

Experimental and Numerical Investigation of Effect of Cadmium Sorption by River Sediments on Longitudinal Dispersion

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Research Article

Keywords: Cadmium, Sorption Ratio, River Bed Sediments, Longitudinal Dispersion

Posted Date: May 25th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-507251/v1>

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20 **Abstract**

21 This paper concerns the cadmium sorptive effects by river bed sediments on longitudinal coefficient in an open-
22 channel flow via experimental and numerical study. For this purpose, a circular flume was used with mean
23 diameter of 1.6 m and a width of 0.2 m. The adsorbing bed was considered as a thin layer of the sediment
24 particles with mean diameter of 0.5 mm and three sediment concentrations of 3, 12, and 20 gr/lit. To determine
25 the sorption parameters of the sediments, some experiments were conducted with three cadmium concentrations
26 of 150, 460, and 770 ppb. Then, the dispersion experiments were carried out with and without the bed
27 sediments. To solve the advection-dispersion equation with considering the sorption term by river bed
28 sediments, a numerical model was then developed. The longitudinal dispersion coefficients were estimated by
29 comparing the experimental and numerical breakthrough curves. The results showed that, with increasing the
30 sediment concentrations, the sediment sorption rate increased and the longitudinal dispersion coefficient
31 decreased by about 38, 36 and 33 percent, respectively, for cadmium concentrations of 150, 460 and 770 ppb. In
32 addition, by increasing the cadmium concentrations, the changes in the longitudinal dispersion coefficient are
33 decreased. Furthermore, a relationship was developed using non-dimensional longitudinal dispersion as a
34 function of the new parameter of sorption ratio. From a practical point of view, the results of this study
35 demonstrated that, at the presence of sediment, the cadmium is longitudinally dispersed with more delay in
36 comparison with no sediment at the river bed.

37 *Keywords:* Cadmium, Sorption Ratio, River Bed Sediments, Longitudinal Dispersion.

38

39 **Introduction**

40 Nowadays, most of the natural rivers are exposed to industrial wastewaters and heavy metal pollutions
41 and the study of different factors affecting on the transport and the fate of these pollutants is important. On the
42 other hand, the rivers typically carry the sediments via erosion and sedimentation processes. In addition, the
43 river is usually contains the different sizes of sediments, most of them is very rich in organic matter, and
44 therefore has a strong potential to adsorb chemical pollutants in a sorbate form (Ng 2006a). As a result, the
45 presence of these sedimentary loads in the rivers, due to the high potential of metal ions to adsorb by sediment
46 particles, may play an important role in the transport and fate of heavy metal pollutants. In this regards, many
47 studies have demonstrated that the sediments have accumulated about 62, 40, 90 and 80 percent of cadmium,
48 copper, lead, and zinc, respectively, in the eastern rivers of the United States (EPA 1998, Uddin 2017).

49 Therefore, considering the presence of sediment loads having very high sorption rates, and the effects of
50 sorption process by sediments on the advection and dispersion of these pollutants is important.

51 After being absorbed by the sediment particles, heavy metal ions are transferred from the dissolved
52 phase into the absorbed phase. This process can be seen as a self-cleaning process of the rivers (Fornster and
53 Gottfried 1981; Herut et al. 1995; Bird and Evenden 1996). It should be mentioned that, there are two
54 approaches for description of this phenomenon in the aquatic systems. Some researchers supposed that the
55 distribution of pollutants may be described as an equilibrium process by an instantaneous partitioning between
56 the dissolved and the adsorbed phases (Falconer and Lin 2003; Wu et al. 2005). Others considered the sorption
57 as a kinetic process (Jonsson and Worman 2001; Jonsson et al. 2004; Huang et al. 2007; Roshanfekar et al. 2008;
58 and Huang 2009). Longitudinal dispersion coefficient can be affected by many hydrodynamic and geometrical
59 parameters, and as a result the dispersion characteristic may vary from one river to another. Till now, three
60 methods, namely the integral method, dye tracing measurements and empirical formulae have been widely used
61 to estimate the longitudinal dispersion coefficient (Zeng and Huai, 2014).

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

$$66 \quad \frac{\partial C}{\partial t} = -V \frac{\partial C}{\partial x} + D_L \frac{\partial^2 C}{\partial x^2} - \rho \frac{\partial q}{\partial t} \quad (1)$$

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

71 Until now, many researchers have studied numerically and analytically the advection-dispersion equation
72 with considering the sorptive effects of pollutants in groundwater (van Kooten 1996, Williams and Tomasko
73 2008, Bruining et al. 2012, Singh and Das 2016, Jaiswal and Gulrana 2019, and Pillai and Raizada 2021) and
74 surface water resources (Phillips et al. 1995, Ng 2000a, b, 2001, 2006), Revelli and Ridolfi 2002, 2003 and Yip
75 and Ng 2003, and Mahdavi et al. 2008).

76 Purnama (1995) found that, for low sorption rates, the boundary retention increases the dispersion rate
77 and considers as the main effect suppressing the boundary absorption, which decreases the dispersion rate. It

78 was, however, pointed out by Jiang and Grotberg (1993) that, for dispersion in oscillatory tube flow, the wall
79 absorption, when it is weak, may increase or decrease the dispersion depending on the oscillation frequency. Ng
80 (2000a) studied the effects of sorptive exchange on the transport of a chemical in a sediment-laden open-channel
81 flow. He found that, for sufficiently large particles and solid fractions, enhancement of the longitudinal
82 dispersion coefficient due to the sorptive exchange can be significant and should be included in a
83 comprehensive model. Revelli and Ridolfi (2002, 2003) have investigated the dispersion in sediment-laden
84 streams where the chemical may undergo sorptive exchange with suspended sediments and nonlinear decay
85 reactions. Ng (2006) has extended the work of Jiang and Grotberg (1993) to dispersion in tube flow subject to
86 both an irreversible process of absorption and a reversible phase exchange process at the tube wall. It has been
87 found that the kinetics of the phase exchange will have dramatic effects on the dispersion, including intensifying
88 the otherwise weak effects due to the wall absorption. Williams and Tomasko (2008) developed an analytical
89 solution of the one-dimensional contaminant transport undergoing advection, dispersion, sorption, and first-
90 order decay, subject to a first-order decaying contaminant concentration. They pointed out that this solution can
91 be used to model the transport of radioactively decaying contaminants and remediation of recalcitrant NAPL. In
92 both cases the boundary concentration can exhibit first-order source decay and undergo transport decay at a
93 different rate.

94 Mahdavi et al. (2013) investigated the effect of sorption of cadmium to sediments through an
95 experimental and numerical study. Their results showed that sorption process reduces the dispersion coefficient
96 but has no effect on advection rate. The results also indicate that the linearization method of estimating sorption
97 parameters is unsuitable. It was also found that a pseudo second-order model for kinetic sorption improves the
98 results obtained in comparison with a first-order model. Comparison between the kinetic and equilibrium
99 models showed that assuming equilibrium conditions underestimates transport velocity. One of the gaps of this
100 study was the experiment just performed at one sediment concentration. Ghoveisi et al. (2014) examined the
101 effect of flow velocity, sediment movement type and concentration in the kinetic adsorption and transport of
102 cadmium in both bed and suspended load conditions. Their results showed that the adsorption rate is directly
103 connected with sediment motion type and flow velocity. For the bed-load conditions, it was observed that the
104 equilibrium capacity increased by 20% as the flow velocity changed from 0.35 to 0.7 m/s. However, for
105 suspended load conditions, the equilibrium capacity was not significantly affected by the flow velocity or
106 sediment motion type. It was experimentally deduced that increasing the sediment concentration load by 300%

107 would decrease the equilibrium cadmium adsorption in unit mass by 170% and 250% for bed and suspended
108 loads, respectively.

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

132 While much work has been performed on the longitudinal coefficient in channels and rivers, there are
133 few studies in the literature, particularly looking into the effects of sorption process on advection and dispersion
134 of heavy metals. On the other hand, there is a gap in knowledge about the effect of heavy metal sorption by
135 natural river sediments in different concentration on advection–dispersion processes. For this purpose, first, the
136 absorption of cadmium ions by riverbed sediments were experimentally investigated for different sediment

137 concentrations to find the adsorption parameters. Accordingly, the research objectives are as follows: 1. study of
138 the effect of sediment concentrations on the longitudinal dispersion coefficient; 2. analysis of the advection-
139 dispersion equation with respect to the sorption term; and 3. numerical solution of the advection-dispersion
140 equation with respect to the sorption term. We are also looking for a relationship between the longitudinal
141 dispersion coefficient and a parameter representative of cadmium sorption rate of the bed sediments, in which,
142 the sediment and cadmium concentrations are considered.

143

144 **Materials and Methods**

145 **Experimental Investigations**

146 The experiments of this study were conducted in a circular flume with a mean diameter of 1.6 m, width
147 of 0.20 m and a depth of 0.15 m (Fig. 1) placed on a platform of 2×2 m². The water-sediment mixture was run
148 using two pedals within the flume. In order to remove any possible impurities (especially, the pollutants due to
149 previous experiments), the flume was filled with 0.1% HNO₃ and was run for 1 hr before each experiment. It
150 was then thoroughly rinsed and filled up to 0.13 m (130 lit) with deionized water. The environmental parameters
151 of pH and EC were respectively adjusted using NaOH or HNO₃ and NaCl, which were constant throughout the
152 experiments (EC=800±10 μS/cm, pH=7.5±0.1). In addition, all the experiments were conducted at temperature
153 of 25°C, adjusting by two 300 W aquarium heaters. A stock solution of 1000 ppm cadmium was prepared for all
154 experiments. Cadmium measurements were conducted by using an ICP-OES (Varian VISTA-MPX device). The
155 detection limit for the cadmium ion was 0.0005 ppm.

156

157 Figure 1. ABOUT HERE

158

159 The sediment samples were collected from shallow waters nearer to the bank of the Karaj River (north of
160 Iran) and were taken from upper 0-15 cm layer of the deposits at the places with low flow rates as sedimentation
161 was assumed to occur (Jain and Ram, 1997). The samples were washed several times with distilled water to
162 remove physical earthen impurities. Then, prior to experiments, they were dried in a hot air oven at 110°C for
163 24 hrs. A sediment size of 0.53 mm was selected by using standard sieving apparatus (particles remained
164 between sieves No. 30 and 40). The cation exchange capacity (CEC) of the riverine sediments was measured
165 using Bower et al.'s method (Bower et al. 1952) equal to 13.873 meq/100gr. Besides, the general physical–

166 chemical features of sediment samples revealed that these samples were mainly composed of SiO₂ (54 wt %),
167 AlSi₃O₈ (14.4 wt %), Fe₂O₃ (7.5 wt %), CaO (6.4 wt %), and other minerals (8.34 wt %).

168 Experimental investigations in this study were performed in two parts: sorption and dispersion
169 experiments. First, the sorption experiments were conducted in order to obtain the sorption parameters (k and
170 q_e) as a function of cadmium and sediment concentrations, which they are needed for numerical modeling.
171 During these experiments, the cadmium solution (with the concentrations of 150, 460 and 770 ppb) was first
172 injected throughout the flume. The cadmium plume was then spread through the flume. After a certain time and
173 reaching an equilibrium conditions, three samples were taken from different points of the flume for measuring
174 the initial concentrations (C₀) and to ensure a constant cadmium concentration throughout the flume. A thin
175 layer of bed sediments were then spilled throughout the flume bed with the concentrations of 3, 12, and 20 gr/lit.
176 The experiment was started by taking 50 mL samples at a given point in the centreline of the flume in different
177 times. According to Mahdavi et al. (2013), the sorption process were kinetically investigated by taking the
178 samples in different times of 0, 1, 2, 5, 10, 15, 30, 45, 60, 90, 120, 180, 240, and 300 min. The amount of
179 adsorbed cadmium at each time (q) is calculated, as follows:

$$180 \quad q = \frac{(C_0 - C)V}{W} \quad (2)$$

181 where, C₀ is the initial cadmium concentration (t = 0) and C is the cadmium concentration at different
182 times (ppb), V is the volume of the water (130 lit), and W is the weight of the sediments (gr). For the kinetic
183 modeling, a pseudo second order equation is used (Ho and McKay 1999; Azizian 2004; and Mahdavi et al.
184 2013), as follows:

$$185 \quad \frac{\partial q}{\partial t} = k_2(q_e - q)^2 \quad (3)$$

186 where, k₂ is the second order rate coefficient and q_e is the equilibrium adsorbed cadmium. Integrating this
187 equation for the boundary conditions of t = 0 to t = t and q = 0 to q = q, gives:

$$188 \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

189 The sorption experiments with different initial cadmium concentrations are used in order to determine the
190 best kinetic equation and to estimate the sorption parameters k₂ and q_e. In order to estimate the kinetic sorption
191 parameters, there are two methods (Mahdavi et al. 2013). The first method is applying the least square method
192 to the linear transformed kinetic model (Eqs. 3 and 4). However, Jiang et al. (2007) and Ho (2006) showed that

193 it is better to use non-linear least square method for the original non-linear equation. Therefore, in this study,
194 both methods are used and compared.

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

210

211 Table 1. Conducted experiments and experimental conditions

212

213 Numerical Modeling

214 Apollo and Postman (1993)'s method was used to solve Eq. (1), numerically. Indeed, the advantage of
215 this procedure is that the different expressions of advection, dispersion, and absorption are individually solved at
216 each step. In other word, at a certain time step, the effect of the advection on the cells is first applied. Then, the
217 effect of the dispersion is calculated in each cell; after that on the resulting cells from advection and dispersion
218 expressions the effect of the absorption will be applied. The advantage of this method is that one can easily add
219 other chemical or physical formulas to the model. In addition, each process can be solved with the most
220 appropriate numerical method.

221

222

Figure 1. ABOUT HERE.

223

224 **Results and Discussion**

225 **Results of Sorption Experiment**

226 In this study, the advection and dispersion of cadmium ion at the presence of river bed sediments were
227 investigated. As mentioned before, the sorption characteristics of the river sediments were first investigated. In
228 addition, the kinetic sorption was investigated in several steps. The overall results of these experiments showed
229 that for most sorption processes, the cadmium sorption rate by bed sediments consists of three phases: the first
230 phase (rapid absorption), the second phase (transition) and the third phase (almost flat) (Fig. 2).

231

232 Figure 2. ABOUT HERE.

233

234 Figure 3 shows the effect of sediment concentration on the cadmium sorption rate for initial cadmium
235 concentrations of 150, 460 and 770 ppb. As can be seen, by increasing sediment concentrations, the absorbed
236 cadmium per unit weight of sediment is reduced. According to this figure, with increasing sediment
237 concentrations from 3 to 20 g/lit, the equilibrium adsorbed cadmium per unit weight of sediment (1 gr) is
238 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
239 highest sediment concentration (20 gr/lit), it can be said that by increasing the sediment concentrations, the
240 sorption percentage increases. In these experiments, by increasing the sediment concentrations, the cadmium
241 removal percentage increased from 50 to 78.15% (for Cd concentration of 150 ppb) from 47.27 to 84.9% (for
242 the concentration of 460 ppb) and from 41 to 80.21% (for Cd concentration of 770 ppb). In other words, it can
243 be concluded that by increasing the sediment concentrations in the solution and because of competition between
244 sediments, the contribution of each gram of sediment in the solution decreases, however, the total absorbed
245 cadmium increases.

246

247 Figure 3. ABOUT HERE.

248

249 The following explanations can be expressed for these changes: 1) at the initial stage of adsorption
250 process, the sediment surface provided more adsorption sites, which contributed to rapidly increased adsorption
251 rate. Due to the negative-charged surface of sediments, it could combine with metal cations through Coulomb
252 force, and this process could be considered as pseudo-adsorption. 2) specific adsorption happened through

253 chemical reaction between Cd(II) and sediment surface was followed. However, it would change the property of
254 surface electric charge. Increased positive sites would prevent the adsorption of Cd(II); and 3) available sorption
255 sites became limiting factor along with increasing adsorption amount. (González Costa et al., 2017;
256 Markiewicz-Patkowska et al., 2005; Vibhawari et al., 2010, Huang et al., 2019). The results of Jain and Ram
257 (1997), Jain and Sharma (2002), Ho (2003 and 2006), Mahdavi et al. (2008) are consistent with the results of the
258 present study.

259

260 Table 2. Results of calculations of sorption parameters.

261

262 **Results of Dispersion Experiments**

263 In order to estimate the longitudinal dispersion coefficient and investigate the effect of cadmium sorption
264 by river bed sediments on this coefficient, some experiments were performed. The results of these experiments
265 are used for calibration and validation of the numerical model. These experiments were performed in three
266 sediment concentrations of 3, 12, and 20 gr/lit as well as sediment-free conditions (control experiment; $C_s = 0$).
267 The results of dispersion experiments for runs No. AD05 and AD08 ($C_s = 0$) and at the presence of bed
268 sediment with a concentration of 20 gr/lit and cadmium concentration of 460 ppb is shown in Fig. 4. As can be
269 seen, the presence of sediments has two major effects on time distribution curve of concentration cadmium.
270 First, due to the cadmium sorption by sediments, the peak values have decreased relative to the sediment-free
271 state. Second, the difference between the minimum and maximum values of each peak has increased.

272

273 Figure 4. ABOUT HERE.

274

275 As mentioned before, one-dimensional advection-dispersion equation (Eq. 1) is used for description of
276 heavy metal transport in the dissolved phase. In this study, the splitting operator method (Appelo and Postma
277 (1995)'s method) was applied to numerically solve Eq. 1.

278 According to Fig. 5, in a circular flume, cell 1 is located next to the last cell (cell n). Therefore, its value
279 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,
280 n-1 and n.

281

282 Figure 5. ABOUT HERE.

283

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

$$286 \begin{cases} C = 0 \\ C = C_{in} \end{cases} \quad \text{for } t = 0 \text{ and } \forall x \quad (5)$$

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

$$289 C_0 = C_L \quad \text{for } \forall t \quad (6)$$

290 In order to estimate the longitudinal dispersion coefficient without sediments and at the presences of
291 sediments with different concentrations, a numerical model was developed in MATLAB and calibrated by
292 experimental data. Therefore, the model was run for different flow velocities and dispersion coefficients and the
293 best coefficient was selected after comparing with the experimental data and calculating Sum of squared error
294 (SSE).

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

297

298 Figure 6. ABOUT HERE.

299

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

307

308 Figure 7. ABOUT HERE.

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

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Figure 8. ABOUT HERE

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:

$$A_R = \frac{C_0 - C_{50}}{t_{50}} \tag{7}$$

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 $\mu\text{g/lit}$, respectively.

In column 6 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 range of this parameter is 0.041-0.067, 0.041-0.065, 0.04-0.058 m for cadmium concentrations of 150, 460, and 770 ppb, respectively.

Table 3. ABOUT HERE

The variations in the longitudinal dispersion coefficient (D_L) are plotted against the absorption ratio (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 it is 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 9. ABOUT HERE

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

$$344 \frac{D_L}{Vh} = 16.05(1.02 + e^{-0.001A_R}) \quad (8)$$

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

350

351 **Conclusions**

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

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368 **Ethics approval**

369 Not applicable

370

371 **Consent to participate**

372 Not applicable

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374 **Consent to Publish**

375 Not applicable

376

377 **Authors Contributions**

378 Mohsen Nasrabadi, as former PhD Candidate, performed the experiments and analyzed and interpreted
379 the data and he was a major contributor in writing the manuscript. Ali Mahdavi Mazdeh is the co-supervisor of
380 this PhD thesis, and Mohammad H. Omid is the main supervisor of this PhD thesis. All authors read and
381 approved the final manuscript.

382

383 **Funding**

384 There is no funding sources for the research reported

385

386 **Competing Interests**

387 The authors declare that they have no competing interests.

388

389 **Data Availability**

390 Some or all data, models, or code that support the findings of this study are available from the
391 corresponding author upon reasonable request.

392

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497 **Figure Captions**

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Figures

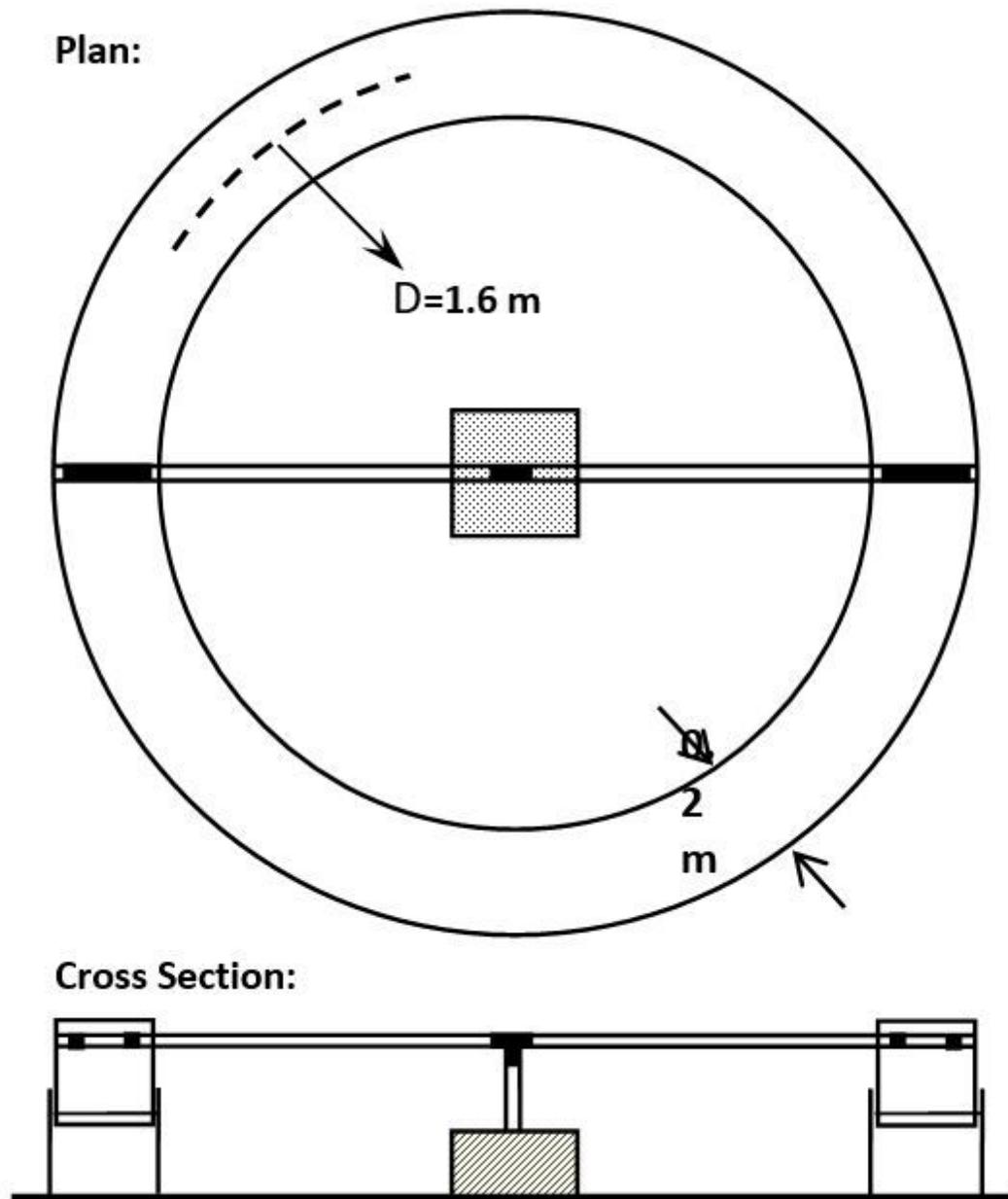


Figure 1

Plan and cross section of the circular flume

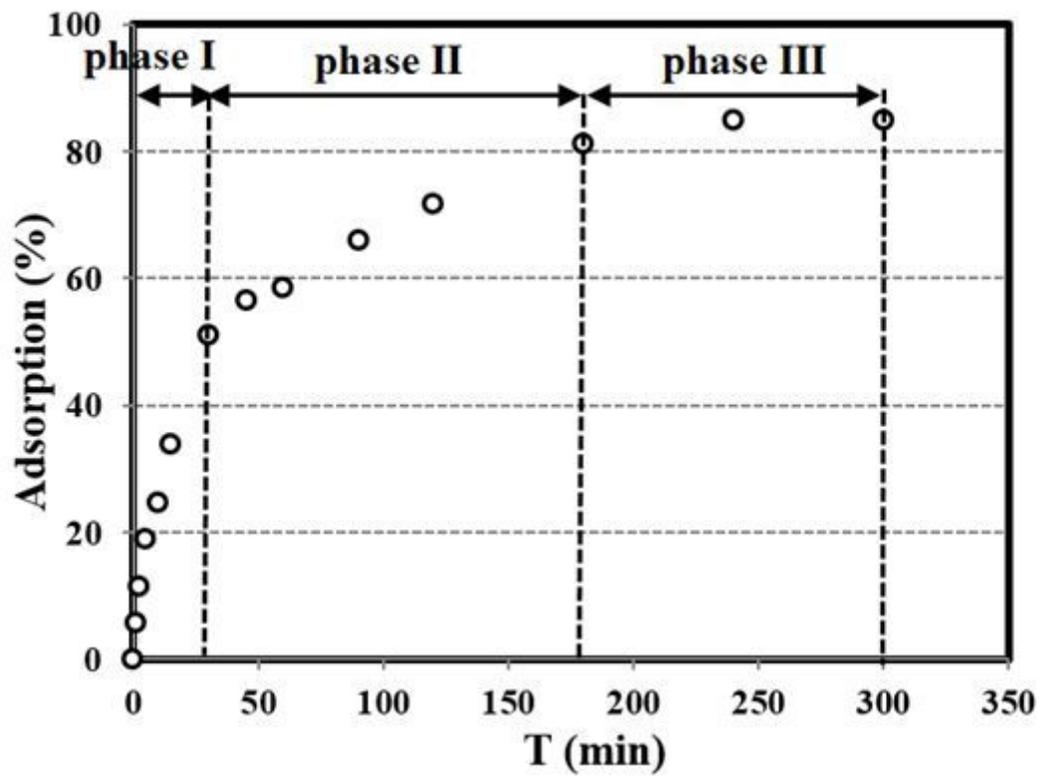


Figure 2

Different phases of the cadmium sorption.

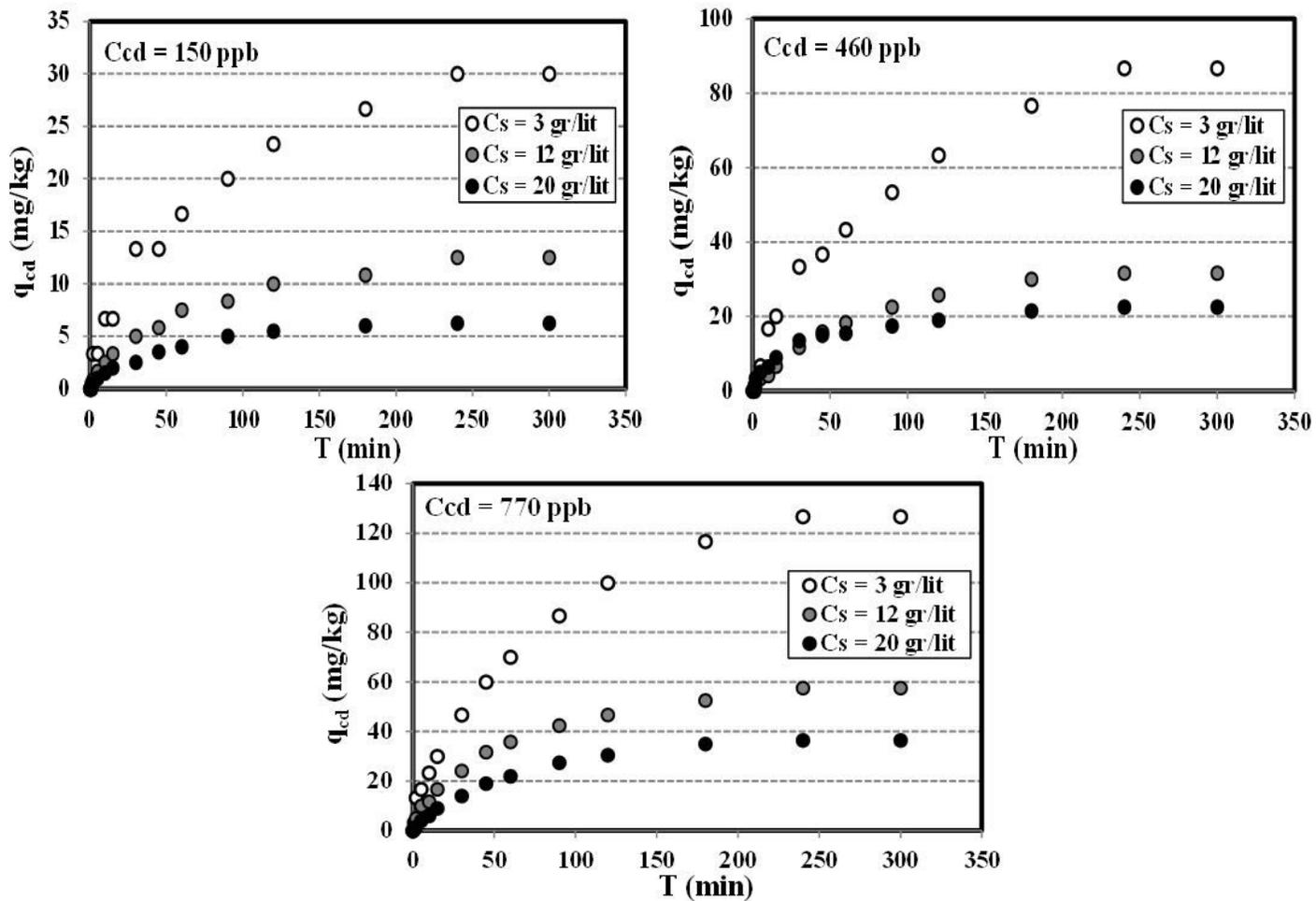


Figure 3

The effect of sediment concentration on the cadmium sorption

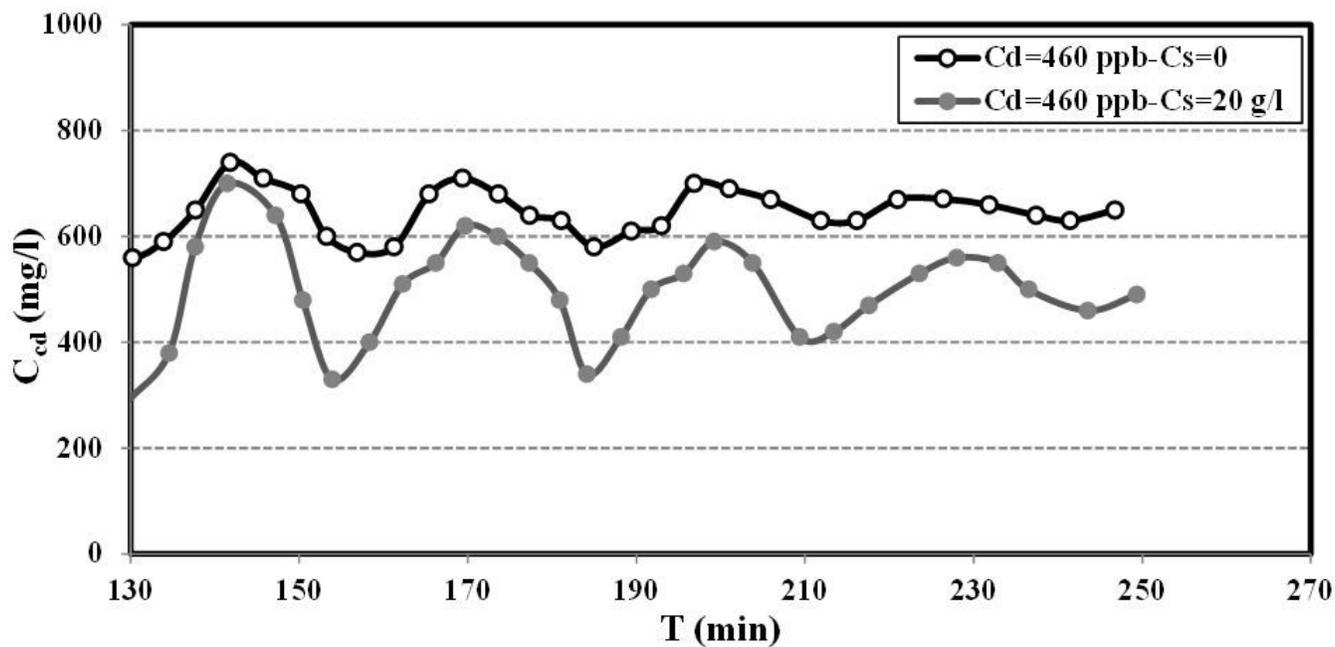


Figure 4

Time distribution of cadmium concentration (ppb 460) without and with sediment concentration of 20 g/lit.

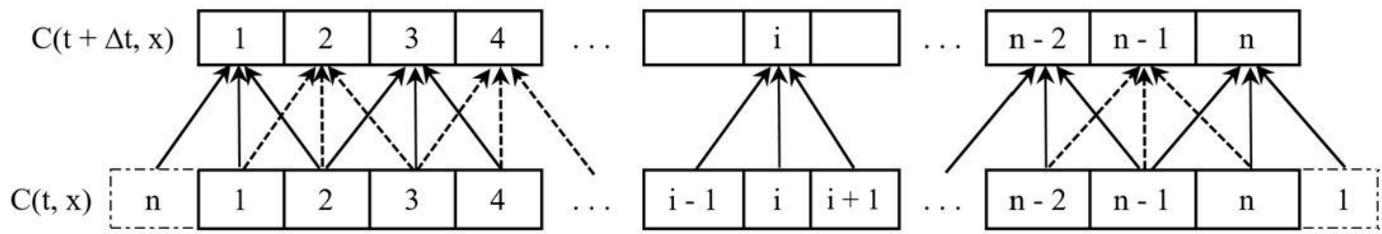


Figure 5

General Scheme for Numerical Modeling

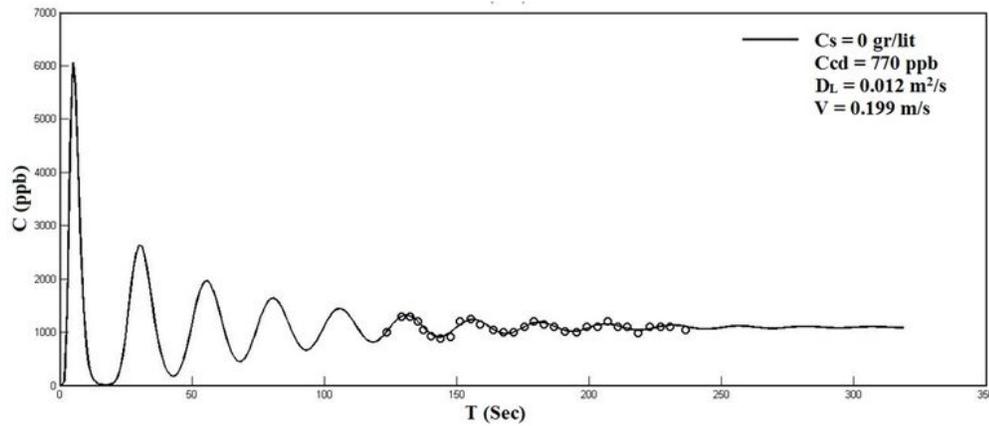
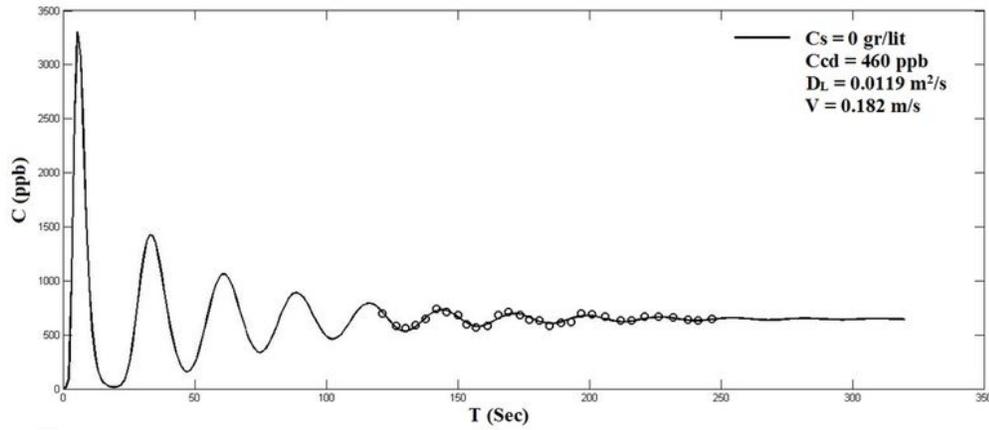
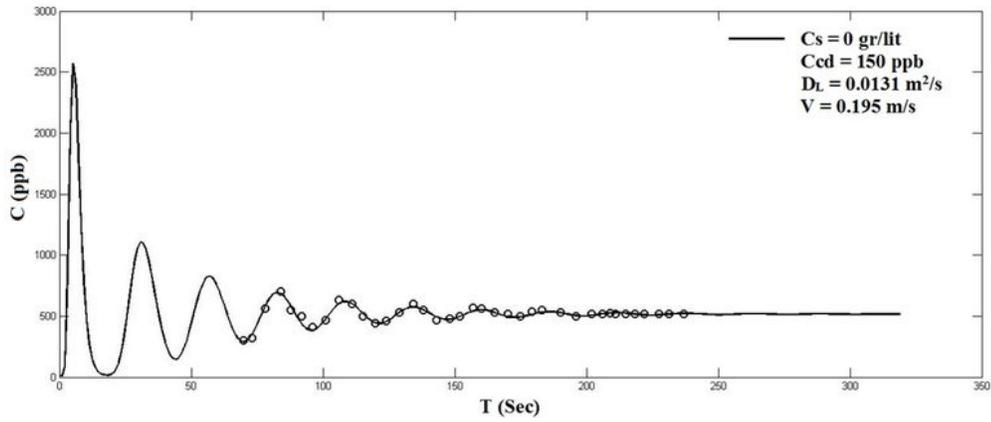


Figure 6

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

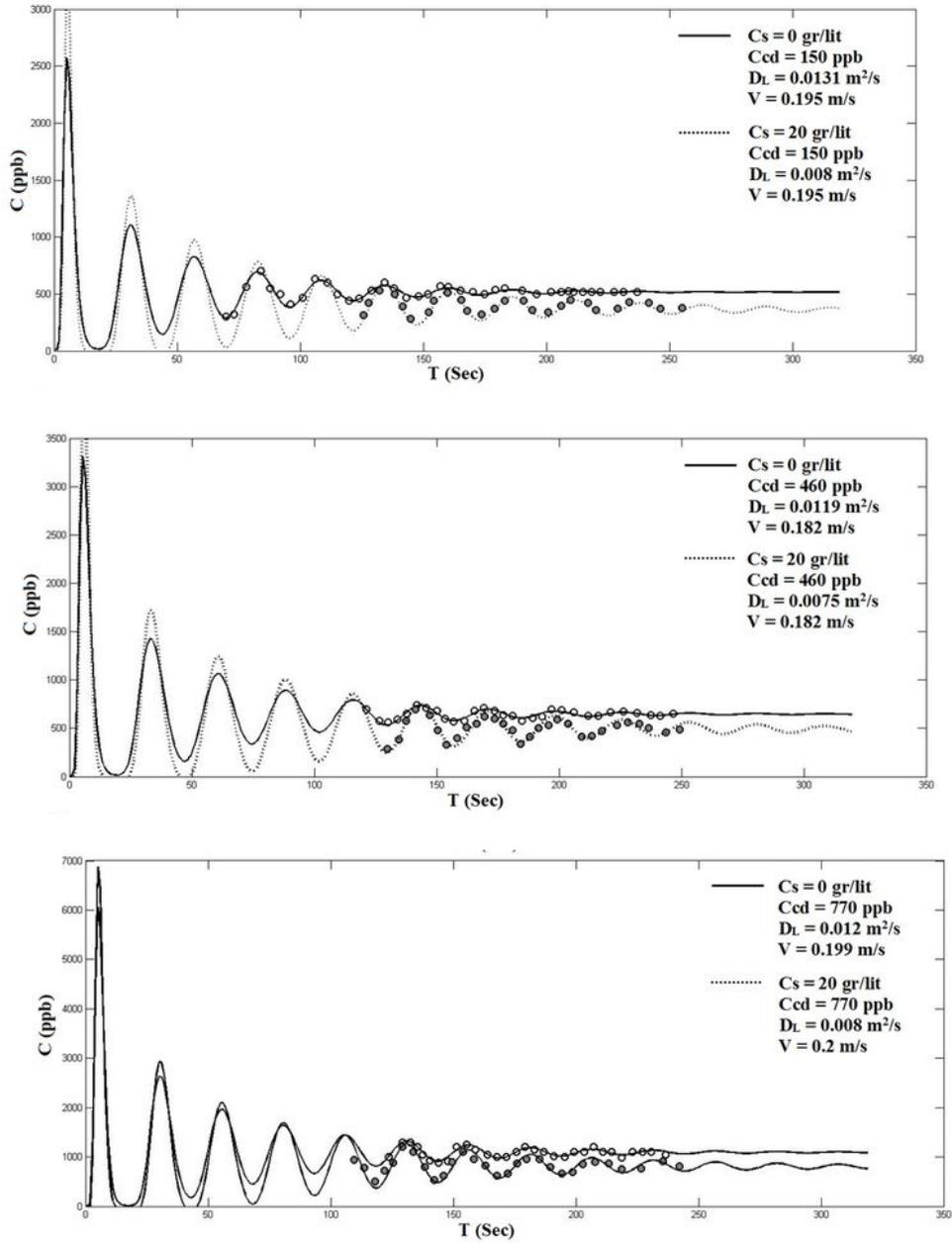


Figure 7

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

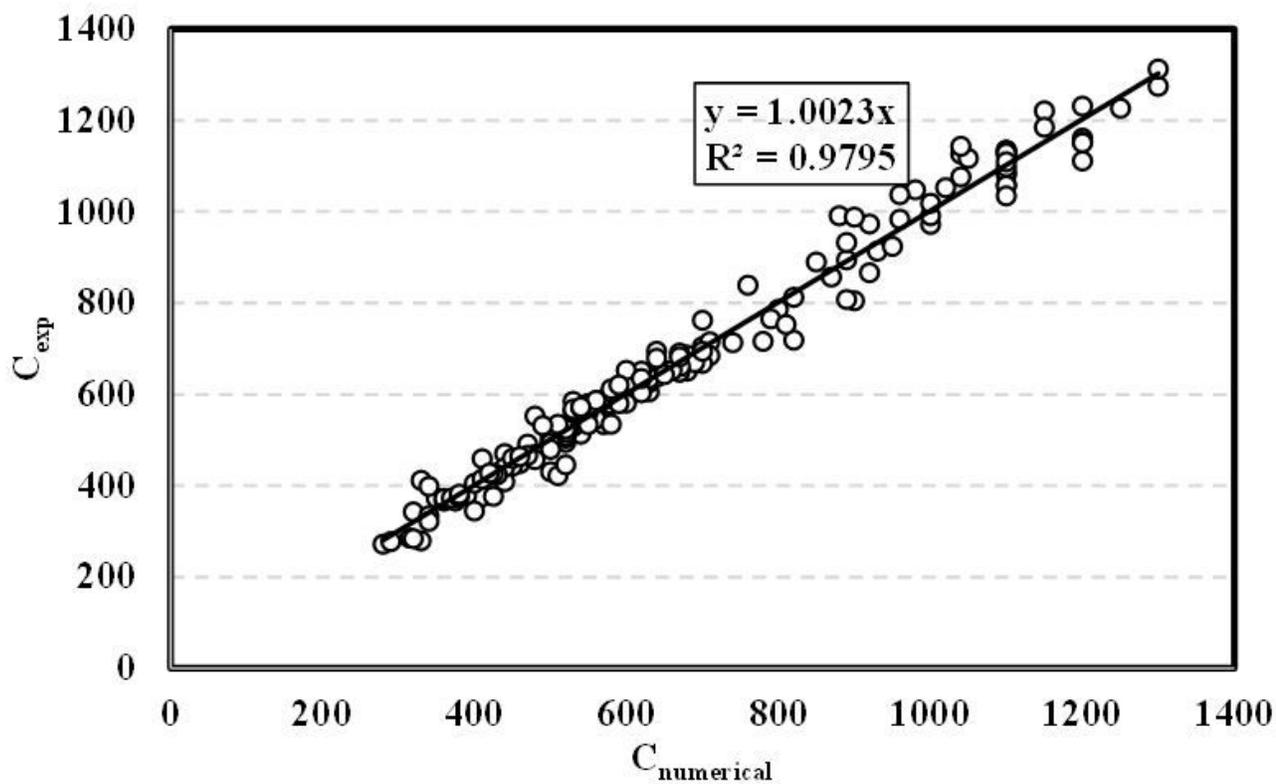


Figure 8

Measured data versus numerical modeling

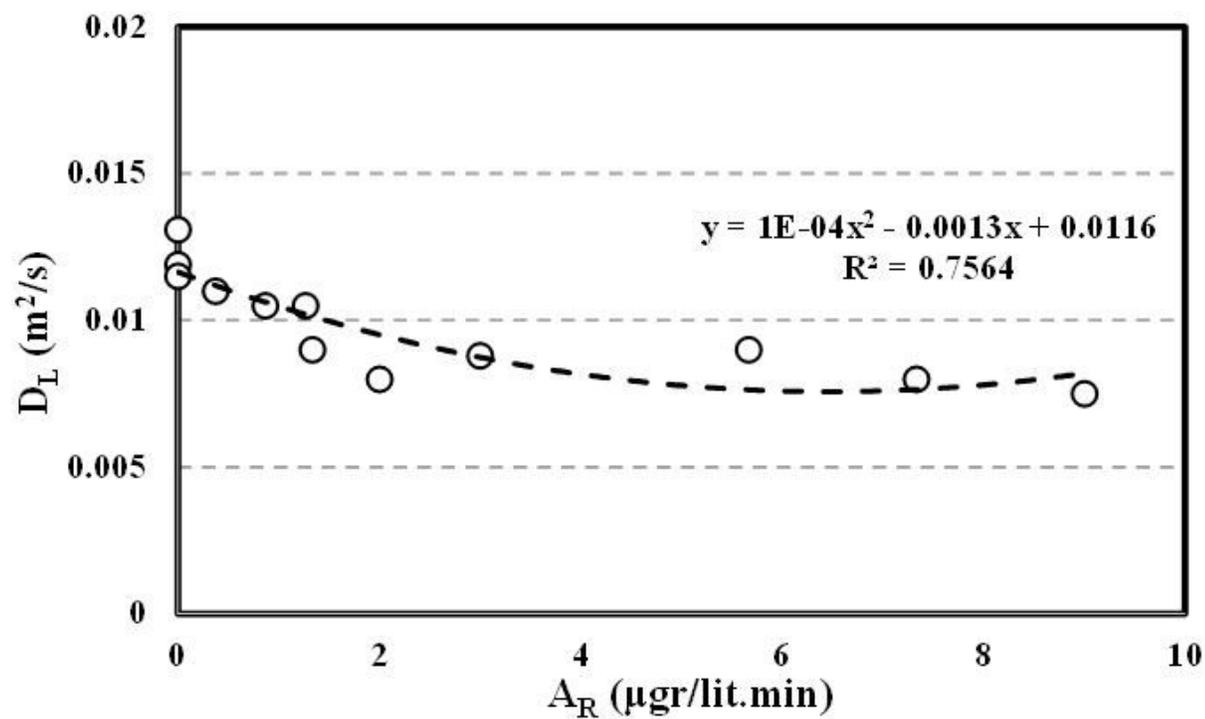


Figure 9

Changes in longitudinal dispersion coefficient of cadmium versus sorption ratio.