

Two-dimensional numerical modeling of chemical transport–transformation in fluvial rivers: formulation of equations and physical interpretation

Sui Liang Huang

ABSTRACT

Based on previous work on the transport–transformation model of heavy metal pollutants in fluvial rivers, this paper presents the formulation of a two-dimensional model to describe chemical transport–transformation in fluvial rivers by considering basic principles of environmental chemistry, hydraulics and mechanics of sediment transport and recent developments along with three very simplified test cases. The model consists of water flow governing equations, sediment transport governing equations, transport–transformation equation of chemicals and convection–diffusion equations of sorption–desorption kinetics of particulate chemical concentrations on suspended load, bed load and bed sediment. The chemical transport–transformation equation is basically a mass balance equation. It demonstrates how sediment transport affects transport–transformation of chemicals in fluvial rivers. The convection–diffusion equations of sorption–desorption kinetics of chemicals, being an extension of batch reactor experimental results, take both physical transport, i.e. convection and diffusion, and chemical reactions, i.e. sorption–desorption into account. The effects of sediment transport on chemical transport–transformation were clarified through three simple examples. Specifically, the transport–transformation of chemicals in a steady, uniform and equilibrium sediment-laden flow was calculated by applying this model, and results were shown to be rational. Both theoretical analysis and numerical simulation indicated that the transport–transformation of chemicals in sediment-laden flows with a clay-enriched riverbed possesses not only the generality of common tracer pollutants, but also characteristics of transport–transformation induced by sediment motion. Future work will be conducted to present the validation/application of the model with available data.

Key words | chemical, fluvial rivers, numerical modeling, transport–transformation, water–sediment–pollutants interaction

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NOTATION

The following symbols are used in this paper.

x and y coordinates of two dimensions in plane;
 dx and dy differential length in x and y directions;
 h_1 , h_2 and h_3 vertical length occupied by suspended load (flowing water), bed load (flowing water) and bed deformation;

Δh active thickness of bed sediment for sorption–desorption;
 h water depth ($h_1 + h_2$);
 c vertically averaged dissolved chemicals concentration;
 u and v vertically averaged flow velocity in x and y directions (flowing water and suspended load);

w_x and w_y	vertically averaged velocity of bed load in x and y directions (flowing water and bed load);	k_1^s, b^s, k_2^s and k_3^s	coefficient of sorption rate (nonlinear part), coefficient of desorption rate (both linear and nonlinear parts), coefficient of sorption rate (linear part) and the maximum sorption capacity for suspended load;
s_s and s_b	suspended load concentration and bed load concentration;		
N_s, N_b and N_m	vertically averaged particulate concentrations of chemicals on suspended load, bed load and sediment of the riverbed perimeter (or chemical contents sorbed by unit weight of suspended load, bed load and unit area of the riverbed sediment);	k_1^b, b^b, k_2^b and k_3^b	coefficient of sorption rate (nonlinear part), coefficient of desorption rate (both linear and nonlinear parts), coefficient of sorption rate (linear part) and the maximum sorption capacity for bed load;
ρ_s	specific weight of sediment particles;	k_1^m, b^m, k_2^m and k_3^m	coefficient of sorption rate (nonlinear part), coefficient of desorption rate (both linear and nonlinear parts), coefficient of sorption rate (linear part) and the maximum sorption capacity for bed sediment;
p'	the porosity of bed	z_0	bed elevation;
k_{ch-bio}	the overall pseudo-first-order reaction kinetics coefficient;	c_0	designated dissolved pollutant concentration;
E_x^s and E_y^s	turbulent diffusion coefficient components of suspended load in x and y directions	$\delta(t)$	δ function with time;
E_x^v and E_y^v	turbulent diffusion coefficients of particulate chemicals concentrations on suspended load in x and y directions;	L	length of the numerical flume;
N_∞	equilibrium particulate chemicals concentration;	s^*	suspended sediment-carrying capacity;
c_∞	equilibrium dissolved chemicals concentration;	k_s and m_s	coefficients in suspended sediment-carrying capacity formula.
k_L	linear partition coefficient;		
k_F	Freundlich binding coefficient;		
m	Freundlich exponent		
b	maximum sorption capacity		
k_{La}	Langmuir affinity constant;		
N	particulate chemicals concentration in batch reactor experiments at any time;		
c	dissolved chemicals concentration in batch reactor experiments at any time;		
k_{L1}, k_{L2}, k_{La1} and k_{La2}	rate coefficients;		
k_1, k_2, k_3 and b	coefficient of sorption rate (nonlinear part), coefficient of desorption rate (both linear and nonlinear parts), coefficient of sorption rate (linear part) and the maximum sorption capacity;		
$E_x^{N_s}$ and $E_y^{N_s}$	turbulent diffusion coefficients of particulate chemicals concentrations on suspended load in x and y directions;		

INTRODUCTION

Properties of pollutants play a significant role when numerical models are used to predict their fate, transport–transformation in the aquatic environment. As sediment motion occurs ubiquitously in natural rivers, lakes and other surface water bodies, pollutants can be grouped into sediment-motion-related pollutants or (particulate-) sediment-associated pollutants (SAPs) and sediment-motion-non-related ones (Hart 1986; Huang 1993; Mahler *et al.* 2000; Ellison & Brett 2006; Huang *et al.* 2007b). The water temperature, which can be taken as typical of sediment-motion-non-related pollutants, has little to do with sediment motion. Heavy metals (Huang *et al.* 2007b), organic chemicals, especially hydrophobic organic compounds (HOCs) (Mossman *et al.* 1988; Allen-King *et al.* 2002; Kim *et al.* 2004), nutrients such as salts of nitrogen and phosphorus (Koelmans *et al.* 2001), certain bacteria (Mahler *et al.* 2000) and various kinds of oils (Khondaker 2000) are representatives of SAPs. Fate,

transport–transformation of these pollutants is heavily dependent on sediment transport in surface water bodies and sediment particles can be considered as one of its most important carriers other than water. In this regards, there is much well-documented literature available, such as Wang & Govind (1993), Hundal *et al.* (2001), Johnson & Weber (2001), Salloum *et al.* (2002), Allen-King *et al.* (2002), Xu *et al.* (2006), Huang *et al.* (2007a,b,c), to cite just a few. Partly due to the sediment transport effect, partly due to data scarcity in validating the numerical model, in which flow, sediment transport and transport–transformation of SAPs in fluvial rivers were simultaneously considered, numerical modeling of SAPs transport–transformation in fluvial rivers has been a challenging subject (Ziegler *et al.* 2000).

Two-dimensional numerical modeling is increasingly applied to study transport–transformation of SAPs in surface water bodies nowadays. The significance of sediment transport on fate, transport–transformation of SAPs has been well recognized and documented; however, the effect of sediment transport was greatly simplified in these model equations. It was usually considered with a source/sink term known as sedimentation–resuspension (Mossman *et al.* 1988; Ji *et al.* 2002; Kim *et al.* 2004; Huang *et al.* 2007b). Thus, the equation describing transport–transformation of SAPs was a traditional convection–diffusion equation plus the “sedimentation–resuspension” term (terms representing degradation, photolysis, volatilization and hydrolysis were also included for the chemical fate model equation) (Mossman *et al.* 1988). Detailed reviews can be found in the literature (Khondaker 2000; Koelmans *et al.* 2001; James 2002; Huang *et al.* 2007b). Also another treatment in the model equation was that the instant equilibrium between particulate SAPs concentration and dissolved SAPs concentration was assumed. The invalidity of this assumption has been questioned by many researchers (Koelmans *et al.* 2001; James 2002; Huang *et al.* 2007b).

Based on previous work (Huang *et al.* 2007b,c), this paper is going to present the formulation of a mathematical model describing transport–transformation of SAPs in fluvial rivers by considering the principles of hydraulics, mechanics of sediment transport, environmental chemistry and recent developments along with three very simplified test cases. Future work will be conducted to present a

validation/application of the model with available data. The transport–transformation equation of heavy metals developed previously was extended to study the transport–transformation of SAPs by considering mechanisms other than adsorption–desorption. The major contribution of this paper was to develop a new set of equations called convection–diffusion equations of sorption–desorption kinetics for particulate SAP concentrations on suspended sediment, bed load and bed material, respectively. These equations were worked out by extending batch-reactor experimental results to natural water bodies.

Based on previous work (Huang *et al.* 2007b,c), governing equations for SAPs consisted of flow-governing equations, sediment transport-governing equations, the transport–transformation equation of SAPs and convection–diffusion equations of sorption–desorption kinetics of SAPs. As two-dimensional governing equations of flow and sediment transport have been well established and widely used, this paper focuses on the governing equations of SAPs. Although the formulated model was considered to be suitable for describing transport–transformation of SAPs, here SAPs are mainly chemicals, especially hydrophobic organic compounds (HOCs) for the sake of simplicity.

EQUATION OF CHEMICAL TRANSPORT–TRANSFORMATION IN FLUVIAL RIVERS

As pointed out in previous papers (Huang *et al.* 2007b,c), it is better and proper to establish a mathematical model of chemical transport–transformation (dynamics) in its integrity, rather than a model of separated phases (dissolved pollutant phase and particulate pollutant phases on suspended load, bed load and bed sediment). This concept and other simplicities in the previous papers were extended and applied in the derivation of the governing equation of chemical transport–transformation in fluvial rivers.

Take a control volume, $dx dy \times h$ ($= h_1 + h_2$, total depth), from a flow domain, as shown in Figure 1. It is assumed that the entire flowing space consists of three parts: the upper part where suspended load and water are conveyed, the middle part where bed load and water are conveyed, and the lower part where degradation or aggradation of bed occurs.

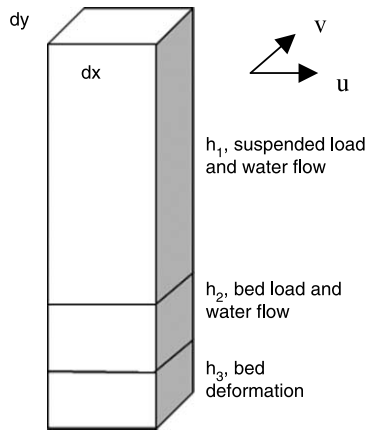


Figure 1 | Sketch of a control volume with $dx dy \times h$ ($h = h_1 + h_2 + h_3$).

The following assumptions were introduced in order to simplify the problem:

- The interchange between pore water and flowing water and the consequent interchange of chemicals are relatively negligible.
- Suspended load moves together with flowing water without any lag, and riverbed slopes in both x and y directions are small. The concentration of suspended load (sediment) is low.
- For variations of particulate chemical phase (on suspended load, bed load and bed sediment), the sorption–desorption is the main mechanism of the chemical–biological reaction.
- For dissolved chemical phase, chemical and biological reactions other than sorption–desorption can be separately considered, which mainly include hydrolysis, photolysis, biodegradation and evaporation, and these reactions can be considered as a pseudo-first-order reaction kinetics, and further it can be represented by an overall term.

The following symbols were used in the deduction: c is the vertically averaged dissolved chemical concentration; u and v are the vertically averaged flow velocity in the x and y directions (flowing water and suspended load), respectively; w_x and w_y are the vertically averaged velocity of bed load in the x and y directions (flowing water and bed load); s_s and s_b are the suspended load concentration and bed load concentration, respectively; N_s , N_b and N_m are the vertically averaged particulate concentrations of chemicals

on suspended load, bed load and sediment of the riverbed perimeter (or chemical contents sorbed by unit weight of suspended load, bed load and unit area of the riverbed sediment), respectively; h_1 , h_2 and h_3 are the depths occupied by suspended load (flowing water), bed load (flowing water) and bed deformation, respectively; ρ_s is the specific weight of sediment particles and p' is the porosity of the bed.

Chemicals entering and leaving the control volume are as follows:

For the dissolved (in the water phase):

$$-\frac{\partial}{\partial x} \left[u c h_1 dy \left(1 - \frac{s_s}{\rho_s} \right) \right] dx dt - \frac{\partial}{\partial x} \left[w_x c h_2 dy \left(1 - \frac{s_b}{\rho_s} \right) \right] dx dt$$

$$-\frac{\partial}{\partial y} \left[v c h_1 dx \left(1 - \frac{s_s}{\rho_s} \right) \right] dy dt - \frac{\partial}{\partial y} \left[w_y c h_2 dx \left(1 - \frac{s_b}{\rho_s} \right) \right] dy dt.$$

The particulate part consists of two parts, which are as follows:

$$\text{On suspended load : } -\frac{\partial}{\partial x} (u s_s N_s h_1 dy) dx dt$$

$$-\frac{\partial}{\partial y} (v s_s N_s h_1 dx) dy dt.$$

$$\text{On bed load : } -\frac{\partial}{\partial x} (w_x s_b N_b h_2 dy) dx dt$$

$$-\frac{\partial}{\partial y} (w_y s_b N_b h_2 dx) dy dt.$$

The difference of chemicals between entering and leaving is

$$-\frac{\partial}{\partial x} \left[u c h_1 dy \left(1 - \frac{s_s}{\rho_s} \right) \right] dx dt - \frac{\partial}{\partial x} \left[w_x c h_2 dy \left(1 - \frac{s_b}{\rho_s} \right) \right] dx dt$$

$$-\frac{\partial}{\partial y} \left[v c h_1 dx \left(1 - \frac{s_s}{\rho_s} \right) \right] dy dt$$

$$-\frac{\partial}{\partial y} \left[w_y c h_2 dx \left(1 - \frac{s_b}{\rho_s} \right) \right] dy dt \quad (1)$$

$$-\frac{\partial}{\partial x} (u s_s N_s h_1 dy) dx dt - \frac{\partial}{\partial y} (v s_s N_s h_1 dx) dy dt$$

$$-\frac{\partial}{\partial x} (w_x s_b N_b h_2 dy) dx dt - \frac{\partial}{\partial y} (w_y s_b N_b h_2 dx) dy dt.$$

The increment of chemicals in the control volume in dt time is

$$\text{For the dissolved : } \frac{\partial}{\partial t} [c(h_1 + h_2) dx dy] dt$$

On suspended load : $\frac{\partial}{\partial t}(s_s N_s h_1 dx dy) dt$

On bed load : $\frac{\partial}{\partial t}(s_b N_b h_2 dx dy) dt$

It was suggested that for the bed sediment, sorption–desorption takes place in a thin layer (Huang *et al.* 2007a,c). Thus, the increment of chemicals on the bed sediment could be expressed as $\partial/\partial t[N_m dx dy(1-p')]dt$ for simplicity (the alternative is to define a very small active depth, Δh . Then it can be expressed as $\partial/\partial t[N_m dx dy \Delta h (1-p')]dt$).

When bed slopes in the x and y directions are larger, the area $dx dy$ should be modified and this can be considered in the numerical codes. The total increment of chemicals is

$$\frac{\partial}{\partial t}[c(h_1 + h_2) dx dy] dt + \frac{\partial}{\partial t}(s_s N_s h_1 dx dy) dt + \frac{\partial}{\partial t}(s_b N_b h_2 dx dy) dt + \frac{\partial}{\partial t}[N_m dx dy(1-p')] dt. \quad (2)$$

Chemical and/or biological reactions other than sorption–desorption, for example, hydrolysis, photolysis, biodegradation and evaporation, generally cause a decrease of dissolved chemicals and can be expressed generally as follows:

$$-k_{ch-bio} c(h_1 + h_2) dx dy dt \quad (3)$$

where k_{ch-bio} is the overall pseudo-first-order reaction kinetics coefficient.

Considering the mass balance, one can write

$$\begin{aligned} & -\frac{\partial}{\partial x}[uch_1 dy(1-\frac{s_s}{\rho_s})] dx dt - \frac{\partial}{\partial x}[w_x ch_2 dy(1-\frac{s_b}{\rho_s})] dx dt \\ & -\frac{\partial}{\partial y}[vch_1 dx(1-\frac{s_s}{\rho_s})] dy dt - \frac{\partial}{\partial y}[w_y ch_2 dx(1-\frac{s_b}{\rho_s})] dy dt \\ & -\frac{\partial}{\partial x}(us_s N_s h_1 dy) dx dt - \frac{\partial}{\partial y}(vs_s N_s h_1 dx) dy dt \\ & -\frac{\partial}{\partial x}(w_x s_b N_b h_2 dy) dx dt - \frac{\partial}{\partial y}(w_y s_b N_b h_2 dx) dy dt \\ & = \frac{\partial}{\partial t}[c(h_1 + h_2) dx dy] dt + \frac{\partial}{\partial t}(s_s N_s h_1 dx dy) dt \\ & + \frac{\partial}{\partial t}(s_b N_b h_2 dx dy) dt + \frac{\partial}{\partial t}[N_m dx dy(1-p')] dt \\ & - k_{ch-bio} c(h_1 + h_2) dx dy dt. \end{aligned} \quad (4)$$

Following the procedures in the literature (Huang 1993, 2001; Huang *et al.* 2007c) and after simplifying and arranging, one gets

$$\begin{aligned} & \frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} - \frac{1}{h} \frac{\partial}{\partial x}(h E_x \frac{\partial c}{\partial x}) - \frac{1}{h} \frac{\partial}{\partial y}(h E_y \frac{\partial c}{\partial y}) = N_s \frac{\rho' \partial h_s}{h \partial t} \quad (I) \\ & - \frac{(1-p') \partial N_m}{h \partial t} + \frac{N_s - N_b}{h} \left[\frac{\partial}{\partial t}(s_b h_2) + \frac{\partial}{\partial x}(w_x h_2 s_b) + \frac{\partial}{\partial y}(w_y h_2 s_b) \right] \quad (II) \\ & - \frac{h_1}{h} \left[s_s \frac{\partial N_s}{\partial t} + s_s u \frac{\partial N_s}{\partial x} + s_s v \frac{\partial N_s}{\partial y} - E_x^s \frac{\partial s_s \partial N_s}{\partial x \partial x} - E_y^s \frac{\partial s_s \partial N_s}{\partial y \partial y} \right] \quad (III) \\ & - \frac{h_2}{h} \left[s_b \frac{\partial N_b}{\partial t} + w_x s_b \frac{\partial N_b}{\partial x} + w_y s_b \frac{\partial N_b}{\partial y} \right] - k_{ch-bio} c \quad (IV) \\ & \quad (V) \quad (VI) \quad (VII) \end{aligned} \quad (5)$$

where E_x and E_y are the turbulent diffusion coefficient components of flow, respectively and E_x^s and E_y^s are the turbulent diffusion coefficient components of suspended load, respectively.

This is the two-dimensional equation describing the transport–transformation of chemicals in fluvial rivers under the condition of uniform sediment particles. The physical meaning of each term is as follows: term (I) is the variation of the dissolved chemical concentration. If it is equal to zero, it is just the convection–diffusion equation of common tracer pollutants. For chemicals, it is generally not equal to zero due to the effect of sediment transport and chemical–biological action on their transport–transformation. Thus, in summary, the right-hand side of Equation (5) is the effect of sediment transport and chemical–biological action on chemical transport–transformation. Term (II) reflects the effect of bed deformation. Term (III) represents the effect of chemical sorption–desorption by bed sediment (mud). Term (IV) is the effect of bed load variation. Term (V) is the effect of chemical sorption–desorption by suspended load. Term (VI) is the effect of chemical sorption–desorption by bed load. Finally, term (VII) is the effect of chemical–biological action.

In the case of negligible bed load motion, which is often the case in fluvial rivers, $h_2 = 0$ and $h = h_1$ can be assumed.

Therefore, Equation (5) can be further simplified as

$$\begin{aligned} & \frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} - \frac{1}{h} \frac{\partial}{\partial x} \left(h E_x \frac{\partial c}{\partial x} \right) - \frac{1}{h} \frac{\partial}{\partial y} \left(h E_y \frac{\partial c}{\partial y} \right) \\ & = N_s \frac{\rho'}{h} \frac{\partial h_3}{\partial t} - \frac{(1-p')}{h} \frac{\partial N_m}{\partial t} \\ & - \left[s_s \frac{\partial N_s}{\partial t} + s_s u \frac{\partial N_s}{\partial x} + s_s v \frac{\partial N_s}{\partial y} - E_x^s \frac{\partial s_s}{\partial x} \frac{\partial N_s}{\partial x} - E_y^s \frac{\partial s_s}{\partial y} \frac{\partial N_s}{\partial y} \right] \\ & - k_{\text{ch-bio}} c \end{aligned} \quad (6)$$

One-dimensional and three-dimensional equations describing the phenomenon for uniform and non-uniform sediments can be deduced similarly or found in Huang (1993, 2001) and Huang *et al.* (2007c).

CONVECTION–DIFFUSION EQUATIONS OF SORPTION–DESORPTION KINETICS OF CHEMICALS

Sorption isotherm model and kinetic model (equations)

Numerous laboratory experiments have been conducted in order to study the mechanism of chemical sorption–desorption on–off soil and sediment particles. A number of sorption isotherm models and kinetic models have been worked out, mostly through data fitting (e.g. Wang & Govind 1993; Burris *et al.* 1995; Schlebaum *et al.* 1999; Hundal *et al.* 2001; Johnson & Weber 2001; Johnson *et al.* 2001; Allen-King *et al.* 2002; Salloum *et al.* 2002; Song & Shin 2005; Li & Huang 2006; Huang & Li 2007). From these and other publications, it can be seen that both the sorption isotherm model and the kinetic model heavily depend on properties of sorbates (chemicals), sorbents (sediment particles), solutions and environmental conditions (Allen-King *et al.* 2002) and there may not exist a unified sorption isotherm and kinetic model.

In the past, for equilibrium sorption, the linear isotherm model, Equation (7) (Salloum *et al.* 2002; Huang & Li 2007), the Freundlich isotherm, Equation (8) (Hundal *et al.* 2001; Salloum *et al.* 2002), the Langmuir isotherm, Equation (9) (Wang & Govind 1993; Burris *et al.* 1995; Huang & Li 2007) and a combination of linear isotherm and Freundlich isotherm or that of linear isotherm and Langmuir isotherm (Allen-King *et al.* 2002; Song & Shin 2005) were discussed

and used to fit the experimental data:

$$N_{\infty} = k_L c_{\infty} \quad (7)$$

$$N_{\infty} = k_F c_{\infty}^m \quad (8)$$

$$N_{\infty} = b \frac{c_{\infty}}{k_{La} + c_{\infty}} \quad (9)$$

where N_{∞} is the equilibrium particulate chemical concentration, c_{∞} is the equilibrium dissolved chemical concentration, k_L is the linear partition coefficient, k_F is the Freundlich binding coefficient, m is the Freundlich exponent, b is the maximum sorption capacity and k_{La} is the Langmuir affinity constant.

For sorption–desorption kinetics, in the past, the diffusion model, multi-compartment first-order model and three-parameter, two-compartment, first-order rate equation, etc (Johnson & Weber 2001; Johnson *et al.* 2001) were used to study the HOCs' sorption–desorption processes. Because most experimental data of equilibrium sorption can be well fitted by a combination of linear sorption and Langmuir sorption isotherm, following the idea from the literature (Schlebaum *et al.* 1999; Johnson & Weber 2001; Johnson *et al.* 2001), this paper suggests a new three-parameter, two-compartment, first-order rate equation as follows:

$$\frac{dN}{dt} = \frac{k_{L1}c - k_{L2}N}{(I)} + \frac{k_{La1}c(b - N) - k_{La2}N}{(II)} \quad (10)$$

where N is the particulate chemical concentration in batch reactor experiments at any time, c is the dissolved chemical concentration in batch reactor experiments at any time, and k_{L1} , k_{L2} , k_{La1} and k_{La2} are rate coefficients.

The advantage of using such a rate equation is that, when equilibrium is reached, it is just a combination of the linear sorption isotherm (term I) and Langmuir sorption isotherm (term II). Also the parameters in the latter isotherm have a clear physical meaning. Actually, term II is just those terms in the derivation of the Langmuir sorption isotherm and term I has been used by a number of authors (Schlebaum *et al.* 1999). For heavy metal pollutants, the separated form, either term I or term II, has been studied by Huang (2001, 2003a,b).

After some arrangement and combination, Equation (10) is

$$\frac{dN}{dt} = k_1 c(b - N) - k_2 N + k_3 c \quad (11)$$

where $k_1 = k_{La1}$, $k_2 = k_{L2} + k_{La2}$ and $k_3 = k_{L1}$. Thus, k_1 , k_2 , k_3 and b are the coefficient of sorption rate (nonlinear part), the coefficient of desorption rate (both linear and nonlinear parts), the coefficient of sorption rate (linear part) and the maximum sorption capacity, respectively.

These parameters can be ascertained in laboratories by batch reactor experiments (Huang & Li 2007) and modified according to field data validation processes (Huang *et al.* 2007a).

Convection–diffusion equations of sorption–desorption kinetics of chemicals

Sorption–desorption of chemicals by sediment particles is influenced by many factors for certain chemicals, including environmental, chemical and biological conditions, and hydraulic and sediment conditions. In natural rivers, environmental chemical and biological conditions generally do not change very much for a certain reach within a certain time. In contrast, hydrology, hydraulics and sediment conditions display significant variations (IWRPR 1988). From the engineering application point of view, thus, one may consider that environmental, chemical and biological conditions remain constant for a certain river reach within a certain time period. Conversely, flow and sediment conditions, the dissolved chemical concentration and particulate chemical concentration vary with space and time. For a small limited element (control volume) in fluvial rivers the concept deduced from laboratory experiments is still valid. Thus, Equation (11) can be used for describing the sorption–desorption phenomenon in natural rivers (the total differential, dN/dt , must be changed to the partial differential, $\partial N/\partial t$, or, in other words, the original ordinary differential equation now becomes a partial differential equation). However, in natural rivers, both physical transport, i.e. convection and diffusion, and chemical reaction, i.e. sorption–desorption, can cause changes in the particulate chemical concentration. Under the condition of two-dimensional flow, specifically, for the particulate chemical

concentration on a uniform suspended load:

$$\begin{aligned} \frac{\partial N_s}{\partial t} + \frac{u \frac{\partial N_s}{\partial x} + v \frac{\partial N_s}{\partial y}}{\text{(I)}} - \frac{\frac{\partial}{\partial x} \left(E_x^{N_s} \frac{\partial N_s}{\partial x} \right) - \frac{\partial}{\partial y} \left(E_y^{N_s} \frac{\partial N_s}{\partial y} \right)}{\text{(II)}} \\ = \frac{k_1^s c(b^s - N_s) - k_2^s N_s + k_3^s c}{\text{(III)}} \end{aligned} \quad (12)$$

where $E_x^{N_s}$ and $E_y^{N_s}$ are the turbulent diffusion coefficients of particulate chemical concentrations on suspended load in the x and y directions, respectively, and k_1^s , b^s , k_2^s and k_3^s are the coefficients for suspended load defined in Equation (11).

From Equation (12), it can be seen that both physical transport (terms (I) and (II) on the left) and chemical reaction (term (III) on the right) were considered, which cause temporal and spatial variations of particulate chemical concentrations on suspended load in fluvial rivers.

For the particulate chemical concentration on uniform bed load:

$$\frac{\partial N_b}{\partial t} + w_x \frac{\partial N_b}{\partial x} + w_y \frac{\partial N_b}{\partial y} = k_1^b c(b^b - N_b) - k_2^b N_b + k_3^b c \quad (13)$$

where k_1^b , b^b , k_2^b and k_3^b are the coefficients for bed load defined in Equation (11).

Due to the fact that bed load moves generally in the form of sliding, jumping and rolling, no diffusion needs to be considered in its transport equation. In Equation (13), which is for the particulate chemical concentration on bed load, there also appears to be no diffusion term.

Equation (14) is for the particulate chemical concentration on bed sediment (sediment on the riverbed perimeter), where no convection and diffusion needs to be considered:

$$\frac{\partial N_m}{\partial t} = k_1^m c(b^m - N_m) - k_2^m N_m + k_3^m c \quad (14)$$

where k_1^m , b^m , k_2^m and k_3^m are the coefficients for bed load defined in Equation (11), respectively.

Equations (13) and (14) can be considered as special cases of Equation (12), which is called the “convection–diffusion equations of sorption–desorption kinetics of chemicals” in this paper.

For non-uniform sediments in fluvial rivers, it is assumed that Equations (12), (13) and (14) are valid for each size of sediments.

TWO-DIMENSIONAL MATHEMATICAL MODEL OF CHEMICAL TRANSPORT–TRANSFORMATION IN FLUVIAL RIVERS

By combining the equations obtained in the preceding two paragraphs with flow and sediment motion equations, a mathematical model for chemical transport–transformation can be established for uniform sediments. The model is comprised of the flow continuity equation, flow momentum equations, sediment transport equation, bed deformation equation, a formula for sediment-carrying capacity, an equation for chemical transport–transformation, i.e. Equations (5) or (6), and convection–diffusion equations of sorption–desorption kinetics of chemicals, i.e. Equations (12)–(14). For the sake of simplicity, flow and sediment transport governing Equations (also used in the next section), and numerical methods for solving these equations, are not detailed here and interested readers can refer to Huang (2007). The numerical schemes used to solve Equations (12) and (13) were the same as those mentioned in Huang (2007).

APPLICATION OF THE MATHEMATICAL MODEL AND DISCUSSION

The preceding mathematical model was applied to three simple cases. The flow is steady and uniform with equilibrium sediment transport, without bed deformation and bed load transport. In case 1, the incoming water is polluted with a pulse source at the inlet and the incoming suspended sediment is clean. In case 2 the incoming water is polluted with a continual source at the inlet and the incoming suspended sediment is clean. In case 3, the incoming water and suspended sediment are clean and initially, the water and suspended sediment are clean but the bed sediment is polluted. A clear water flow with the same flow parameters (but without sediment motion) was also computed for comparison for cases 1 and 2. Some concepts considering

the effect of sediment transport on the transport–transformation of chemicals may be deduced from these three cases.

Since the physical meaning of the chemical–biological term in Equation (5) is straightforward, in a short time its effect can be ignored in the test cases: thus, $k_{\text{ch-bio}}$ is set to zero.

Under the condition of uniform sediment and without bed load motion and bed deformation, the governing equations for flow, sediment and chemicals can be simplified as follows:

$$\text{Flow : } u = \text{constant}; \quad v = 0; \quad h = \text{constant};$$

$$E_x = \text{constant}; \quad E_y = \text{constant}.$$

$$\text{Sediment : } \frac{\partial z_0}{\partial t} = 0; \quad s_s = s_* = k_s \left(\frac{u^3}{gR\omega} \right)^{m_s};$$

$$E_x^s = \text{constant}; \quad E_y^s = \text{constant}$$

where z_0 is the bed elevation, s_* is the suspended sediment carrying capacity, and k_s and m_s are coefficients.

The chemical transport–transformation equation is

$$\begin{aligned} \frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} - \frac{1}{h} \frac{\partial}{\partial x} \left(h E_x \frac{\partial c}{\partial x} \right) - \frac{1}{h} \frac{\partial}{\partial y} \left(h E_y \frac{\partial c}{\partial y} \right) \\ = - \frac{(1-p')}{h} \frac{\partial N_m}{\partial t} - \left[s_s \frac{\partial N_s}{\partial t} + s_s u \frac{\partial N_s}{\partial x} + s_s u \frac{\partial N_s}{\partial y} \right] \end{aligned} \quad (15)$$

The convection–diffusion equation of sorption–desorption kinetics of chemicals for suspended load is

$$\begin{aligned} \frac{\partial N_s}{\partial t} + u \frac{\partial N_s}{\partial x} - \frac{\partial}{\partial x} \left(E_x^{N_s} \frac{\partial N_s}{\partial x} \right) - \frac{\partial}{\partial y} \left(E_y^{N_s} \frac{\partial N_s}{\partial y} \right) \\ = k_1^s c (b^s - N_s) - k_2^s N_s + k_3^s c \end{aligned} \quad (16)$$

and the convection–diffusion equation of sorption–desorption kinetics of chemicals for bed sediment is

$$\frac{\partial N_m}{\partial t} = k_1^m c (b^m - N_m) - k_2^m N_m + k_3^m c. \quad (17)$$

The numerical flume is 50 m wide and 2,000 m long and water depth in the flume is 2.5 m with a flow discharge of 130 m³/s. The bed slope and water surface slope is 0.00025 and Manning's roughness coefficient is 0.025. The sediment size is 0.015 mm and the falling velocity is 0.0141 mm/s. The computational mesh is uniform with a mesh size of 10 m.

In the computation, the parabolic eddy-viscosity model was selected with a full slip wall boundary. Time step was 5 s. Under such conditions, the other flow and sediment parameters computed by the model were: $u = 1.04$ m/s; $E_x = E_y = E_x^s = E_y^s = E_x^{N_s} = E_y^{N_s} = 0.0125$ m²/s; $s_s = s_* = 1.84$ kg/m³.

The pollutant transport equation with the same flow parameters and without sediment motion is as follows:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} - \frac{1}{h} \frac{\partial}{\partial x} \left(h E_x \frac{\partial c}{\partial x} \right) - \frac{1}{h} \frac{\partial}{\partial y} \left(h E_y \frac{\partial c}{\partial y} \right) = 0. \quad (18)$$

Based on laboratory experiments with dimethyl phthalate (Huang & Li 2007), parameters on the right-hand side of Equation (16) were: $k_1^s = 6.50 \times 10^{-7}$ l/(μ g s); $b^s = 30.68$ μ g/g, $k_2^s = 4.11 \times 10^{-7}$ 1/s and $k_3^s = 0.0$ (unit is l/(g s)) (The Langmuir sorption isotherm can describe the equilibrium sorption of dimethyl phthalate into the Haihe River sediment very well, and the correlation coefficient was 0.97). Based on the experimental result in the literature (Huang *et al.* 2007a), parameters on the right-hand side of Equation (17) can be set as: $k_1^m = 1.625 \times 10^{-7}$ l/(μ g s), $b^m = 306.8$ μ g/m², $k_2^m = 1.03 \times 10^{-7}$ 1/s and $k_3^m = 0.0$.

Under the uniform flow conditions with transversely constant pollutant concentrations at the inlet, as a matter of fact, there is no change of all the concentration transversely. For the sake of saving space and simplicity, results along the centreline of the flume were analysed and displayed.

Case 1: pulse incoming polluted water and clean incoming suspended sediment at inlet

In the case of pulse incoming polluted water and clean incoming suspended sediment at the inlet, the boundary conditions and initial conditions were as follows (for simplicity, c means $c(x, y, t)$, N_s means $N_s(x, y, t)$ and N_m means $N_m(x, y, t)$):

$$c|_{t=0} = 0; \quad N_s|_{t=0} = 0; \quad N_m|_{t=0} = 0; \quad c|_{x=0} = c_0 \delta(t),$$

$$\delta(t) = \begin{cases} 1 & 20s \leq t \leq 25s \\ 0 & t > 20s \text{ or } t < 25s \end{cases}, \text{ and } c_0 = 10 \mu\text{g/l};$$

$$N_s|_{x=0} = 0; \quad \frac{\partial c}{\partial x}|_{x=L} = 0; \quad \frac{\partial N_s}{\partial x}|_{x=L} = 0$$

where L is the length of the flume calculated from upstream.

The simulated result was shown in Figures 2–4. It can be seen from Figure 2 that peaks of particulate dimethyl phthalate concentrations on suspended sediment in the flume moved with peaks of dissolved dimethyl phthalate concentrations, and peak values of particulate dimethyl phthalate concentrations on suspended sediment increased with time increasing. This is due to the fact that sorption of dissolved dimethyl phthalate onto suspended sediment takes a certain time. For particulate dimethyl phthalate concentrations on bed sediment, because the dissolved dimethyl phthalate concentration upstream was higher than downstream, the bed sediment thus absorbed quite a lot of dissolved dimethyl phthalate there; therefore it was higher upstream than downstream. This also can be seen clearly from Figure 3, which showed variations of dissolved and particulate dimethyl phthalate concentrations with time at the middle point of the flume. Actually, after the peaks moved downstream, the bed sediment started desorption.

Due to sediment sorption, the peak value of dissolved dimethyl phthalate concentrations with sediment motion was smaller than that without sediment motion at the same location, as shown in Figure 3. Figure 4 also displayed this feature. With sediment sorption and time increasing, the difference between peak values of dissolved dimethyl phthalate concentrations with and without sediment motion became larger.

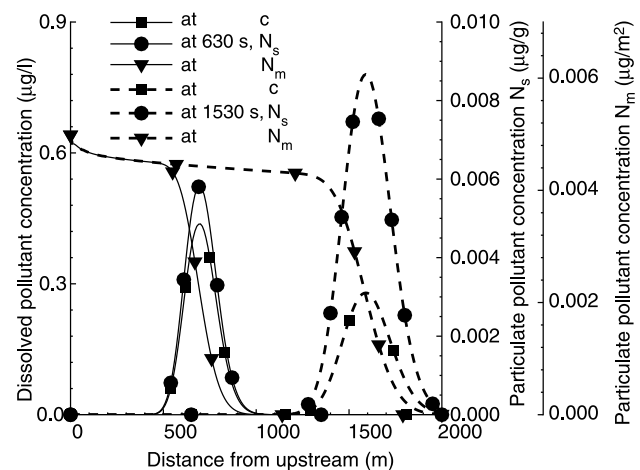


Figure 2 | Variations of dissolved and particulate dimethyl phthalate concentrations with distance at different times for Case 1.

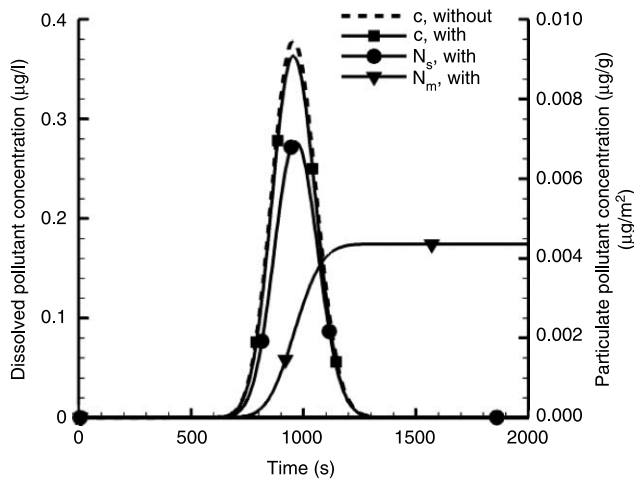


Figure 3 | Variations of dissolved and particulate dimethyl phthalate concentrations at 1,000 m from upstream with time for Case 1.

Case 2: continually polluted incoming water and clean incoming sediment at inlet

In the case of continually polluted incoming water and clean incoming sediment at the inlet, the boundary and initial conditions were as follows:

$$c|_{t=0} = 0; \quad N_s|_{t=0} = 0; \quad N_m|_{t=0} = 0; \quad c|_{x=0} = c_0 \quad \text{and} \\ c_0 = 10 \mu\text{g/l}; \quad N_s|_{x=0} = 0; \quad \frac{\partial c}{\partial x}|_{x=L} = 0; \quad \frac{\partial N_s}{\partial x}|_{x=L} = 0$$

With polluted water coming continually at the inlet, particulate dimethyl phthalate concentrations on suspended and bed sediment in the flume increased with

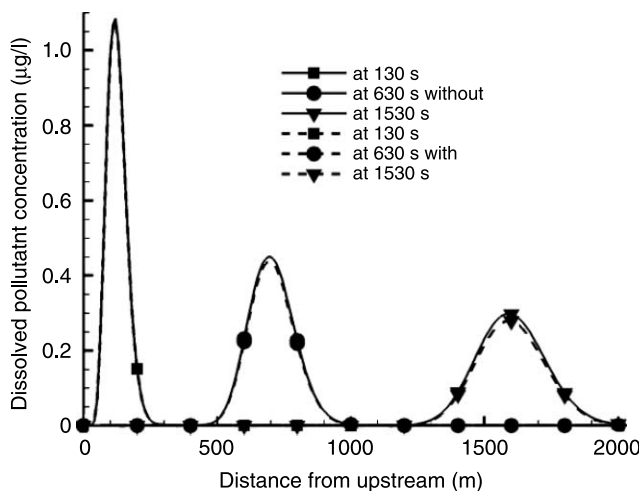


Figure 4 | Comparisons of dissolved dimethyl phthalate concentrations at different times between with and without sediment transport for Case 1.

increasing time, as shown in Figure 5, and peaks of particulate dimethyl phthalate concentrations on suspended sediment always appeared in the vicinity of the vanguard of dissolved dimethyl phthalate concentrations. This is because the suspended sediment moves with water and the suspended sediment here has more time to absorb dissolved dimethyl phthalate. Due to the fact that the dissolved dimethyl phthalate upstream was always larger than that downstream, the particulate dimethyl phthalate concentrations on bed sediment upstream were also always higher than those downstream.

Due to sediment sorption, the dissolved dimethyl phthalate concentrations with sediment motion were smaller than those without sediment motion at the middle point of the flume, as shown in Figure 6. At this place, the particulate dimethyl phthalate concentration in the bed sediment increased with time increasing, while the particulate dimethyl phthalate concentration in the suspended sediment initially increased very fast with time increasing, and after some time it increased only a little. This “dynamic equilibrium”, determined by Equations (15) and (16), is different from the equilibrium in the batch reactor experiments, where it can be considered as the static (or absolute) equilibrium. Because equilibrium sorption of dimethyl phthalate onto (Haihe River) sediment in batch reactor experiments fits the Langmuir sorption isotherm very well (Huang & Li 2007), the equilibrium particulate dimethyl

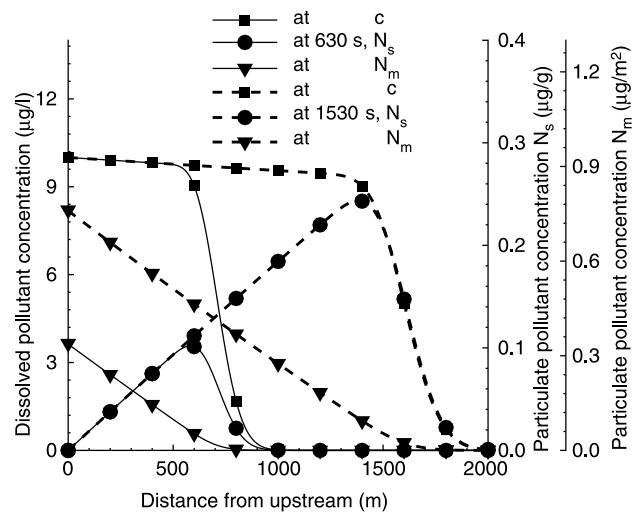


Figure 5 | Variations of dissolved and particulate dimethyl phthalate concentrations with distance at different times for Case 2.

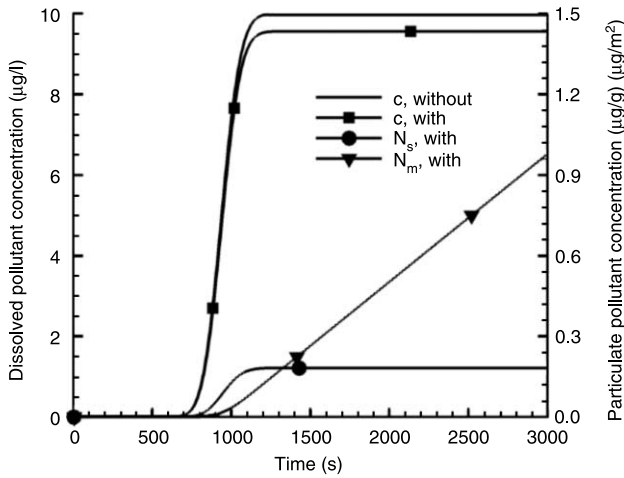


Figure 6 | Variations of dissolved and particulate dimethyl phthalate concentrations at 1,000 m from upstream with time for Case 2.

phthalate concentration is about 28.8 µg/g when the dissolved dimethyl phthalate concentration is about 10 µg/l as calculated by Equation (9), being much larger than the value here.

Figure 7 also showed the effect of sediment transport on dimethyl phthalate transport–transformation. At the very beginning of 130 s, differences of dissolved dimethyl phthalate concentrations in the flume between with and without sediment motion were very small, with time increasing, for example, at 1,530 s the difference became larger. With sediment motion, it is obvious that the dissolved dimethyl phthalate concentration is smaller than that without sediment motion.

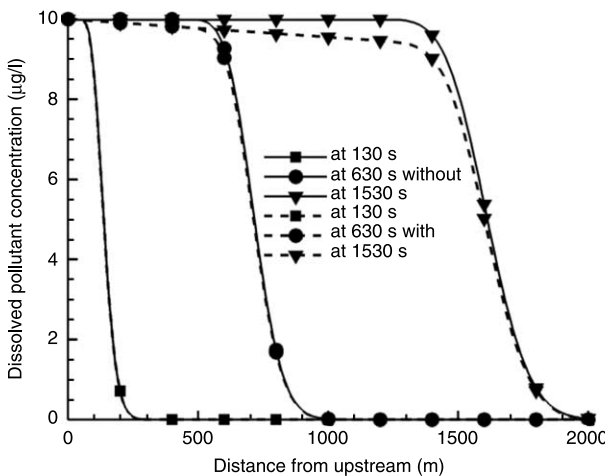


Figure 7 | Comparisons of dissolved dimethyl phthalate concentrations between with and without sediment transport for Case 2.

Case 3: clean incoming water and suspended sediment with initially clean water and suspended sediment but polluted bed

In the case of clean incoming water and sediment at the inlet, and initially, clean water and suspended sediment and polluted bed in the flume, the boundary and initial conditions were as follows:

$$c|_{t=0} = 0; \quad N_s|_{t=0} = 0; \quad N_m|_{t=0} = N_m = 150 \mu\text{g}/\text{m}^2;$$

$$c|_{x=0} = 0; \quad N_s|_{x=0} = 0; \quad \frac{\partial c}{\partial x}|_{x=L} = 0; \quad \frac{\partial N_s}{\partial x}|_{x=L} = 0.$$

Under the above conditions, it can be expected that the polluted bed sediment desorbs dimethyl phthalate, thus causing the water to be polluted and then suspended sediment in the flume to be polluted, as shown in Figures 8 and 9. Due to the effect of dilution from clean incoming water and of scavenging from clean incoming suspended sediment upstream (at the inlet) (sorption of dissolved dimethyl phthalate onto suspended sediment upstream functions as a scavenger), the dissolved and particulate dimethyl phthalate concentrations on suspended sediment gradually increased in the upstream part of the flume, as shown in Figure 8. Then, after some distance, these dilution and scavenging effects became weak; the dissolved and particulate dimethyl phthalate concentrations on suspended sediment kept a high level and increased only little with increasing distance. Figure 9 showed variations of the dissolved and particulate dimethyl phthalate concentrations

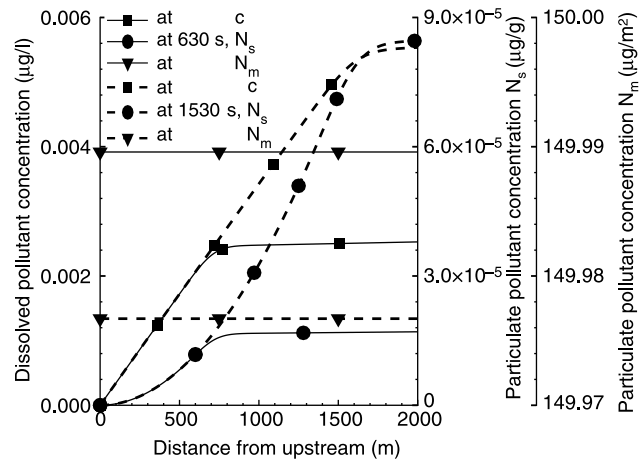


Figure 8 | Variations of dissolved and particulate dimethyl phthalate concentrations with distance at different times for Case 3.

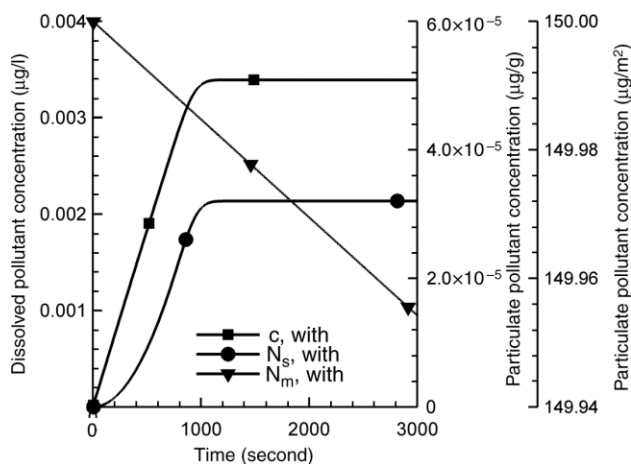


Figure 9 | Variations of dissolved and particulate dimethyl phthalate concentrations at 1,000 m from upstream with time for Case 3.

at the middle of flume with time. It can be seen from the figure that the bed desorbed pollutants continuously in the simulated period, and at the very beginning, the dissolved and particulate dimethyl phthalate concentrations on the suspended sediment increased very fast and, after some time, both increased only a little with time increasing. This is also a “dynamic equilibrium”, as indicated in Case 2.

Although these were very simple cases with a very limited simulation period of time, they did present us with some ideas and concepts of the effect of sediment transport on chemical transport–transformation in fluvial rivers. In the world, there are numerous rivers with heavily sediment-laden flows and clay-enriched riverbeds; thus such an effect should be fully considered and studied.

CONCLUSIONS

Based on previous work, this paper presented a mathematical model describing chemical transport–transformation in fluvial rivers. In the model, governing equations include the flow continuity equation, flow momentum equation, sediment transport equation, bed deformation equation, the formula for sediment-carrying capacity, the equation of chemical transport–transformation and convection–diffusion equations of sorption–desorption kinetics of chemicals. This model describes the effect of sediment transport on chemical transport–transformation in fluvial rivers with clear physical meanings. Parameters b , k_1 , k_2 and k_3 can be

ascertained without difficulty through preliminary laboratory experiments. Thus the model is suitable for practical applications. Three case studies of the application of this model to a simple two-dimensional uniform flow in a flume clarified and elucidated concepts of the effect of sediment transport on chemical transport–transformation. It is obvious that the model could be improved upon in practical applications in natural rivers, especially the kinetic model (equation) of chemicals (Equation (11)).

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