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MODELING OF HEAVY METALS IN A RESERVOIR WITH DIFFUSIVE BOTTOM LAYER

P. V. Tkalitch, W. Chen and J. H. Tay

School of Civil and Structural Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 2263

ABSTRACT

A model of heavy metal kinetics in the well mixed reservoir with respect to vertical diffusion in the active bottom layer is presented. The model incorporates the mechanisms of a heavy metal reaction process between "overlying water -suspended sediments - interstitial water - bottom sediment". Application of long-term modeling is provided to simulate the self-cleaning abilities of the Kranji Reservoir. The adsorption rate of Zn on bottom sediments was determined by a modified batch test. The analytical results demonstrate the high retention and concentration of Zn in the interstitial water, which indicates the importance of including the interstitial water quality in the assessment of potential ecological effects. The numerical simulations show the influence of the bottom diffusive layer on Zn long-term dynamics in the aquatic system. Copyright © 1996 IAWQ. Published by Elsevier Science Ltd.

KEYWORDS

Bottom diffusive layer; distribution and diffusion coefficients; interstitial water; kinetic model; sediments; tropical reservoir; zinc.

INTRODUCTION

Heavy metals from urban runoff are well documented as having a number of potential ecological effects on receiving waters (Ellis *et al.*, 1991). Bottom sediments have the tendency to become the sink component for accumulation of heavy metals and consequently may adversely affect benthic organisms. In the long-term, the contaminated sediments could be a second source of pollution of the overlying water when the environmental conditions to which the sediment is exposed are altered (Nriagu, 1988).

In Singapore, artificial reservoir water which originates from urban runoff is a major source of water supply because of lack of natural fresh water resources. Therefore it is even more important to protect the reservoirs from contamination. Kranji Reservoir is one of the major water supply sources in Singapore. It is formed behind the tidal gate in the mouth of Kranji River at the north-west coast. The reservoir receives stormwater discharge over the nature reserves, fairly dense commercial and residential areas. The water quality of the reservoir has been previously investigated by Appan (1977), Phang (1987), Chen (1995) and Chen (in press) (see Tables 1, 2 and 3). It was shown that concentration of heavy metals in the interstitial water exceeded the water quality criteria for aquatic life by three to eleven times, which may lead to a potential threat to the benthic and overlying near-bed aquatic organisms.

To manage and control the water quality in the reservoir, a long-term prediction model is required. A numerical model can be a tool for predicting the fate of chemical pollutants in the reservoir, proposing and evaluating clean up remediations (Lung, 1993). With the development from static to dynamic models, emphasis on the kinetics and fate of pollutants have increased rapidly in recent years (Brezonik, 1993). A process-oriented box-type approach would allow us to answer most questions about the long-term effects of input parameters that are responsible for the physical phenomena involved on the distribution of chemical pollutants in the overlying water, suspended and bottom sediments. Each of the parameters depends on the physical-chemical properties of local sediments and water in the reservoir, and can only be obtained reliable by measurement rather than predicted.

HEAVY METAL MODEL STRUCTURE

Dissolved in the overlying water metals can react with the active upper bottom layer by means of the vertical molecular diffusion in the interstitial water, where it also actively interacts with the bottom sediments. The diffusion process in the active bottom layer (Fig. 1) can be described using the equation

$$\frac{\partial C^i}{\partial t} = D\frac{\partial^2}{\partial z^2}C^i + \text{Reactions}, \quad \text{with the boundary conditions:} \quad C^i\Big|_{z=0} = k_3 C^w, \quad C^i\Big|_{z=b} = C^g.$$

C^w, C^i and C^g = metal concentration in the overlying water, interstitial water of the upper active bottom layer and of the down inactive bottom layer, respectively, [g/cub.m].
b = efficient thickness of the contaminated upper bottom sediment layer [m].
D = diffusion coefficient for the soluble metal in the active bottom layer [sq.m/sec].
k_3 = exchange coefficient "overlying water- interstitial water" [-]; with respect to volumetric water content of the bottom sediments, dilution rate of outcome interstitial water and armoring effect.
z = vertical axes [m].

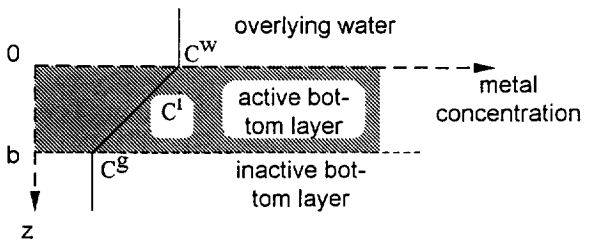

Figure 1. Schematic distribution of the dissolved heavy metals.

The complete mass-balance equations for the heavy metals in the system "overlying water - suspended sediments - interstitial water - bottom sediments" can be described as:

$$\begin{aligned}
&\frac{d}{dt}VC^w = -a_1\left(k_1 C^w - C^s\right) V S - \frac{4DF}{b}\left(k_3 C^w - C^i\right) + Q_i C_i^w - Q_o C^w ;\\
&\frac{d}{dt}VSC^s = a_1\left(k_1 C^w - C^s\right) V S + \left(q^b C^b - q^s C^s\right) F + Q_i S_i C_i^s - Q_o S C^s ;\\
&\frac{d}{dt}MC^b = a_2\left(k_2 C^i - C^b\right) M - \left(q^b C^b - q^s C^s\right) F ;\\
&\frac{d}{dt}C^i = -a_2\left(k_2 C^i - C^b\right)\rho_s + \frac{4D}{b^2}\left(k_3 C^w - 2C^i + C^g\right) ;\\
&\frac{d}{dt}VS = \left(q^b - q^s\right) F + Q_i S_i - Q_o S ; \quad \frac{d}{dt}M = \left(q^b - q^s\right) F ; \quad \frac{d}{dt}V = Q_i - Q_o .
\end{aligned} \tag{1}$$

where

$$a_1 = (\delta_1^s / \tau_1^s + \delta_1^d / \tau_1^d) / (1 + k_1 S); \quad a_2 = (\delta_2^s / \tau_2^s + \delta_2^d / \tau_2^d) / (1 + k_2 \rho_s);$$

$$q^s \equiv \begin{cases} w(S - S^*), & S > S^* \\ 0, & S \le S^* \end{cases}; \quad q^b \equiv \begin{cases} w(S^* - S), & S < S^* \\ 0, & S \ge S^* \end{cases}.$$

C^s and C^s_i = metal contamination of the suspended sediments in the reservoir and income water, respectively, [g/kg].
C^b = metal concentration in bottom sediments[g/kg].
Q_i and Q_o = input and output water discharge into a reservoir, respectively, [cub.m/sec].
V = water volume at a reservoir [cub.m].
M = mass of contaminated bottom deposits from the active layer [kg]($=r_s bF$).
F = area of a reservoir [sq.m].
k_1 and k_2 = distribution coefficients "overlying water-suspended sediments" and "interstitial water-bottom sediments", respectively, [cub.m/kg].
S and S_i = concentration of suspended sediments in the reservoir and income water, respectively, [kg/cub.m].
S^* = equilibrium concentration of suspended sediments in the reservoir [kg/cub.m].
w = settling velocity of the suspended sediments [m/sec].
r_s = bottom sediments' density [kg/cub.m].
d = delta-function for the determination of the contaminant transfer direction, with upper indexes "s" and "d" refer to the sorption and desorption phenomena, and down indexes "1" and "2" refer to the interface "solution-suspended sediments" and "interstitial water-bottom sediments", respectively.
t = time scales of the respective phenomena [sec].

In the absence of the contaminants' sources in the inactive bottom layer, if variation of the contamination in the interstitial water is small and speed of the metal exchange in the system "overlying water - bottom sediments" can be presented as $a_2 = 4D/(b^2 \rho_s k_2)$ the equations (1) can be simplified to those, derived and extensively verified by Zheleznyak *et al.* (1992).

The general set of the equations (1) can be rewritten in the following form

$$\frac{dX_j}{dt} = -A_j X_j + B_j; \quad (j=1,7) \tag{2}$$

where

$$\{X\}_{j=1,7} \equiv (C^w, C^s, C^b, C^i, S, M, V);$$

$$A_1 \equiv Q_i / V + a_1 k_1 S + 4k_3 DF/(Vb); \qquad B_1 \equiv Q_i C_i^w / V + a_1 S C^s + 4DF/(Vb);$$

$$A_2 \equiv Q_i S_i / (V S) + F q^b / (V S) + a_1; \qquad B_2 \equiv Q_i S_i C_i^s / (V S) + F C^b q^b / (V S) + a_1 k_1 C^w;$$

$$A_3 \equiv F q^s / M + a_2; \quad A_6 \equiv 0; \qquad B_3 \equiv F C^s q^s / M + a_2 k_2 C^w; \quad B_7 \equiv Q_i - Q_o;$$

$$A_4 = a_2 k_2 \rho_s + 8D/b^2; \qquad B_4 = 4D(k_3 C^w + C^g)/b^2 + a_2 \rho_s C^b;$$

$$A_5 \equiv Q_i / V + F w / V; \quad A_7 \equiv 0; \qquad B_5 \equiv Q_i S_i / V + F w S^* / V; \quad B_6 \equiv F w (S - S^*).$$

The (n+1)-th time-step D for the solution of equations (3) can be written in the unconditional stable form:

$$X_j^{(n+1)} = (X_j^{(n)} + B_j^{(n+1)} \Delta) / (1 + A_j^{(n)} \Delta), \quad j=1,7. \tag{4}$$

Finally, an explicit numerical solution of the model (1) can be developed using the approximation (4):

$$
\begin{aligned}
V^{(n)} &= V^{(n-1)} + B_7^{(n)}\Delta;\\
S^{(n)} &= \left(S^{(n-1)} + B_5^{(n)}\Delta\right)/\left(1 + A_5^{(n)}\Delta\right);\\
M^{(n)} &= M^{(n-1)} + B_6^{(n)}\Delta;\\
C^{i(n+1)} &= G_1^{(n)}/E_{14}^{(n)};\\
C^{s(n+1)} &= \left(G_2{}^{(n)} - E_{24}^{(n)}C^{i(n+1)}\right)/E_{22}^{(n)};\\
C^{b(n+1)} &= G_3^{(n)} + E_{32}^{(n)}C^{s(n+1)} + E_{34}^{(n)}C^{i(n+1)};\\
C^{w(n+1)} &= \left[C^{i(n+1)} - G_4^{(n)} - E_{43}^{(n)}C^{b(n+1)}\right]/E_{41}^{(n)};
\end{aligned}
\qquad (5)
$$

where

$$E_{14} = -(1-\alpha_{12}\alpha_{21} + E_{32}\alpha_{23})E_{24} - (\alpha_{14}\alpha_{21} - E_{34}\alpha_{23})E_{22}; \quad E_{22} = -E_{41} - E_{32}(E_{41}\alpha_{23} - E_{43}\alpha_{21});$$

$$E_{24} = -\alpha_{21} - E_{34}(E_{41}\alpha_{23} - E_{43}\alpha_{21}); \quad E_{32} = -q^{s}FC^{s}\Delta/(1 + A_3\Delta)/M; \quad E_{34} = -a_2k_2C^{i}\Delta/(1 + A_3\Delta);$$

$$E_{41} = -4Dk_3C^{w}\Delta/(1 + A_4\Delta)/b^2; \quad E_{43} = -a_2\rho_sC^{b}\Delta/(1 + A_4\Delta);$$

$$G_1 = (\beta_1\alpha_{21} + \beta_2 + G_3\alpha_{23})E_{22} - (1 - \alpha_{12}\alpha_{21} + E_{32}\alpha_{23})G_2; \quad G_4 = (C^{i} + 4\Delta DC^{g}/b^2)/(1 + A_4\Delta);$$

$$G_3 = C^{b}/(1 + A_3\Delta); \quad G_2 = -\beta_2E_{41} - G_4\alpha_{21} - G_3(E_{41}\alpha_{23} - E_{43}\alpha_{21}); \quad \alpha_{12} = a_1SC^{s}\Delta/(1 + A_1\Delta);$$

$$\alpha_{14} = 4DFC^{i}\Delta/(1 + A_1\Delta)/(Vb); \quad \alpha_{23} = Fq^{b}C^{b}\Delta/(1 + A_2\Delta)/(VS); \quad \alpha_{21} = a_1k_1C^{w}\Delta/(1 + A_2\Delta);$$

$$\beta_1 = (C^{w} + Q_iC_i^{w}\Delta/V)/(1 + A_1\Delta); \quad \beta_2 = (C^{s} + Q_iS_iC_i^{s}\Delta/(VS))/(1 + A_2\Delta);$$

MATERIALS AND METHODS

Sampling

Field samples used in the experiments were taken from Kranji Reservoir. Three sampling sites were selected. The water temperature, dissolved oxygen (DO) concentration and pH were measured in the field.

Samples for analysis of heavy metals in the overlying water, suspended and bottom sediments were taken at three sites in the reservoir. Grab sampling was used for the collection of sediments. All samples were moved to the laboratory in a temperature-controlled box. The overlying water was filtered through 0.45 μm filter paper. The filtered water was used for heavy metal analysis and kinetic batch testing. All containers had been soaked in 10% HNO_3 overnight and then rinsed with deionized water before storing samples and chemical reagents.

Analytical methods

The interstitial water was separated from the bottom sediment by centrifugation at 3500 rpm for 20 min. The supernatant was filtered through a 0.45 μm filter paper. The filtrate was collected for the analysis of Zn concentration. Raw overlying water and its filtrates (through 0.45 μm filter paper) were pre-concentrated by

evaporating the samples from 1000 mL to 20 mL in an oven at 65°C and made up to 50 mL. Metal analysis was conducted on the concentrated water samples. Total sediment-bound metals were released by adding 10 mL concentrated HNO_3 to 0.6 g of dried sediment which is then subjected to microwave digestion at 70% power for 10 min. After the digestion, the sample was diluted to 50 mL with deionized water for metal analysis. The concentration of Zn in the overlying water samples both with and without filtered, interstitial water and bottom sediments were determined by Perkin-Elmer Inductively Coupled Plasma Emission Spectrometry 400.

Table 1. Physical and chemical characteristics of sampling sites in Kranji Reservoir (KA, KB AND KC)

Sampling sites	Station 1 (KA)	Station 2 (KB)	Station 3 (KC)
Water depth (m)	6	12	17
Temperature (°C,Top/Bottom)	29.5/29.0	29.4/29.0	29.4/28.3
pH (Top/Bottom)	7.2/6.8	7.5/6.9	6.6/6.5
TSS (mg/l, Top/Bottom)	13.2/39.6	14.4/16.0	12.0/16.8
DO(mg/l, Top/Bottom)	8.76/0.44	8.64/3.72	6.06/3.70
Water Content (%, of bottom sediments)	85.78	91.96	82.86
Loss on Ignition(%, of bottom sediments)	16.90	21.88	16.54
COD (mg O_2/g dry sediments)	165.85	276.96	239.56

Table 2. Heavy metal concentration in the interstitial water and bottom sediment

Sampling site	Zn	Pb	Cu
Station 1 (KA)			
Interstitial water (μg/L)	1640.85	19.75	22.79
Bottom sediments (μg/g)	134.55	61.45	24.50
Station 2 (KB)			
Interstitial water (μg/L)	495.76	13.93	10.47
Bottom sediments (μg/g)	263.25	69.20	26.15
Station 3 (KC)			
Interstitial water (μg/L)	186.97	12.20	11.54
Bottom sediments (μg/g)	149.2	57.40	24.85

Kinetic experiments

The adsorption kinetics of Zn were measured using the batch test described by Amacher (1988) with modification. A total of 5 g of wet bottom sediment (with 87% water content) from sampling station 1(KA) in Kranji Reservoir was placed in a polyethylene bottle, two for each given time. 50 mL of overlying water (with addition of Zn) was mixed with sediment to give a final concentration of Zn, 2.4 mg/L. Sediment was separated from solution after 10, 12, 15, 17, 22, 30, 40 and 60 min by centrifugation at 3500 rpm for 10 min. 20 mL of 99.9 % ethanol was added to the separated sediment and shaken for 10 min and then centrifuged to extract the remaining solution. The supernatant was decanted and the residual sediment was dried at 65°C for 24 h. Heavy metals adsorbed in the sediment were extracted by 25 mL of 0.01M EDTA for 5 h. The extractant was separated from the sediment by centrifugation at 3500 rmp for 10 min and used for metal analysis.

MATHEMATICAL MODEL APPLICATION

The developed mathematical model was used for the evaluation of the self-cleaning abilities of the Kranji Reservoir under the assumption that all external sources of the contaminants are removed from the urban stormwater (starting point for simulation). All the water quality processes in the Kranji Reservoir are governed by the rate of release of the contaminants (by way of molecular diffusion) from the active bottom layer to the overlying water and suspended sediments. Most of the data and coefficients for the model were obtained from the laboratory experiments, as described in Table 3.

There are no reliable data for the value of the diffusion coefficient in the bottom layer of the Kranji Reservoir, but one can be assumed from the measurements by Shackelford (1989) for different chemicals and different types of soils. In the present study the value 1.7×10^{-10} has been chosen as the result of the numerical experiments directed to the model calibration on the real data. This value also agreed with the data range of Shackelford (1989). The specific dispersion coefficient should be more precisely evaluated in future laboratory experiments. Zinc is adsorbed, complexed and accumulated by bottom sediments under anoxic conditions. Low concentration was found in the overlying water. Loss of Zn induces a gradient in concentration between the overlying water and interstitial water. This induces a diffusive flux of Zn across the bottom sediments / overlying water interface. Character time for adsorption - desorption processes much more fast than diffusion time and does not affect the simulation results significantly. It is indicated that the major control fact for the Zn distribution in the absence of strong external sources is diffusion from the bottom layer, rather than desorption. For clarifying the water discharge influence on the reservoir's clean up abilities it was assumed that during the period of 25-35 years from the starting point, water discharge increased from an averaged level 10.6 to a maximal level 17.3 cub.m/s (Phang and Quah, 1987).

Table 3. Parameters for the numerical simulation

Parameter	Value	Parameter	Value	Parameter	Value	Parameter	Value
k_1[cub.m/kg]	10.06	τ_1 [s]	10	w [m/s]	0.02	F [sq.m]	5.E+6
k_2[cub.m/kg]	0.14	τ_2 [s]	10	ρ_s[kg/cb.m]	2000	V [c.m]	1.5E+7
k_3 [-]	180.4	D [sq.m/s]	1.7E-10	b [m]	0.05	Q_i ,Q_o-aver. [cub.m/s]	10.6
$C^{w(0)}$[g/cb.m]	7.26E-3	$C^{s(0)}$ [g/kg]	7.3E-2	S*[kg/cb.m]	0.013	Q_i ,Q_o-max. [cub.m/s]	17.3
$C^{i(0)}$[g/cub.m]	1.31	$C^{b(0)}$[g/kg]	1.82E-1	S_i[kg/cb.m]	0.013	Δ [year]	1

The interface surface between active and inactive bottom layers satisfies the permeability condition

$$\partial C^i / \partial z\Big|_{z=b} = 0 \quad \text{or} \quad C^{g(n+1)} = (C^{g(n)} + 4D\Delta C^{i(n)} / b^2) / (1 + 4D\Delta / b^2).$$

Results of the long-term simulation (up to 50 years) are shown in Fig. 2. During this period, contamination of the suspended sediments with Zn will be clean up to natural level 20 mg/g (Alloway, 1990). Concentration of Zn in overlying water all the time satisfies the water quality criteria for protection of aquatic life (Frits, 1990), however, the level of the interstitial water contamination exceeds the criteria even at the end of the simulation period. If it is assumed that interstitial water contains the mobile and bioavailable fraction of Zn in the bottom sediments, then the results of this study demonstrate the importance of interstitial water in sediment toxicity studies and in the assessment of potential ecological effects.

Increasing the water discharge leads to the temporal decreasing of the overlying water contamination level. However, this phenomenon does not significantly affect contamination of the active bottom layer, which restores the previous trend of overlying water contamination reduction after the discharge normalizing.

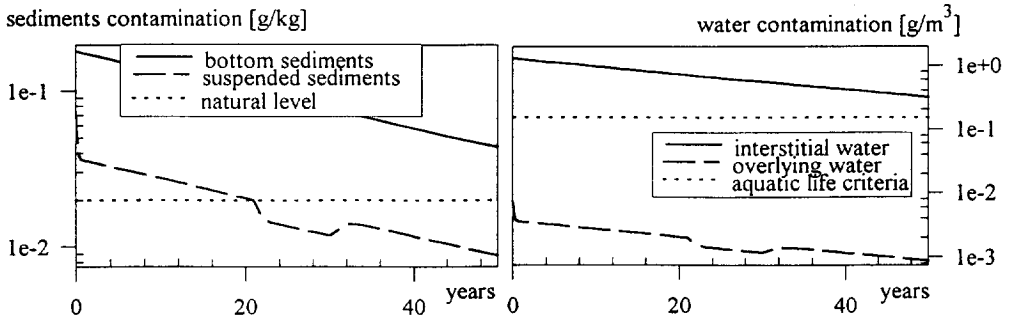

Figure 2. Numerical simulation of Zn concentration in Kranji Reservoir after elimination imagined pollution sources.

CONCLUSIONS

A model for heavy metals kinetics in reservoirs with respect to the diffusive boundary layer has been developed. Transport through the diffusive sediments boundary layer is the limiting factor of equilibrium conditions within the system "overlying water - interstitial water - bottom sediments".

The model application shows that for the long-term simulations, results are rather sensitive to the diffusion coefficient D and the variation of the distribution coefficients k_1 and k_2. The precise evaluation of these parameters should be the most significant contribution of the laboratory experiments to the model calibration.

During the 50 years of self clean up, Kranji Reservoir can reduce the concentration level of Zn in soluble and particulate form by one order of magnitude and reach near-natural conditions.

High retention and concentration of Zn in the interstitial water indicate the high risk of bottom sediments to the aquatic ecosystem.

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