

## Numerical modelling of heavy metals for riverine systems using a new approach to the source term in the ADE

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### ABSTRACT

This paper describes a modelling study of dissolved heavy metals in riverine systems, undertaken to introduce a new approach of the varied reaction coefficients used in the Advection–Dispersion Equation (ADE). The dissolved heavy metals, i.e. lead and cadmium, were modelled using a 1D hydro-environmental model. It is found that pH and EC play an essential role in adsorption and desorption of heavy metals by the particles in solution. Therefore, in this study we have tried to find the best relationships between pH and EC with the reaction coefficient. Relatively close agreement between predicted results and field-measured dissolved lead and cadmium concentrations were obtained for different varied reaction coefficients. Finally, the best relationships for the reaction coefficients for dissolved lead and cadmium were introduced and the results were successfully compared with the corresponding measured values.

**Key words** | advection–dispersion equation, dissolved heavy metals modelling, reaction coefficient, river pollution, water quality modelling

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### NOMENCLATURE

ADE	Advection–Dispersion Equation
FASTER	Flow And Solute Transport in Estuaries and Rivers
ULTIMATE QUICKEST	Universal Limiter Transient Interpolation Modelling for Advection Term Equation – Quadratic Upstream Interpolation for Convective Kinematics with Estimated Streaming Terms
$T$	top width of the channel
$\xi$	water elevation above (or under) datum
$Q$	discharge
$\beta$	momentum correlation factor due to non-uniform velocity over the cross section
$A$	wetted cross-sectional area
$R$	$A/P =$ hydraulic radius

$P$	wetted parameter of the cross section
$c_z$	Chezy coefficient
$g$	acceleration due to gravity
$x, t$	river flow direction and time, respectively
$C$	area's average dissolved heavy metal concentration
$D_x$	longitudinal dispersion coefficient
$S_t^d$	transformation term defining absorbed and desorbed particulate fluxes to or from sediments (source and sink term or rate of reaction)
$S_0^d$	source of dissolved heavy metal from lateral inflow or outflow
$Q_L$	lateral inflow or outflow discharge
$C_L$	lateral inflow or outflow dissolved heavy metal concentration
$\Delta x$	distance between two consecutive cross sections which can be either constant or variable

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$t$	time
$H$	averaged depth over the cross section
$U$	cross-sectional average velocity
$U_*$	local shear velocity
$\kappa$	the rate of reaction coefficient
$\kappa_{20}$	reaction coefficient at 20°C
TEMP	temperature of water
$O$	temperature coefficient
pH	the mean pH of the river at the site for each time
EC	electrical conductivity: the mean EC of the river at the site for each time ( $\mu\Omega^{-1}/\text{cm}$ )

## INTRODUCTION

In recent years there has been growing international public concern and an increased awareness of riverine pollution problems, particularly with regard to water pollution (Falconer & Lin 2003). Human and aquatic life is often threatened by the transport of pollutants through riverine systems to coastal waters and it is therefore not surprising to find that, from a water quality point of view, rivers have been studied very extensively and for longer than any other water bodies (Thomann & Mueller 1987). This is probably due to the fact that people live close to, or interact with, rivers and streams. Many rivers and estuaries have suffered environmental damage due to discharges from manufacturing processes and wastewater from centres of pollution over several decades. In recent years these environmental concerns have made the development of computer models that predict the dispersion of pollutants in natural water systems more urgent. The main attraction of such models, in contrast with physical models, is their low cost and their ease of adaptability to new situations. Thus the widespread popularity of mathematical modelling techniques for the hydrodynamic and pollutant transport in rivers justifies any attempt to develop new models based on novel and rigorous approaches (Nassehi & Bikangaga 1993).

For modelling dissolved heavy metal transport in rivers, a good understanding of the phenomenon is necessary. Heavy metals generally exist in two phases in river waters, i.e. in the dissolved phase in the water column and in the particulate phase adsorbed on the sediments. The behaviour of heavy metals in the aquatic environment is strongly influenced by

adsorption on organic and inorganic particles. The dissolved fraction of heavy metals may be transported via the process of advection–dispersion (Wu *et al.* 2005). These pollutants are non-conservative in nature and their concentrations depend on salinity and pH, which may vary with time and along a river. As a result, the dissolved metal may come out of solution or even redissolve, depending on conditions along the time or channel (Nassehi & Bikangaga 1993). Figure 1 illustrates the dissolved heavy metal transport process in a riverine system. In many studies (such as Nassehi & Bikangaga (1993), Shrestha & Orlob (1996), Wu *et al.* (2001, 2005), etc.) the researchers assumed a constant reaction coefficient with time, whereas in the field this coefficient may vary according to the rate of pH, salinity, temperature or even other chemical substances and other hydraulic characteristics of the river.

Numerical models provide a valuable tool for predicting the fate and transport of dissolved heavy metals in river environments and are increasingly used for such hydro-environmental management studies of river waters. However, computer-based tools used for predicting such heavy metal concentrations are still used infrequently, even though they can support decision-making by the regulatory authorities, marine environment agencies and industry (Ng *et al.* 1996).

## OBJECTIVES OF THIS STUDY

Based on the effect of different substances such as pH and salinity on dissolved heavy metal concentrations in rivers, the necessity of heavy metal modelling with more accuracy

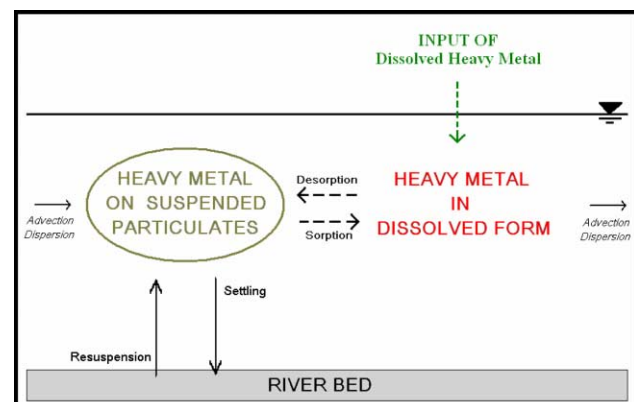


Figure 1 | Schematic illustration of dissolved heavy metal process in riverine waters.

in predicting the concentration is inevitable. Therefore the general objective of the research described in this paper is to provide a methodology predicting a varying reaction coefficient for dissolved lead and cadmium heavy metals using pH and EC (as a function of salinity) which affects the reaction coefficient in the ADE for improved accuracy.

This paper gives details of the development of a modelling approach for predicting dissolved heavy metal fluxes (lead and cadmium) and the application of the model to the Karoon River, located in the south west of Iran. The model was calibrated and verified against field-measured time series data for discharges, water levels and dissolved lead and cadmium heavy metal concentrations.

## MATHEMATICAL MODEL DETAILS

Any numerical model used to predict the flow and dissolved heavy metal transport processes in rivers depends primarily on solving the governing hydro-environmental equations. In most riverine systems, the basin is regarded as a 1D system, with longitudinal flow dominating throughout the system. The governing equations are as follows.

### For flow modelling

The one-dimensional governing hydrodynamic equations describing flow and water elevations in rivers are based on the St. Venant equations, applicable to 1D unsteady open-channel flows. The most widely used form of these equations, in practice, are generally written as (Cunge et al. 1980)

$$T \frac{\partial \xi}{\partial t} + \frac{\partial Q}{\partial x} = 0 \quad \text{continuity equation} \quad (1)$$

$$\underbrace{\frac{\partial Q}{\partial t}}_1 + \beta \underbrace{\frac{\partial}{\partial x} \left( \frac{Q^2}{A} \right)}_2 + \underbrace{gA \frac{\partial \xi}{\partial x}}_3 + \underbrace{g \frac{Q|Q|}{c_z^2 AR}}_4 = 0 \quad (2)$$

momentum equation

The individual terms in the momentum equation refer to: (1) local acceleration, (2) advective acceleration, (3)

pressure gradient and (4) bed resistance. Equations (1) and (2) are solved numerically to provide the varying values of discharge and water elevations at any point and time.

### For dissolved heavy metals modelling

The transport of heavy metals in the dissolved phase can be described by the following one-dimensional advection–dispersion Equation (ADE) (Kashefipour 2002):

$$\underbrace{\frac{\partial CA}{\partial t}}_1 + \underbrace{\frac{\partial CQ}{\partial x}}_2 - \underbrace{\frac{\partial}{\partial x} \left[ AD_x \frac{\partial C}{\partial x} \right]}_3 = \underbrace{S_0^d}_4 + \underbrace{S_t^d}_5 \quad (3)$$

The individual terms in the advection–dispersion equation refer to: (1) local effects, (2) transport by advection, (3) longitudinal dispersion and turbulent diffusion, (4) sources of dissolved heavy metals through lateral inflow and outflow and (5) transformation term defining absorbed and desorbed particulate fluxes to or from sediments (source term or rate of reaction).  $S_0^d$  can be defined as

$$S_0^d = \frac{Q_L C_L}{\Delta x} \quad (4)$$

The longitudinal dispersion coefficient in natural rivers is dependent upon many hydrodynamic parameters including depth, width, velocity and shear stress (Fischer et al. 1979). In this paper the Kashefipour & Falconer (2002) relationship for the longitudinal dispersion coefficient has been used. This coefficient was based on applying the dimensional analysis procedure to more than 80 datasets in 30 natural rivers in the USA and the most accurate relationship for estimating the longitudinal dispersion coefficient was found to be of the following form:

$$D_x = \left[ 7.428 + 1.775 \left( \frac{T}{H} \right)^{0.620} \left( \frac{U_*}{U} \right)^{0.572} \right] HU \left( \frac{U}{U_*} \right) \quad (5)$$

In addition Tavakolizadeh (2006) used this dispersion coefficient for water quality modelling in the Karoon River and achieved acceptable results for different water quality parameters using this coefficient.

## MODEL DEVELOPMENT

The main part of the ADE is the transformation term defining absorbed and desorbed particulate fluxes to or from sediments ( $S_t^d$ ). For water bodies close to outfalls the conditions are not generally consistent with equilibrium conditions. For equilibrium conditions it can be assumed that the parameter  $S_t^d$  in Equation (3) is equal to zero. On the other hand, no source or sink term is assumed. A review of the literature has shown that many researchers include this type of assumption in their models, such as Wu *et al.* (2005). However, another group of researches, for example Nassehi & Bikangaga (1993), assumed a reaction term having a form of Equation (6) with a constant coefficient.

In recent years much effort has been focused on correlating the partitioning rate of heavy metals in the particulate and dissolved phases to several environmental factors and water properties. This relation was always a problem for heavy metals modelling due to the complexity of the phenomenon and the amount of measured data. Since the dissolved heavy metals in solution can be transported, and this may produce much damage to the environment, it seems to be better to only model this part of the heavy metals concentrations. Therefore, for heavy metals entrainment and going out of solution can be defined as a first-order reaction equation. This idea was first applied by Nassehi & Bikangaga (1993) with a constant reaction coefficient. In this research new reaction coefficients for dissolved lead and cadmium modelling are introduced due to pH and EC changes in the water column. The key point is that the chemical characteristics of the flow, such as pH and EC, can affect the sorption and desorption of the dissolved heavy metals to or from the sediments, and these characteristics can have an important effect on the dissolved heavy metal concentrations. Therefore, for more accurate heavy metal modelling, a varying reaction coefficients has been suggested in this paper, linking these chemical parameters to the kinetic processes. The first-order reaction equation may be defined as

$$S_t^d = -\kappa CA \quad (6)$$

where  $\kappa$  is the reaction coefficient rate, which may have a positive or negative value as the dissolved heavy metals

disappear or accumulate in a given river section. The reaction coefficient can be affected by several environmental factors such as temperature, pH, salinity, etc. Therefore,  $\kappa$  can be defined as

$$\kappa = f(\text{pH, Salinity, Temperature, ...}) \quad (7)$$

The  $\kappa$  value may be related to temperature as given by the following Equation (see Orlob 1983):

$$\kappa = \kappa_{20} \times O^{(\text{TEMP}-20)} \quad (8)$$

where the temperature coefficient ( $O$  in Equation (8)) may vary from 1.047 to 1.135. Based on the different characteristics of each heavy metal (such as lead, cadmium, etc.) the varying reaction coefficient should be computed and the corresponding relation of the reaction coefficient should be used separately for each metal. Kashefipour *et al.* (2006) showed that the accuracy of the predicted faecal indicator concentrations were significantly increased when they applied a time series varying decay equation instead of a constant coefficient.

In the current study, effort was focused on finding suitable functions to represent the reaction coefficient rate for dissolved lead and cadmium in rivers. In calibrating the model against measured dissolved lead and cadmium data, five approaches for each dissolved metal were used: (i) no rate of reaction for dissolved heavy metal (used by some researchers for equilibrium conditions), (ii) a constant reaction coefficient for the rate of reaction during the whole simulation time, (iii) a time-varying reaction coefficient for the rate of the reaction, using pH as a variable, (iv) a time-varying reaction coefficient for the rate of the reaction, using EC as a variable, and (v) a time-varying reaction coefficient for the rate of the reaction, using both pH and EC variables. For the first approach (case (i)) the reaction coefficient ( $\kappa$ ) was set to zero, and to find an appropriate constant  $\kappa$  (case (ii)) a number of simulation calibration runs were carried out and the initial reaction coefficient was subsequently adjusted by comparing the predicted dissolved lead or cadmium concentrations with the corresponding measured values for the whole simulation time. The appropriate constant  $\kappa$  was chosen for the best fit curve between both series of data values.

For the other approaches (cases (iii)–(v)) the procedure was as follows:

1. For each measured value of lead or cadmium a number of calibration runs were carried out and the initial  $\kappa$  value was subsequently adjusted until the predicted and measured heavy metal concentrations at an appropriate time and site were exactly equal, without considering the other measured values.
2. This procedure was separately done for all of the measured heavy metals concentration values.
3. At any time of measuring data, the appropriate  $\kappa$  value was specified according to the above two stages and it was therefore possible to correlate these values to the corresponding measured pH and EC values to find the best equations describing the relationships between  $\kappa$  and pH and/or EC.
4. The obtained relationships were then added to the water quality module of the model as a part of the numerical solution of the ADE.

For all approaches the model was then verified with another set of measured lead or cadmium data at the site.

## FIELD DATA COLLECTION

The Karoon River is the largest and only navigable river in the south west of Iran (see [Figure 2\(a\)](#)). In this study the Mollasani–Farsiat reach of the Karoon River, a distance of 110 km was selected due to the high amount of heavy metal concentrations along this reach (see [Figure 2\(b\)](#)). The Karoon River basin has a network of gauging stations (see [Figure 2\(b\)](#)) and there are several effluent inputs to the river between gauging stations at Mollasani and Farsiat, including industrial units such as piping, steel, paint making, agriculture, paper mills, fish cultivation and power plant industries draining from wastewater works into the river (see [Figure 2\(c\)](#)) ([Diagomanolin \*et al.\* 2004](#)).

Hydrodynamic and water quality data were acquired via the Khuzestan Water and Power Authorities (KWPA). A set of six field-measured data were available from March 2004, including discharge and water levels measurements at the Mollasani, Ahwaz and Farsiat gauging stations and pH, EC, dissolved lead and cadmium concentrations at the

Mollasani and Shekare gauging stations (see [Figure 2\(c\)](#)). Also, concentrations of dissolved lead and cadmium were measured from more than 15 outfalls and industrial locations along this reach. A number of 113 cross sections were used as the initial topology inputs of the model for the river. Cross sections nos.1, 36, 49 and 113 corresponded to the cross sections at the gauging stations of Farsiat, Shekare, Ahwaz and Mollasani, respectively.

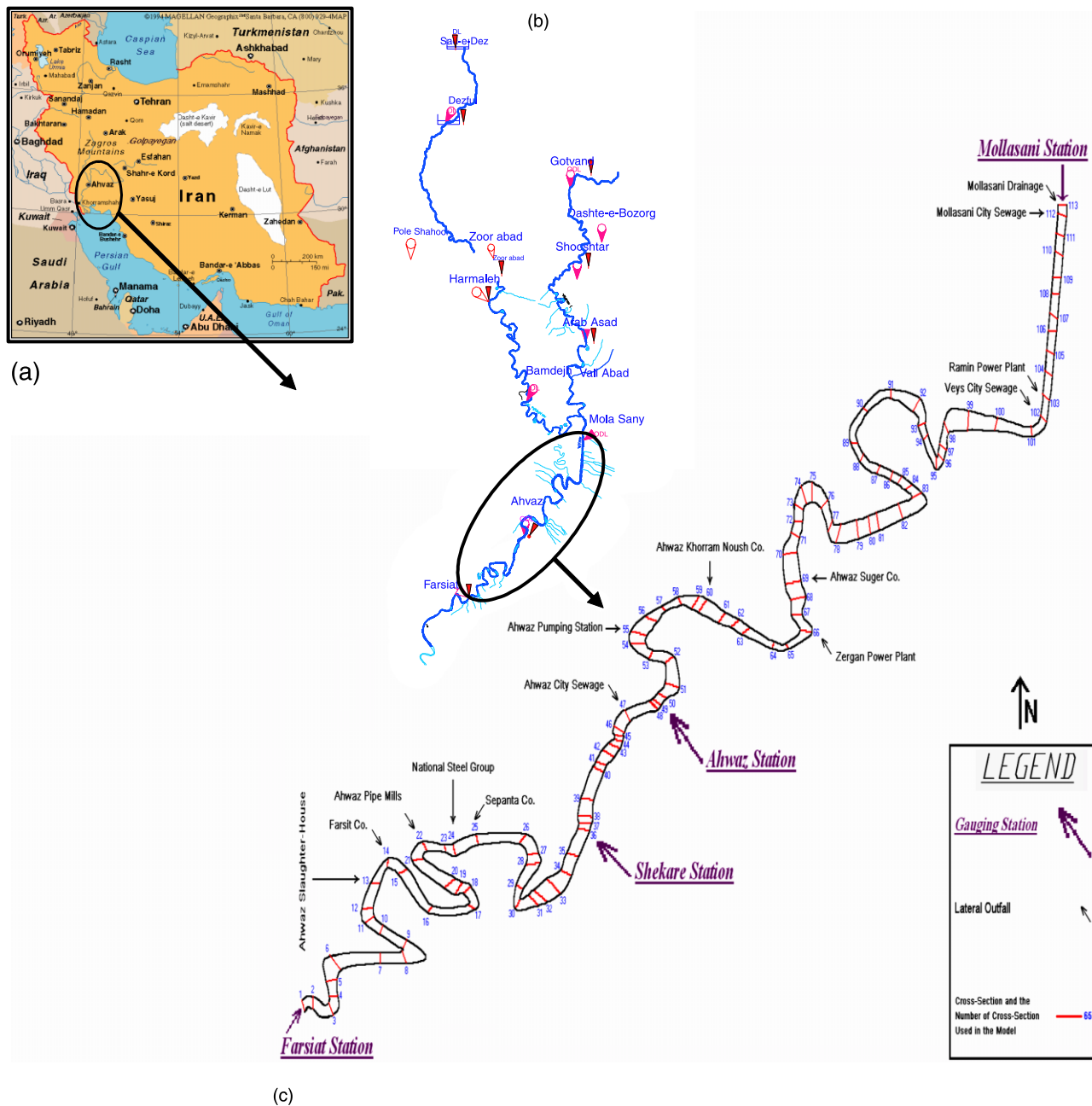
## MODEL SET-UP

The numerical FASTER model was set up to simulate the flow field and dissolved lead and cadmium concentrations in the Karoon River between the Mollasani and Farsiat stations. The water elevations recorded at the Farsiat hydrometric station were chosen as the downstream boundary and the measured discharges and heavy metal concentrations at the Mollasani station were used as the upstream boundary conditions for flow and water quality modules of the main model.

The 1D grid, covering the region from Mollasani to Farsiat, was represented using 113 segments, with extensive bathymetric data at each cross section being collected during the most recent bathymetric survey conducted by KWPA in 2000.

## Hydrodynamic model results

The hydrodynamic module of the FASTER model was calibrated against the data provided for 2003 and 2004. The main hydrodynamic parameter used for calibration was the Manning roughness coefficient. The river was separated into four parts, with the Manning coefficient being varied from 0.026–0.050. Good agreement was obtained between the predicted water levels and field data at the Ahwaz gauging station, with a difference in results being less than 3% (see [Figure 3\(a\)](#)) and also the model discharges agreed well with the field data obtained at the Ahwaz gauging station, with the difference being less than 16% (see [Figure 3\(b\)](#)). The hydrodynamic module was then validated using another series of measured data (see [Figure 4](#)). As can be seen from this figure the predicted data also gave relatively good correlation with the corresponding measured values. A summary of the statistical analysis of the model results is illustrated in [Table 1](#).

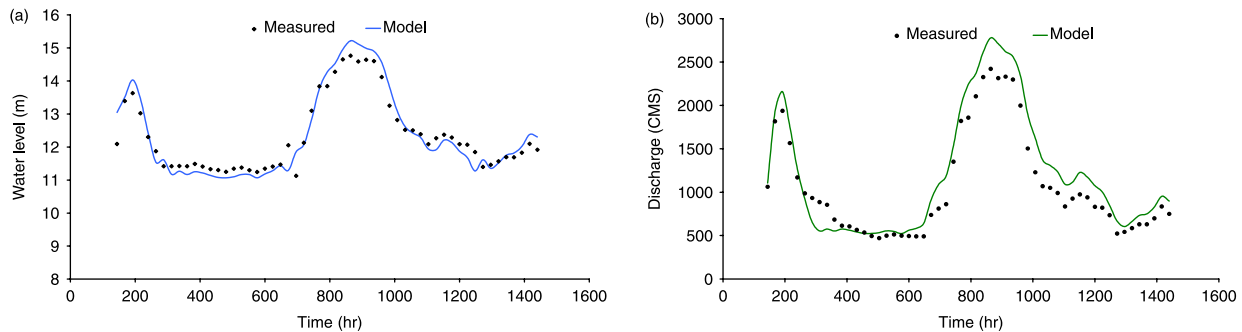


**Figure 2** | (a) Location of the Karoon River, (b) the Karoon River network and gauging stations and (c) outfalls, the gauging stations of Karoon River and the cross sections used in the model between Mollasani and Farsiat.

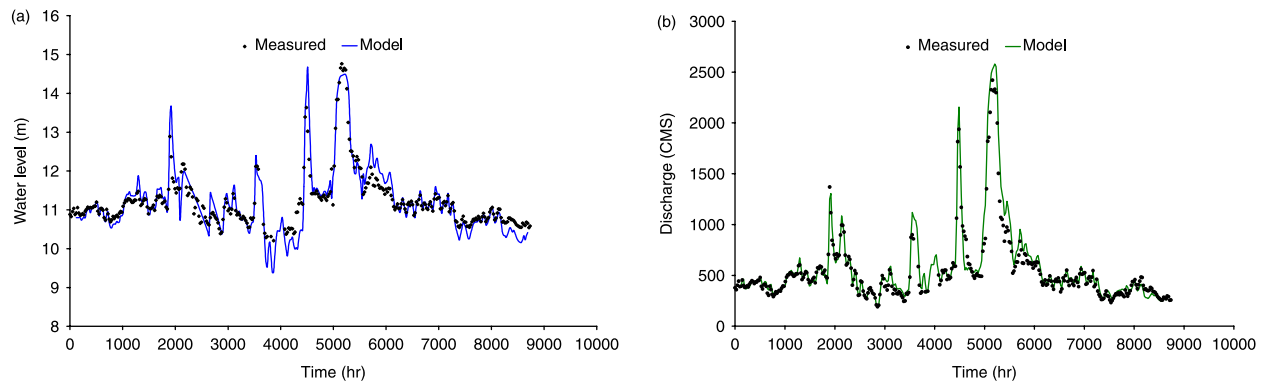
### Dissolved heavy metal model results

The rate of reaction coefficient plays an important role in accurately predicting the concentration distribution of the dissolved heavy metals for river, estuarine and coastal waters. As was mentioned, in this study five different approaches were used to estimate the reaction coefficients for simulating the

dissolved lead and cadmium concentrations. The measured lead and cadmium concentration values in the Shekareh gauging station (see Figure 2) were used to calibrate and generate appropriate functions between reaction coefficient and pH and/or EC. Another set of data in this gauging station was applied to verify the model.



**Figure 3** | (a) Comparison of water levels with the corresponding measured data for model calibration. (b) Comparison of discharges with the corresponding measured data for model calibration.



**Figure 4** | (a) Comparison of water levels with the corresponding measured data for model verification. (b) Comparison of discharges with the corresponding measured data for model verification.

### Dissolved lead model results

For the first run a conservative dissolved lead value was assumed, leading to a zero value for the rate of reaction coefficient. The fit between the predicted and measured data showed 25.2% and 33.3% errors for calibration and verification of the model, respectively. As can be seen from Figure 5(a, b) the predicted dissolved lead in this case did not agree well with the corresponding measured data at the site.

In the second run, the dissolved metal concentration was assumed to be non-conservative, with the reaction coefficient in Equation (3) being constant. The best fit between the predicted and measured dissolved lead concentrations occurred for a reaction coefficient of  $0.12 \text{ d}^{-1}$ . This assumption led to a prediction error of 3.4% and 17.1% for calibration and verification of the model, respectively (see Figure 5(a, b)). However, some research results suggest that the reaction coefficients for

different pH and salinity conditions were not constant. A more detailed investigation is being planned to determine the rate of reaction coefficient for different pH and EC. According to this finding, it seems that using a variable reaction coefficient, which can be adjusted automatically within a numerical model, as a function of the pH, EC or pH and EC values may give better calibration results.

**Table 1** | A summary of the hydrodynamic model results

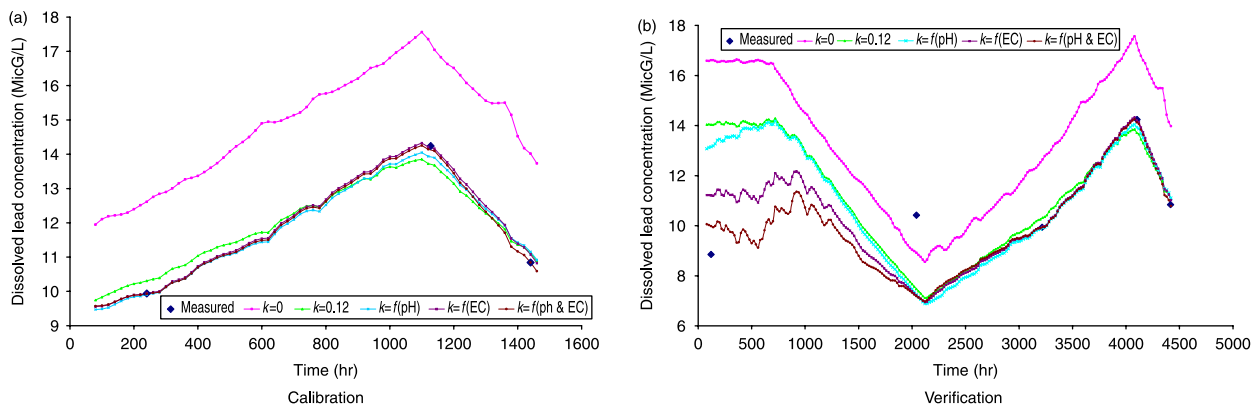
	Calibration			Verification		
	RMSE <sup>*</sup>	R <sup>2†</sup>	%Error <sup>‡</sup>	RMSE	R <sup>2</sup>	%Error
Water elevation	0.350	0.935	2.17	1.013	0.869	2.98
Discharge	1.580	0.960	15.20	1.870	0.930	13.21

where:  $X_{ip}$  = Predicted Data,  $X_{im}$  = Measured Data and  $n$  = Number of Data (Azmathullah *et al.* 2005).

<sup>\*</sup>Root Mean Square Error  $\text{RMSE} = \left[ \frac{\sum_{i=1}^n (X_{ip} - X_{im})^2}{n} \right]^{0.5}$

<sup>†</sup>Coefficient of Determination ( $R^2$ )  $R^2 = \frac{(\sum_{i=1}^n X_{ip} X_{im})^2}{\sum_{i=1}^n X_{ip}^2 \sum_{i=1}^n X_{im}^2}$

<sup>‡</sup>Average Absolute Error  $\% \text{Error} = \frac{\sum_{i=1}^n |X_{ip} - X_{im}|}{\sum_{i=1}^n X_{im}} \times (100)$



**Figure 5** | Comparison of predicted dissolved lead with the corresponding measured values.

A number of simulations were carried out to find a formulation for describing the relationship between the reaction coefficient and the pH value. Using the measured dissolved lead concentrations, it was found that the most suitable relationship was of the following form:

$$\kappa = -0.1646 \times \text{pH} + 1.4934 \quad (R^2 = 0.643) \quad (9)$$

The predicted results, for which the reaction coefficients were calculated using Equation (9) in the model, were compared with the corresponding measured values for calibration and verification in Figure 5(a, b), respectively. The comparison showed that the error of simulation had reduced to 1.9% and 15% for calibration and verification of the model, respectively.

In the next stage a number of simulations were also carried out to find a suitable formulation for describing the reaction coefficient with the EC value. It was found that the most suitable relationship between the reaction coefficient for dissolved lead and EC of the river was of the following form:

$$\kappa = -0.00023 \times \text{EC} + 0.581 \quad (R^2 = 0.924) \quad (10)$$

The predicted results, for which the reaction coefficients were calculated using Equation (10) in the model, were compared with the corresponding measured values for calibration and verification in Figure 5(a, b), respectively. This showed that the error of simulation had also declined to 0.8% and 10.8% for calibration and verification of the model, respectively.

The same procedure was applied to find the best relationship for  $\kappa$  with both EC and pH:

$$\kappa = 0.160 \times \text{pH} - 0.000402 \times \text{EC} - 0.401 \quad (R^2 = 1.000) \quad (11)$$

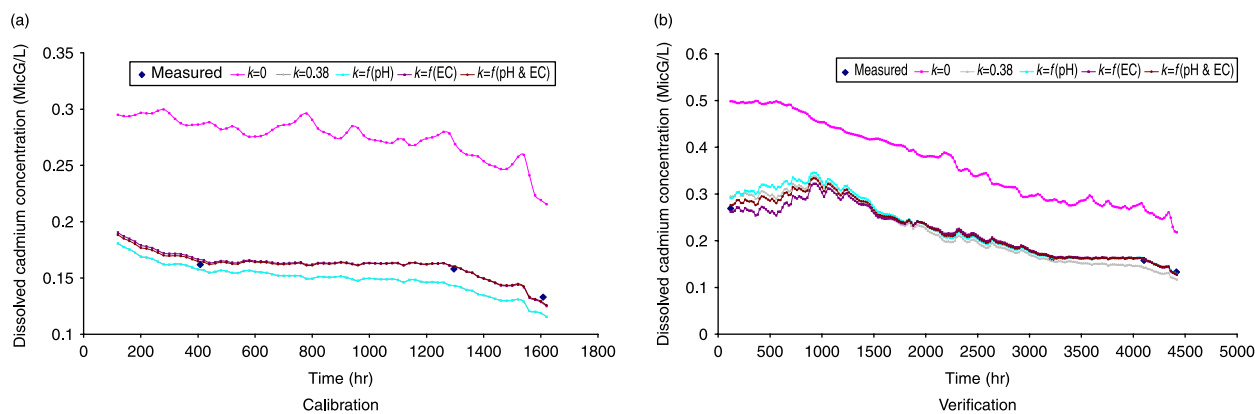
Again the predicted results, for which the reaction coefficients were calculated using Equation (11) in the model, were then compared with the corresponding measured values for calibration and verification in Figure 5(a, b), with the errors being calculated 0.4% and 8.3%, respectively. These results showed another improvement in the predicted dissolved lead concentrations.

### Dissolved cadmium model results

The same procedure was carried out for dissolved cadmium modelling. For the first run cadmium was assumed to be conservative, for which the predicted data did not show reasonable agreement with the measured data and the error was estimated to be 71.1% and 76.4% for model calibration and verification, respectively (see Figure 6(a, b)). For the second run cadmium was assumed to be non-conservative, with a constant reaction coefficient and the best fit between the predicted and measured data occurred for a reaction coefficient of  $0.38 \text{ d}^{-1}$ . This assumption significantly reduced the error to 7.7% and 8.5% for model calibration and verification, respectively (see Figure 6(a, b)).

The same procedure was applied and the following relationships between the reaction coefficient and pH and





**Figure 6** | Comparison of predicted dissolved cadmium with the corresponding measured values.

EC were suggested, as are listed in Table 2. As can be seen from this table the calculated errors for estimating cadmium concentrations were decreased from 71.1% and 76.42% to 2.18% and 2.29% for the calibration and verification stages of the heavy metal modelling, respectively.

## DISCUSSION

Salinity has been found by many investigators to be more influential on the reaction coefficient than any other environmental or water properties in riverine and estuarine waters. The results published by Turner *et al.* (2002) showed that the trace metal distribution coefficient in estuarine waters is primarily a function of salinity. Nassehi & Bikangaga (1993) calculated the value of the reaction coefficient for dissolved zinc in different elements of a river. Wu *et al.* (2005) used salinity for modelling the partitioning coefficient of heavy metals in the Mersey estuary and concluded that the modelling results agreed well with the measured data.

It should be noted that the proposed method in this paper is valid for rivers with large variations in salinity and pH. Therefore, this method could be used for rivers either close to the coastal waters, and thus affected by tides, or such rivers that have many agricultural inputs from saline soils draining into them. The chosen reach of the Karoon River in this research was an example of the second type of river. The average minimum and maximum EC for three years' data collection (2002–2004) at the Ahwaz hydro-metric station (see Figure 2) were 707 and 2254  $\mu\Omega^{-1}/\text{cm}$ , respectively. The pH values also ranged from a minimum of 7.3 to a maximum of 8.5 at this station.

In deriving Equations (9)–(11) for lead and the similar ones for cadmium (Table 2), it was assumed that the environmental factors and water properties remained constant during the whole simulation period. Since the model was calibrated using measured dissolved lead and cadmium at the site this assumption was thought to be valid. However, there are some limitations in using these equations. Firstly, simultaneous measurements of dissolved lead and cadmium were only made at one site and for six

**Table 2** | A summary of the dissolved cadmium model results

	Calibration			Verification		
	RMSE	$R^2$	%Error	RMSE	$R^2$	%Error
$\kappa = 0$	0.1086	0.991	71.11	0.1483	0.999	76.42
$\kappa = 0.38$	0.0126	0.947	7.67	0.0171	0.997	8.47
$\kappa = -0.2462 \times \text{pH} + 2.3738$	0.0028	0.996	1.78	0.0114	0.999	4.16
$\kappa = -0.000201 \times \text{EC} + 0.7286$	0.0041	1.000	2.54	0.0050	0.993	2.56
$\kappa = -0.1231 \times \text{pH} - 0.0001 \times \text{EC} + 1.5512$	0.0035	0.999	2.18	0.0046	0.998	2.29

months. More field-measured data are needed to validate and improve the formulae, which relate the pH and EC values to the reaction coefficient for dissolved lead and cadmium. Secondly, a one-dimensional model was used. Although one-dimensional models have been successfully used in riverine hydrodynamic and water quality studies, it seems that applying a two- or three-dimensional model may improve the derived equations. However, using two- or three-dimensional models needs extensive field-measured data. The importance of the models is to estimate the desirable variables as accurately as possible. Measuring some special environmental variables, such as heavy metals, in the field is sensitive and ideally needs extensive laboratory studies with sophisticated instruments and with large investments. Measuring pH and EC in riverine systems is relatively straightforward and can be done with even portable instruments. The main idea from this research work is therefore to introduce a procedure that relates the pH and EC values to reaction coefficients of heavy metal substances, such as lead and cadmium, for model predictions. Hence, for heavy metals modelling studies, measurements of pH and EC would be a suitable tool for relatively accurate estimation of these substances.

The results show an average improvement of 25% and 71.5% in error estimations of lead and cadmium, respectively, when using pH and EC as two variables affecting the dynamic processes of these heavy metals.

## CONCLUSIONS

Details are given of the hydro-environmental study to predict the heavy metals concentrations along rivers using a new approach to the source term of the advection–dispersion Equation (ADE). The main purpose of this study was to assess the impact of pH and EC on the reaction coefficient used in dissolved lead and cadmium modelling. The hydrodynamic module was first calibrated and validated using the field-measured data taken at a site located along the Karoon River, the largest river in the south west of Iran. In order to find the best equation between pH and EC with the reaction coefficient used in the ADE too, many model runs were carried out and the water quality module was subsequently calibrated by adjusting the reaction

coefficient. For each measured lead or cadmium value at any time the most appropriate reaction coefficient was specified and from there for the considered heavy metals a few equations between pH and EC with the reaction coefficient were proposed and added to the water quality module of the model. The main findings from the model simulations can be summarized as follows:

1. Five different procedures were used for estimating the rate of reaction coefficient for dissolved lead and cadmium, including: a zero reaction coefficient, a constant reaction coefficient, a varying reaction coefficient with pH, a varying reaction coefficient with EC and a varying reaction coefficient with both pH and EC.
2. Improvements were achieved in the predicted dissolved lead and cadmium concentration distributions when varying reaction coefficients were used.
3. The best fit between the predicted and measured values for simulation with a constant reaction coefficient was obtained when the coefficient was set to 0.12 and  $0.38 \text{ d}^{-1}$  for dissolved lead and cadmium, respectively.
4. According to Equations (9)–(11) for lead and the similar ones in Table 2 for cadmium and the measured pH and EC values, the ranges of reaction coefficients were calculated to be: (0.11–0.18, 0.10–0.29, 0.10–0.43) and (0.31–0.40, 0.31–0.48, 0.31–0.44) for lead and cadmium for the three suggested procedures, respectively. The error estimation was decreased from an average of 30% to 4% for lead and 74% to 2.2% for cadmium when pH and EC were used as two variables affecting the reaction coefficient.

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