

Study on the Transport of Sediment Oxygen Demand -Related Organic Matter in Bottom Sediment System

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ABSTRACT: Approach of organic material anaerobic biodegradation and species of organic matter in sediment are discussed, and then a classifying method of the species is proposed on a new viewpoint. The pore water sediment oxygen demand (SOD) numerical model in bottom sediment system is proposed originally, which differs from other advection-dispersion-sorption (ADS) model in adding a SOD-creating term. The model was preliminarily validated via pilot experiment. Finally, this model was used to simulate SOD concentration of pore water in bottom sediment, and the sensitivity of parameters in the model was analyzed. The results indicate that SOD-creating factor at beginning stage and pore water SOD-attenuating factor in bottom sediment are the most important coefficients in the new model and should be estimated accurately. Because of the assumption of equilibrium of sorption/desorption, the new model appears to be valid only with less than 5 m/d vertical velocity of pore water.

Key words: SOD, Bottom sediment, Biodegradation, Mathematical model, Pore water

INTRODUCTION

Scour, deposition and re-suspension of bottom sediment are the key factors that dominate the action of endogenic contaminants in natural water system (Nedohin & Elefsiniotis, 1997; Park & Park, 2009), and as a result of those processes, releasing of contaminants in pore water acts as a main polluting approach (Jorgensen & Marais, 1990; Widdowson *et al.*, 1988). The fate of organic matter in the subsurface is known to be dependent on many different processes, advection, dispersion, sorption, decay, chemical reactions and biological degradation (Kim, 2005; Steeby *et al.*, 2004; Geetha *et al.*, 2008). Assuming that sorption can be described in terms of equilibrium, a advection-dispersion-sorption (ADS) model can be obtained (Freeze & Cherry, 1979). Lindqvist and Enfield (1992) (Lindqvist & Enfield, 1992) used the ADS-equation to model bacterial dispersal in groundwater microcosms. The sorption term was represented in four different ways: as a linear, reversible equilibrium process with an irreversible term; as a linear, reversible equilibrium process without an irreversible sorption term; as a two-site process with equilibrium and non-equilibrium processes; and as a filtration process. A reactive term expressing degradation can also be added to the ADS-model. Reddy and Ford (1996) (Vangenuchten & Wagenet, 1989) incorporated Monod kinetics into the ADS-model to analyze degradation of 1,2-

dichlorobenzene. Additionally, other models in addition to the ADS-model have been used to predict transport and degradation of organic compounds in the subsurface (Veenstra & Nolen, 1991; Gamerdinger *et al.*, 1990).

For further understanding of the microbial degradation of organic substances in aquifers, research was carried out to establish a new mathematic model to describe variation of SOD concentration in pore water of a homogeneous bottom sediment system.

MATERIALS & METHODS

Due to the difficulty in oxygen diffusion, biodegradation of organic matter in sediment system is usually in anaerobic condition (Adams & Van Eck, 1988; Reddy & Ford, 1996). There are three main kinds of organic matter in bed sediment system, A, B and C (in Fig. 1. classified by the broken lines). A is organic matter with high molecular weight (MW), which can not dissolve in pore water. B is one with moderate and low MW, which can dissolve in pore water and may be absorbed on the surface of solid particle simultaneously. C is the ultimate product, which can leave the system as gas or transform to carbonates, sulfide, ammonium, etc (McQuillan & Webb, 1994; Canfield *et al.*, 1993; Pinhassi *et al.*, 1999). On this classification, the biological reactions in bottom sediment system can be summarized as

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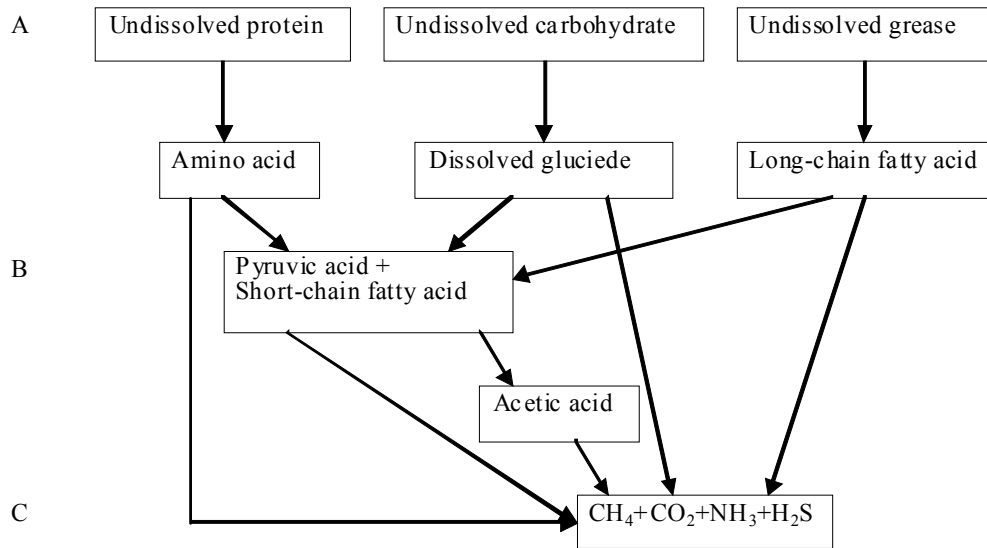


Fig. 1. A schematic of biological degradation accesses of organic matter in bottom sediment system with anaerobic condition

following simple Eq. (1), which is favorable for expressing this kind of chemical reaction in mathematic format.



The vertical concentration distribution of organic matter (the releasable SOD concentration of pore water was selected as an indicative parameter of releasable organic contaminant) in bottom sediment system is seriously influenced by some factors, including diffusion, advection, sorption, reaction, etc. And it can be described as advection-diffusion-sorption-reaction (ADSR) equation (Murphy & Ginn, 2000; Murphy *et al.*, 1997; Zysset *et al.*, 1994; Baveye & Valocchi, 1989):

$$\frac{\partial C_B}{\partial t} = D \frac{\partial^2 C_B}{\partial z^2} - \bar{v} \frac{\partial C_B}{\partial z} - \frac{\rho_b}{\theta} \frac{\partial C_{B,s}}{\partial t} + r \quad (2)$$

Where C_B (M/L^3 ; dimensions, such as mass, length and time, are symbolized by M, L, T, respectively) is the SOD concentration of pore water in bottom sediment system. $C_{B,s}$ (M/L^3) is a index of quantity of B on the surface of sediment particle, and for convenience of measurement, is expressed as the ratio of the mass of B adsorbed on the surface of particle to the volume of pore water in a certain bottom sediment system. D (L^2/T) is the vertical diffusion coefficient in the system. \bar{v} (L/T) is the average vertical velocity of pore water, having the positive direction in upward. ρ_b (M/L^3) is the bulk density of bottom sediment, θ (L^3/L^3) is the porosity, t (T) is time, and r (M/L^3T) is a reaction term. z (L) is

vertical distance, and $z=0$ is located at the interface of water and sediment .

Pore water SOD concentration in bottom sediment system is controlled directly by the amount of B in Eq. (1), and B is subject to those two reactions in the chemical equation. So the reaction term in Eq. (2) can be separated into two parts,

$$r = r_1 - r_2 \quad (3)$$

where r_1 , r_2 are the reaction rate terms, corresponding to the reaction, $A \rightarrow B$, and $B \rightarrow C$ in chemical Eq. (1), respectively.

In the organic-contaminating bed sediment system, there is abundant reactant, A, participating in the reaction, $A \rightarrow B$. At the same time, because of the effect of space particularity of sediment pore on the activity of microorganism, the reaction, $A \rightarrow B$, usually is performed only by bacteria in pore water to metabolize the solid organic matter on the surface of sediment particle (Bales *et al.*, 1995; Harvey *et al.*, 1993). The reaction product, B, is dissolved in pore water partly (expressed as $C_{B,w}$), and the other is adsorbed on the surface of sediment particle (expressed as $C_{B,s}$), which occupies some surface of reactant A exposed to pore water. Following the production of B, the reaction rate, declines correspondingly and can be expressed as a function of concentration of B.

$$r_1(z,t) = \frac{k_1}{(C_B / C_{B,0})} \quad (4)$$

where k_1 is defined as SOD-creating factor (M/TL^3). The reaction, $B \rightarrow C_{B,s}$ is assumed as first-order attenuating reaction (Bekins *et al.*, 1998; Borden & Bedient, 1986; Molz *et al.*, 1986), then corresponding attenuation term in Eq. (3), r_2 , can be written as:

$$r_2 = k_2 C_B \quad (5)$$

where k_2 is defined as SOD-attenuating factor (T^{-1}).

In Eq. (2), $\frac{\rho_b}{\theta} \frac{\partial C_{B,s}}{\partial t}$ is the sorption term, and the relationship of C_B and $C_{B,s}$ can be written as:

$$\frac{\partial C_{B,s}}{\partial t} = \frac{\partial C_{B,s}}{\partial B} \frac{\partial C_B}{\partial t} \quad (6)$$

The novel approach here is the splitting of the reaction term. When the vertical velocity of pore water is sufficiently low, we can assume that there is sorption/desorption equilibrium of B between pore water and sediment particle in the sediment system,

then $\frac{\partial C_{B,s}}{\partial C_B}$ can be described as an isotherm sorption with linear condition,

$$C_{B,s} = k_d C_B \quad (7)$$

$$\frac{\partial C_{B,s}}{\partial C_B} = k_d \quad (8)$$

Eq.(6) can be expressed as,

$$\frac{\partial C_{B,s}}{\partial t} = k_d \frac{\partial C_B}{\partial t} \quad (9)$$

Substitute Eq. (4), (5), (9) into Eq. (2), we got

$$\left(1 + \frac{\rho_b}{\theta} k_d\right) \frac{\partial C_B}{\partial t} = D \frac{\partial^2 C_B}{\partial z^2} - \bar{v} \frac{\partial C_B}{\partial z} + \frac{k_1}{(C_B / C_{B,0})} - k_2 C_B \quad (10)$$

This equation is the control equation of SOD concentration of pore water in the bottom sediment system, and can be rewritten as:

$$\frac{\partial C_B}{\partial t} = A_1 \frac{\partial^2 C_B}{\partial z^2} + A_2 \frac{\partial C_B}{\partial z} + A_3 \frac{1}{(C_B / C_{B,0})} + A_4 C_B \quad (11)$$

Where

$$A_1 = \frac{D}{\left(1 + \frac{\rho_b}{\theta} k_d\right)}, \quad A_2 = \frac{-\bar{v}}{\left(1 + \frac{\rho_b}{\theta} k_d\right)}$$

$$A_3 = \frac{k_1}{\left(1 + \frac{\rho_b}{\theta} k_d\right)}, \quad A_4 = \frac{-k_2}{\left(1 + \frac{\rho_b}{\theta} k_d\right)}$$

In different environmental and hydrological cases, Eq. (11) has different initial and boundary conditions. For natural fresh water system with bed sediment, it is assumed that, the SOD concentration of pore water at beginning time, $C_{B,0}$, is equal to that of the overlying water. Because the upper interface of bottom sediment touches with the overlying water entirely, the bottom sediment and overlying water should be looked as a successive system. In this case, the initial and boundary conditions are

$$C_B(z, 0) = C_{B,0} \quad (12)$$

$$C_B(0, t) = C_B(z_0, t) = C_{B,0} \quad (13)$$

Where z_0 is the maximal depth, being the top line of free groundwater. Ordinarily, the C_B of overlying water is much less than that of bottom sediment. Later, the simulation showed the fluctuation of the initial and boundary concentration almost did not act on the results.

For validating Eq. (11) with experiment, a microcosm system of fresh water with bottom sediment was built in laboratory and the data of experiment were compared with simulation results of the model. In March of 2002, the sediment samples were collected from the Qinhuai River near Nanjing City, P. R. China, using a van Veen-type grabber, which yielded material from the sediment surface to a depth of approximately from 0 cm to 15 cm. The wet sediments were stored in glass bottle with Teflon caps at 4 °C in the dark.

About 500 ml stored wet sediment was put into a 2000 ml container with 500 ml distilled water, and completely mixed for 1 min, then left to settle for about 30 min and then the overlying water was removed. The previous releasing procedure was repeated 5 times to prepare a sample, with low pore-water SOD

concentration. (Some of the sediment was sampled to measure SOD concentration of pore water.) The prepared sample was displaced into a 100 mm diameter glass column with thickness of 6 cm, and about 1000 mL distilled water was added to mixed fully for 1 min. The mixed system was sampled for measuring the SOD concentration of pore water, and then cultured at 20 °C or 4 °C in dark for 10 days. At the end of 10 days, the upper water was removed completely; the sediment system was sliced at intervals of 1.0 cm using a mini type slice sampler. Pore water of sediment was prepared by centrifugation at 3,600 rpm for 15 min at 20 °C. The SOD concentration was measured as given in Kuroda et al.(1997) (Kuroda *et al.*, 1997). Immediately, the SOD concentration of pore water was measured and the result was shown in Fig. 2.

On other hand, the SOD in pore water was simulated with the new model. The transport part of equation (11) is solved with an explicit finite difference scheme that is forward in time, central in space for dispersion, and backward in space for advective transport part (Appelo and Postma, 1993). The chemical interaction terms are calculated separately from the transport part for each time step for all solute components. The spatial and time step used in the solutions were, respectively, 0.005 cm and 0.01 day. The numerical values of the parameters in Eq. (11) were shown in Table 1. The SOD concentration in pore water of the system was simulated with Eq. (11), and shown in the Fig. 2 as the solid line, which is fit to the experimental data very well.

RESULTS & DISCUSSION

For research on the sensitivity of coefficients in Eq. (11), the simulated calculation with the new model was carried out on different D , k_1 , k_2 , \bar{v} and the initial and boundary conditions. In all simulations, the initial SOD concentration was 2.5 mg/L, the thickness of bottom sediment was 5 cm and all coefficients were same as those in Tab. 1, except the noted one in each case. The results showed that, with the exception of D with low sensitivity, the other coefficients are with high sensitivity, which were illustrated in Fig. 3 & Fig. 6. In simulation process, three values were selected for D , i.e. 3×10^{-6} , 6×10^{-6} , 12×10^{-6} cm²/s, and the three simulating patterns were given in almost same diversification as in Fig. 3. So the other coefficients were analyzed below.

Table 1. Parameters in the SOD Model

<i>Coefficient</i>	<i>Numerical value</i>
$D/(cm^2/s)$	6×10^{-6} ^a
k_d	23.04 ^b
$\rho_b/(g/cm^3)$	2.0 ^b
θ	0.5 ^a
$k_1/(mg/L \cdot d)$	78.28 (in 20°C), 4.21 (in 4°C) ^b
$C_{B0}/(mg/L)$	4.5 ^b
$k_2/(d^{-1})$	0.0373 (in 20°C) 0.0020 (in 4°C) ^b

^a from (Zysset *et al.*, 1994). ^b from (Lee *et al.*, 2002).

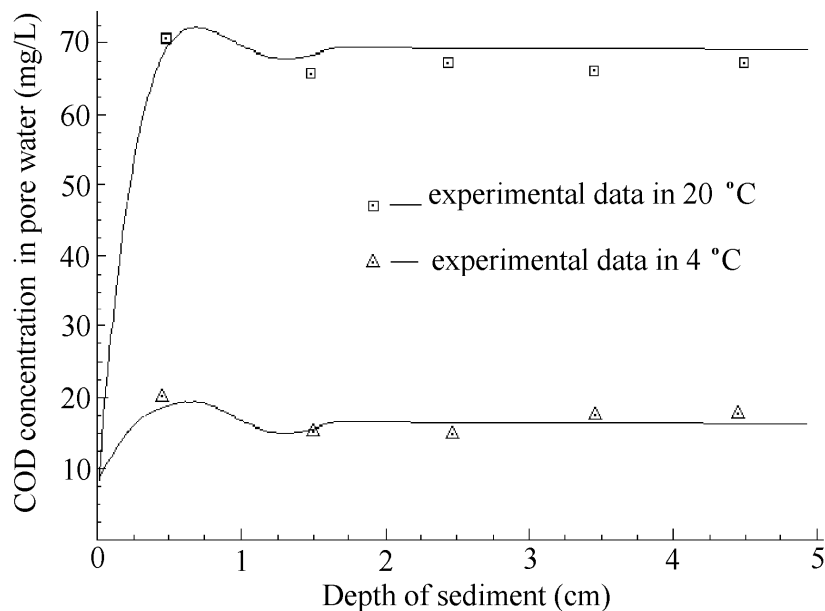


Fig. 2. Verification of the novel sediment pore water SOD model using experimental data

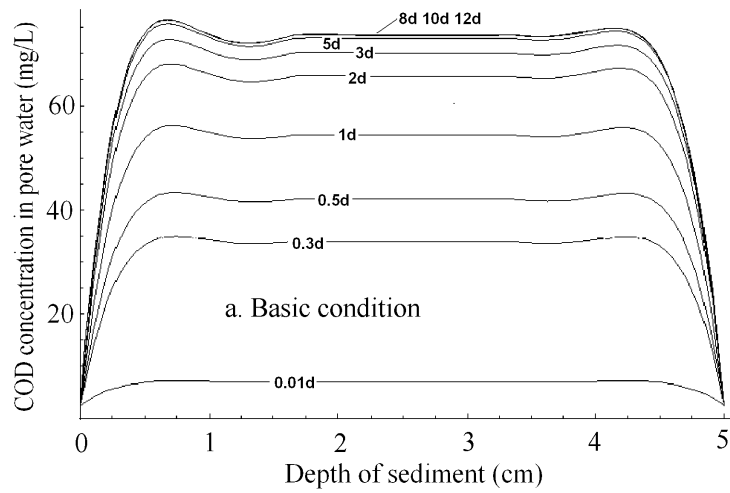


Fig. 3. Simulated SOD concentration in bottom sediment system: 20 °C with the parameters presented in Table 1

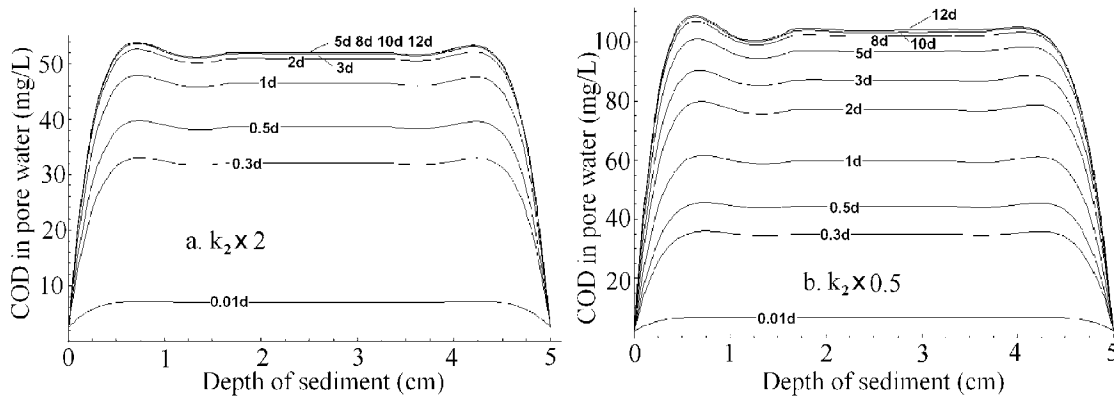


Fig. 4. Simulated SOD concentration in bottom sediment system with different values of k_2 : a. $k_2 \times 2$ and b. $k_2 \times 0.5$

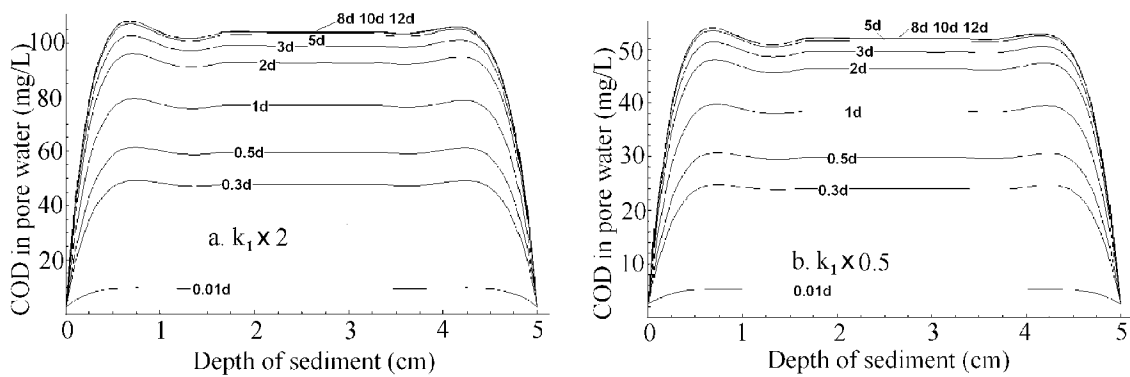


Fig. 5. Simulated SOD concentration in bottom sediment system: a. $k_1 \times 2$ and b. $k_1 \times 0.5$.

In Fig. 3, when $t = 0$ d, SOD concentration was 2.5 mg/L in whole depth; after 0.3 d, it was about 33 mg/L in middle depth and $t = 1$ d, it had reached 53 mg/L. Beyond 8 d, all result curves were coincident actually, which suggests that, in the profile of SOD concentration in pore water, the equilibrium was reached on day 8, and the maximum is about 75 mg/L in the middle depth.

Fig. 4 shows the cases with variation of SOD-attenuating factor, k_2 . It was suggested that k_2 effects the equilibrium concentration and the time to reach it. When k_2 is increased by 100%, the equilibrium concentration drops from 72 mg/L (Fig. 3) to 53 mg/L (Fig. 4a). With k_2 decreasing by 50%, it is up to more than 100 mg/L (Fig. 4b). The time to reach the ultimate concentration is shortened from 8 days to about 3 days (Fig. 4a).

Fig. 5 shows the cases with variation of pore water SOD-creating factor, k_1 . It is suggested that the effect of k_1 is rather on the equilibrium concentration than on the equilibrium time. When k_1 increased by 100%, the equilibrium concentration rises from 72 mg/L (Fig. 3) to 103 mg/L (Fig. 5a), and when k_1 decreased by 50%, it drops to about 51 mg/L (Fig. 5b).

Fig. 6 shows the cases with different vertical flow velocity \bar{v} and initial and boundary conditions. When \bar{v} is increased from 1 m/d to 2 m/d, the SOD profile showed no significant change (Fig. 6a), but when the velocity was 5 m/d, the profile changes significantly (Fig. 6b), but when it was 10 m/d, the profile fluctuated throughout the full thickness seriously (Fig. 6c), which may be attributed to the assumption of equilibrium of sorption/desorption and suggests that when beyond 5m/day eq. (11) appears no longer valid.

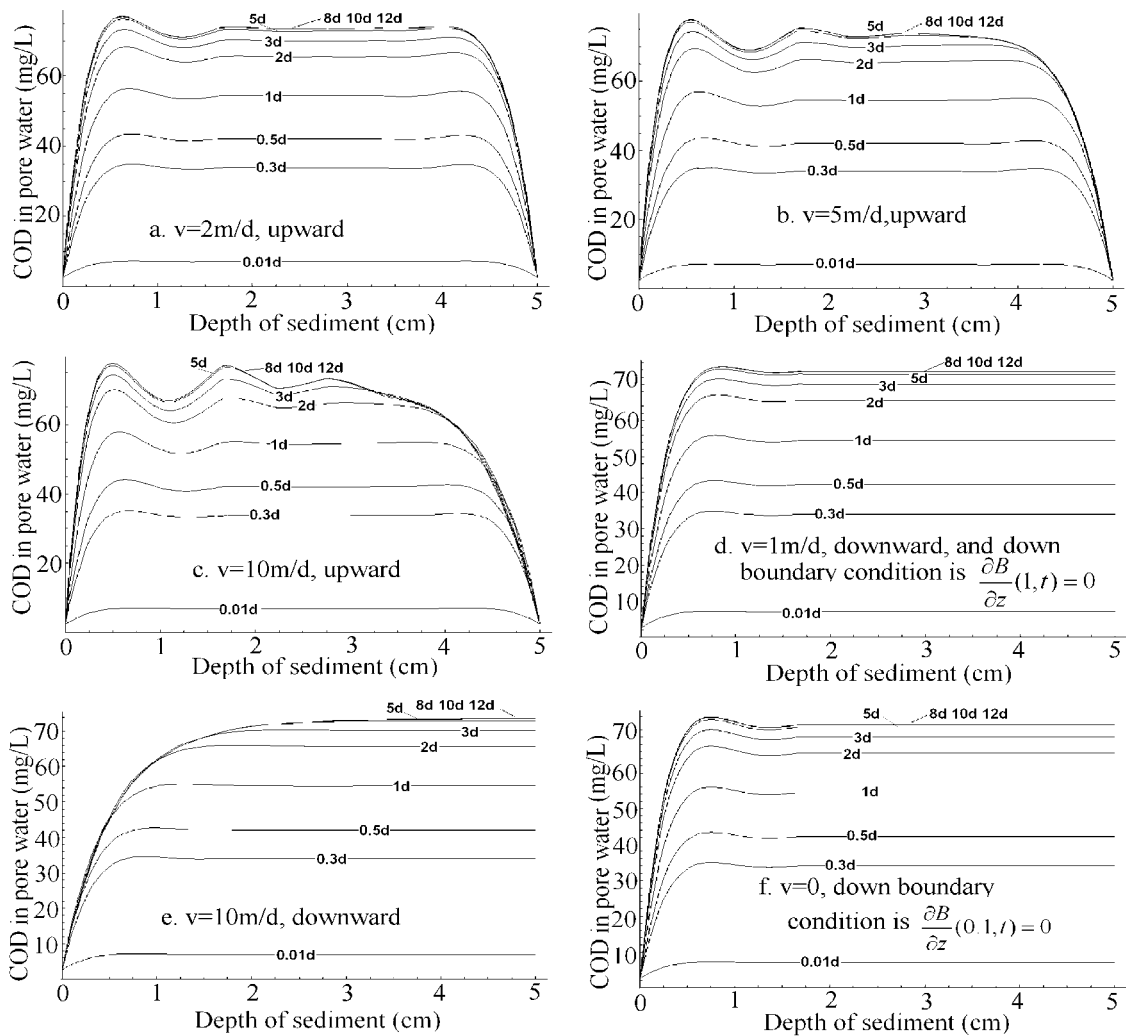


Fig. 6. Simulated SOD concentration in bottom sediment system with variation of the average vertical velocity, \bar{v} and boundary conditions

In natural water environment, the vertical flow is accommodated by the underground water level. The upward fluid conveys the contaminants in bottom sediment into the overlying water, and the downward flow will take the contaminants into underground water. Direction of \bar{v} was upward in previous calculations, and Fig. 6d and Fig. 6e showed the case with downward \bar{v} , accordingly with a new boundary condition, $\partial B / \partial z(0.1, t) = 0$. The case with $\bar{v} = 0$ was shown in Fig. 6f. Fig. 6d to 6f suggested that the boundary conditions impact on the pore water SOD profile in sediment system significantly.

CONCLUSION

Approach of organic material anaerobic biodegradation and species of organic matter in sediment were discussed and, then a classifying method of the species was proposed on a new viewpoint. A novel pore water SOD numerical model in bottom sediment system was proposed originally, which differs from other ADS model in adding a SOD-creating term. Via microcosm experiment, the reliability of the model was ascertained preliminarily. In the investigation of the sensitivity of parameters presenting in the model, two ones, k_1 , k_2 , are more influential to the simulating process. In natural water systems, those two parameters are controlled by the microbial activities, and then should be estimated accurately for a given state. In addition, the new model is based on an assumption that the SOD equilibrium of sorption/desorption between the sediment solid and the pore water. But it can be found that this assumption may be unreasonable when the vertical velocity of pore water is more than 5 m/d. Although we established the model and explored some properties of it, we suggest further studies on a greater variety of sediments. In addition we think that the further research on the two new parameters, k_1 , k_2 , especially via field experiment, would be useful for evaluating the SOD contaminants in bottom sediment and, for improving these kinds of model.

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