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Research Article

Modelling of Cd Transformation in Water

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Abstract: Based on the model of transforming of Cd in the water, in the detritus and in the sediment, an improved box model of the multiple medium transforming of Cd in water environment was developed, including another two state variables, the content of Cd in the zooplankton and the phytoplankton. With this model, the influence to Cd cycle by adsorbent process and exogenous input was studied and a method of estimating environmental capacity of Cd was pointed out.

Keywords: Cd, heavy metal, modelling, plankton

INTRODUCTION

Metal Cd is widely used in many kinds of industries such as electroplating, alloy and battery. Cd is toxic and can enter and accumulate in animal and human body through their digestive and respiratory tract. Accumulated Cd in liver or kidney can affect the normal function of enzyme system. Cd in waste water is hazardous to the environment and health. Therefore, it is very necessary to study how to simulate the migration and transformation of Cd in water and how to control it.

Three state variables are considered in typical multi-phase model, including heavy metal dissolved in water, absorbed in detritus and in sediment. This kind of model is widely used all over the world, for example, the Pb transforming model in Jiaozhou Bay (Li *et al*., 2009a), the migration and transformation model of heavy metal in Xiangjiang River (Dou *et al*., 2007), the three-dimensional model of Cu and Pb in Boston Harbor (Li *et al*., 2010), etc. The effect of different operation conditions on heavy metal bio-sorption such as pH is becoming a focus of research (Li *et al*., 2009a; Zeng *et al*., 2011).

The state variables described above are most concerned in recent researches. However, the effect of plankton on heavy metal transforming process needs to be studied, because the accumulation of heavy metal in plankton is significant (Pyrzyńska and Bystrzejewski, 2010). On one hand, the plankton has metabolic ability and has different composition from suspended detritus, so suspended detritus cannot be used to represent the plankton role. On the other hand, the study of biological accumulation is helpful for analysis of the heavy metal threat to the plankton. Thus, an improved multi-phase model of Cd migration and transformation was developed in this study. Another two state variables were added to typical model-Cd concentration in phytoplankton and in zooplankton.

METHODOLOGY OF MODEL

This model can be used to simulate the Cd cycle in water and when parameters and initial condition are determined, Cd transformation can be predicted by this model.

This box model included five state variables, the dissolved Cd concentration in water (M: μg/L), the concentration of adsorbed Cd in detritus (M_D: μg/L), the concentration of Cd in sediment (M_M: μg/L) and Cd concentration in phytoplankton (M_P: μg/g) and in zooplankton (M_Z: μg/g).

The formula of a certain matter in box model was given by:

$$\frac{\partial HC}{\partial t} = H(S^C + Q^C) \tag{1}$$

where,
H = The water depth
C = The Cd concentration in a certain state
S^C = The source item
Q^C = Includes interactions between state variables, growth, death and sedimentation

According to the transformation of Cd between different states, the model was built as shown in Fig. 1.

Runoff input and atmospheric sedimentation are the source of this system. Dissolved Cd can be absorbed by suspended detritus. The phytoplankton can absorb and accumulate the dissolved Cd. Cd in water, detritus

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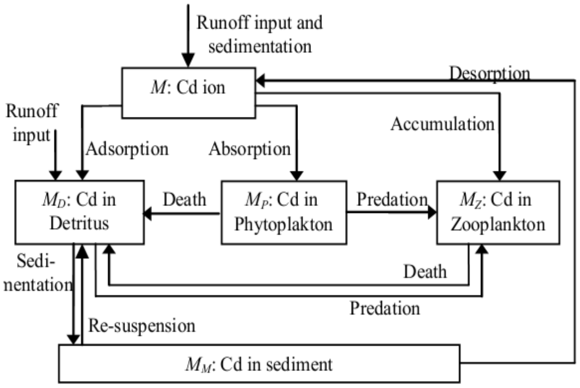

Fig. 1: Cd cycle in water

and phytoplankton can be predated by zooplankton and accumulating in its body. The dead body of zooplankton and phytoplankton return to water in form of suspended particles. Cd in detritus can enter into sediment and then return to water in certain condition (Dong *et al*., 2010). In polluted area, the heavy metal in sediment has a high level of concentration and can be desorbed sometimes, so Cd can return to water from sediment. Strictly speaking, Cd in detritus can also be desorbed, but this process can be ignored, because the desorption scale is relatively small (Blackmore, 2001).

Formulas in model: In formula (1), the interaction item Q^C varies from state variables and formula for each variable will be discussed in this section.

Dissolved Cd: Under the hypothesis that the concentration Cd in detritus is uniformed in the spatial distribution, considering the mass transfer process in the liquid-solid interface on detritus, the adsorption of dissolved Cd (Huang *et al*., 2008) and the release of Cd from sediment, the change of dissolved Cd concentration was given by Li *et al*. (2009b):

$$Q^M = -k_1\left(\theta f_0 M_D - M\right) + k_2\left(f_1 M_M - M\right) \tag{2}$$

where,
M : Dissolved Cd (µg/L)
k_1 : Adsorption coefficient between dissolved and particulate Cd (1/d)
θ : The content of suspended particles in unit volume water (µg/L)
f_0 : The distribution coefficient between water and particles
M_D : The concentration of Cd in particles (µg/L)
k_2 : The desorption coefficient between water and sediment (1/d)

Cd in sediment: Sedimentation of Cd in detritus contributes a lot to Cd in sediment (M_M: µg/L). Cd in sediment can return to water in certain condition of water flow and the formula was given by Li *et al.* (2010):

$$Q^{M_M} = -k_2\left(f_1 M_M - M\right) + \frac{w_0 M_D}{H} - \frac{K w_0}{H} M_M \tag{3}$$

where,
w_0 = The rate of sedimentation (1/d)
K = The factor of re-suspension

Cd adsorbed in detritus: The interaction item of Cd adsorbed in detritus was given by Li *et al*. (2010):

$$\begin{aligned} Q^{M_D} &= -\frac{w_0 M_D}{H} + \frac{K w_0}{H} M_M \\ &\quad + k_1\left(\theta f_0 M_D - M\right) + \mu_{ZM} M_Z C_Z + \mu_{PM} M_P \end{aligned} \tag{4}$$

where,
$\mu_{ZM} M_Z C_Z$ & $\mu_{PM} M_P$: The contribution to the Cd in detritus, from death process of zooplankton and phytoplankton respectively
μ_{ZM} : The death rate of zooplankton
C_Z : The content of zooplankton in water
μ_{PM} : The death rate of phytoplankton

Cd concentration in zooplankton: Cd concentration in zooplankton is the mass of Cd per unit mass of phytoplankton in µg/g. Cd in zooplankton is mainly from dissolved Cd and its food, including phytoplankton and detritus. According to the principle of bio-accumulation and bio-magnification, Cd will accumulate in zooplankton's body. In case of death and breeding, Cd in zooplankton can return to water in form of detritus. Its interactive formula was given by Pan and Wang (2008):

$$\begin{aligned} Q^{M_Z} &= k_u M + AE(IR \times {}^{M_D}\!/_{\theta} + IP \times M_P) \\ &\quad - \left(k_e + g\right) M_Z \end{aligned} \tag{5}$$

where,
k_u : The uptake rate constant from dissolved Cd
AE : The Cd assimilation efficiency of zooplankton
IR : The ingestion rate of zooplankton
IP : The ingestion rate of phytoplankton
k_e : The Cd efflux rate constant
g : Growth rate constant of zooplankton
M_D/θ : The concentration of Cd in detritus, which can be taken by zooplankton

Cd concentration in phytoplankton: Cd concentration in phytoplankton (M_P: µg/g) was given like zooplankton:

$$Q^{M_P} = k_{up} M - AE \times IP \times M_P - g_P M_P \tag{6}$$

Table 1: Initial condition

Variables	Value	Units
Dissolved Cd	0.037	µg/L
Cd adsorbed in particles	1	µg/L
Cd in sediment	0.190	µg/L
Cd concentration in phytoplankton	0.120	µg/g
Cd concentration in zooplankton	1.400	µg/g

Table 2: Parameters in model

Symbol	Value	Definition
k_1	3.630×10^{-3} d^{-1}	Adsorption coefficient between dissolved and particulate Cd
θ	2.430×10^{3} µg/L	Content of suspended particles in unit volume water
f_0	20	Distribution coefficient between water and particles
k_2	5.200×10^{-4} d^{-1}	Desorption coefficient between water and sediment
f_1	4.000	Distribution coefficient between water and sediment
K	0.200	Factor of re-suspension
k_u	0.455 L/ (g·d)	Uptake rate constant from dissolved Cd of zooplankton
AE	0.876	Cd assimilation efficiency of zooplankton
IR	0.400 g/ (g·d)	Ingestion rate of zooplankton
k_e	0.090 d^{-1}	Cd efflux rate constant of zooplankton
g	0.195 d^{-1}	Growth rate constant of zooplankton
IP	0.400 g/ (g·d)	Ingestion rate of phytoplankton
k_{up}	2.280 L/ (g·d)	Uptake rate constant from dissolved Cd of phytoplankton
g_P	0.471 d^{-1}	Growth rate constant of phytoplankton

where,

k_{up} = The uptake rate constant from dissolved Cd of phytoplankton

g_P = The growth rate constant of phytoplankton

Implement of the model: The initial concentration of state variables was given in Table 1 and parameters in this study were determined according to relative papers (Pan and Wang, 2008; Reinfelder *et al.*, 1998), as shown in Table 2.

The exogenous input was mainly composed of runoff input and atmospheric sedimentation and the input amount in this model were 3.33×10^{-3} mg/m^3·d and 6.67×10^{-3} mg/m^3·d, respectively.

The classical Runge-Kutta method was adopted to solve the model. After verification of time step independence, the time step was fixed for 1 h.

RESULTS AND DISCUSSION

Example: The water depth was 10 m and water stayed still. Computing time was 720 h (30 days). And the result was shown in Fig. 2.

As shown in Fig. 2, dissolved Cd concentration tends to be stable and Cd in detritus keeps growing, because dissolved Cd can be absorbed by suspended detritus. Most suspended particles fall to sediment, so Cd is accumulated in sediment. The Cd concentration of phytoplankton keeps decreasing because of metabolism. The Cd in zooplankton keeps increasing at first because of bio-accumulation and then drops down.

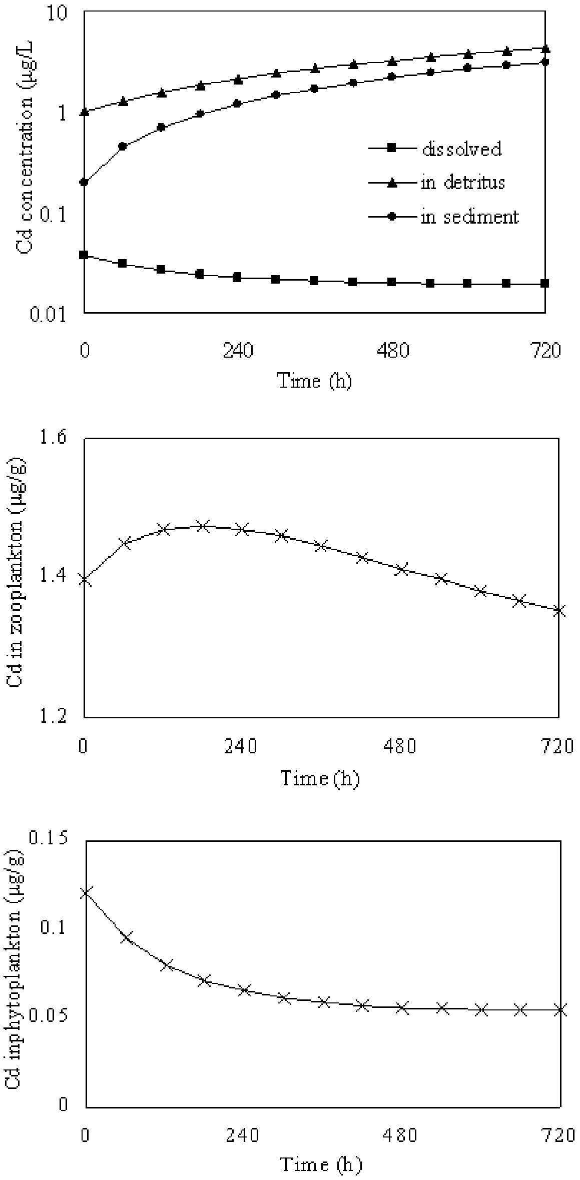

Fig. 2: Cd concentration of different states in water in 720 h (30 days)

The influence of adsorption process: Through a series of experiments of different adsorption coefficient values, the influence of adsorption process to the Cd cycle was analyzed. The adsorption coefficient values from 2.71 to 9.07×10^{-3} d^{-1} and 3.60×10^{-3} d^{-1} was adopted in the example according to the value measured in laboratory (Dong *et al.*, 2010). Three adsorption coefficient values were adopted in experiments, which were 2.88×10^{-3} d^{-1}, 3.60×10^{-3} d^{-1} and 4.32×10^{-3} d^{-1}. The result was shown in Fig. 3.

Dissolved Cd is strongly influenced by the adsorption coefficient. Higher adsorption coefficient

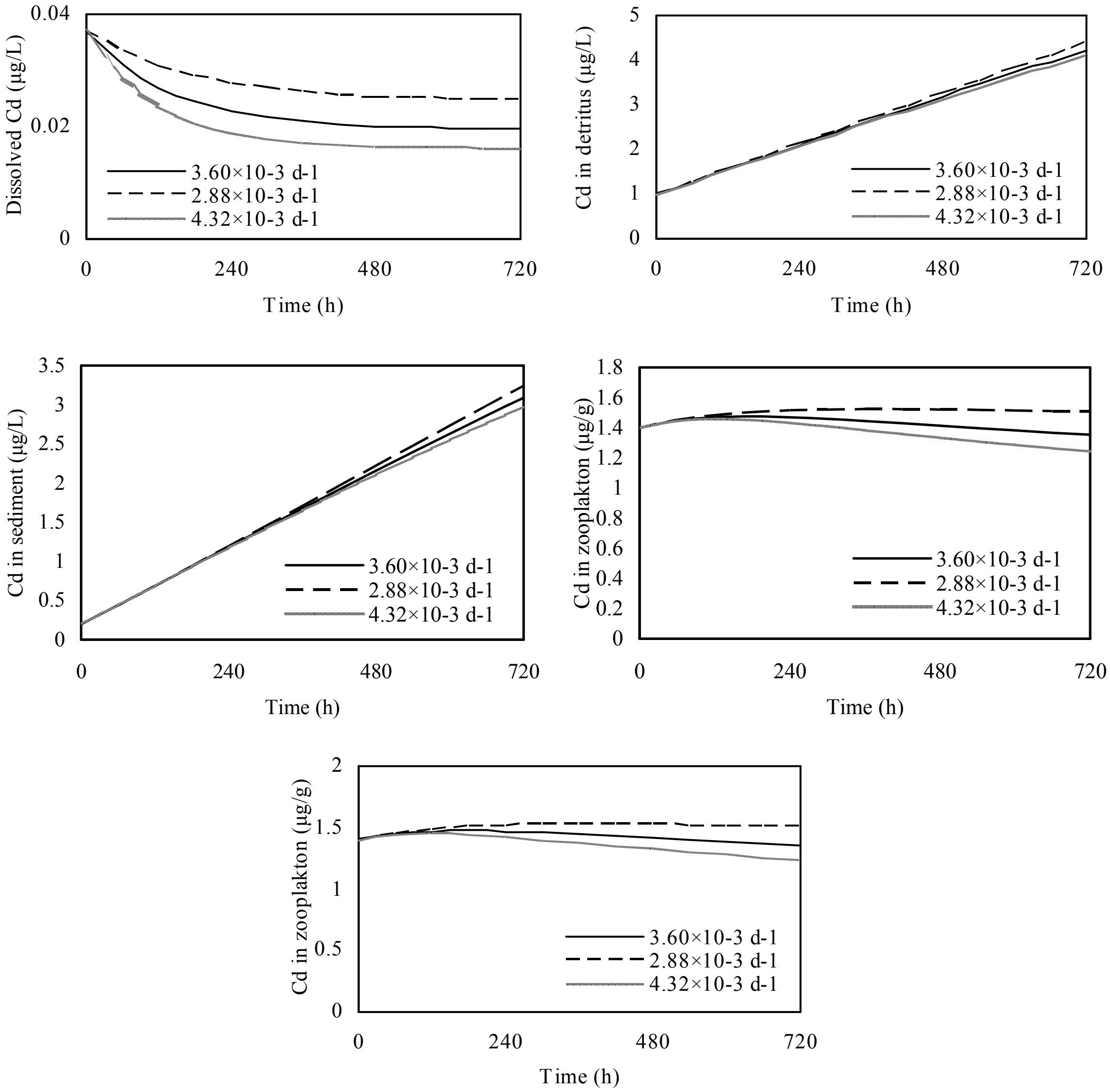

Fig. 3: Influence of adsorption coefficient

value brings stronger absorption reaction and lower dissolved Cd concentration. On the contrary, lower adsorption coefficient value brings higher dissolved Cd concentration. Adsorption process is significant to dissolved Cd in water. This process has a weak influence on Cd concentration in detritus and sediment, but it has a strong influence on Cd content in phytoplankton and zooplankton. Because Cd ion can be uptaked by phytoplankton and zooplankton, the Cd content in phytoplankton and zooplankton will be higher when dissolved Cd concentration is higher.

The influence of exogenous input: In order to study the influence of exogenous input, the two exogenous sources are increased by 50, 100 and 200%, respectively and the result of simulation is shown in Fig. 4.

When the sources are increased by 50%, every state variable is increased distinctly. Cd in phytoplankton keeps increasing instead of decreasing. The tendency of the other state variables is basically the same as in the example. This implies zooplankton is more sensitive to exogenous input. When water is in a certain degree of Cd pollution, Cd in zooplankton body will be gradually accumulated and is hard to be metabolic. When the sources are increased by 100%, Cd ion concentration keeps increasing at first and tends to be stable at last. It suggests that adsorbing dissolved Cd is more difficult in this situation. When the sources are increased by 200%, dissolved Cd is increasing significantly and Cd concentration of phytoplankton is reduced at first and then goes up and tendsto be stable at last. It indicates that as a primary productivity, phytoplankton has strong metabolic ability and low

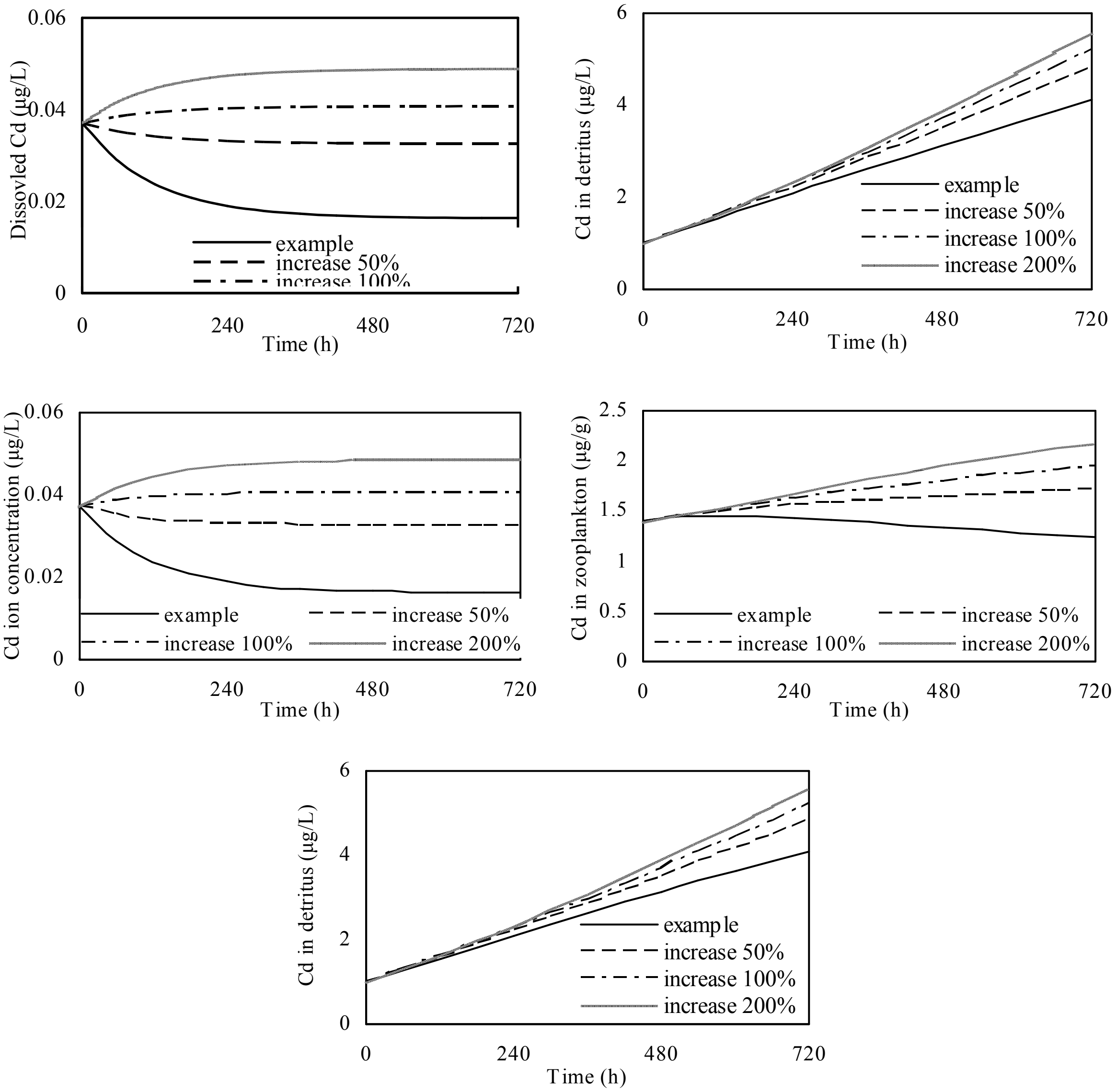

Fig. 4: Influence of exogenous input

sensitive degree of exogenous input and can suffer strong exogenous input. On the other hand, the increase of every state variable implies that Cd pollution is beyond the environmental capacity completely and the water cannot recover through self-purification without water treatment. Environmental capacity can be estimated by adapting the exogenous input and observing the tendency of state variables in a series of results.

CONCLUSION

Based on the traditional model of transforming of Cd in water, in detritus and in sediment, an improved box model of Cd cycle in water was developed, including another two state variables-the content of Cd in the zooplankton and the phytoplankton. And classical Rage-Kutta method was adopted to solve this model. As was shown in the results, some conclusions can be drawn as follow. Adsorption process was significant to Cd cycle in water, especially to Cd dissolved in water. Higher adsorption coefficient value brings stronger absorption reaction and lower dissolved Cd concentration. Another conclusion can be drawn that Cd content of phytoplankton and zooplankton is positive correlative to exogenous input, by comparing among different exogenous input conditions. When exogenous resources are increased by 200%, Cd pollution is beyond environmental capacity and Cd concentration keeps increasing in the whole water environment and plankton. Environmental capacity could be estimated by adapting resources and observing the results.

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