



# Investigating the contaminant transport of heavy metals in estuarine waters

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**Abstract** A three-dimensional contaminant transport model of heavy metal (copper) was coupled with the hydrodynamics and suspended sediment transport module to simulate the transport and distribution of heavy metal (copper) of the Danshui River estuarine system in northern Taiwan. The coupled model was validated with observational data including the water level, tidal current, salinity, suspended sediment concentration, and copper concentration. The model simulation results quantitatively reproduce the measurements. Furthermore, the validated model was employed to explore the influences of the freshwater discharge and suspended sediment on the distribution of copper concentrations in the tidal estuarine system. The results demonstrate that a high freshwater discharge results in a decreasing copper concentration, while a low freshwater discharge raises the copper concentration along the estuarine system. If the suspended sediment transport module was excluded in the model simulations, the predicted copper concentration underestimated the measured data. The distribution of copper concentrations without the suspended sediment transport module was lower than that with the suspended sediment transport module. The simulated results indicate that the

freshwater discharge and suspended sediment play crucial roles in affecting the distribution of copper concentrations in the tidal estuarine system.

**Keywords** Copper · Hydrodynamics · Salinity · Suspended sediment · Tidal estuarine system · Three-dimensional model

## Introduction

The tidal estuaries and adjacent coastal seas in Taiwan have received anthropogenic loads of heavy metals and bio-accumulative organic and inorganic materials for many years. In fact, the untreated point and nonpoint sources entering into the receiving waters have caused a significant influence on the aquatic environment and ecosystems of tidal estuaries (Huang and Lin 2003). Suspended sediments are regarded as a sink (or source) for heavy metals entering into rivers. The resuspension of a highly contaminated sediment bed during a high flow period would release heavy metals into the water columns. The desorption of contaminants such as fecal bacteria and heavy metals would significantly affect the aquatic ecosystems (Menon et al. 1998; He et al. 2010; Witke et al. 2003; Wu et al. 2005; Murdoch et al. 2010; de Souza Machado et al. 2016). The advection and diffusion, settling, solubilization, and speciation are vital processes which are affected by the physical, chemical, and biological actions in tidal estuaries. These processes determine the temporal variation and spatial distribution of heavy metals (Benoit et al. 1994).

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Field measurements of heavy metals allow for a direct way of understanding the contaminant conditions in tidal estuaries. Huang and Lin (2003) analyzed the bulk sediment heavy metal concentration in the Keelung River, a tributary of the Danshui River, to analyze the heavy metal content in sediment bed for further assessing the effectiveness as a result of pollution control. Jiann et al. (2005) investigated the distribution and behavior of heavy metals at downstream of the Danshui River and the Keelung River by means of heavy metal fractionation techniques. However, field measurements require significant efforts and money and do not cover the entirety of the spatial distributions and temporal variations.

Numerical models provide another way to better understand the fate and transport of suspended sediments and heavy metals in tidal estuaries. They are also widely used for investigating the hydroenvironmental management in estuarine waters (Ng et al. 1996; Wu et al. 2005). Contaminant models that couple hydrodynamic, suspended sediment, and heavy metal transport models are needed, because heavy metals can adsorb and desorb with particles in the water column and sediment bed. One-dimensional, horizontally averaged two-dimensional, vertically averaged two-dimensional, and coupled one-dimensional and two-dimensional hydrodynamic, suspended sediment, and heavy metal transport models have been developed and applied to investigate the fate and transport of heavy metals in rivers, estuaries, and coasts (e.g., Ji et al. 2002; Wu et al. 2005; Hartnett et al. 2006; Murdoch et al. 2010; Trento and Alvarez 2011; Hartnett and Berry 2012; Alvarez and Trento 2014; Samano et al. 2014; Horvat and Horvat 2016). Because of the models' complexity, difficulty in operation, and requirement of large time for simulations, few coupling three-dimensional hydrodynamic, suspended sediment, and heavy metal transport models were developed and applied in tidal estuaries. For example, Lu et al. (2014) applied a three-dimensional heavy metal transport model by integrating the hydrodynamic and sediment transport models (Environmental Fluid Dynamic Code, three-dimensional model, EFDC 3D) to predict the distribution of heavy metal contaminant (copper) concentrations in the Qujiang estuary in China. Cho et al. (2016) used the EFDC 3D to model heavy metal-sediment interaction processes to investigate the parameter sensitivity assessment using a one-step-at-a-time approach and uncertainty analysis using the Bayesian Monte

Carlo method. Premier et al. (2019) also applied the Delft3D model to explore the fate and transport of metal contaminants that relied on the resuspension of suspended sediment in the Thames Estuary.

The Danshui River estuarine system in Taiwan has received huge anthropogenic pollution in the past 30 years via nutrients, fecal coliform, and heavy metals (Lin et al. 2007; Wen et al. 2008; Liu and Huang 2012). Because of the high concentration of heavy metals, specifically copper (Cu), in the Danshui River-Dahan River, the Hsintien River, and the Keelung River, there is an urgent need to develop a high resolution heavy metal fate and transport model coupled with a hydrodynamic and suspended sediment model to allow for a better prediction and management of heavy metal (Cu) in tidal estuaries.

There were many published studies regarding the modeling of the Danshui River system. The target of these published studies focused on salt intrusion and residual circulation, residence time and age, water quality, suspended sediment, and fecal coliform (Liu et al. 2007a, b, 2008; Etemad-Shahidi et al. 2010; Chen et al. 2010, 2011; Liu and Chan 2014; Chen and Liu 2017). The purpose of this study is to develop a coupling hydrodynamic, salinity, suspended sediment, and heavy metal transport model and to predict the transport and distribution of the heavy metal (Cu) in the tidal estuarine system. The coupled model, called SELF-SED-HM, was validated with measured data collected in 2015, which includes the water level, velocity, salinity, suspended sediment concentration, and copper concentration. Furthermore, the validated model was employed to explore the influences of the freshwater discharge and suspended sediment on the transport and distribution of copper concentrations in the tidal estuarine system. The main contribution of this study focuses on developing a three-dimensional hydrodynamic, suspended sediment, and heavy metal transport coupled model instead of modeling application and experiment.

## Research area

The Danshui River estuarine system, located on the outskirts of Taipei, is the largest tidal river and one of the most heavily polluted rivers in northern Taiwan (Wang et al. 2007; Chen et al. 2011). Three main tributaries: the Dahan River, the Hsintien River, and the Keelung River (Fig. 1a) constitute the Danshui River

estuarine system (Chen et al. 2011). The drainage area of the river basin is 2726 km<sup>2</sup>, which is approximately 7.6% of the total area of Taiwan. Among these three major tributaries, the Dahan River is the longest, with a length of 135 km (Liu et al. 2007a, b). The population density of the area (2500 persons/km<sup>2</sup> approximately) is also the highest in Taiwan (Liu et al. 2007a, b). The river depth is shallow from 1 m to 15 m and the estuarine system receives a mean annual discharge of  $6.6 \times 10^9$  m<sup>3</sup>/y (Water Resources Agency 2017). The drainage basin has been subjected to large amounts of nutrients, resulting from industrial and agricultural activities.

The major forcing mechanics of the barotropic flows are astronomical tides and river discharges, while the baroclinic flows forced by salt water intrusion are the most important transport mechanism in the Danshui River estuarine system (Hsu et al. 1999). Principal lunar semidiurnal constituent tide ( $M_2$ ) and principal solar semidiurnal constituent tide ( $S_2$ ) are major tidal components, with a mean tidal range and a spring tidal range are 2.22 m and 3.1 m, respectively, resulting in a tidal excursion distance 25–28 km from the Danshui River to upriver reaches (Liu et al. 2007a, b). The variation in the salinity depends on the magnitude of the freshwater discharges, flood-ebb tidal flows, spring-neap tidal variations, and vertical mixing characteristics. Wang et al. (2004) reported that the residence time in the Danshui River estuarine system is approximately 1–2 days based on various freshwater discharges from upstream reaches.

A population of 6.5 million, about a quarter of Taiwan's residents, resides along the Danshui River system covering the Keelung City, Taipei City, New Taipei City, Taoyuan City, and Hsinchu County to form a highly developed area. Different kinds of wastewater including treated and untreated industrial and domestic wastewater, livestock wastewater, and river bank landfill seepage water discharge from the Danshui River system, resulting in huge pollution loadings from heavy metals, organic and inorganic materials, and fecal coliform bacteria (Wang et al. 2007). We analyzed the different kinds of measured data of heavy metals including copper, lead, cadmium, chromium, arsenic, mercury, silver, and zinc collected from the Taiwan Environmental Protection Administration (TEPA) in the period from 2006 to 2017 and found that the distribution of copper concentration in the Danshui River-Dahan River exceeded the surface water classification and water quality standards (0.03 mg/L). However, in

the Hsintien River and the Keelung River the heavy metal (Cu) concentrations were less than the standards. Therefore the copper (Cu) was regarded as research target in this study. Figure 2 displays the mean value plus/minus one standard deviation of the Cu concentration in the Danshui River-Dahan River, the Hsintien River, and the Keelung River. It shows that the prominent areas of the highly polluted copper concentration are located at the Chung-Siao Bridge (Main Danshui River), the Hsin-Hai Bridge (Dahan River), and the Fu-Chou Bridge (Dahan River), which is probably due to the nearby sanitary landfill site.

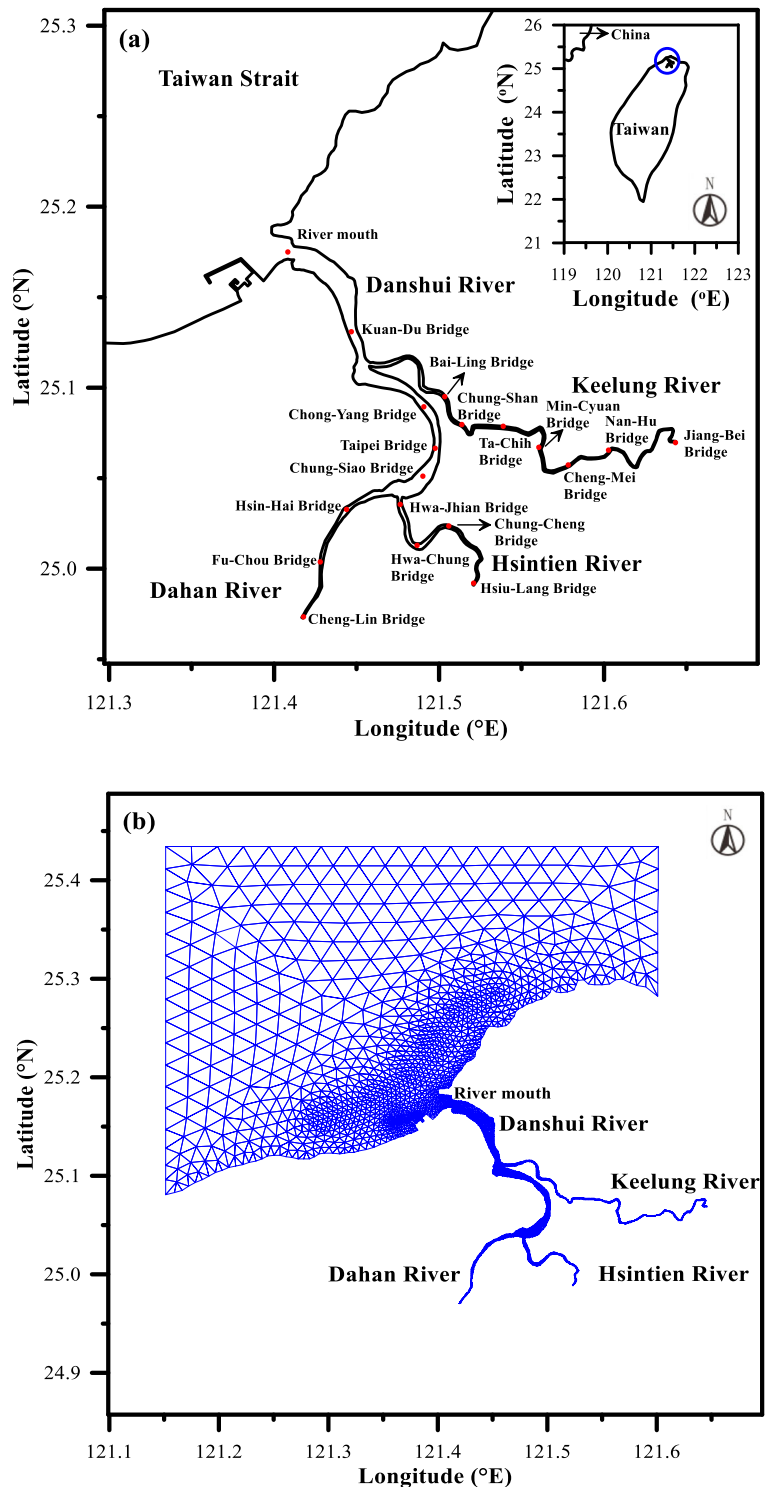
## Materials and methods

### Hydrodynamic model

There are several common codes including structured and unstructured grids used for numerical modeling of hydrodynamics. The models of structured grid include POM (Blumberg and Mellor 1987), TRIM (Casulli and Cheng 1992), ROMS (Shchepetkin and McWilliams 2005), and others, while the models of unstructured grid have UnTRIM (Casulli and Walters 2000), ELCIRC (Zhang et al. 2004), FVCOM (Chen et al. 2003), and others. Numerical simulations for the hydrodynamics were implemented with an unstructured grid, semi-implicit Eulerian-Lagrangian finite element model (SELFE, Zhang and Baptista 2008) because SELFE used a formal Galerkin finite-element framework and a flexible hybrid SZ coordinates. It is the reason that in the present study SELFE was selected for hydrodynamic modeling.

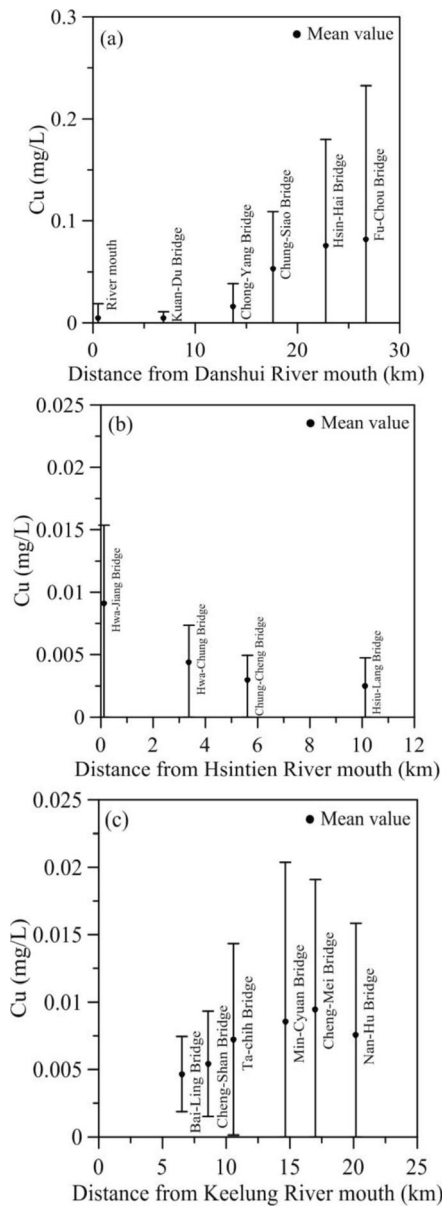
All equations in the SELFE model are solved in Cartesian space ( $x$ ,  $y$ , and  $z$ ). In order to construct a three-dimensional prismatic element, the SELFE model adopts triangular meshes in the horizontal plane, which are inserted in the vertical plane. In the water surface equation, continuous linear is used to discretize water surface elevation with wet and drying algorithms. The nonconfirming basic function is implemented to yield horizontal velocity. The vertical diffusion is solved implicitly and advection of momentum is treated using Eulerian-Lagrangian method (Karna et al. 2015). The terrain-following  $S$  grid and the equipotential  $Z$  grid can be selected to build the vertical grid (Song and Haidvogel 1994). The Courant-Friedrichs-Lewy (CFL) stability condition constrains the choice of time step.

**Fig. 1** a Map of the Danshui River estuarine system and the adjacent coastal sea and b the unstructured grid in the horizontal plane used for the model simulation



The Generic Length Scale (GLS) turbulence closure model in SELEF is used to calculate vertical eddy diffusivity and viscosity. In the current study, the  $k-\epsilon$

model (Rodi 1984) is adopted in the model simulation. The detailed solution processes of the SELFE model can be found in Zhang and Baptista (2008).



**Fig. 2** Mean and standard deviation of the measured Cu concentration collected between 2006 and 2017 in **a** the Danshui River-Dahan River, **b** the Hsintien River, and **c** the Keelung River

### Suspended sediment model

The hydrodynamic model coupled with a suspended sediment transport module with the same spatial and temporal resolutions is used to simulate the concentration of the suspended sediment in tidal estuaries. The suspended sediments in the water column are transported by advection and diffusion, but the sediments on the bed are not. The suspended sediment

concentrations are solved by the advection-diffusion equation with setting term in vertical direction, which is expressed as (Chen and Liu 2017):

$$\begin{aligned} \frac{\partial C_s}{\partial t} + u \frac{\partial C_s}{\partial x} + v \frac{\partial C_s}{\partial y} + w \frac{\partial C_s}{\partial z} - w_s \frac{\partial C_s}{\partial z} \\ = \frac{\partial}{\partial z} \left( \kappa \frac{\partial C_s}{\partial z} \right) + F_h \end{aligned} \quad (1)$$

where  $C_s$  indicates the suspended sediment concentration (SSC) in water column,  $u$ ,  $v$ , and  $w$  represent the velocities in the  $x$ ,  $y$ , and  $z$  directions, respectively,  $\kappa$  and  $F_h$  express the vertical eddy diffusivity and horizontal diffusion term, respectively, and  $w_s$  denotes the sediment settling velocity.

No sediment flux is applied at the water surface. Therefore, the diffusion flux and settling flux counterbalance each other at the boundary condition. At the sediment bed, the net sediment flux is equal to the combination of the sediment erosion flux ( $E$ ) and the sediment deposition flux ( $D$ ). When the threshold of erosion ( $\tau_e$ ) is smaller than the bottom shear stress ( $\tau_b$ ), the sediment erosion flux ( $E$ ) takes place. Conversely, when the threshold of deposition ( $\tau_d$ ) exceeds the bottom shear stress ( $\tau_b$ ), the sediment deposition ( $D$ ) occurs (Partheniades 1965). The detailed description of suspended sediment model can be found in Chen and Liu (2017).

### Heavy metal transport model

The major mechanism of copper partitioning between dissolved and particulate phases in the Danshui River estuary has been documented by Jiann et al. (2005). At the same time, the processes of sediment deposition, resuspension, and settlement affect the heavy metal concentration in the water column (Shrestha and Orlob 1996). The heavy metal concentration in the water column is influenced by advection and diffusion processes. These transport mechanisms are all considered in the heavy metal transport model to portray the copper movement in tidal estuary. Therefore the three-dimensional hydrodynamic (SELFE) and suspended sediment transport model (SED) coupled with the heavy metal (Cu) transport module (HM) becomes a SELFE-SED-HM model. The governing equations for heavy metal transport module are written as:

$$\frac{\partial C_{HM}}{\partial t} + u \frac{\partial C_{HM}}{\partial x} + v \frac{\partial C_{HM}}{\partial y} + w \frac{\partial C_{HM}}{\partial z} = \frac{\partial}{\partial z} \left( \kappa \frac{\partial C_{HM}}{\partial z} \right) \quad (2)$$

$$+ F_h + C_{HM0} - f_s w_s \frac{\partial C_{HM}}{\partial z} \text{ if } \tau_b \leq \tau_d$$

$$\frac{\partial C_{HM}}{\partial t} + u \frac{\partial C_{HM}}{\partial x} + v \frac{\partial C_{HM}}{\partial y} + w \frac{\partial C_{HM}}{\partial z} = \frac{\partial}{\partial z} \left( \kappa \frac{\partial C_{HM}}{\partial z} \right) \quad (3)$$

$$+ F_h + C_{HM0} + f_d C_{HMB} \frac{\partial M}{\partial z} \text{ if } \tau_b > \tau_d$$

where  $C_{HM}$  represents the concentration of the heavy metal (Cu),  $C_{HM0}$  denotes the source or sink of the heavy metal concentration,  $C_{HMB}$  expresses the heavy metal concentration in the sediment bed,  $F_h$  indicates the horizontal diffusion term,  $f_s$  is the fraction of heavy metal attached to the suspended sediment in the water column,  $f_d$  is the fraction of heavy metal dissolved in the water column,  $M$  represents the erosion rate parameter, and  $\tau_b$  and  $\tau_d$  denote the bottom shear stress and critical shear stress for deposition, respectively.

Two parameters  $f_s$  and  $f_d$  can be expressed as:

$$f_s = \frac{K_d C_s}{1 + K_d C_s} \quad (4)$$

$$f_d = \frac{1}{1 + K_d C_s} \quad (5)$$

$$K_d = \frac{f_s}{f_d} \quad (6)$$

where  $C_s$  denotes the suspended sediment concentration (SSC),  $K_d$  represents the partition coefficient, and  $f_s + f_d = 1$ .

### Model implementation

Even though the study area is focused on the Danshui River estuarine system, the modeling domain is extended to cover adjacent coastal sea (Fig. 1b) for easily setting up the open boundary conditions. The deepest position is located at the northeast corner of modeling domain, with a depth of 110 m (see Fig. 1b). To set up the unstructured grids for the model simulation, the topographic and bathymetric data of the Danshui River estuarine system and the Taiwan’s Strait were collected

from different resources including the Water Resources Agency, Ministry of Economic Affairs and Taiwan’s Ocean Data Bank, Ministry of Science and Technology. A total of 6335 elements and 4092 nodes were generated in the horizontal domain. The maximum and minimum grid sizes are 2500 m and 40 m, respectively, at the coastal sea and upper reaches of the Danshui River system. The vertical grid used in the computational domain consists of 10 evenly spaced layers in the  $S$ -coordinates and 10 layers in the  $Z$ -coordinates. According to CFL stability condition, the time step was set to 120 s in the model simulations to insure the numerical stability (Chen and Liu 2017).

### Metrics for model performance

To convince how the model is reliable and feasible for prediction, the statistical error indicators were used to compare the simulated results and the measured data to assess the performance of the coupled model. There are many statistical error indicators can be used to quantify the difference of simulated results and measured data. However, two-dimensional indicators and one nondimensional score were used to evaluate the model performance. Three criteria included the mean absolute error (MAE), root mean square error (RMSE), and Skill. The MAE and RMSE metrics are the dimensional indicators, while the predictive Skill is a nondimensional score developed by Willmott (1981) and was, for example, used by Warner et al. (2005), Das et al. (2012), and Zhang et al. (2013). The smaller the MAE and RMSE values are, the closer the simulated results are close to the measured data, and the better the model performance. There is not acceptable range for MAE and RMSE reported in the literature. However, different Skill ranges have different evaluations for model performance. The metric of model performance for Skill can be expressed as:

$$Skill = 1 - \frac{\sum_{i=1}^N |(Y_m)_i - (Y_o)_i|^2}{\sum_{i=1}^N (|(Y_m)_i - Y_o| + |(Y_o)_i - Y_o|)^2} \quad (7)$$

where  $N$  represents the total number of data,  $(Y_m)_i$  denotes the model prediction at location (or time)  $i$ ,  $(Y_o)_i$  expresses the corresponding observed value at  $i$ , and  $Y_o$  represents the mean value of observation ( $= \frac{1}{N} \sum_{i=1}^N (Y_o)_i$ ).



A value of Skill = 1.0 indicates a perfect model performance, while a value of Skill = 0.0 represents very poor performance.

## Model validation

### Hydrodynamics and salinity

The water level, tidal current, and salinity are fundamental variables in hydrodynamic model to be validated. In order to allow the hydrodynamic model to be driven, the water level and salinity were imposed at the open boundaries. The time-series water level was generated by five tidal constituents ( $M_2$ ,  $S_2$ ,  $N_2$ ,  $K_1$ , and  $O_1$ ) at the open boundaries to drive the model simulation (Liu et al. 2007a, b). The measured data of the freshwater discharges in 2015 were used to specify the upstream boundaries where are located at the Cheng-Lin Bridge (Dahan River), the Hsiu-Lang Bridge (Hsintien River), and the Jiang-Bei Bridge (Keelung River). The salinities at the open boundaries and upstream boundaries were set at 35 ppt (part per thousand) and 0 ppt, respectively. The water level, velocity, and salinity were specified to be 1.5 m, 0.5 m/s, and 25 ppt, respectively, for initial condition. A 15-day warm up time was required to achieve a regime situation. The bottom roughness height ( $z_0$ ) was the only parameter needed to be determined in the hydrodynamic model. In this study, a constant bottom roughness height of 0.005 m was used in the model simulations.

A good agreement between the measured and calculated hydrodynamic conditions can promote confidence in the prediction of heavy metal. Therefore, to ensure that the calculated heavy metal concentrations were genuine, we first validated the model against the hydrodynamic and salinity measurements in the Danshui River estuarine system. Fig. S1 in the Supplementary Material illustrates the comparison between the measured and simulated time-series water levels at the different gauge stations during the period from June 27, 2015 to July 3, 2015. The MAE values at the Danshui River mouth, Tu-Ti-Kung-Pi, the Taipei Bridge, the Hsin-Hai Bridge, the Chung-Cheng Bridge, the Bai-Ling Bridge, and the Ta-Chih Bridge are 0.14 m, 0.13 m, 0.09 m, 0.26 m, 0.17 m, 0.15 m, and 0.13 m, respectively, while the RMSE values are 0.15 m, 0.14 m, 0.11 m, 0.31 m, 0.19 m, 0.18 m, and 0.17 m, respectively. The Skill scores range between 0.97 and

0.99, demonstrating the capability of the model to accurately mimic the time-series water levels. Fig. S2 in the Supplementary Material shows the comparison between the time-series measured data of the depth-averaged velocity and the calculated velocity at the Kuan-Du Bridge, Taipei Bridge, and Hsin-Hai Bridge on June 30, 2015. The MAE values at the Kuan-Du Bridge, the Taipei Bridge, and the Hsin-Hai Bridge are 0.09 m/s, 0.24 m/s, and 0.07 m/s, respectively, while the RMSE values at these stations are 0.11 m/s, 0.26 m/s, and 0.09 m/s, respectively. The Skill scores range between 0.74–0.96, signifying that the model performance is indicated as excellent.

The salinity data measured on June 30, 2015 were used for model validation. Fig. S3 in the Supplementary Material compares the measured and simulated time-series salinities at the Kuan-Du Bridge, the Taipei Bridge, and the Hsin-Hai Bridge. The mean value plus/minus one standard deviation of measured salinity and the simulated salinity at the surface and bottom layers are shown in the figure (see Figs. S3a and S3b in the Supplementary Material). Because of low salinity at the Hsin-Hai Bridge (see Fig. S3c in the Supplementary Material), the simulated depth-averaged salinity is presented in the figure. The low salinity represents that the limit of salt intrusion in the Dahan River is located around the Hsin-Hai Bridge. Fig. S3 (in the Supplementary Material) shows that while the simulated salinity underestimates the measured salinity during the flood tide it reproduces the measured salinity during the ebb tide at the Taipei Bridge. The MAE values at the Kuan-Du Bridge, the Taipei Bridge, and the Hsin-Hai Bridge are 3.34 ppt, 1.53 ppt, and 0.05 ppt, respectively, while the RMSE values are 3.71 ppt, 2.36 ppt, and 0.06 ppt, respectively. The Skill scores range between 0.36–0.89, indicating that the model performance falls between good and excellent.

Based on a good quantitative comparison between model simulations and measurements in water level, velocity, and salinity at different gauge stations, we demonstrate that the hydrodynamic model is reliable and capable for prediction.

### Suspended sediment distribution

To ascertain the predictive capability of the suspended sediment module, the SSC data measured on June 4 and December 1 in 2015 were used for model validation. The monthly SSC data recorded by the TEPA at the

upstream reaches of the Dahan River, the Hsintien River, and the Keelung River served as the upstream boundary conditions. A constant SSC of 5 mg/L was specified as the open boundary conditions to drive the model simulation. The initial condition was specified with the constant value of SSC (=4 mg/L).

Figures 3 and S4 (in the Supplementary Material) present comparisons between the measured and simulated SSC distributions along the Danshui River-Dahan River, the Hsintien River, and the Keelung River on June 4, 2015 and December 1, 2015, respectively. The simulated suspended sediment concentrations at the surface and bottom layers are shown in the figures. The figures show that the simulated SSC reproduces the measured data at different locations along the river, except for the Hwa-Jhian Bridge (Fig. 3b) and the Hwa-Chung Bridge (Fig. 3b and b) in the Hsintien River, where the model overestimates the measured SSC. Comparing with the simulated results and measurements in Figs. 3b and S4b (in the Supplementary Material), the suspended sediment concentration in the Hsintien River on December 1 was higher than that on June 4, 2015. It is the reason that the high suspended sediment concentration was found at the upstream on December 1, where the dominant concentration at the downstream reaches. The MAE and RMSE values respectively range from 1.9 mg/L to 10.5 mg/L and from 2.7 to 15.1 mg/L for the Danshui River-Dahan River, the Hsintien River, and the Keelung River. The Skill scores are in the range of 0.52–0.84, which indicates that the model performance is between very good and excellent. Based on the model validation, the parameters for the suspended sediment model are determined. They are  $w_s = 4.5 \times 10^{-4} \text{ m/s}$ ,  $\tau_e = 0.35 \text{ N/m}^2$ ,  $\tau_d = 0.35 \text{ N/m}^2$ , and  $M = 3.0 \times 10^{-5} \text{ kg/m}^2/\text{s}$ .

### Heavy metal (Cu) distribution

Modeling heavy metal (Cu) in an estuarine system is dependent on accurately simulating the hydrodynamics, salinity, and suspended sediment concentration. The numerical predictions of the total Cu concentration along the main river and its tributaries are presented in this section. To validate the heavy metal transport model, the quarterly data of the heavy metal (Cu) concentrations measured by the TEPA were collected in 2015 at the river boundaries and used to drive the model simulation. The heavy metal (Cu) concentration at the open boundaries was set at a constant value of 0.007 mg/L. It

means that each grid at open boundaries (Fig. 1b) was specified with the same value (i.e., 0.007 mg/L). The constant value of heavy metal (Cu) concentration (0.001 mg/L) was specified for the initial condition.

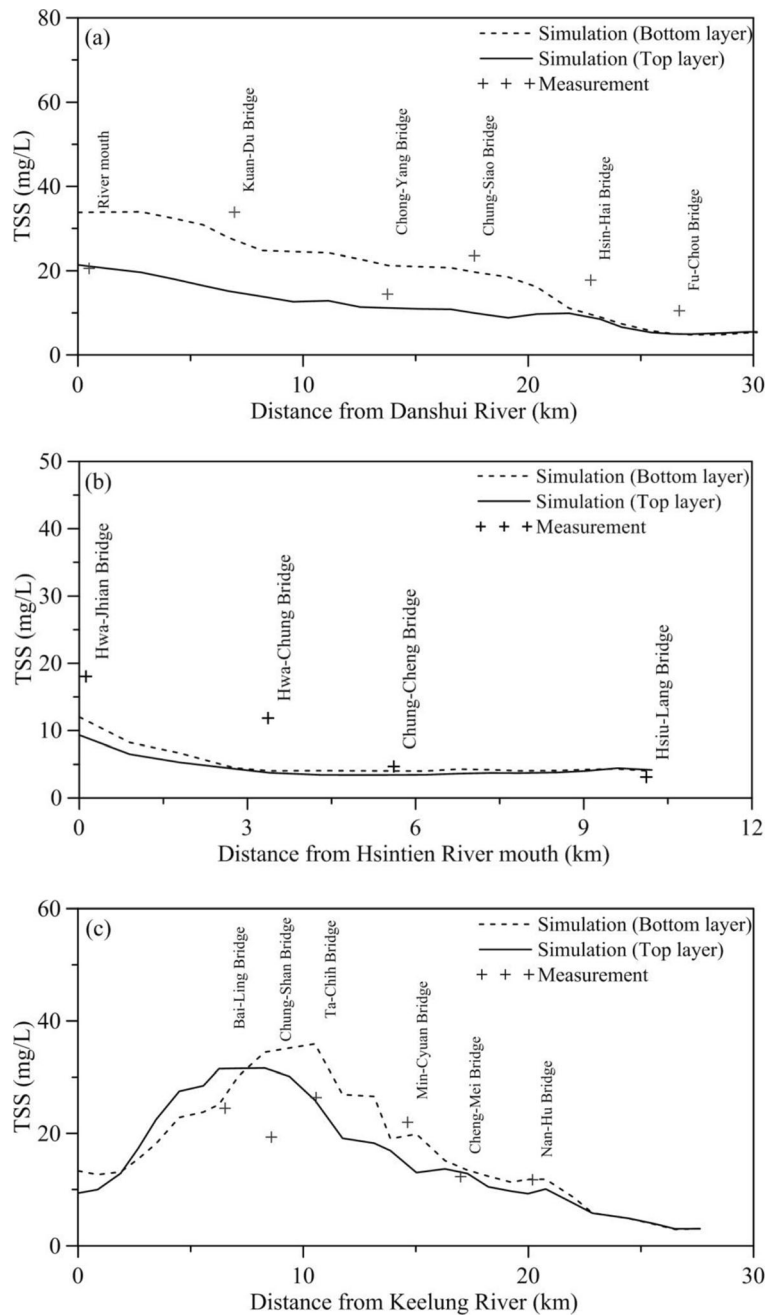
Figures 4 and S5 (in the Supplementary Material) illustrate comparisons of the simulated and measured Cu concentrations along the Danshui River-Dahan River, the Hsintien River, and the Keelung River on June 4, 2015, and December 1, 2015, respectively. These figures indicate that the highest Cu concentration is located at the upstream reaches of the Dahan River (i.e., the Hsin-Hai Bridge and the Fu-Chou Bridge). Even though the simulated Cu concentrations underestimate/overestimate the measured Cu concentrations at some stations, the simulated Cu concentrations mostly mimic the measured Cu concentrations in the main river and its tributaries. Table 1 indicates the statistical errors between the measured and simulated Cu concentrations along the Danshui River-Dahan River, the Hsintien River, and the Keelung River on March 6, June 4, September 3, and December 1 of 2015. The MAE values range from 0.0004–0.0094 mg/L; the RMSE values range from 0.0005–0.014 mg/L; and the Skill scores range from 0.70–0.97, indicating that the model performance is excellent. Based on the model validation, the parameters used in the heavy metal transport model are:  $C_{HMB} = 0.01 \text{ kg/m}^3$  and  $K_d = 45 \text{ L/g}$ .

### Diagnostic experiments and discussion

The validated model was then applied to analyze how the heavy metal (Cu) transport and distribution were affected by river discharge and suspended sediment concentration. The model was first used to predict the distribution of heavy metal in the estuarine system under different freshwater discharges from upstream reaches in the Dahan River, the Hsintien River, and the Keelung River. Then, the validated model was run with suspended sediment concentration and without suspended sediment concentration. The baseline condition including the suspended sediment transport module is based on the results of the model-data comparison on December 1, 2015. Even though the Skill scores of three rivers on December 1, 2015, are relatively low compared to the simulated results of the other three periods (Table 1), the stable discharges from upstream reaches of three tributaries during the winter season would be more appropriate to consider as the baseline condition.



**Fig. 3** Comparison between the measured and simulated suspended sediment concentrations on June 4, 2015 along **a** the Danshui River-Dahan River, **b** the Hsintien River, and **c** the Keelung River

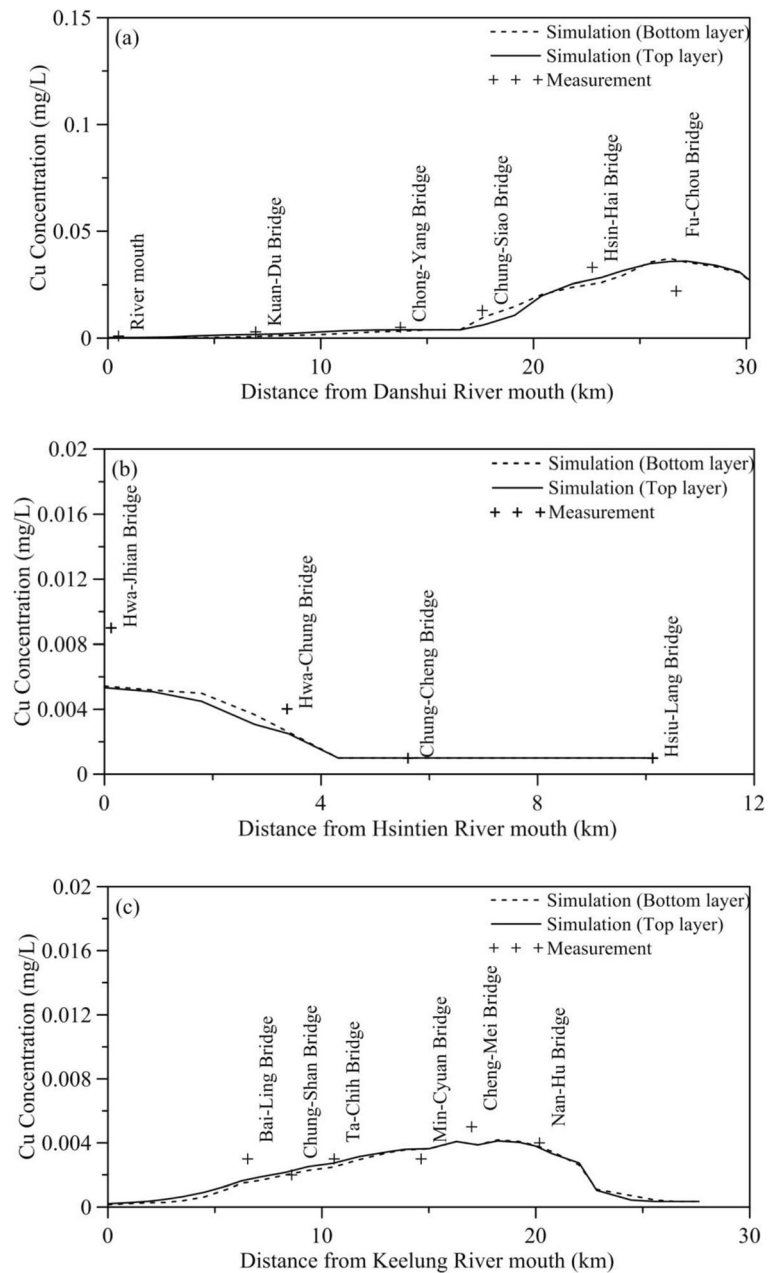


Effect of freshwater discharge

To explore the effect of different freshwater discharges from three major tributaries on the distribution of copper concentration, the simulated condition was the same as when executing the model validation on December 1, 2015, except that the freshwater discharges at the upstream boundary condition were replaced with  $Q_{75}$  and

$Q_{10}$  flow conditions, representing low and high discharges, respectively. The  $Q_{75}$  and  $Q_{10}$  flow conditions express the discharges that are equal or exceeded the time with 75% and 10%, respectively (Liu et al. 2007a, b). As the high discharges ( $Q_{10}$  flow) at the upstream boundaries of the major tributaries were used in the model simulation, they were  $64.8 \text{ m}^3/\text{s}$ ,  $131.4 \text{ m}^3/\text{s}$ , and  $67.0 \text{ m}^3/\text{s}$  for the Dahan River, the Hsintien River,

**Fig. 4** Comparison between the measured and simulated copper concentrations on June 4, 2015 along **a** the Danshui River-Dahan River, **b** the Hsintien River, and **c** the Keelung River



and the Keelung River, respectively. The  $Q_{75}$  discharges, representing a low flow condition at the upstream boundaries for the Dahan River, the Hsintien River, and the Keelung River, were  $3.74 \text{ m}^3/\text{s}$ ,  $11.6 \text{ m}^3/\text{s}$ , and  $3.5 \text{ m}^3/\text{s}$ , respectively.

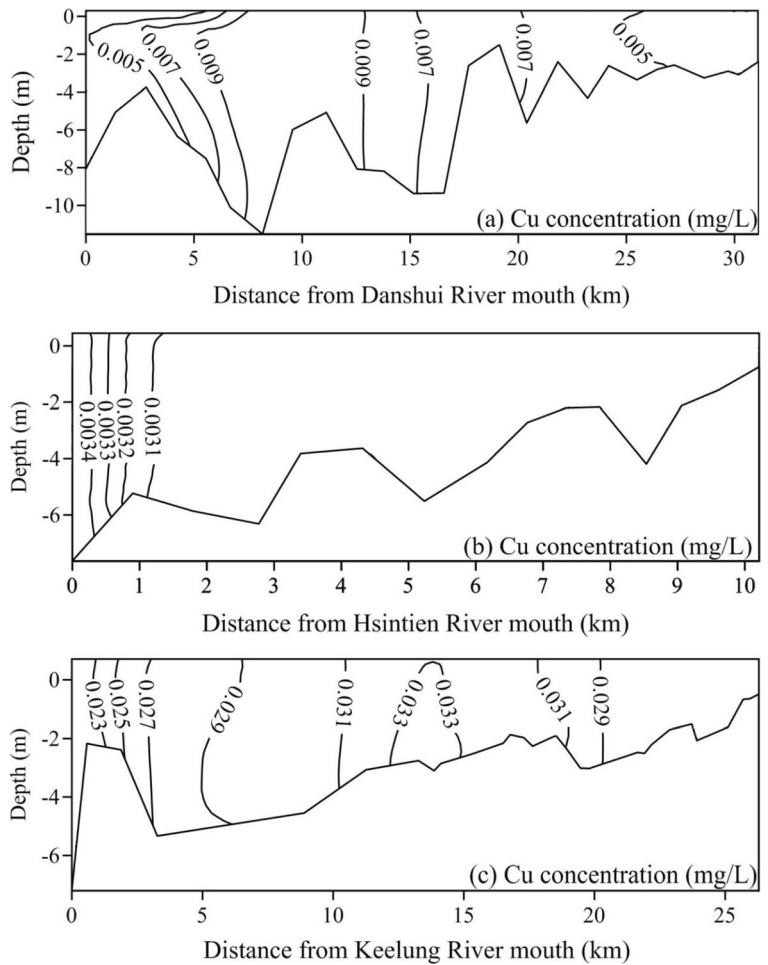
Figures 5 and 6 display the tidally averaged distribution of copper concentrations in the Danshui River-Dahan River, the Hsintien River, and the Keelung River under  $Q_{10}$  and  $Q_{75}$  flow conditions, respectively.

Comparing the simulated results in Figs. 5 and 6 shows that the copper concentration in the estuarine system under the  $Q_{75}$  low flow condition is higher than that under the  $Q_{10}$  flow condition. This may be the reason that the copper concentration is flushed out the estuary: it is a result of a high freshwater discharge coming from the upstream reaches of the three major tributaries. The simulated copper concentration under the  $Q_{75}$  low flow condition increases 1.9~3.1, 1.3~2.9, 0.4~0.8 times

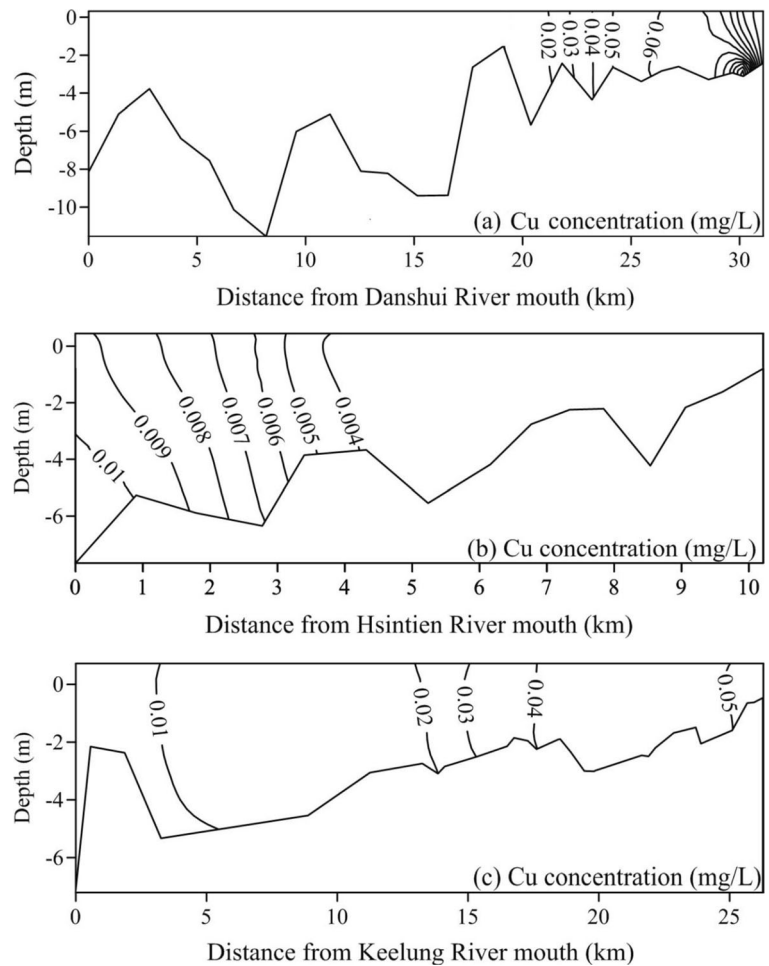
**Table 1** Statistical errors between the measured and simulated heavy metal (Cu) concentrations on different dates in 2015

Date in 2015	Metrics	Danshui River-Dahan River	Hsintien River	Keelung River
March 6	MAE (mg/L)	0.0047	0.0011	0.0016
	RMSE (mg/L)	0.0071	0.0015	0.0019
	Skill	0.83	0.96	0.90
June 4	MAE (mg/L)	0.0057	0.0019	0.0007
	RMSE (mg/L)	0.0071	0.0029	0.0008
	Skill	0.93	0.95	0.76
September 3	MAE (mg/L)	0.0042	0.0011	0.0004
	RMSE (mg/L)	0.0049	0.0014	0.0005
	Skill	0.95	0.97	0.83
December 1	MAE (mg/L)	0.0093	0.0018	0.0025
	RMSE (mg/L)	0.0140	0.0025	0.0028
	Skill	0.73	0.77	0.83

**Fig. 5** Calculated tidally averaged distribution of copper concentrations under  $Q_{10}$  flow conditions in **a** the Danshui River-Dahan River, **b** the Hsintien River, and **c** the Keelung River



**Fig. 6** Calculated tidally averaged distribution of copper concentrations under  $Q_{75}$  flow conditions in **a** the Danshui River-Dahan River, **b** the Hsintien River, and **c** the Keelung River



approximately in the Danshui River-Dahan River, the Hsintien River, and the Keelung River, respectively, compared with that under the  $Q_{10}$  flow condition. A similar pattern in the reduction of the heavy metal concentration in the water column due to an increasing discharge was also found by Wang et al. (2009) and de Souza Machado et al. (2016). Figure 6a shows that the local highest copper concentration is located around the Hsin-Hai Bridge and the Fu-Chou Bridge in the Dahan River under a low flow condition. Under a high flow condition ( $Q_{10}$  flow), the highest copper concentration is moved to the middle reaches of the Danshui River (Fig. 5a).

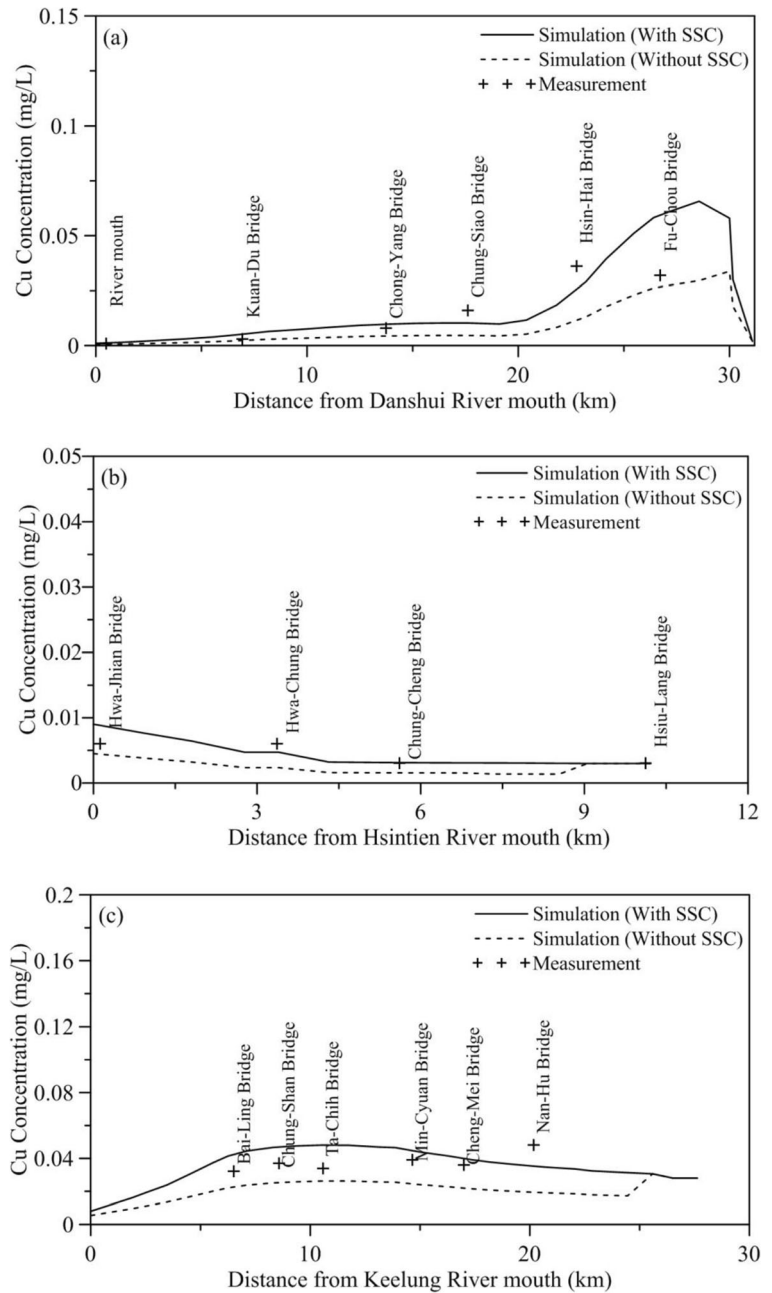
#### Effect of the suspended sediment concentration

To understand how the suspended sediment module is of critical importance in the coupled model (SELFE-SED-

HM), the validated model was conducted without taking into account the suspended sediment module, and then compared with the condition including the suspended sediment module (baseline condition).

Figure 7 illustrates the simulated results of the copper concentration with and without including the suspended sediment module on December 1, 2015, in the Danshui River-Dahan River, the Hsintien River, and the Keelung River. The measured data of copper concentration are also shown in Fig. 7. The results indicate that when the suspended sediment module is not included in the model simulations, the simulated copper concentrations along the estuarine system decrease compared with the simulated copper concentrations when the suspended sediment module is considered in the model simulations. Figure 7 also reveals that the simulated copper concentrations in the estuarine system do not mimic the measured data on December 1, 2015, if the suspended

**Fig. 7** Influence of the suspended sediment on the distribution of copper concentrations on December 1, 2015 in **a** the Danshui River-Dahan River, **b** the Hsintien River, and **c** the Keelung River



sediment module is excluded from the model simulations.

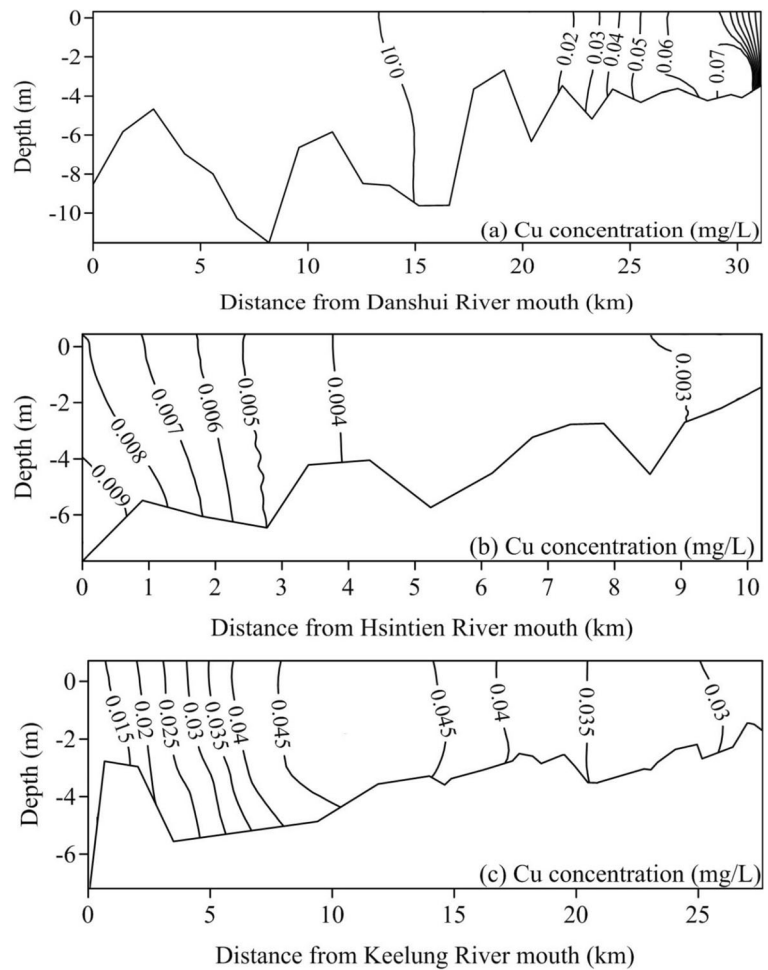
The maximum rates (*MR*) for excluding the suspended sediment module in the model simulations were  $-55\%$ ,  $-55\%$ , and  $-45\%$  for the Danshui River-Dahan River, the Hsintien River, and the Keelung River, respectively. The maximum rate (*MR*) can be expressed as (Chen and Liu 2017),

$$MR = \frac{C_{HM,without\ SSC} - C_{HM,with\ SSC}}{C_{HM,with\ SSC}} \times 100\% \quad (8)$$

where  $C_{HM, without\ SSC}$  denotes the simulated copper concentration without a suspended sediment module and  $C_{HM, with\ SSC}$  represents the simulated copper concentration with a suspended sediment module (baseline).



**Fig. 8** The tidally averaged distribution of copper concentrations including the suspended sediment transport module (Baseline) in **a** the Danshui River-Dahan River, **b** the Hsintien River, and **c** the Keelung River



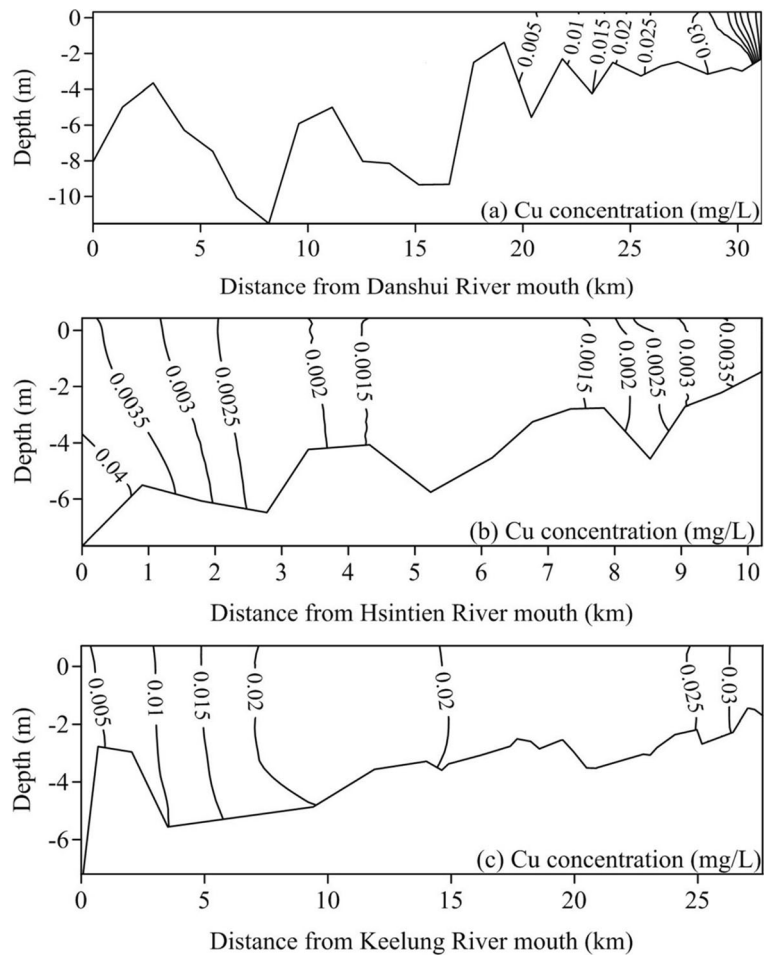
Figures 8 and 9 display the vertical distribution of the tidally averaged copper concentration with (baseline) and without including the suspended sediment module, respectively. Comparing the simulated results shown in Figs. 8 and 9, the copper concentrations in the tidal estuarine system appear to have a significant difference. Notably, the simulated copper concentrations with a suspended sediment transport module (baseline) are higher than those without a suspended sediment transport module in the model throughout the tidal estuaries. The simulated copper concentration with a suspended sediment transport module (baseline) increases 1.0~1.4, 0.5~1.7, 0.7~1.5 times approximately in the Danshui River-Dahan River, the Hsintien River, and the Keelung River, respectively, compared with that without suspended sediment. This demonstrates that the suspended sediment concentration in tidal estuarine systems plays

a crucial role to affect the transport and distribution of the copper concentration.

Recently, Samano et al. (2014), Lu et al. (2014), and Horvat and Horvat (2016) used the suspended sediment and heavy metal transport model to simulate the concentration of heavy metal in rivers and estuaries. However, to the best of our knowledge, the importance of the suspended sediment transport module in the model simulations was not yet demonstrated and quantified. In the current study, we proved that the suspended sediment transport for heavy metal concentration is extremely significant in the Danshui River estuarine system. The simulated copper concentrations in the estuarine system would underestimate the measured data if the suspended sediment module was not considered in model simulations.

There are several important pollutant sources along the Danshui River estuarine system to aggravate the

**Fig. 9** The tidally averaged distribution of copper concentration excluding the suspended sediment transport module in **a** the Danshui River-Dahan River, **b** the Hsintien River, and **c** the Keelung River



heavy metal contamination. In future research, the coupled contaminant transport model will be utilized to analyze the effect of different pollutant reduction options on the transport and distribution of heavy metal in tidal estuaries.

**Conclusions**

A heavy metal (copper) transport model was developed and coupled with a three-dimensional hydrodynamic, salinity, and suspended sediment module (SELFED-HM) to predict the transport and distribution of copper concentrations in the Danshui River estuarine system of northern Taiwan. The coupled model was validated with data from 2015 on the observed water level, velocity, salinity, suspended sediment concentration, and copper concentration. The simulated results

satisfactorily reproduced the measured data including the hydrodynamics, salinity, suspended sediment concentration, and copper concentration.

The validated model was then used to explore the effects of the freshwater discharge and suspended sediment on the distribution of copper concentrations. The predicted results indicate that the copper concentration in the estuarine system under low flow conditions is higher than that under high flow conditions. The model was also conducted with and without considerations of the suspended sediment module in model simulations. The simulated results reveal that the influence of the suspended sediment on the copper concentration is of crucial importance. The simulated copper concentrations in the model simulations including the suspended sediment transport module, which represents a baseline, are higher than those excluding the suspended sediment transport module. The results demonstrate that the

suspended sediment has extreme importance to affect the transport and distribution of copper concentrations in estuaries.

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## References

- Alvarez, A. M., & Trento, A. E. (2014). Analytical and numerical solutions for sediment and heavy metal transport: a 1D simplified case. *Water Quality Research Journal*, *49*(3), 258–272.
- Benoit, G., Oktay-Marshall, S. D., Cantu, A., Hood, E. M., Cokeman, C. H., Corapcioglu, M. O., & Santschi, P. H. (1994). Partitioning of Cu, Pb, Ag, Zn, Fe, Al, and Mn between filter-retained particles, colloids, and solution in six Texas estuaries. *Marine Chemistry*, *45*(4), 307–336.
- Blumberg, A. F., & Mellor, G. L. (1987). A description of a three-dimensional coastal ocean circulation model. In N. Heaps (Ed.), *Three-dimensional coastal ocean models*. Coastal and Estuarine Studies (Vol. 4, pp. 1–16). Washington, DC: AGU.
- Casulli, V., & Cheng, R. T. (1992). Semi-implicit finite difference methods for three-dimensional shallow water flow. *International Journal for Numerical Methods in Fluids*, *15*(6), 629–648.
- Casulli, V., & Walters, R. A. (2000). An unstructured grid, three-dimensional model based on the shallow water equations. *International Journal for Numerical Methods in Fluids*, *32*(3), 331–348.
- Chen, W. B., & Liu, W. C. (2017). Investigating the fate and transport of fecal coliform contamination in a tidal estuarine system using a three-dimensional model. *Marine Pollution Bulletin*, *116*, 366–384.
- Chen, C., Liu, H., & Beardsley, R. C. (2003). An unstructured grid, finite-volume, three-dimensional primitive equations ocean model: application to coastal ocean and estuaries. *Journal of Atmospheric and Oceanic Technology*, *20*, 159–186.
- Chen, W. B., Liu, W. C., Kimura, N., & Hsu, M. H. (2010). Particle release transport in Danshui River estuarine system and adjacent coastal ocean: a modeling assessment. *Environmental Monitoring and Assessment*, *168*(1–4), 407–428.
- Chen, W. B., Liu, W. C., & Hsu, M. H. (2011). Water quality modeling in a tidal estuarine system using a three-dimensional model. *Environmental Engineering Science*, *28*(6), 443–459.
- Cho, E., Arhonditsis, G. B., Khim, J., Chung, S., & Heo, T. Y. (2016). Modeling metal-sediment interaction process: parameter sensitivity assessment and uncertainty analysis. *Environmental Modelling & Software*, *80*, 159–174.
- Das, A., Justic, D., Inoue, M., Hoda, A., Huang, H., & Park, D. (2012). Impacts of Mississippi River diversions on salinity gradients in a deltaic Louisiana estuary: ecological and management implications. *Estuarine, Coastal and Shelf Science*, *111*, 17–26.
- de Souza Machado, A. A., Spencer, K., Kloas, W., Toffolon, M., & Zarfl, C. (2016). Metal fate and effects in estuaries: a review and conceptual model for better understanding of toxicity. *Science of the Total Environment*, *541*, 268–281.
- Etemad-Shahidi, A., Shahkolahi, A., & Liu, W. C. (2010). Modeling of hydrodynamics and cohesive sediment processes in an estuarine system: case study in Danshui River. *Environmental Modeling and Assessment*, *15*(4), 261–271.
- Hartnett, M., & Berry, A. (2012). Numerical modelling of the transport and transformation of trace metals in a highly dynamic estuarine environment. *Advances in Engineering Software*, *44*(1), 170–179.
- Hartnett, M., Lin, B., Jones, P. D., & Berry, A. (2006). Modelling the fate and transport of nickel in the Mersey Estuary. *Journal of Environmental Science and Health, Part A*, *41*(5), 825–847.
- He, M., Wang, Z., & Tang, H. (2010). Modeling the ecological impacts of heavy metals on aquatic ecosystems: a framework for the development of an ecological model. *Science of the Total Environment*, *266*(1–3), 291–298.
- Horvat, Z., & Horvat, M. (2016). Two-dimensional heavy metal transport model for natural watercourses. *River Research and Applications*, *32*(6), 1327–1341.
- Hsu, M. H., Kuo, A. Y., Kuo, J. T., & Liu, W. C. (1999). Procedures to calibrate and verify numerical models of estuarine hydrodynamics. *Journal of Hydraulic Engineering*, *125*(2), 166–182.
- Huang, K. M., & Lin, S. (2003). Consequences and implication of heavy metal spatial variations in sediments of the Keelung River drainage basin, Taiwan. *Chemosphere*, *53*(9), 1113–1121.
- Ji, G., Hamrick, J. H., & Pagenkopf, J. (2002). Sediment and metal modeling in shallow river. *Journal of Environmental Engineering*, *128*(2), 105–119.
- Jiann, K. T., Wen, L. S., & Santschi, P. H. (2005). Trace metal (Cd, Cu, Ni and Pb) partitioning, affinities and removal in the Danshuei River estuary, a micro-tidal, temporally anoxic estuary in Taiwan. *Marine Chemistry*, *96*(3), 293–313.
- Karna, T., Baptista, A. M., Lopez, J. E., Turner, P. J., McNeil, C., & Sanford, T. B. (2015). Numerical modeling of circulation in high-energy estuaries: a Columbia River estuary benchmark. *Ocean Modelling*, *88*, 54–71.
- Lin, H. J., Shao, K. T., Jan, R. Q., Hsieh, H. L., Chen, C. P., Hsieh, L. Y., & Hsiao, Y. T. (2007). A trophic model for the Danshuei River Estuary, a hypoxic estuary in northern Taiwan. *Marine Pollution Bulletin*, *54*(11), 1789–1800.

- Liu, W. C., & Chan, W. T. (2014). Assessing the influence of nutrient reduction on water quality using a three-dimensional model: case study in a tidal estuarine system. *Environmental Monitoring and Assessment*, 186(12), 8807–8825.
- Liu, W. C., & Huang, W. C. (2012). Modeling the transport and distribution of fecal coliform in a tidal estuary. *Science of the Total Environment*, 431, 1–8.
- Liu, W. C., Chen, W. B., Cheng, R. T., Hsu, M. H., & Kuo, A. Y. (2007a). Modeling the influence of river discharge on salt intrusion and residual circulation in Danshui River estuary. *Continental Shelf Research*, 27(7), 900–921.
- Liu, K. K., Kuo, S. J., Wen, L. S., & Chen, K. L. (2007b). Carbon and nitrogen isotopic composition of particulate organic matter and biogeochemical processes in the eutrophic Danshuei Estuary in northern Taiwan. *Science of the Total Environment*, 382, 103–120.
- Liu, W. C., Chen, W. B., Kuo, J. T., & Wu, C. (2008). Numerical determination of residence time and age in a partially mixed estuary using three-dimensional hydrodynamic model. *Continental Shelf Research*, 28(8), 1068–1088.
- Lu, S., Li, R., Xia, X., & Zheng, J. (2014). Use of a three-dimensional model to predict heavy metal (copper) fluxes in the Qujiang estuary. *Water Science and Technology*, 69(6), 1334–1343.
- Menon, M. G., Gibbs, R. J., & Phillips, A. (1998). Accumulation of muds and metals in the Hudson River estuary turbidity maximum. *Environmental Geology*, 34(2–3), 214–222.
- Murdoch, N., Jones, P. J. C., Falconer, R. A., & Lin, B. (2010). A modelling assessment of contaminant distributions in the Severn Estuary. *Marine Pollution Bulletin*, 61(1–3), 124–131.
- Ng, B., Turner, A., Tyler, A. O., Falconer, R. A., & Millward, G. E. (1996). Modelling contaminant geochemistry in estuaries. *Water Research*, 30(1), 63–74.
- Partheniades, E. (1965). Erosion and deposition of cohesive soils. *Journal of the Hydraulics Division*, 91(1), 105–139.
- Premier, V., de Souza Machado, A. A., Mitchell, S., Zarfl, C., Spencer, K., & Toffolon, M. (2019). A model-based analysis of metal fate in the Thames Estuary. *Estuaries and Coasts*, 42(4), 1185–1201.
- Rodi, W. (1984). *Turbulence models and their applications in hydraulics: a state of the art review*. Delft: International Association for Hydraulics Research.
- Samano, M. L., Garcia, A., Revilla, J. A., & Alvarez, C. (2014). Modeling heavy metal concentration distributions in estuarine waters: an application to Suances Estuary (Northern Spain). *Environmental Earth Sciences*, 72(8), 2931–2945.
- Shchepetkin, A. F., & McWilliams, J. C. (2005). The regional oceanic modeling system (ROMS): a split-explicit, free-surface, topography-following-coordinate, oceanic model. *Ocean Modelling*, 9(4), 347–404.
- Shrestha, O. L., & Orlob, G. T. (1996). Multiphase distribution of cohesive sediments and heavy metals in estuarine systems. *Journal of Environmental Engineering*, 122(8), 730–740.
- Song, Y., & Haidvogel, D. (1994). A semi-implicit ocean circulation model using a generalized topography-following coordinate system. *Journal of Computational Physics*, 115(1), 228–244.
- Trento, A. E., & Alvarez, A. M. (2011). A numerical model for the transport of chromium and fine sediments. *Environmental Modeling and Assessment*, 16(6), 551–564.
- Wang, C. F., Hsu, M. H., & Kuo, A. Y. (2004). Residence time of the Danshuei River estuary, Taiwan. *Estuarine, Coastal and Shelf Science*, 60(3), 381–393.
- Wang, C. F., Hsu, M. H., Liu, W. C., Hwang, J. S., Wu, J. T., & Kuo, A. Y. (2007). Simulation of water quality and plankton dynamics in the Danshuei River estuary. *Journal of Environmental Science and Health, Part A*, 42(7), 933–953.
- Wang, C., Wang, X., Wang, B., Zhang, C., Shi, Z., & Zhu, C. (2009). Level and fate of heavy metals in the Changjiang estuary and its adjacent waters. *Oceanology*, 49(1), 64–72.
- Warner, C. J., Geyer, W. R., & Lerczak, J. A. (2005). Numerical modeling of an estuary: a comprehensive skill assessment. *Journal of Geophysical Research*, 110, C05001.
- Water Resources Agency. (2017). *Hydrological year book of Taiwan*. Nantun District: Water Resources Agency, Ministry of Economic Affairs.
- Wen, L. S., Jiann, K. T., & Liu, K. K. (2008). Seasonal variation and flux of dissolved nutrients in the Danshuei Estuary, Taiwan: a hypoxic subtropical mountain river. *Estuarine, Coastal and Shelf Science*, 78(4), 694–704.
- Willmott, C. J. (1981). On the validation of models. *Physical Geography*, 2(2), 184–194.
- Woitke, P., Wellmütz, J., Helm, D., Kube, P., Lepom, P., & Litherat, P. (2003). Analysis and assessment of heavy metal pollution in suspended soils and sediments of the river Danube. *Chemosphere*, 51(8), 633–642.
- Wu, Y., Falconer, R. A., & Lin, B. (2005). Modelling trace metal concentration distributions in estuarine waters. *Estuarine, Coastal and Shelf Science*, 64(4), 699–709.
- Zhang, Y., & Baptista, A. M. (2008). SELFE: A semi-implicit Eulerian-Lagrangian finite-element model for cross-scale ocean circulation. *Ocean Modelling*, 21(3–4), 71–96.
- Zhang, Y., Baptista, A. M., & Myers, E. P. (2004). A cross-scale model for 3D baroclinic circulation in estuary-plume-shelf systems: I. Formulation and skill assessment. *Continental Shelf Research*, 24(18), 2187–2214.
- Zhang, W., Feng, H., Zheng, J., Houtink, A. J. F., van der Vegt, M., Zhu, Y., & Cai, H. (2013). Numerical simulation and analysis of saltwater intrusion lengths in Pearl River Delta, China. *Journal of Coastal Research*, 29(2), 372–382.

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