

Incorporating sorption/desorption of organic pollutants into river water quality model

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Abstract: Preliminary research was conducted about how to incorporate sorption/desorption of organic pollutants with suspended solids and sediments into single-chemical and one-dimensional water quality model of Jinghang Canal. Sedimentation-resuspension coefficient k_3 was deduced; characteristics of organic pollutants, concentrations and components of suspended solids/sediments and hydrological and hydraulic conditions were integrated into k_3 and further into river water quality model; impact of sorption/desorption of organic pollutants with suspended solids and sediments on prediction function of the model was discussed. Results demonstrated that this impact is pronounced for organic pollutants with relatively large K_{oc} and K_{ow} , especially when they are also conservative and f_{oc} of river suspended solids/sediments is high, and that incorporation of sorption/desorption of organic pollutants into river water quality model can improve its prediction accuracy.

Keywords: water quality model; sorption/desorption; sedimentation-resuspension coefficient

Introduction

Since Streeter-Phelps (Streeter, 1925) set up the first water quality model, application of water quality model is becoming increasingly extensive in environmental pollution control and water quality programming.

Organic compounds are principal pollutants in river water body, whereas sediments are their source and sink in water. Organic pollutants in the water column can be sorbed by suspended solids and transferred to the sediment layer by settling; on the other hand, organic pollutants in bottom sediments can be released to overlying water by resuspension of sediments. So sorption/desorption of organic pollutants with suspended particulates and sediments is potential to significantly influence on their concentrations in water and further on their transport, degradation and fate in water environment. In order to indicate this effect, Thomas (Thomas, 1980) introduced the sedimentation-resuspension coefficient k_3 into river water quality model. However, in setting-up and application of the model, sorption/desorption of organic compounds with suspended particulates and sediments has not been paid enough attention, for example, k_3 is often disregarded or is calculated only by such means of simple methods as inverse deduction (Gao, 1985); also, the concentrations and components of suspended particulates/sediments are not efficiently taken into account, which often makes prediction results of water quality model deviate markedly from observations. This is disadvantageous to water environmental management and water pollution control.

In addition, most of present river water quality models are about BOD and DO, and BOD is a comprehensive index of organic pollutants. Because different organic pollutants

have different toxicity and environmental endangerments that are often concealed by BOD, it is increasingly necessary to set up river water quality model of single organic pollutant, especially for persistent toxic substances. For above reasons, we chose single-chemical river water quality model, selected Jinghang Canal as a target river, studied about how to integrate sorption/desorption of organic pollutants (*p*-chloronitrobenzene, nitrobenzene and *p*-nitrotoluene) with suspended particulates and sediments into water quality model, and to deduce the coefficient k_3 , and discussed influence of such factors as physicochemical properties of organic pollutants, contents and components of suspended solids/sediments and hydrological-hydraulic conditions on prediction function of river water quality model, the objective of which was to provide theoretical basis and practicable method for improving prediction accuracy of the model and protecting more effectively water environment.

1 Experimental

1.1 Materials

The test organic compounds, *p*-chloronitrobenzene, nitrobenzene, and *p*-nitrotoluene, analytical grade (99.5 + %), were purchased from Shanghai Chemical Reagent Company. Their water solubilities (S_w 's) and octanol-water partition coefficients ($\log K_{ow}$'s) are listed in Table 1. The sediment (its organic carbon content $f_{oc} = 3.98\%$) used was collected from the top 0–20 cm of the sediment surface of Hangzhou reach of Jinghang Canal near the Gongzhen Bridge. The procedures (i. e., being dried, ground, and homogenized to pass a 100-mesh sieve) were performed before experiments.

Table 1 Physicochemical properties and sorption isotherm linear regression equations of three organic compounds

Compounds	<i>p</i> -chloronitrobenzene	Nitrobenzene	<i>p</i> -nitrotoluene
S_w , mg/L, 25 °C	248.4	1936	339.3
$\log K_{ow}$	2.39	1.85	2.37
Linear regression equations of sorption isotherms ^a	$Q_e = 4.98 C_e$ ($r^2 = 0.9933$)	$Q_e = 1.68 C_e$ ($r^2 = 0.9920$)	$Q_e = 5.28 C_e$ ($r^2 = 0.9987$)

Notes: ^a Q_e : $\mu\text{g/g}$; C_e : mg/L

1.2 Decay experiments

Water sample was collected from the same point as the sediment, placed statically for one day, and then the river water as solvent was obtained by decanting. Specific concentrations of *p*-chloronitrobenzene, nitrobenzene and *p*-nitrotoluene (these reagents is of analytical purity) in the river water made above were prepared respectively, and these solutions were transferred into taper bottles of 1000 ml, and then they were shaken slightly (80 r/min) in constant temperature ($25 \pm 1^\circ\text{C}$) in order to simulate oxygen-filling process of natural waters; their concentrations were determined at regular intervals. Based on experiments, decay plots of three organic pollutants in the river water were obtained, and then their respective decay coefficients k_1 's were calculated. Blank experiments (without target chemicals) were conducted simultaneously for correction of results.

1.3 Sorption experiments

The isotherms were determined by batch technique at room temperature ($25 \pm 1^\circ\text{C}$). An amount of sediment and the total of 20 ml solution were added in 25 ml centrifugation tubes that were then capped tightly with Teflon-lined screw caps. The ratio of water and sediment was adjusted to achieve 20%—80% uptake of the sorbate in the sorption experiments. The solution in the tubes contained 0.005 mol/L CaCl_2 and 100 mg/L NaN_3 as biocide to inhibit biodegradation. The tubes were placed on a shaker table and incubated for 2 d. A 2-day contact time was demonstrated to be enough for equilibrium in preliminary experiments. After equilibrium, the solid and the aqueous phases were separated by centrifugation (3000 r/min) for 20 min. The concentrations of target organic compounds in the aqueous phase were determined by UV-spectrophotometer. The maximum absorbance wavelength of *p*-chloronitrobenzene, nitrobenzene and *p*-nitrotoluene is 280.2, 267.5 and 284.5 nm, respectively. Simultaneously, the sediment blank experiments without solutes were run in order to correct the determination results. The control experiments with solutes without any sediment were also carried out so as to evaluate solute losses due to volatilization and uptake by glass wall of tubes, and the result showed that the solutes losses were negligible.

2 Choose of river water quality model

2.1 Model formulation

It is assumed that a chemical factory will be set up near Gongzhen Bridge (in the suburbs of Hangzhou City) of Jinhang Canal. According to the design, it will discharge waste of 2000 m^3/d including one of *p*-chloronitrobenzene, nitrobenzene, and *p*-nitrotoluene as a concentration of 5 mg/L, into Jinhang Canal. In order to survey impact of discharge waste on water quality of Jinhang Canal, it is planed to set up water quality model of the organic pollutant. The reach of Jinhang Canal starting from Gongzhen Bridge and extending 500 km downwards, chosen as target reach, may be regarded as having constant hydraulic and hydrological conditions, and sediments during this reach is assumed to have identical f_{oc} . The average parameters of the reach is: water discharge is 27 m^3/s ; the depth is 6 m; the width is 45 m; the current velocity is 0.1 m/s; the concentration of suspended solids (ρ_{ss}) is 0.8812 g/L; the organic carbon content (f_{oc}) of suspended solids/sediments is 3.98%; and the slope of the river bed (I) is 2×10^{-4} . Due to small depth and width of the river, discharged pollutants are assumed to reach average distribution instantaneously in the cross section, and it is reasonable to treat the river as a one-dimensional system.

The basic governing formulation of one-dimensional model (Xie, 1996) is as follows:

$$\frac{\partial c}{\partial t} + u_x \frac{\partial c}{\partial x} = D_x \frac{\partial^2 c}{\partial x^2} - (k_1 + k_3)c, \quad (1)$$

where c is the average cross-sectional concentration of the pollutant; x is the downstream distance from initial section in longitudinal direction; t is the time; u_x is the average cross-sectional current velocity; D_x is the longitudinal dispersion coefficient, and k_1 is the decay coefficient; k_3 is the sedimentation-resuspension coefficient that embodies the effect of sorption/desorption of the pollutants with suspended solids and sediments on their concentrations in water. The second term on the left side of Eq. (1) is the advection contribution and the first term on the right side is the diffusion contribution. Without consideration of change of hydraulics and pollutants discharge with time and space, Eq. (1) can be simplified as steady-state form (Xie, 1996):

$$u_x \frac{\partial c}{\partial x} = D_x \frac{\partial^2 c}{\partial x^2} - (k_1 + k_3)c. \quad (2)$$

In above equations, in order to express conveniently, $k = k_1 + k_3$ was assumed.

2.2 Analytical solution of the model

2.2.1 Analytical solution of Eq. (1)

(1) Instantaneous area source: Instantaneous area source implies that the pollutant is discharged one time and evenly distributed instantaneously. The analytical solution of Eq. (1) under this condition is as follows (Xie, 1996):

$$c(x, t) = \frac{m}{A \sqrt{4\pi D_x t}} \exp \left[-\frac{(x - u_x t)^2}{4D_x t} - kt \right], \quad (3)$$

where m (g) is the mass of the pollutant discharged instantaneously, and A (m^2) is the sectional area of the river.

(2) Continuous area source: Continuous area source implies that the pollutant is discharged continuously by the rate of m (g/s) at the section($x = 0$) of the river. At $x = 0$, $\partial c/\partial t = 0$. As long as $x > 0$, the analytical solution of the Eq.(1) under this condition is gained.

When $t \rightarrow \infty$, the following equation was deduced (Jiang, 1997):

$$c(x) = \frac{m}{Au_x} \exp\left(-\frac{kx}{u_x}\right), \quad (4)$$

where m may be noted as $c_0 q_0$, and c_0 (mg/L) is the average concentration of the pollutant at initial section, and q_0 (m^3/s) is the average flow at the section.

In practice, sometimes background concentration(c_b) of the pollutant in the river needs to be considered. So $c(x)$ was expressed:

$$c(x) = \frac{c_0 q_0}{Au_x} \exp\left(-\frac{kx}{u_x}\right) + c_b \exp\left(\frac{kx}{u_x}\right). \quad (5)$$

2.2.2 Analytical solution(Xie, 1996) of Eq.(2)

Boundary condition of Eq.(2) is $c(0) = c_0$, $c(\infty) = 0$, then

$$c(x) = c_0 \exp\left[\frac{u_x x}{2} \left(1 - \sqrt{1 + 4D_x k/u_x^2}\right)\right]. \quad (6)$$

3 Determination of model coefficients

3.1 Longitudinal dispersion coefficient D_x

There exist a few methods to determine longitudinal coefficient D_x , such as Elder Eq., Fischer Eq., Golovna Eq. (Xie, 1996) and Koussis-Rodriguez Eq. (Koussis, 1998). Herein we use two equations with high stability and accuracy that was proposed in 2002 by Kashefipour and Falconer(Kashefipour, 2002):

$$D_x = 10.612h(u_x/u_*), \quad (\text{suitable for } w/h > 50) \quad (7)$$

$$D_x = [7.428 + 1.775(w/h)^{0.620} (u_* / u_x)^{0.572}] hu_x(u_x/u_*), \quad (\text{suitable for } w/h < 50), \quad (8)$$

where h is the average depth, w is the average width, u_* is the shear flow velocity. In the reach studied, $w/h = 45/6 = 7.5 < 50$, so D_x was calculated according to Eq.(8):

$$u_* = \sqrt{ghI} = 0.108(m/s), D_x = 7.72(m^2/s).$$

3.2 Decay coefficient k_1

Decay plots of three organic pollutants in the river water were obtained by experiments, and then their respective decay coefficient k_1 were calculated. Fig.1 shows the decay trend of p -chloro -nitrobenzene in the river water. From Fig. 1 we can find that the plot nearly accords with exponent equation. Their fitting equation is

$$c = 19.77e^{-0.0227t}, \quad (R^2 = 0.9869)$$

then

$$-\frac{dc}{dt} = 0.0227c. \quad (9)$$

So the decay coefficient of p -chloronitrobenzene is $k_1 = 0.0227(d^{-1})$. Likewise, decay coefficients of other two chemicals were gained: nitrobenzene, $k_1 = 0.281(d^{-1})$; p -nitrotoluene, $k_1 = 0.0387(d^{-1})$.

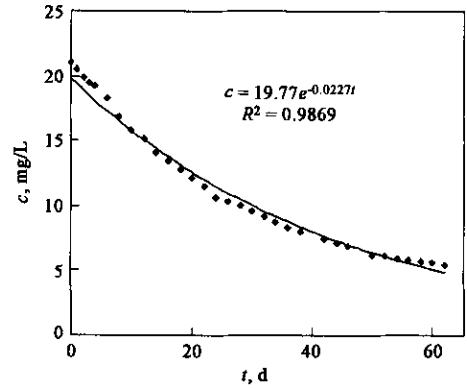


Fig.1 The decay plot of p -chloronitrobenzene in water of Jinghang Canal

3.3 Sedimentation-resuspension coefficient k_3

In order to model river water quality, the river water body was divided into two compartments: water column and sediment, as shown in Fig.2, and the sediment was further segmented into a well-mixed surface layer(or named active layer), which can resuspend in certain conditions, and deep layer with relative stability. The water column was furthermore divided into sub-compartments: water and suspended particulates. Fig.2 also shows transportation of organic pollutants among different phases of concern.

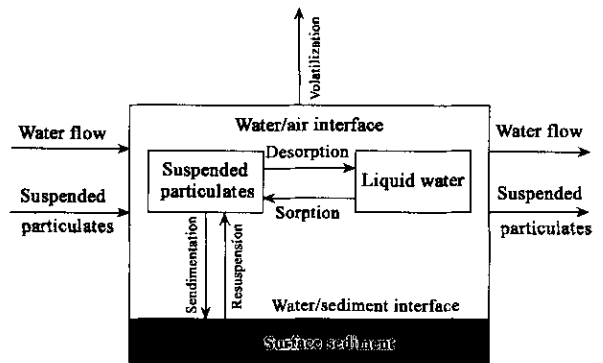


Fig.2 Transportation of organic pollutants in the river

Additionally, sorption isotherms of most sparingly soluble nonionic organic chemicals on sediments/soils are largely linear(Chiou, 1979), for example, sorption of three compounds studied in this research (p -chloronitrobenzene, nitrobenzene and p -nitrotoluene) on Jinghang Canal sediment (Fig.3). Their linear regression equations are listed in Table 1. So distribution of organic pollutants between water and suspended particulates was assumed to be described by linear isotherm. Moreover, their transportation between aqueous and solid phases was assumed to reach equilibrium quickly.

The concentration of the pollutant in water was denoted as c_{aq}^* ($\mu g/L$), the concentration of sorbed pollutant on

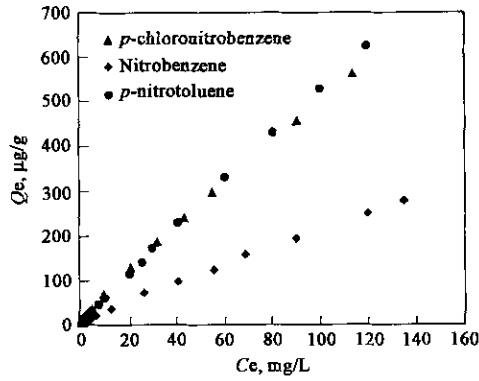


Fig. 3 Sorption isotherms of *p*-chloronitrobenzene, nitrobenzene and *p*-nitrotoluene on the sediment of Jinghang Canal

suspended particulates and sediment were denoted as q_{ss}^* and q_s ($\mu\text{g/g}$) respectively, then it was obtained that

$$q_{ss}^* = K_d c_{aq}^*,$$

also, it was assumed that $q_s = K_d^* c_{aq}^*$, where K_d is the equilibrium distribution coefficient of organic pollutants between water phase and suspended particulates, K_d^* is the the distribution coefficient between water phase and sediment (difference between K_d and K_d^* is that K_d implies equilibrium, but K_d^* is not sure).

The concentration and settling velocity of suspended solids were regarded as ρ_{ss} (g/L) and u_{ss} (m/s), bulk density and resuspension velocity of active sediment as ρ_s (g/L) and u_s (m/s), then the total concentration of the pollutant in water column is

$$c = c_{aq}^* + q_{ss}^* \rho_{ss} = c_{aq}^* + K_d c_{aq}^* \rho_{ss} = c_{aq}^* (1 + K_d \rho_{ss}). \quad (10)$$

As shown in Fig. 2, sorption of organic pollutants on suspended particulates and their common settling can result in decreasing of the pollutant concentration in water column, whereas effect of sediment resuspension on it depends on K_d^* . Increasing of pollutant concentration in unit time resulting from the above two factors is described as:

$$\begin{aligned} \frac{dc}{dt} &= \frac{q_{ss}^* \rho_{ss}}{h/u_{ss}} + \frac{q_s \rho_s}{h/u_s} = -\frac{q_{ss}^* \rho_{ss} u_{ss}}{h} + \frac{q_s \rho_s u_s}{h} \\ &= \frac{1}{h} [q_s \rho_s u_s - q_{ss}^* \rho_{ss} u_{ss}] \\ &= \frac{1}{h} [K_d^* c_{aq}^* \rho_s u_s - K_d c_{aq}^* \rho_{ss} u_{ss}] \\ &= \frac{c_{aq}^*}{h} [K_d^* \rho_s u_s - K_d \rho_{ss} u_{ss}]. \end{aligned} \quad (11)$$

from Eq. (10), it was obtained that

$$c_{aq}^* = \frac{c}{1 + K_d \rho_{ss}}, \quad (12)$$

then, from Eq. (11) and Eq. (12), the following formulations were deduced:

$$\begin{aligned} \frac{dc}{dt} &= \frac{c}{h(1 + K_d \rho_{ss})} (K_d^* \rho_s u_s - K_d \rho_{ss} u_{ss}) = -k_3 c, \\ k_3 &= \frac{1}{h(1 + K_d \rho_{ss})} (K_d \rho_{ss} u_{ss} - K_d^* \rho_s u_s). \end{aligned} \quad (13)$$

In the reach of Jinghang Canal studied in this paper, $K_d^* = 0$ (implying that sediments have not been polluted by the target pollutants) was assumed. Then, from Eq. (13), k_3 was expressed as:

$$k_3 = \frac{K_d \rho_{ss} u_{ss}}{h(1 + K_d \rho_{ss})}. \quad (14)$$

Settling velocity of suspended solids was measured: $u_{ss} \approx 2.0 \times 10^{-4}$ m/s. Distribution coefficients (K_d) of three organic pollutants on the sediment were determined by means of batch balance method (described in the experiment part of this paper). Furthermore, their sedimentation-resuspension coefficients (k_3) were calculated according to Eq. (14). The values of K_d and k_3 are all listed in Table 2.

4 Influence of sorption/desorption of organic pollutants on prediction function of water quality model

From Eq. (13), it is shown that k_3 comprehends impacts of various factors on changes of river water quality; K_d and K_d^* are decided by physicochemical characteristics of organic pollutants and components of suspended solids and sediments; h , ρ_{ss} , ρ_s , u_{ss} and u_s depend on hydrological and hydraulic conditions of the river, degree of sediment contamination, and components of suspended solids/sediments. Furthermore, k_3 can be positive or negative.

When $K_d \rho_{ss} u_{ss} > K_d^* \rho_s u_s$, k_3 is positive and the pollutant concentration in water column decrease. The prevalent process is that organic pollutants are sorbed on suspended particulates and sink together.

When $K_d \rho_{ss} u_{ss} < K_d^* \rho_s u_s$, k_3 is negative and the pollutant concentration in water column increase. The prevalent process is that contaminated sediment resuspends and possibly releases organic pollutants.

When $K_d \rho_{ss} u_{ss} = K_d^* \rho_s u_s$, k_3 is equal to zero and both sedimentation and resuspension do not effect the pollutant

Table 2 Coefficients and one-chemical water quality model of three organic contaminants

Compounds		<i>p</i> -chloronitrobenzene	Nitrobenzene	<i>p</i> -nitrotoluene
K, d ⁻¹	K_d , l/kg	4.98	1.68	5.28
	K_1 , d ⁻¹	2.27×10^{-2}	2.81×10^{-1}	3.87×10^{-2}
	K_3 , d ⁻¹	1.26×10^{-2}	4.27×10^{-3}	1.39×10^{-2}
	With k_3	3.53×10^{-2}	2.85×10^{-1}	5.26×10^{-2}
	Without k_3	2.27×10^{-2}	2.81×10^{-1}	3.87×10^{-2}
Water quality model	With k_3	$c(x) = 4.29 \exp(-4.09 \times 10^{-3} x)$ $\mu\text{g/L}(x: \text{km})$	$c(x) = 4.29 \exp(-3.30 \times 10^{-2} x)$ $\mu\text{g/L}(x: \text{km})$	$c(x) = 4.29 \exp(-6.09 \times 10^{-3} x)$ $\mu\text{g/L}(x: \text{km})$
	Without k_3	$c(x) = 4.29 \exp(-2.63 \times 10^{-3} x)$ $\mu\text{g/L}(x: \text{km})$	$c(x) = 4.29 \exp(-3.25 \times 10^{-2} x)$ $\mu\text{g/L}(x: \text{km})$	$c(x) = 4.29 \exp(-4.48 \times 10^{-3} x)$ $\mu\text{g/L}(x: \text{km})$

concentration in water column.

According to Eq. (4) and relevant parameters and coefficients obtained above, water quality models of the three organic pollutants are respectively acquired with considering or ignoring k_3 (Table 2). Fig. 4 shows plots of their concentrations versus downstream distance predicted by their quality modes under two cases. At sites of 20, 50, 100 and 200 km from the starting point (Gongzhen Bridge of Jinghang Canal), predicted concentrations for *p*-chloronitrobenzene, under no considering k_3 , deviate 3.0%—33.9% from that under considering k_3 , 2.3%—9.4% for nitrobenzene, and 8.4%—38.0% for *p*-nitrotoluene. It is clear that sorption on suspended solids and concurrent settling for *p*-chloronitrobenzene and *p*-nitrotoluene will influence more significantly prediction function of water quality model than for nitrobenzene. This phenomenon could reasonably be ascribed to the fact that distribution coefficients of the former two organic pollutants are two times larger than that of the latter (Table 2). According to Eq's ($K_d = K_{oc} f_{oc}$, $\log K_{oc} = a \times \log K_{ow} + b$) (Kopinke, 1995; Grathwohl, 1990; Xing, 1994, here, f_{oc} is organic carbon content of soil/sediment; K_{oc} is organic carbon normalized partition coefficient, and a , b are empirical coefficient in nature), influence of sorption/desorption of organic pollutants on their concentrations in water becomes more significant with increasing of their K_{oc} and K_{ow} and f_{oc} of suspended solids/sediments. On the other hand, according to Eq. $k = k_1 + k_3$, difficulty of degradation and volatilization of organic pollutants will increase this effect in some degree.

5 Conclusions

Sorption/desorption of organic pollutants on/from suspended solids and sediments was incorporated into river water quality model, and sedimentation-resuspension coefficient k_3 was deduced as follows:

$$k_3 = \frac{1}{h(1 + K_d \rho_{ss})} (K_d \rho_{ss} u_{ss} - K_d^* \rho_s u_s).$$

Such factors as distribution coefficient (K_d) of organic pollutants, contents and components (ρ_{ss} , f_{oc} , etc.) of suspended solids/sediments and hydrological and hydraulic conditions (h , u_{ss} , u_s , etc.) were incorporated into k_3 and further into river water quality model. Moreover, single-chemical and one-dimensional water quality models of three organic pollutants were set up taking Jinghang Canal as a target river. Results indicated that for organic pollutants with large K_{ow} and K_{oc} , especially for conservative substances, and rivers with suspended solids and sediments of high f_{oc} , significant errors will occur if disregarding sorption/desorption of organic pollutants with suspended solids and sediments in application of river water quality model. Although only preliminary work has been done in this research, its consequences may provide theoretical basis and practical method for improving prediction accuracy of water quality model.

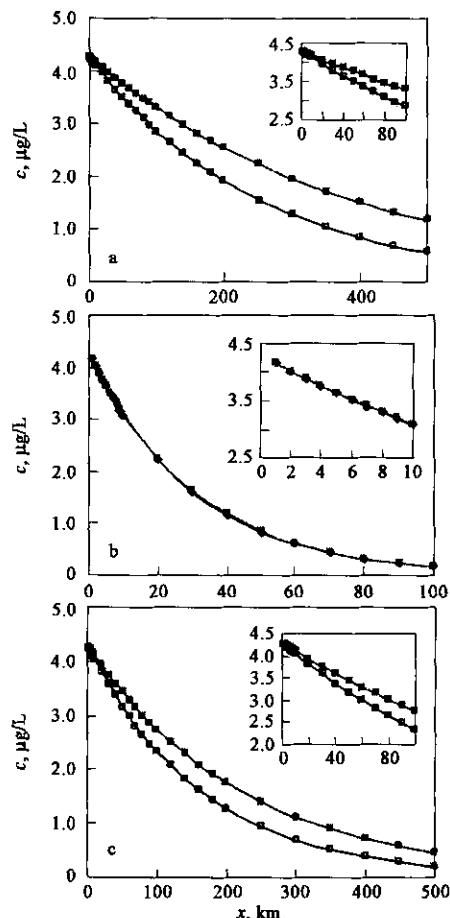


Fig.4 Comparison of water quality models for prediction of pollutants(a: *p*-chloronitrobenzene; b: nitrobenzene; c: *p*-nitrotoluene) concentrations versus downstream distance along Jinghang Canal under two cases (open symbol represents the model into which sorption and desorption were incorporated, solid symbol represents that of no incorporation)

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