

Effect of cadmium sorption by river sediments on longitudinal dispersion

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ABSTRACT

This paper concerns the cadmium sorptive effects by river bed sediments on longitudinal dispersion coefficient in an open-channel flow via experimental and numerical study. For this purpose, a circular flume was used with mean diameter of 1.6 m and a width of 0.2 m. The adsorbing bed was considered as a thin layer of the sediment particles with mean diameter of 0.53 mm and three sediment concentrations of 3, 12, and 20 gr/lit. To determine the sorption parameters of the sediments, some experiments were conducted with three cadmium concentrations of 150, 460, and 770 ppb. Then, the dispersion experiments were carried out with and without the bed sediments with the same cadmium concentration as the sorption experiments. A numerical model was then developed to solve the advection–dispersion equation with considering the sorption term by river bed sediments. The longitudinal dispersion coefficients were estimated by comparing the experimental and numerical breakthrough curves. The results showed that, with increasing the sediment concentrations, the sediment sorption rate increased and the longitudinal dispersion coefficient decreased by about 38, 36 and 33 percent, respectively, for cadmium concentrations of 150, 460 and 770 ppb. In addition, by increasing the cadmium concentrations, the changes in the longitudinal dispersion coefficient are decreased. Furthermore, a relationship was developed using non-dimensional longitudinal dispersion as a function of the new parameter of sorption ratio. From a practical point of view, the results of this study demonstrated that, at the presence of riverbed sediment, the cadmium is longitudinally dispersed with more delay in comparison with no sediment at the river bed.

Key words: cadmium, longitudinal dispersion, river bed sediments, sorption ratio

HIGHLIGHTS

- The advection–dispersion equation was numerically solved with considering the sorption term by river bed sediments.
- Longitudinal dispersion coefficients were estimated by comparing the experimental and numerical breakthrough curves.
- With increasing the sediment concentrations, the sediment sorption rate increased and the longitudinal dispersion coefficient decreased.

INTRODUCTION

Nowadays, most of the natural rivers are exposed to industrial wastewaters and heavy metal pollutions and the study of different factors affecting on the transport and the fate of these pollutants is important. On the other hand, the rivers typically carry the sediments through erosion and sedimentation processes. In addition, the natural river usually contains the different sizes of sediments, most of them very rich in organic matter, and therefore has a strong potential to adsorb chemical pollutants in a sorbate form (Ng 2006). As a result, the presence of these sedimentary loads in the rivers, due to the high potential of metal ions to adsorb by sediment particles, may play an important role in the transport and fate of heavy metal pollutants. In this regard, many studies have demonstrated that the sediments have accumulated about 62, 40, 90 and 80 percent of cadmium, copper, lead, and zinc, respectively, in the eastern rivers of the United States (EPA 2003; Uddin 2017). Therefore, considering the presence of sediment loads having very high sorption rates, and the effects of sorption process by sediments on the advection and dispersion of these pollutants is important.

After being absorbed by the sediment particles, heavy metal ions are transferred from the dissolved phase into the absorbed phase. This process can be seen as a self-purification process of the rivers (Fornster & Gottfried 1981; Herut *et al.* 1995; Bird & Evenden 1996). It should be mentioned that there are two approaches for description of this phenomenon in the aquatic

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systems. Some researchers supposed that the distribution of pollutants may be described as an equilibrium process by an instantaneous partitioning between the dissolved and the adsorbed phases (Falconer & Lin 2003; Wu *et al.* 2005). Others considered the sorption as a kinetic process (Jonsson & Worman 2001; Jonsson *et al.* 2004; Huang *et al.* 2007; Roshanfekr *et al.* 2008; Huang 2009). Longitudinal dispersion coefficient can be affected by many hydrodynamic and geometrical parameters and, as a result the dispersion characteristics may vary from one river to another. To date, three methods, namely the integral method, dye tracing measurements and empirical formulae have been widely used to estimate the longitudinal dispersion coefficient (Zeng & Huai 2014).

When the pollutants enter the rivers, they may move through flow velocity along with the river flow and spread vertically, transversely, and longitudinally due to turbulent diffusion within the channel and absorption into the suspended and bed sediments through the sorption process. The advection–dispersion equation for the pollutants is defined by considering the absorption process, as follows (Runkel & Bencala 1995):

$$\frac{\partial C}{\partial t} = -V \frac{\partial C}{\partial x} + D_L \frac{\partial^2 C}{\partial x^2} - \rho \frac{\partial q}{\partial t} \quad (1)$$

where, C is the concentration of solution (g/lit), V is flow velocity (m/s), D_L is longitudinal dispersion coefficient (m^2/s), ρ is the sediment concentration (g/lit), and q is the amount of cadmium absorbed in μg per unit weight of the sediments. The expression $\partial q/\partial t$ represents the release of cadmium ions from the soluble phase by the sorption process, for which various equilibrium and kinetics models have been proposed.

To date, many researchers have studied numerically and analytically the advection–dispersion equation as well as considering the sorptive effects of pollutants in groundwater (van Kooten 1996; Williams & Tomasko 2008; Bruining *et al.* 2012; Singh & Das 2016; Jaiswal & Gulrana 2019; Pillai & Raizada 2021) and surface water resources (Phillips *et al.* 1995; Ng 2000a, 2000b, 2001, 2006; Revelli & Ridolfi 2002, 2003; Yip & Ng 2003; Mahdavi *et al.* 2008; Chabokpour *et al.* 2020; Nasrabadi *et al.* 2021).

Purnama (1995) found that, for low sorption rates, the boundary retention increased the dispersion rate and was considered as the main effect suppressing the boundary absorption, which decreased the dispersion rate. It was, however, pointed out by Jiang & Grotberg (1993) that, for dispersion in oscillatory tube flow, the wall absorption, when it is weak, may increase or decrease the dispersion depending on the oscillation frequency. Ng (2000a) studied the effects of sorptive exchange on the transport of a chemical in a sediment-laden open-channel flow. He found that, for sufficiently large particles and solid fractions, enhancement of the longitudinal dispersion coefficient due to the sorptive exchange can be significant and should be included in a comprehensive model. Revelli & Ridolfi (2002, 2003) have investigated the dispersion in sediment-laden streams where the chemical may undergo sorptive exchange with suspended sediments and non-linear decay reactions. Ng (2006) has extended the work of Jiang & Grotberg (1993) to dispersion in tube flow subject to both an irreversible process of absorption and a reversible phase exchange process at the tube wall. It was found that the kinetics of the phase exchange will have significant effects on the dispersion, including intensifying the otherwise weak effects due to the wall absorption. Williams & Tomasko (2008) developed an analytical solution of the one-dimensional contaminant transport undergoing advection, dispersion, sorption, and first-order decay, subject to a first-order decaying contaminant concentration. They pointed out that this solution can be used to model the transport of radioactively decaying contaminants and remediation of recalcitrant NAPL. In both cases, the boundary concentration can exhibit first-order source decay and undergo transport decay at a different rate.

Mahdavi *et al.* (2013) investigated the effect of sorption of cadmium to sediments through an experimental and numerical study. Their results showed that the sorption process reduced the dispersion coefficient but has no effect on advection rate. It was also found that a pseudo-second-order model for kinetic sorption improves the results obtained in comparison with a first-order model. Comparison between the kinetic and equilibrium models showed that assuming equilibrium conditions underestimates transport velocity. One of the gaps of this study was the experiment just performed at one sediment concentration. Ghozeisi *et al.* (2014) examined the effect of flow velocity, sediment movement type and concentration in the kinetic adsorption and transport of cadmium in both bed and suspended load conditions. Their results showed that the adsorption rate is directly connected with sediment motion type and flow velocity. For the bed-load conditions, it was observed that the equilibrium capacity increased by 20% as the flow velocity changed from 0.35 to 0.7 m/s. However, for suspended load conditions, the equilibrium capacity was not significantly affected by the flow velocity or sediment motion type. It was

experimentally deduced that increasing the sediment concentration load by 300% would decrease the equilibrium cadmium adsorption in unit mass by 170 and 250% for bed and suspended loads, respectively.

Hlushkou *et al.* (2014) developed a microscopic numerical model combining simulations of advective–diffusive transport with a stochastic approach to the sorption process at the solid–liquid interface for flow through a circular tube. The retention factor of an adsorbed solute is constructed by independent adjustment of the adsorption probability and mean adsorption sojourn time. The presented three-dimensional modelling approach can realize any microscopic model of the adsorption kinetics based on a distribution of adsorption sojourn times expressed in analytical or numerical form. They addressed the impact of retention factor, adsorption probability, and distribution function for adsorption sojourn times on solute dispersion depending on the average flow velocity. Their results demonstrated that the distribution function for adsorption sojourn times is a key parameter affecting dispersion and show that models of advection–diffusion–sorption cannot describe mass transport without specifying microscopic details of the sorption process. In contrast to previous one-dimensional stochastic models, the presented simulation approach can be applied as well to study systems where diffusion is a rate-controlling process for adsorption. Wang & Chen (2016) analytically studied the evolution of two-dimensional concentration distribution for solute dispersion in a laminar open-channel flow with bed absorption. Their results showed the extremely non-uniform cross-sectional concentration distribution, and demonstrated that concentration at the bed instead of the mean should be used for reliable quantification of the absorption flux. Mondal *et al.* (2020) described the longitudinal dispersion of passive tracer materials released into an incompressible viscous fluid, flowing through a channel with walls having first-order reaction. Its model was based on a steady advection–diffusion equation with Dirichlet’s and mixed boundary conditions, and whose solution represented the concentration of the tracers in different downstream stations. A finite difference implicit scheme was used to solve the advection–diffusion equation in the computational region, and an inverse transformation was employed for the solution in the physical region. They showed how the mixing of the tracer molecule was influenced by the shear flow and due to the action of the absorption parameter at both the walls of the channel.

While much work has been performed on the longitudinal coefficient in channels and rivers, there have been few previously published studies, particularly looking into the effects of sorption process on advection and dispersion of heavy metals. Conversely, there is a gap in knowledge about the effect of heavy metal sorption by natural river sediments in different concentrations on advection–dispersion processes. Since different pollution sources containing heavy metal ions are usually discharged to natural and alluvial rivers, the results of this study will be useful for the researchers, decision-makers, and river engineers to quantify the influence of heavy metal sorption due to the presence of river sediments on longitudinal dispersion. For this purpose, first, the adsorption of cadmium ions by riverbed sediments were experimentally investigated for different sediment concentrations to find the adsorption parameters. Accordingly, the research objectives were as follows: 1. study of the effect of sediment concentrations on the longitudinal dispersion coefficient; 2. analysis of the advection–dispersion equation with respect to the sorption term; and 3. numerical solution of the advection–dispersion equation with respect to the sorption term. We are also looking for a relationship between the longitudinal dispersion coefficient and a parameter representative of cadmium sorption rate of the bed sediments, in which the sediment and cadmium concentrations are considered.

MATERIALS AND METHODS

Experimental investigations

The experiments of this study were conducted in a circular flume with a mean diameter of 1.6 m, width of 0.20 m and a depth of 0.15 m placed on a platform of $2 \times 2 \text{ m}^2$ (Figure 1). The water–sediment mixture was run using two pedals within the flume. In order to remove any possible impurities (especially, the remaining pollutants due to previous experiments), the flume was filled with 0.1% HNO_3 and was run for 1 hr before each experiment. It was then thoroughly rinsed and filled up to a height of 0.13 m (130 lit) with deionized water. The environmental parameters of pH and EC (Electrical Conductivity) were respectively adjusted using NaOH or HNO_3 and NaCl, which were constant throughout the experiments ($\text{EC} = 800 \pm 10 \text{ }\mu\text{S}/\text{cm}$, $\text{pH} = 7.5 \pm 0.1$). In addition, all the experiments were conducted at temperature of $25 \text{ }^\circ\text{C}$, adjusted by two 300 W aquarium heaters. A stock solution of 1,000 ppm cadmium was prepared for all experiments. Cadmium measurements were conducted by using an ICP-OES instrument (Varian VISTA-MPX device). The detection limit for the cadmium ion was 0.0005 ppm.

The sediment samples were collected from shallow waters nearer to the bank of the Karaj River (north of Iran) and were taken from upper 0–15 cm layer of the deposits at the places with low flow rates as sedimentation was assumed to occur (Jain

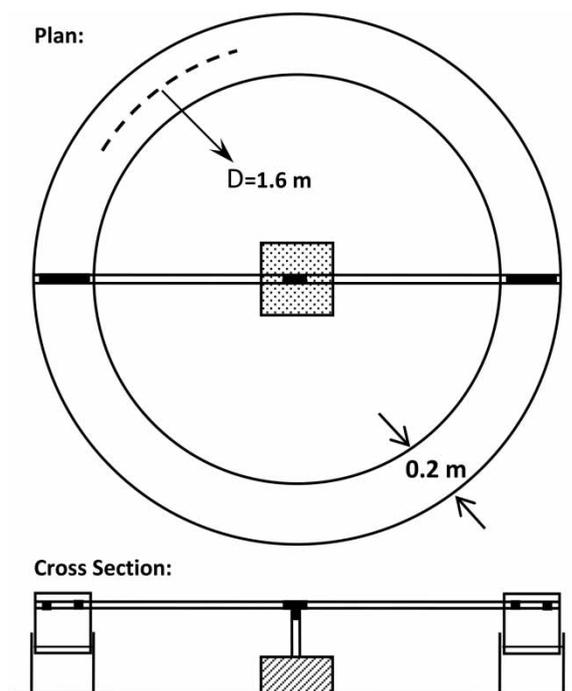


Figure 1 | Plan and cross section of the circular flume.

& Ram 1997). The samples were washed several times with distilled water to remove physical earthen impurities. Then, prior to experiments, they were dried in a hot air oven at 110 °C for 24 hr. A sediment size of 0.53 mm was selected by using a standard sieving apparatus (particles remained between sieves Nos. 30 and 40). The cation exchange capacity (CEC) of the riverine sediments was measured using Bower *et al.*'s method (Bower *et al.* 1952) equal to 13.873 mEq/100 g. In addition, the general physical-chemical features of sediment samples revealed that these samples were mainly composed of SiO₂ (54 wt%), AlSi₃O₈ (14.4 wt%), Fe₂O₃ (7.5 wt%), CaO (6.4 wt%), and other minerals (8.34 wt%).

Experimental investigations in this study were performed in two parts: sorption and dispersion experiments. First, the sorption experiments were conducted in order to obtain the sorption parameters (k and q_e) as a function of cadmium and sediment concentrations, which they are needed for numerical modelling. During these experiments, the cadmium solution (with the concentrations of 150, 460 and 770 ppb) was first injected throughout the flume. The cadmium plume was then spread through the flume. After a certain time and reaching an equilibrium conditions, three samples were taken from specified points of the flume for measuring the initial concentrations (C_0) and to ensure a constant cadmium concentration throughout the flume. A thin layer of bed sediments were then spilled throughout the flume bed with the concentrations of 3, 12, and 20 gr/lit. The experiment was started by taking 50 mL samples at a given point in the centreline of the flume in different times. According to Mahdavi *et al.* (2013), the sorption process were kinetically investigated by taking the samples in different times of 0, 1, 2, 5, 10, 15, 30, 45, 60, 90, 120, 180, 240, and 300 min. The amount of adsorbed cadmium at each time (q) is calculated, as follows:

$$q = \frac{(C_0 - C)V}{W} \quad (2)$$

where, C_0 is the initial cadmium concentration ($t = 0$) and C is the cadmium concentration at different times (ppb), V is the volume of the water (130 litres), and W is the weight of the sediments (g). For the kinetic modelling, a pseudo-second-order equation is used (Ho & McKay 1999; Azizian 2004; Mahdavi *et al.* 2013), defined as follows:

$$\frac{\partial q}{\partial t} = k_2(q_e - q)^2 \quad (3)$$

where, k_2 is the second-order rate coefficient and q_e is the equilibrium adsorbed cadmium. Integrating this equation for the boundary conditions of $t = 0$ to $t = t$ and $q = 0$ to $q = q$, gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

The sorption experiments with different initial cadmium concentrations are used in order to determine the best kinetic equation and to estimate the sorption parameters of k_2 and q_e . In order to estimate the kinetic sorption parameters, there are two methods (Mahdavi *et al.* 2013). The first method is applying the least squares method to the linear transformed kinetic model (Equations (3) and (4)). However, Jiang *et al.* (2007) and Ho (2006) showed that it is better to use the non-linear least squares method for the original non-linear equation. Therefore, in this study, both methods were used and compared.

In the second part of the experiments, the dispersion process was investigated in a different manner from the sorption experiments. In this section of the tests, a thin layer of sediments were first spread over the bottom of flume at a specified concentration (3, 12, and 20 g/litre). After adjusting the environmental parameters (temperature, pH, and EC), the cadmium solution with a given concentration was injected in one point of the flume ($x = 0$); then the cadmium plume was transported and spread longitudinally through the flume by advection and dispersion processes, respectively, until it dispersed throughout the flume. It should be mentioned that the transverse spreading of the plume was ignored because the flume width was small. The changes in the cadmium concentrations were monitored at a distance of $x = 1.256$ m from the injection point. The samples were taken from this point at about 3 s intervals. By repeating these experiments with and without the presence of sediments, the effect of sorption by sediments can be investigated on longitudinal dispersion of the cadmium. The list of conducted experiments as well as experimental conditions are presented in Table 1. The experiments were always started with the constant flow velocities of about 0.2 m/s. In order to estimate the flow velocity, the salt was only injected once from one point of the flume and the conductivity (EC) values were measured at this point with time, and the average velocity was measured using the measured time for a number of circulations and the spatial distance between the peaks.

Numerical modelling

Appelo & Postman (1993)'s method was used to solve Equation (1), numerically. Indeed, the advantage of this procedure is that the different expressions of advection, dispersion, and absorption are individually solved at each step. In other words, at a

Table 1 | Conducted experiments and experimental conditions

Exp. sets	Run no.	Cadmium con. (ppm)	Sediment con. (g/litre)
Sorption experiments	AS01	0.15	3
	AS02	0.46	3
	AS03	0.77	3
	AS04	0.15	12
	AS05	0.46	12
	AS06	0.77	12
	AS07	0.15	20
	AS08	0.46	20
	AS09	0.77	20
Dispersion experiments	AD01	0.15	0
	AD02	0.15	3
	AD03	0.15	12
	AD04	0.15	20
	AD05	0.46	0
	AD06	0.46	3
	AD07	0.46	12
	AD08	0.46	20
	AD09	0.77	0
	AD10	0.77	3
	AD11	0.77	12
	AD12	0.77	20

Table 2 | Results of calculations of sorption parameters

Parameter	AS01	AS02	AS03	AS04	AS05	AS06	AS07	AS08	AS09
k_2	0.0004	0.0001	0.0001	0.0001	0.0003	0.0003	0.0029	0.0016	0.0004
q_e	36.62	112.70	159.55	36.52	40.71	67.17	7.42	23.94	45.71

certain time step, the effect of the advection on the cells is first applied. Then, the effect of the dispersion is calculated in each cell; after that on the resulting cells from advection and dispersion expressions the effect of the absorption will be applied. The advantage of this method is that one can easily add other chemical or physical formulae to the model. In addition, each process can be solved with the most appropriate numerical method. Table 2 shows the values obtained for the sorption parameters (k and q_e) as a function of cadmium and sediment concentrations.

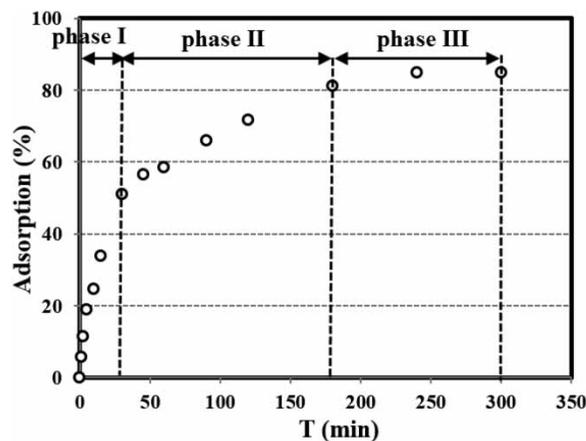
RESULTS AND DISCUSSION

Results of sorption experiment

In this study, the advection and dispersion of cadmium ion at the presence of river bed sediments were investigated. As mentioned before, the sorption characteristics of the river sediments were first investigated. To do this, the sorption experiment was started by taking 50 mL samples at a given point at different times of 0, 1, 2, 5, 10, 15, 30, 45, 60, 90, 120, 180, 240, and 300 min. The amount of adsorbed cadmium at each time (q) was calculated using Equation (2). In addition, the kinetic sorption was investigated in several steps. The overall results of these experiments showed that, for most sorption processes, the cadmium sorption rate by bed sediments consists of three phases: the first phase (Phase I; rapid absorption), the second phase (Phase II; transition) and the third phase (Phase III; almost flat) (Figure 2). The interesting thing is that the cadmium concentration does not affect these phases. As can be seen, the remaining concentration of cadmium ions became asymptotic to the time axis such that there was no appreciable change in the remaining concentration after 5 hr. This time was presumed to represent the equilibrium time at which an equilibrium concentration was presumably attained. It should be mentioned that this time is approximately independent of cadmium and sediment concentrations. The other sorption experiments were conducted for 5 hr.

As mentioned, these experiments were conducted in a circular flume. Until now, many researchers have performed some experiments in batch reactors (Nasrabadi *et al.* 2020). It should be mentioned that the equilibrium time for the batch experiments is more than that for flume experiments (Mahdavi *et al.* 2013; Ghozeisi *et al.* 2014; Nasrabadi *et al.* 2017, 2018). The reason is that the turbulence is much more in the batch reactors; however, for the flume experiments the experimental conditions are very close to the natural rivers.

In addition, the results of measuring physicochemical composition of the minerals using X-ray diffraction (XRD) showed that the sediment was mostly composed of sand (more than 99%; $d_{50} = 0.53$ mm) and the organic content of the sediment was

**Figure 2** | Different phases of the cadmium sorption.

negligible (0–1%). In addition, the weight percentages of the geochemical constituents for the sediments showed that the main constituent was SiO_2 (54%) and CaO is also present in significant amounts (6.4%) in the sediment. In addition, as previously mentioned by different researchers (Koelmans & Lijklema 1992; Jain *et al.* 2004), the most important geochemical phases (iron and manganese) may play an important role in the adsorption process. The amounts of Fe_2O_3 and MnO were 7.5 and 3%, respectively. These values indicate that two geochemical phases may act as supportive materials for Cd adsorption by sediments.

Figure 3 shows the effect of sediment concentration on the cadmium sorption rate for initial cadmium concentrations of 150, 460 and 770 ppb. As can be seen that, by increasing sediment concentrations, the absorbed cadmium per unit weight of sediment is reduced. According to this figure, with increasing sediment concentrations from 3 to 20 g/lit, the equilibrium adsorbed cadmium per unit weight of sediment (1 gr) is reduced from 30 to 6.25, 86.68 to 22.52, and 67.66 to 36.5 μg . Although the sorption rate is lower for the highest sediment concentration (20 g/litre), it can be said that by increasing the sediment concentrations, the sorption percentage increases. In these experiments, by increasing the sediment concentrations, the cadmium removal percentage increased from 50 to 78.15% (for Cd concentration of 150 ppb) from 47.27 to 84.9% (for the concentration of 460 ppb) and from 41 to 80.21% (for Cd concentration of 770 ppb). In other words, it can be concluded that by increasing the sediment concentrations in the solution and because of competition between sediments, the contribution of each gram of sediment in the solution decreases, however, the total absorbed cadmium increases.

The following explanations can be expressed for these changes: (1) at the initial stage of adsorption process, the sediment surface provided more adsorption sites, which contributed to rapidly increased adsorption rate. Due to the negative-charged surface of sediments, it could combine with metal cations through Coulomb force, and this process could be considered as pseudo-adsorption. (2) specific adsorption happened through chemical reaction between Cd(II) and sediment surface was followed. However, it would change the property of surface electric charge. Increased positive sites would prevent the adsorption of Cd(II); and (3) available sorption sites became limiting factors along with increasing adsorption amount.

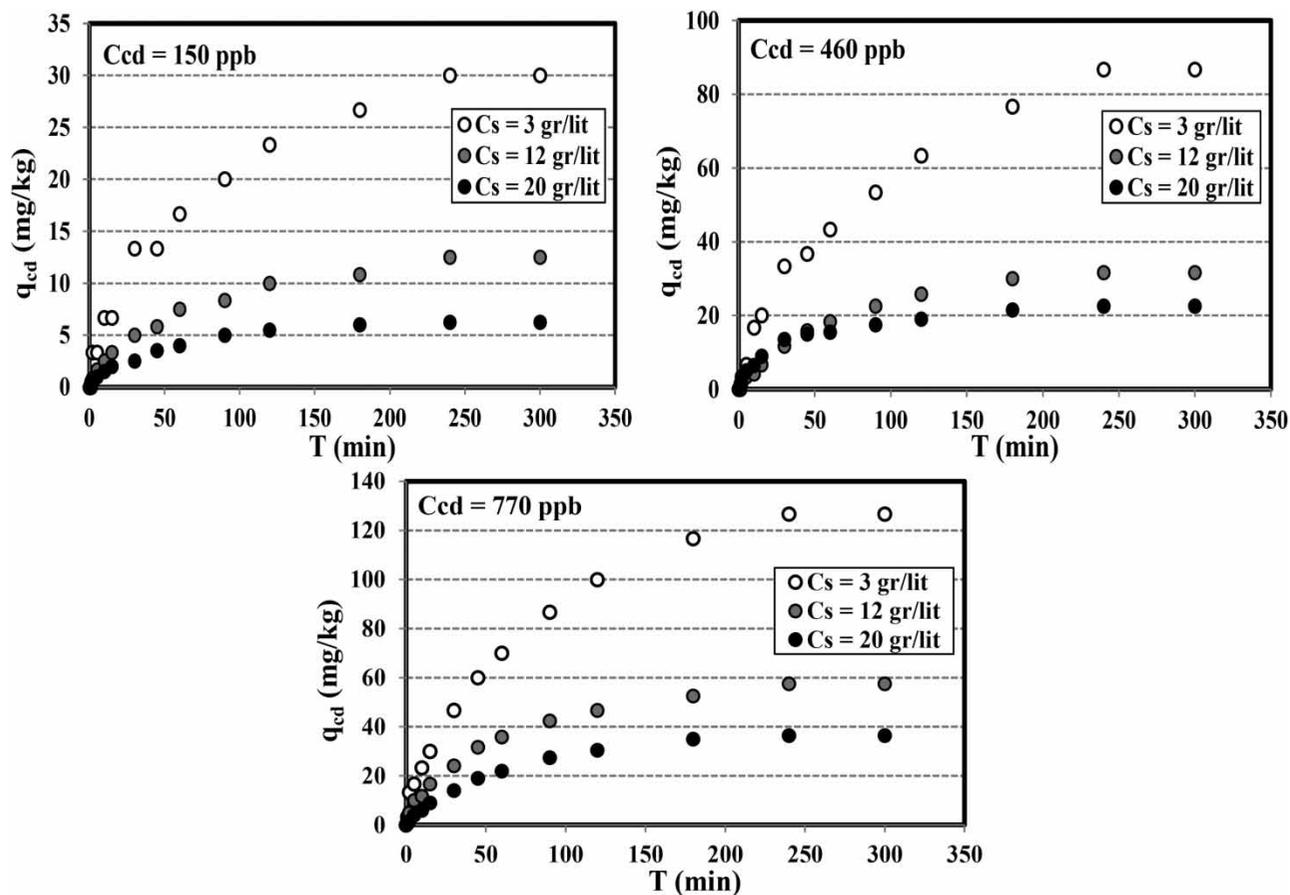


Figure 3 | The effect of sediment concentration on the cadmium sorption.

(Markiewicz-Patkowska *et al.* 2005; Vibhawari & Pandey 2010; González Costa *et al.* 2017; Huang *et al.* 2019). The results of Jain & Ram (1997), Jain & Sharma (2002), Ho (2004, 2006), Mahdavi *et al.* (2008) are consistent with the results of the present study.

Results of dispersion experiments

In order to estimate the longitudinal dispersion coefficient and investigate the effect of cadmium sorption by river bed sediments on this coefficient, some experiments were performed. The results of these experiments were used for calibration and validation of the numerical model. These experiments were performed in three sediment concentrations of 3, 12, and 20 g/litre as well as sediment-free conditions (control experiment; $C_s = 0$). The results of dispersion experiments for runs Nos. AD05 and AD08 ($C_s = 0$) and at the presence of bed sediment with a concentration of 20 g/litre and cadmium concentration of 460 ppb is shown in Figure 4. As can be seen, the presence of sediments has two major effects on breakthrough curve of concentration cadmium. First, due to the cadmium sorption by sediments, the peak values have decreased relative to the sediment-free state. Second, the difference between the minimum and maximum values of each peak has increased.

As mentioned before, a one-dimensional advection–dispersion equation (Equation (1)) is used for description of heavy metal transport in the dissolved phase. In this study, the splitting operator method (Appelo & Postma (1993)’s method) was applied to numerically solve Equation (1).

According to Figure 5, in a circular flume, cell 1 is located next to the last cell (cell n). Therefore, its value is calculated at the next step using cells 1, 2 and n at a previous time step. The cell n is also calculated by cells 1, n–1 and n.

The initial condition is that at time $t = 0$, the concentration across the flume other than the cadmium injection region is zero:

$$\begin{cases} C = 0 \\ C = C_{in} \end{cases} \text{ for } t = 0 \text{ and } \forall x \quad (5)$$

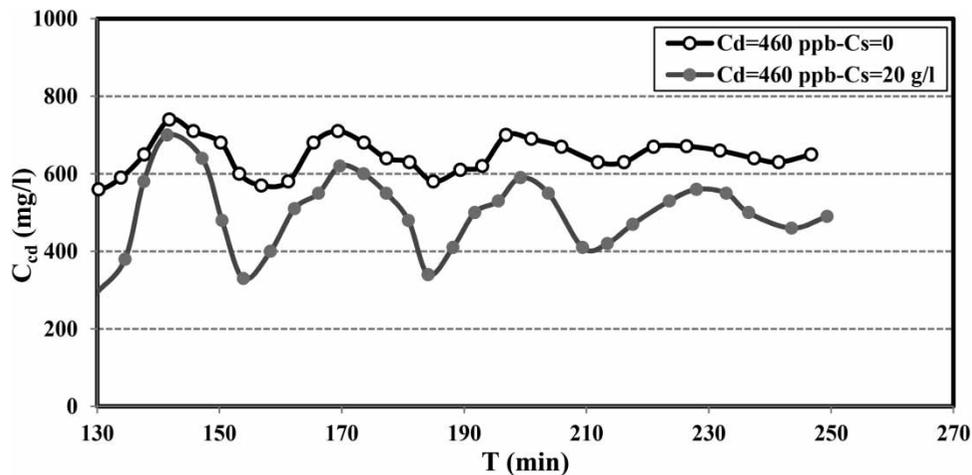


Figure 4 | Time distribution of cadmium concentration (ppb 460) without and with sediment concentration of 20 g/litre.

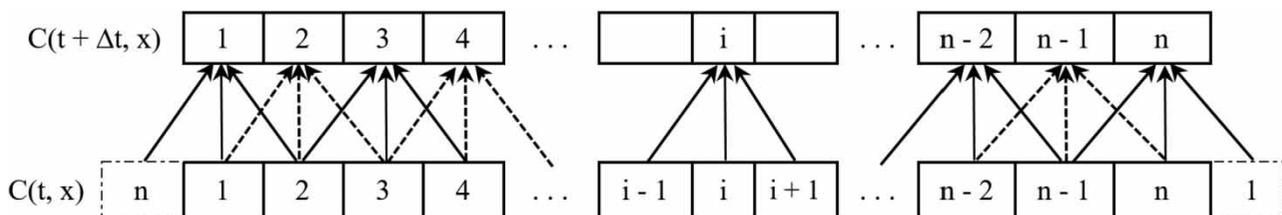


Figure 5 | General scheme for numerical modelling.

In addition, the boundary condition is that the cadmium concentrations at $x = 0$ and $x = L$ are equal at all times:

$$C_0 = C_L \quad \text{for } \forall t \quad (6)$$

In order to estimate the longitudinal dispersion coefficient without sediments and in the presence of sediments with different concentrations, a numerical model was developed on the MATLAB platform and calibrated by experimental data. Therefore, the model was run for different flow velocities and dispersion coefficients and the best coefficient was selected after comparing with the experimental data and calculating the sum of squared error (SSE).

The numerical results and the experimental data are compared in Figure 6. As can be seen, there is a good correlation between experimental results and numerical modelling.

Figure 7 shows the breakthrough curve of cadmium concentration in a sediment-free experiment (solid line) and for a sediment concentration of 20 g/litre (dotted line). As can be seen, the presence of sediments significantly affects advection and dispersion of cadmium, by increasing the cadmium sorption. Increasing the adsorptive capacity of the sediment particles delays breakthrough of the adsorbing solute. In addition, the leading edge of the concentration profile is similar in shape to the zero adsorption case (sediment-free experiment). It has been obviously shown that the sorption process by sediments at maximum concentration reduces the longitudinal dispersion coefficients.

Another notable change in these diagrams is that the number of circulations in breakthrough curves for the experiment with sediment concentration of 20 mg/lit are significantly increased compared to the control experiment (sediment-free experiment). For example, in Figure 7(c), the number of circulations increased from nine circulations in control experiment (sediment-free experiment) to 13 circulations for the experiment with cadmium and sediment concentrations of 770 ppb and 20 mg/lit, respectively.

In Figure 8, the measured data are plotted against numerical results. This figure represents that the numerical modelling has a great capability in estimating the concentration of pollutant in the flow.

Effect of sorption on longitudinal dispersion coefficient

As shown in Figures 5 and 7, the presence of sediments and sorption process reduces the longitudinal dispersion of cadmium. In this study, in order to evaluate the effect of sorption by sediment, a new parameter, named 'absorption ratio (A_R)' was defined, as follows:

$$A_R = \frac{C_0 - C_{50}}{t_{50}} \quad (7)$$

in which, C_0 is the initial concentration ($\mu\text{g/lit}$), C_{50} is cadmium concentration when the sorption percentage is 50% ($\mu\text{g/lit}$) and t_{50} is the required time (min) to achieve an sorption percentage of 50%.

The results of the analysis of cadmium advection and dispersion experiments in the presence of bed sediments are presented in Table 3. As can be observed, with increasing the sediment concentrations, the sorption rate of sediments increased and the longitudinal dispersion coefficient decreased by 38, 36 and 33% for cadmium concentrations of 150, 460 and 770 $\mu\text{g/litre}$, respectively. Increasing the sediment concentrations enhance the sorption rate of cadmium. This process delayed the advection and dispersion of cadmium and reduced the longitudinal dispersion coefficient. According to main aim of the present study, the presence of bed sediment may significantly affect the longitudinal dispersion of cadmium in natural streams.

In column 9 of Table 3, λ is the longitudinal dispersivity, derived by dividing the longitudinal dispersion coefficient to the average flow velocity ($= D_L/V$, in m). As can be seen, with increasing the sediment concentrations in a constant cadmium concentration, the longitudinal dispersion coefficients are decreased. The ranges of this parameter are 0.041–0.067, 0.041–0.065, and 0.04–0.058 m for cadmium concentrations of 150, 460, and 770 ppb, respectively.

The variations in the longitudinal dispersion coefficient (D_L) are plotted against the A_R in Figure 9. This figure shows that, with increasing sorption ratio, the longitudinal dispersion coefficient decreased. The reduction in the longitudinal dispersion coefficients is minimized for high sorption ratio. As was observed, there is a critical value for A_R , in which, the longitudinal dispersion coefficient will not decrease for values greater than this critical value.

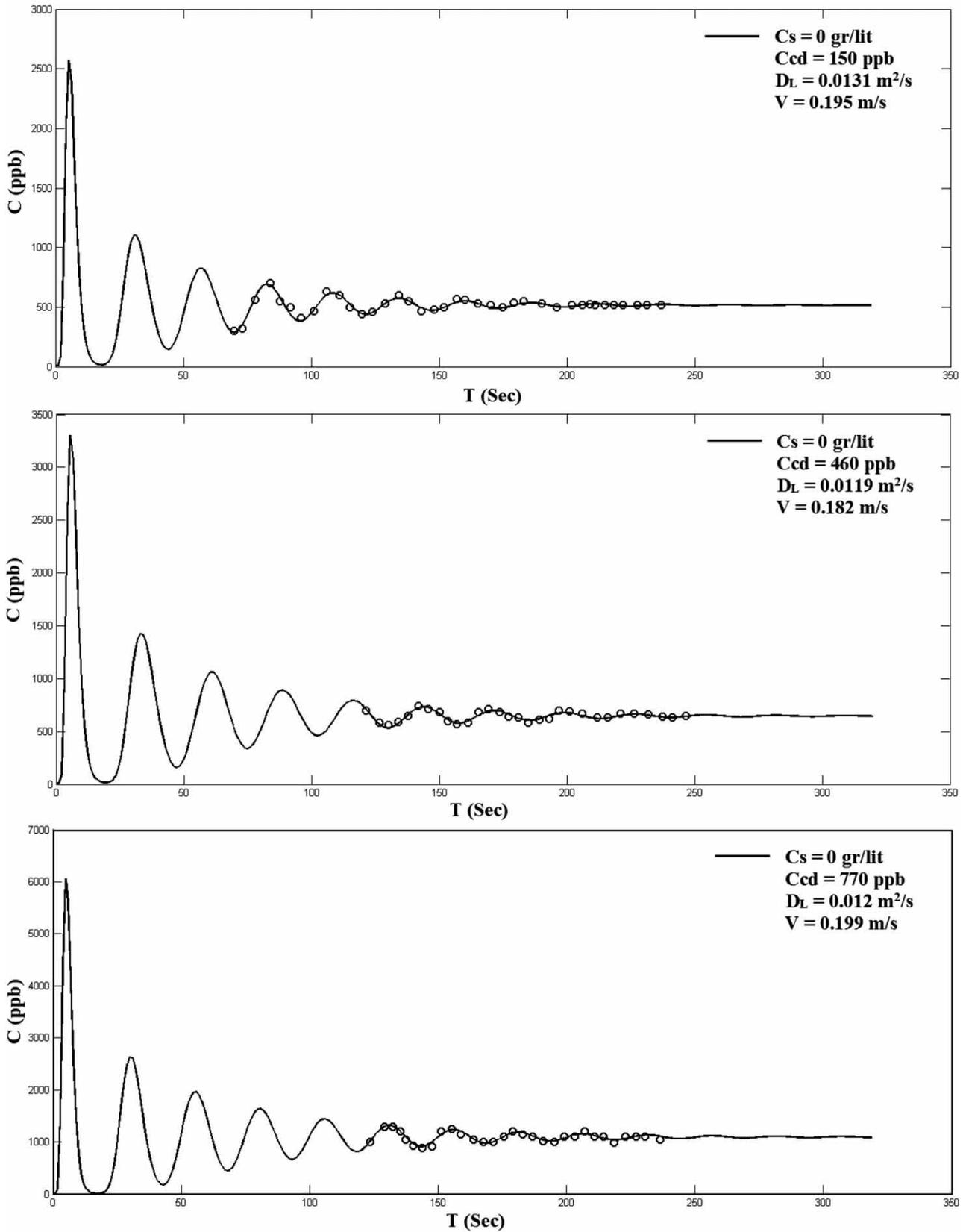


Figure 6 | Time distribution of cadmium concentration; numerical results and experimental data.

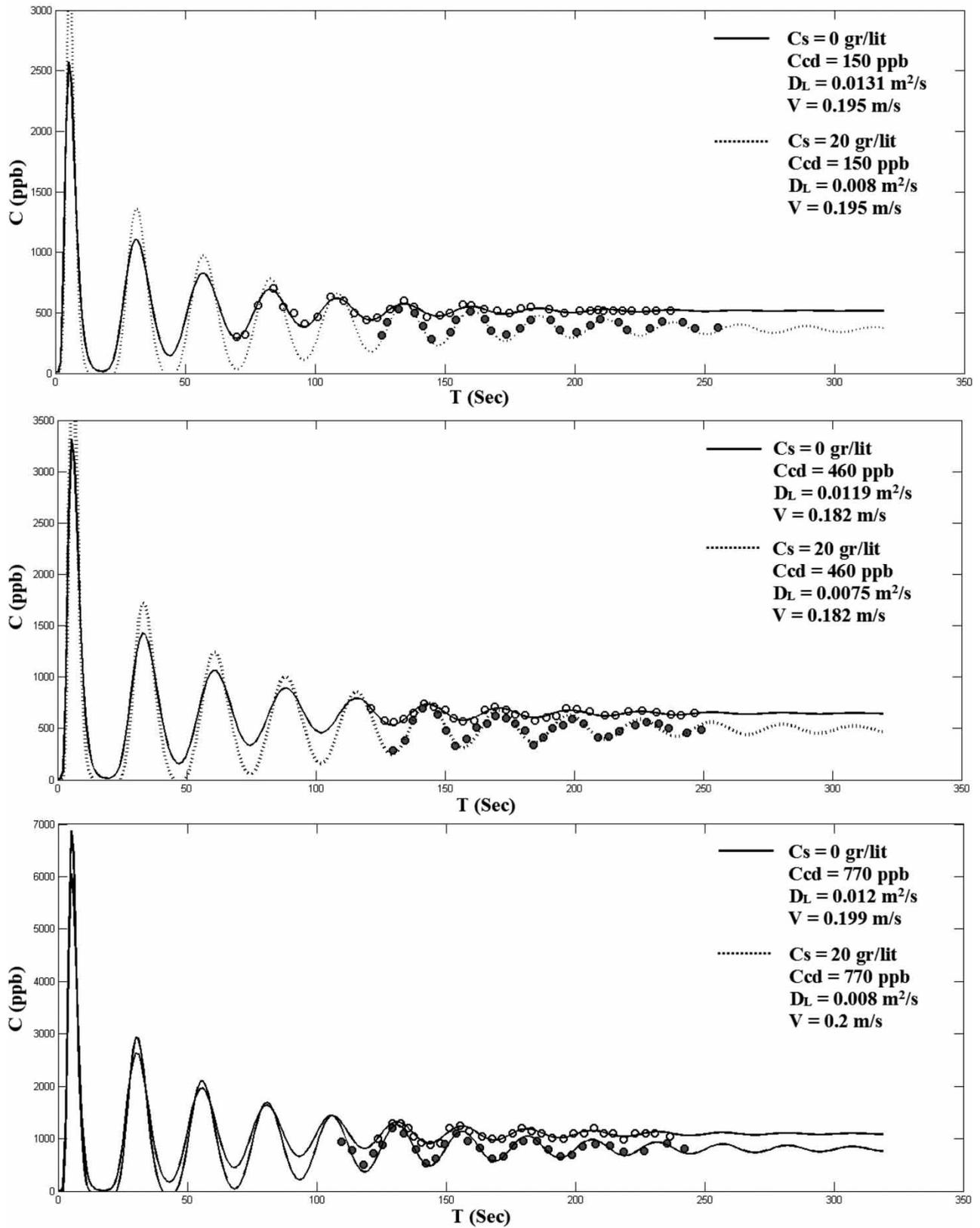


Figure 7 | Time variations of cadmium concentrations with river bed sediments; numerical results and experimental data.

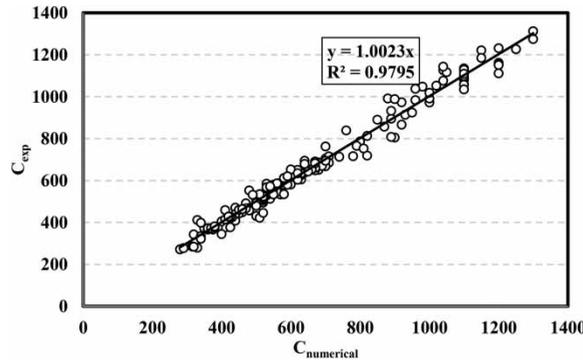


Figure 8 | Measured data versus numerical modelling.

Table 3 | Results of the analysis of cadmium advection and dispersion experiments

C_{cd} (ppb)	C_s (gr/lit)	C_0 (ppb)	C_{90} (ppb)	t_{50} (min)	A_R	V (m/s)	D_L (m ² /s)	λ (m)	D_L/Vh	$\Delta D_L/D_{L0}$
150	0	0	0	0	0	0.195	0.0131	0.067	0.52	0
150	3	180	90	240	0.375	0.189	0.011	0.058	0.45	16.03
150	12	160	80	60	1.333	0.193	0.009	0.047	0.36	31.30
150	20	180	60	60	2	0.195	0.008	0.041	0.32	38.93
460	0	0	0	0	0	0.182	0.0119	0.065	0.50	0
460	3	550	290	300	0.867	0.178	0.0105	0.059	0.45	11.76
460	12	510	240	90	3	0.187	0.0088	0.047	0.36	26.05
460	20	530	260	30	9	0.182	0.0075	0.041	0.32	36.97
770	0	0	0	0	0	0.2	0.0115	0.058	0.44	0
770	3	920	540	300	1.267	0.185	0.0105	0.057	0.44	8.70
770	12	940	430	90	5.667	0.195	0.009	0.046	0.36	21.74
770	20	910	470	60	7.333	0.2	0.008	0.040	0.31	30.43

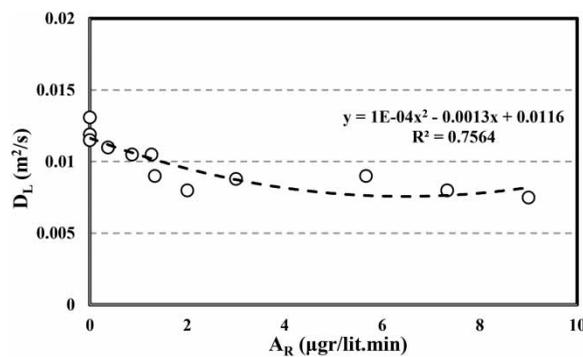


Figure 9 | Changes in longitudinal dispersion coefficient of cadmium versus sorption ratio.

In order to develop a relationship between longitudinal dispersion coefficients and sorption ratios, non-dimensional dispersion coefficients (D_L/Vh) was used. The following equation was developed between the dimensionless dispersion coefficients and the sorption ratio:

$$\frac{D_L}{Vh} = 16.05(1.02 + e^{-0.001A_R}) \tag{8}$$

where, D_L is the longitudinal dispersion coefficient, V is the average flow velocity, h is the average flow depth, and A_R is the A_R . Two statistical indices of mean absolute error and sum of squared errors were used and the results showed that the average error of this relationship is 8.28% and the sum of the squared error is 0.0248. These values represent the very great accuracy of this relationship in estimating the longitudinal dispersion coefficient of cadmium in the presence of river bed sediments.

CONCLUSIONS

This study is solely focused on the effects of sorptive exchange with river bed sediments on the mass transport of cadmium in an open-channel flow. In this research, the effect of cadmium sorption by river bed sediments on the advection and dispersion processes was investigated experimentally and numerically. The results of dispersion experiments showed that with increasing the sediment concentrations, the sediment sorption rate increased and the longitudinal dispersion coefficient decreased by about 38, 36 and 33 percent for cadmium concentrations of 150, 460 and 770 ppb, respectively. In addition, by increasing the cadmium concentrations in the solution, the changes in the longitudinal dispersion coefficient are decreased. Furthermore, a relationship was developed using non-dimensional longitudinal dispersion as a function of A_R . The results of this analysis showed the high ability of developed relationships to estimate the longitudinal dispersion coefficient and to consider the effect of cadmium absorption by sediments on the longitudinal dispersion coefficient. In general, such strong dependence of the dispersion coefficient on the kinetics sorptive exchange may lead to interesting phenomena especially during the initial developing stage of the transport. A future study into these phenomena is worth pursuing, especially for other heavy metals with high concentrations, as well as a wide range of sediment concentrations and flow velocities.

One of the limitations of the present study is the impossibility of comparing the results with the findings of other researchers, as this study has been performed in a circular flume. In addition, this study delivered detailed information on dispersion coefficient on small scales with low-width and there a crucial need for the study of the advection–dispersion process in high-width channels. As natural rivers may contain different heavy metals, it is suggested that further studies to be performed on different heavy metal ions, such as Zn, As, Cu, Pb, Hg, Ni, and Cr.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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