and given by (3.8) and (3.21) respectively.
4. Transport of chemical species

Let us now focus our attention on the transport of the chemical species. The formal procedure of deduction resembles that in the preceding section, and therefore only the key results are presented below. From (2.30), the chemical partitioning between the dissolved and sorbed phases is in local equilibrium only at the leading order:

$$C_{s0} = K_d C_0,$$

(4.1)

where $C_{s0}$ and $C_0$ are respectively the leading-order sorbate and solute concentrations, and $K_d$ is the equilibrated sorption partition coefficient. Hence the $O(1)$ total chemical concentration can be written as

$$C_{tot0} = C_0(1 + K_d \zeta_0) = R C_0,$$

(4.2)

where

$$R(x, z, t) = 1 + K_d \zeta_0 = 1 + K_d \zeta_0(x, t) f(z) \geq 1$$

(4.3)

is the retardation factor resulting from the chemical partitioning. A retardation factor is so termed because in groundwater mass transport it is the ratio of the water seepage velocity to the transport speed which is diminished by phase partitioning. The terminology is adopted here since the form is the same. Physically the factor is the ratio of the total concentration to the solute concentration, and reflects the extent of sorption.

It follows from the $O(1)$ terms of (2.28) and (2.29) that $C_0$ is independent of $z$, and therefore

$$C_0 = C_0(x, t) \quad \text{and} \quad C_{s0} = C_{s0}(x, t) = K_d C_0(x, t).$$

(4.4)

At leading order, the solute and sorbate concentrations are uniformly distributed locally across the water column.

At $O(e)$, (2.30) gives

$$\frac{\partial C_{s0}}{\partial t} = k(K_d C_1 - C_{s1}),$$

(4.5)

where $k$ is the rate constant for the first-order sorption kinetics. Hence the rate of change of the sorbate concentration is driven by the departure from local equilibrium between the $O(e)$ concentrations. The leading-order transport equation for the solute is obtained after taking a depth-average of the $O(e)$ terms of (2.28):

$$\frac{\partial C_0}{\partial t} + u_e \frac{\partial C_0}{\partial x} = 0,$$

(4.6)

where $C_0(x, t)$ is the leading-order solute concentration, and

$$u_e(x, t) = \bar{R} \bar{u} / \bar{R}$$

(4.7)

is the leading-order effective advection velocity in which $R(x, z, t)$ is given by (4.3). This is essentially an average velocity weighted by the retardation factor $R$. One may find from (3.7) and (4.6) that the sediment and the solute clouds are in general advected at different speeds, since

$$u_e = u_s + (\bar{u} - u_s) / \bar{R} = \bar{u} - (\bar{R} - 1)(\bar{u} - u_s) / \bar{R}.$$  

(4.8)

As discussed earlier, $\bar{u} - u_s > 0$ for settling particles, $R \geq 1$ and therefore $\bar{u} \geq u_e > u_s$. In other words the advection speed of the solute is larger than that of sediments, but will be smaller than the discharge velocity in the presence of sediments.
Effects of kinetic sorptive exchange on solute transport

Similar to $\zeta_1$ in (3.13), the following form for $C_1$ can be suggested:

$$C_1(x,z,t) = P \frac{\partial C_0}{\partial x}.$$  \hspace{1cm} (4.9)

The function $P(x,z,t)$, which describes the vertical variation for the $O(\epsilon)$ correction to the solute concentration, is given by

$$P - P_0 = \int_z^0 \frac{dz'}{RE_z} \int_0^{z'} R(u - u_c)dz''.$$  \hspace{1cm} (4.10)

where $R(x,z,t)$ is the retardation factor given by (4.3), and $P_0 = P(z = 0)$ is also undetermined unless a uniqueness condition is specified for the above problem. Now, we may obtain from (3.13), (4.1), (4.5), (4.6) and (4.9) the following expressions for the $O(\epsilon)$ correction to the sorbate concentration and the total chemical concentration:

$$C_{s1}(x,z,t) = K_d \frac{P + u_c/k}{\partial C_0}{\partial x}$$  \hspace{1cm} (4.11)

and

$$C_{tot1} = (RP + K_d \zeta_0 u_c/k) \frac{\partial C_0}{\partial x} + K_d N \frac{\partial \zeta_b}{\partial x} C_0.$$  \hspace{1cm} (4.12)

Recall that we still have the freedom to choose uniqueness conditions for $N$ and $P$ in order to determine their boundary values. With a view to simplifying the advection terms in the effective transport equations, we add the condition that

$$C_{tot1} = 0,$$  \hspace{1cm} (4.13)

which can be satisfied if, evident from (4.12),

$$RP + K_d \zeta_0 u_c/k = 0 \quad \text{and} \quad N = 0.$$  \hspace{1cm} (4.14)

These constraints ensure that $C_{tot0}$ and $\zeta_0$ are correct to $O(\epsilon)$ since their first-order corrections are zero: $C_{tot1} = \zeta_1 = 0$. Conditions similar to (4.14) have also been applied by Chatwin (1970), Mei (1992) and Ng (1999).

If conditions (4.14) are chosen, we may obtain, after some algebra, from the $O(\epsilon^2)$ terms of (2.28) a higher-order transport equation for the solute:

$$\frac{\partial C_0}{\partial t_2} + u_c \frac{\partial C_0}{\partial x} = \frac{\partial}{\partial x} \left( D_c \frac{\partial C_0}{\partial x} \right),$$  \hspace{1cm} (4.15)

where

$$u'_c(x,t) = -\frac{K_d \zeta}{R} (D_s + D_c) \frac{\partial \zeta_b}{\partial x}$$  \hspace{1cm} (4.16)

is the $O(\epsilon)$ correction to the advection velocity in which $D_s$ is given by (3.21), and

$$D_i(x,t) = RE_z/R + D_{Te} + D_{Ke}.$$  \hspace{1cm} (4.17)

is the effective dispersion coefficient. Similar to $D_s$, the first component of $D_c$ is a depth-averaged longitudinal eddy diffusivity, but now weighted by the retardation factor $R$. The other components, $D_{Te}$ and $D_{Ke}$, are dispersion coefficients formally given by

$$D_{Te}(x,t) = (RE_z)^{-1} \left[ \int_z^0 R(u - u_c)dz' \right]^2 / R,$$  \hspace{1cm} (4.18)
and

\[ D_{Kc}(x,t) = -\frac{K_d \zeta_b u_c}{k R^2} (f - \bar{f})(u - \bar{u}). \]  

(4.19)

Like (3.23), \( D_{Tc} \) does not depend on the value of \( P_0 \), and hence is not affected by the uniqueness condition. Also, it is always positive and virtually a Taylor dispersion coefficient, where the flow quantities have been weighted by the retardation factor \( R \).

The other coefficient \( D_{Kc} \), which was first obtained by Ng (2000b), is an additional dispersion coefficient due to the kinetics of solid–water sorptive exchange. It is proportional to the bulk solid–water distribution ratio \( K_d \zeta_b \) and the depth covariance between the sediment concentration and the fluid velocity, and inversely proportional to the sorption rate constant \( k \). For settling particles, the covariance is negative and therefore the dispersion coefficient \( D_{Kc} \) is always positive as well. Also, the stronger the kinetics of sorptive exchange, the larger the value of \( D_{Kc} \). See Ng (2000b) for further discussion on this coefficient.

We may now combine (4.6) and (4.15) to get an effective transport equation for the solute with an error of \( O(\epsilon^2) \):

\[ \frac{\partial C_0}{\partial t} + (u_c + u') \frac{\partial C_0}{\partial x} = \frac{\partial }{\partial x} \left( D_c \frac{\partial C_0}{\partial x} \right), \]  

(4.20)

where \( u_c, u' \) and \( D_c \) are respectively given by (4.7), (4.16) and (4.17). It is remarkable that despite the strictly uniform flow both the advection velocity and dispersion coefficient are functions of \( x \) and \( t \) via dependence on the local sediment concentration.

One may readily show that as the fall velocity \( w_f \) becomes an order of magnitude smaller, the above theory reduces to the case presented by Ng (2000a). In this limiting case, the sediment distribution factor \( f \) approaches unity by which \( u_c \sim u_c \sim \bar{u}, D_s \sim D_T \) and \( D_{Kc} \sim 0 \).

At this point, we have completed applying the homogenization method to the development of effective transport equations for suspended sediments and a sorbing solute. Advection velocities and dispersion coefficients now show up as explicit functions of the hydrodynamic and sorption effects. The present problem is not amenable to analysis by the method of moments at all. For easy reference, the formulae for the advection velocities and dispersion coefficients that have been derived in this work are summarized in table 1.

For simplicity, we shall from here on drop the subscript zero from the leading-order variables (e.g. \( C_0 \)). Also, as the longitudinal eddy diffusivities are in general much smaller than the dispersion coefficients, the first components of \( D_s \) and \( D_c \) in (3.21) and (4.17) will no longer be considered in the following discussion.

5. Numerical example – a plane source of polluted sediments

For illustration, let us revisit an example previously considered by Ng (2000a). This is a case in which fine solid particles and a chemical pollutant are discharged simultaneously at the same point in a stream as a pulse input (i.e. a mathematically instantaneous plane source of both substances). By virtue of the one-dimensional equation (3.29) with constant coefficients, the sediment concentration can be described by a Gaussian distribution in the frame \( \xi = x - u_c t \) which moves at the speed of the centre of mass of the sediment cloud:

\[ \zeta_b(\xi, t) = \frac{m}{f(4\pi D_s t)^{1/2}} \exp \left( -\frac{\xi^2}{4D_s t} \right), \]  

(5.1)
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<table>
<thead>
<tr>
<th>Material</th>
<th>Transport coefficient</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>sediment</td>
<td>advection velocity</td>
<td>( u_s = \overline{u}/f )</td>
</tr>
<tr>
<td>chemical</td>
<td>Taylor dispersion coefficient</td>
<td>( D_{Ts} = (fE_z)^{-1} \left[ \int_0^h f(u - u_s)dz \right]^2 / \overline{f} )</td>
</tr>
<tr>
<td></td>
<td>zeroth-order advection velocity</td>
<td>( u_c = \frac{R \zeta}{R} )</td>
</tr>
<tr>
<td></td>
<td>first-order advection velocity</td>
<td>( u'_c = -\left[ K_d f (D_s + D_c) / R \right] \frac{\partial \zeta}{\partial \xi} )</td>
</tr>
<tr>
<td></td>
<td>Taylor dispersion coefficient</td>
<td>( D_{Tc} = (RE_z)^{-1} \left[ \int_0^h R(u - u_c)dz \right]^2 / R )</td>
</tr>
<tr>
<td></td>
<td>sorption-kinetics-induced dispersion coefficient</td>
<td>( D_{Kc} = -K_d \zeta \bar{u} (f - f) (u - \bar{u}) / k )</td>
</tr>
</tbody>
</table>

Table 1. Summary of formulae for the advection velocities and dispersion coefficients, where \( u \) is the fluid velocity, \( E_z \) is the vertical eddy diffusivity, \( K_d \) is the sorption partition coefficient, \( \zeta_b \) is the sediment concentration at the bed level, \( k \) is the sorption rate constant, and \( f, R, D_s \) and \( D_c \) are respectively given by (3.4), (4.3), (3.21) and (4.17) where \( m \) is the total mass of sediment divided by the cross-sectional area of the stream. Transforming from \((x,t)\) to \((\xi,t)\) and using (4.8), the chemical transport equation (4.20) becomes

\[
\frac{\partial C}{\partial t} + \left[ \frac{\pi - u_s}{R} + u'_c \right] \frac{\partial C}{\partial \xi} = \frac{\partial}{\partial \xi} \left( \frac{D_c}{R} \frac{\partial C}{\partial \xi} \right). \tag{5.2}
\]

Note that because of the apparent advection (inside the square brackets), the centre of mass of the aqueous phase of the chemical will be gradually drifting away from that of the sediment.

Physically we assume that before discharge the particles are completely dry and a chemical pollutant is uniformly sorbed onto the solid with a sorbate concentration \( C_{b,0} \). Immediately after discharge into the stream, dissolution happens instantaneously and the aqueous chemical distribution can be found from (2.3):

\[
C = \frac{C_{d,0}}{1 + K_d \zeta_b} = \frac{C_{d,0} \zeta_b \overline{f}}{1 + K_d \zeta_b} \quad \text{as} \quad t \to 0^+. \tag{5.3}
\]

Note that at all times the conservation of mass requires that

\[
\int_{-\infty}^{\xi} \zeta_b d\xi = m/\overline{f} \quad \text{and} \quad \int_{-\infty}^{\infty} \zeta_b d\xi = C_{d,0} m \quad \text{for} \quad t > 0, \tag{5.4}
\]

where \( C_{d,0} = (1 + K_d \zeta_b f)C = R \zeta \) is the total mass of chemical per bulk volume.

Let us now introduce the following normalized quantities (distinguished by a caret):

\[
\xi = L \hat{\xi}, \quad z = h \hat{z}, \quad t = (L^2 / u_s) \hat{t}, \quad \zeta_b = (m/\overline{f} L) \zeta_{b,0}, \quad (C, C_{tot}) = (C_{d,0} m / L)(\hat{C}, \hat{C}_{tot}), \quad (E_z, D_s, D_c) = u_s (\hat{E}_z, \hat{D}_s, \hat{D}_c), \quad (u, \pi, u_s, u_c, u'_c) = u_s (\hat{u}, \hat{\pi}, \hat{u}_s, \hat{u}_c, \hat{u}'_c), \tag{5.5}
\]

where \( u_s \) is the shear velocity given by (2.10), and \( L \) is a longitudinal length scale for the transport, which according to (2.11) and (2.13) is of the order \((D / E_z)^{1/2} h\). In
terms of the normalized quantities, the equations can be expressed as follows. The sediment concentration distribution is

$$\hat{\zeta}_b(\hat{\xi}, \hat{t}) = (4\pi \hat{D}_s \hat{t})^{-1/2} \exp \left( -\frac{\hat{\xi}^2}{4 \hat{D}_s \hat{t}} \right),$$

(5.6)

while the sediment distribution factor is

$$f(\hat{\xi}) = \exp \left( -\kappa \hat{\xi} \int_0^{\hat{\xi}} \hat{E}_{z-1} \hat{d} z' \right)$$

(5.7)

where $\kappa$ is von Kármán’s constant, and the retardation factor is

$$R(\hat{\xi}, \hat{z}, \hat{t}) = 1 + \beta f_{\hat{\zeta}}$$

(5.8)

Transport of the aqueous phase of chemical is governed by

$$\frac{\partial \hat{C}}{\partial \hat{t}} + \hat{u}_d \frac{\partial \hat{C}}{\partial \hat{\xi}} = \frac{\partial}{\partial \hat{\xi}} \left( \hat{D}_c \frac{\partial \hat{C}}{\partial \hat{\xi}} \right),$$

(5.9)

where $\hat{u}_d$ is the drifting velocity given by

$$\hat{u}_d(\hat{\xi}, \hat{t}) = -\frac{L}{h f} \frac{f - \overline{f}}{\overline{f} - \overline{u}} (\hat{u} - \hat{u}_s) - \frac{\beta}{R} (\hat{D}_s + \hat{D}_c) \frac{\partial \hat{\zeta}_b}{\partial \hat{\xi}}.$$

(5.10)

Ignoring the components due to the longitudinal eddy diffusivity, the dispersion coefficients can be expressed as

$$\hat{D}_s = \left( f \hat{E}_z \right)^{-1} \left[ \int_{\hat{\xi}}^{1} f (\hat{u} - \hat{u}_s) d\hat{z}' \right]^2 \overline{f},$$

(5.11)

and

$$\hat{D}_c(\hat{\xi}, \hat{t}) = \hat{D}_{Tc} + \hat{D}_{Kc},$$

(5.12)

where

$$\hat{D}_{Tc}(\hat{\xi}, \hat{t}) = \left( R \hat{E}_z \right)^{-1} \left[ \int_{\hat{\xi}}^{1} R (\hat{u} - \hat{u}_c) d\hat{z}' \right]^2 \overline{R},$$

(5.13)

and

$$\hat{D}_{Kc}(\hat{\xi}, \hat{t}) = -\frac{\beta \hat{\zeta}_b \hat{u}_c}{f \overline{R}} (f - \overline{f}) (\hat{u} - \overline{u}).$$

(5.14)

The normalized initial condition (5.3) is

$$\hat{C} = \frac{\hat{\zeta}_b}{1 + \beta \hat{\zeta}_b} \quad \text{as} \quad \hat{t} \to 0^+, \quad \text{(5.15)}$$

while the far-field boundary conditions are

$$\hat{C} \to 0 \quad \text{as} \quad \hat{\xi} \to \pm \infty. \quad \text{(5.16)}$$

Also, the integrals in (5.4) now become

$$\int_{-\infty}^{\infty} \hat{\zeta}_b d\hat{\xi} = 1 \quad \text{and} \quad \int_{-\infty}^{\infty} R \hat{C} d\hat{\xi} = 1 \quad \text{for} \quad \hat{t} > 0. \quad \text{(5.17)}$$

In the above equations, the following dimensionless parameters have been introduced:

$$\alpha = w_f/\kappa u_s, \quad \beta = Kdm/L \quad \text{and} \quad \gamma = u_*/kh. \quad \text{(5.18)}$$
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Table 2. Values of $\alpha$ (suspension number), $\gamma$ (sorption kinetics parameter) and $\beta$ (bulk solid–water distribution ratio) for six cases of computation, where cases 1–3 correspond to fine-grained sediments and cases 4–6 correspond to coarser-grained sediments

<table>
<thead>
<tr>
<th>Case</th>
<th>$\alpha$</th>
<th>$\gamma$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>50</td>
<td>10</td>
</tr>
</tbody>
</table>

The parameter $\alpha$ is a form of the suspension number (Rouse 1937), which typically is less than unity when most particles in suspension reside above the constant-stress layer (Sumer 1974). The second parameter $\beta$ is the bulk solid–water distribution ratio of the chemical, which has been assumed to be of order unity when (2.23) is introduced. The third parameter $\gamma$ is the sorption kinetics parameter, which according to (2.19) and (2.22), should be of order unity or greater.

For turbulent open-channel flows, the following logarithmic velocity and parabolic eddy diffusivity (Reynolds analogy is supposed to hold) profiles are commonly adopted in practice:

$$\hat{u}(\hat{z}) = 2.5 \ln(30\hat{z}/\hat{\varepsilon}_s) \quad \text{and} \quad \hat{E}_z(\hat{z}) = 0.4\hat{z}(1 - \hat{z})$$ (5.19)

where von Kármán’s constant $\kappa = 0.4$ has been used, and $\hat{\varepsilon}_s = \varepsilon_s/h$ is the bottom roughness size normalized with respect to the flow depth. Note that by the above profile the velocity vanishes at $\hat{z} = \hat{\varepsilon}_s/30$ (the actual bed) instead of $\hat{z} = 0$ (the theoretical bed). In addition, the parabolic diffusivity profile leads to the following sediment distribution factor, which is widely used in the literature (e.g. Vanoni 1975; van Rijn 1984, 1986, 1993):

$$f(\hat{z}) = \left[\frac{\hat{\alpha}(1 - \hat{z})}{\hat{z}(1 - \hat{\alpha})}\right]^\hat{\kappa},$$ (5.20)

where $\hat{\alpha} \ll 1$ is a small distance above the theoretical bed at which the reference concentration of suspended sediment is defined. In this example, we also choose to use the above relations. The suspended sediment concentration at the bed level is now $\hat{\zeta}_b = \hat{\zeta}(\hat{z} = \hat{\alpha})$, and the section of flow is virtually within $\hat{\alpha} \ll \hat{z} \ll 1$. For a bottom without bedform, an empirical relationship $\alpha = 2d$ where $d$ is the sediment particle diameter has been suggested by Madsen (1975).

Equation (5.9) is solved numerically using a standard second-order implicit scheme of forward-time and centred-space differences. With approximation by implicit finite differences, the one-dimensional equation yields a tridiagonal linear system which can be solved with a simple routine. The conditions in (5.17) are checked by numerical integrations at each time step to ensure that mass conservation is observed throughout the computation. Sufficiently small spatial discretizations ($\Delta\hat{\zeta} = 0.01$, $\Delta\hat{z} = 0.0005$) and time step ($\Delta\hat{t} = 0.002$) have been used so that the maximum error is kept below 1%. To see the various effects, results have been generated for six cases of parameters as listed in table 2. Two sets of values for $\alpha$ and $\gamma$ are considered. The smaller values, as in cases 1–3, correspond to rather fine-grained sediments, while the larger values, as in cases 4–6, correspond to coarser-grained sediments. We have assumed from (2.20) that a slower sorption rate is associated with a coarser particle. Values of $\beta$
Figure 1. Distributions of the sediment concentration $\hat{\zeta}_b$, chemical Taylor dispersion coefficient $\hat{D}_{Tc}$, sorption-kinetics-induced dispersion coefficient $\hat{D}_{Kc}$ and drifting velocity $\hat{u}_d$ for case 1 (fine-grained sediments and a unity bulk solid–water distribution ratio).

Let us first examine the coefficients that control the transport of the chemical pollutant. Recall that $\hat{D}_{Tc}$ and $\hat{D}_{Kc}$ are the components of the dispersion coefficient due to shear flow and sorption kinetics respectively, and $\hat{u}_d$ is the apparent advection velocity as viewed from the centre of mass (or centroid) of the sediment cloud. These coefficients are functions of the sediment concentration, and therefore vary with distance along the channel and time. Figures 1–3 show their spatial distributions at instants $\hat{t} = 0.1, 1.0, 2.0$ and 3.0 for cases 1, 3 and 6 respectively. In the absence of sediments at large $|\hat{\xi}|$, $\hat{D}_{Tc}$ reduces to the Taylor dispersion coefficient for clear water (i.e. $D_T$ given by equation (3.24)), while $\hat{D}_{Kc}$ drops to zero. From these figures the following observations can be made.

(a) In all cases $\hat{D}_{Tc}$ is only modestly enhanced by the presence of sediments; the increase is typically less than 10%.

(b) The distribution and magnitude of $\hat{D}_{Kc}$ strongly depend on the cases. In case 1, its significance is limited to early times and localized near the centre of mass of the sediment cloud. However, it dominates over $\hat{D}_{Tc}$ as the solid–water distribution ratio are varied from 1 to 10, corresponding to an increasingly large fraction of mass in sorbed form. Other parameters have the following values in all cases of computation: $L/h = 100$, $\hat{\varepsilon}_s = 0.002$ and $\hat{a} = 0.004$. 

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\( \beta \) becomes larger (case 3), and as the sorption kinetics parameter \( \gamma \) becomes greater (case 6). In these two cases there exist two off-centre maxima at initial times in the distributions of \( \hat{D}_{Kc} \). While the coefficient continues to maintain a high value in the neighbourhood of the centre, its effect reaches farther upstream and downstream as the sediment cloud spreads out more extensively. It is remarkable that the maximum value of \( \hat{D}_{Kc} \) is comparable with that of \( \hat{D}_{Tr} \) in case 3, but many times that of \( \hat{D}_{Tr} \) in case 6. Therefore, when sorptive exchange becomes highly kinetic, the dispersion of the chemical cloud will be strongly influenced by \( \hat{D}_{Kc} \).

(c) The apparent drifting velocity \( \hat{u}_d \) obviously is larger when the sediments are heavier. More noteworthy is its association with the sediment concentration gradient. The distribution of \( \hat{u}_d \) exhibits a peak and a trough, respectively, immediately downstream and upstream of the centroid of the sediment cloud. The minimum of \( \hat{u}_d \) can even be negative at early stages in cases 3 and 6. Physically, it means that the chemical is being advected at a faster rate if it is downstream of the sediment cloud centroid but at a slower rate (even in the opposite direction) if upstream. These differential advection rates will effectively induce additional dispersion, which is unsymmetrical about \( \xi = 0 \), on the spreading of the chemical cloud, thereby leading to enhanced broadening and skewness of the chemical concentration distribution at an early stage.

Snapshots of the concentration distributions for \( \hat{C} \) (solid curves) and \( \hat{\zeta}_b \) (dashed curves) for case 3 (fine-grained sediments and a large bulk solid–water distribution ratio).
curves) are plotted in figures 4 and 5 for the six cases. In order to better analyse the evolving characteristics of these distributions, the following statistical parameters are also presented as functions of time in figures 6–8: (i) the location of the centre of mass \( \hat{\xi}_c \), (ii) the variance \( \sigma^2 \), and (iii) the skew coefficient \( \chi \). These parameters are computed according to their usual definitions:

\[
\hat{\xi}_c \equiv \frac{\mu_1}{\mu_0},
\]

\[
\sigma^2 \equiv \frac{1}{\mu_0} \int_{-\infty}^{\infty} (\hat{\xi} - \hat{\xi}_c)^2 \hat{C} \, d\hat{\xi} = \frac{\mu_2}{\mu_0} - \frac{\mu_1^2}{\mu_0^2},
\]

and

\[
\chi \equiv \frac{1}{(\sigma^2)^{3/2} \mu_0} \int_{-\infty}^{\infty} (\hat{\xi} - \hat{\xi}_c)^3 \hat{C} \, d\hat{\xi} = \frac{1}{(\sigma^2)^{3/2}} \left[ \frac{\mu_3}{\mu_0} - 3 \frac{\mu_1 \mu_2}{\mu_0 \mu_0} + 2 \frac{\mu_1^3}{\mu_0^3} \right],
\]

where \( \mu_n \) is the \( n \)th integral moment of \( \hat{C} \):

\[
\mu_n = \int_{-\infty}^{\infty} \hat{\xi}^n \hat{C} \, d\hat{\xi} \quad \text{for} \quad n = 1, 2, 3, \ldots.
\]

Chatwin (1972) has shown that a higher-order term that is omitted in a heat-
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Figure 4. Snapshots of the distributions of the solute concentration $\hat{C}(\hat{\xi}, \hat{t})$ (solid lines) and the sediment concentration $\hat{\zeta}_b(\hat{\xi}, \hat{t})$ (dashed lines) for cases 1, 2 and 3. The degree of asymmetry of the solute concentration distribution increases with the solid–water distribution ratio.

Figure 5. As figure 4 but for cases 4, 5 and 6. The solute concentration distribution can exhibit a marked tailing at large times when sorption effects are strong.
conduction-type equation like (5.9) is required in order to correctly predict the long-term behaviour of the skewness due to asymmetry in the initial distribution. Such skewness tends to zero as \((t/T_0)^{-1/2}\) where \(T_0\) is the time scale for diffusion across the channel. We are however examining skewness of the solute concentration distribution that is caused by sorptive exchange and occurs on a much longer time scale \(T_2 \gg T_0\). Any effects of the omitted higher-order term on the skewness can therefore be ignored as long as a time scale longer than \(T_0\) is considered.
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From figures 4–8, one may draw the following conclusions.

(a) As expected, the chemical cloud drifts more rapidly ahead of the sediment cloud in cases 4–6 where sediments are heavier than in cases 1–3 (figure 6). Also, for the same settling velocity the retardation to the chemical advection speed is larger for a higher bulk solid–water distribution ratio $\beta$. Owing to phase exchange, which is substantial only when the sediment and chemical clouds are overlapping, the rate of increase of $\xi_c$ is initially nonlinear but tends to a constant at larger times when the two clouds are mostly separated.

(b) The rate of increase of the variance, which amounts to the dispersion coefficient averaged over the stretch of the distribution, also changes nonlinearly with time in the initial stages (figure 7). The rate of increase eventually becomes constant, corresponding to the coefficient of dispersion in clear water. This happens the soonest in case 1 and the latest in case 6. As discussed earlier the dispersion is the largest in case 6, owing to the highest values of the bulk solid–water distribution ratio $\beta$ and sorption kinetics parameter $\gamma$. It is however obvious from figures 4 and 5 that the differences in the extent of spreading among the cases only lie in the portion of distributions behind the peak concentrations. There are remarkably long tailings in cases 3, 5 and 6; the distributions in these cases are highly unsymmetrical about their peaks. Tailing means a very slow decay of the concentration, which is often due to non-equilibrium phase partitioning. Kinetic sorptive exchange in this example can indeed lengthen the time of impact of the pollutant on a particular point in the stream; the pollution persists even though the maximum concentration has long passed the point.

(c) The asymmetry of the concentration distributions is confirmed by the skew coefficient (figure 8), which in each case starts from a value of zero (Gaussian) initially, and decreases (as the tailing is developing) until it reaches a maximum negative value at a certain point before diminishing back to zero in the long term. In cases 4–6 (figure 5), the non-Gaussianity of the chemical distribution is very conspicuous even at an early stage of spreading. The distribution in case 4 however recovers symmetry.
much sooner than those in cases 5 and 6. For a pulse input of a passive fluid dispersant in a shear flow, the skew coefficient tends to zero according to \((t/T_0)^{-1/2}\) (Aris 1956; Sayre 1968; Chatwin 1970). It is shown here that because of sorptive exchange the deviation from normality of the concentration distribution can be more extensive and last much longer.

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