

Modelling of sediment oxygen demand and organic flux for a pulsed sediment organic load

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Abstract Biodegradation of organic matter in the sediment affects both the level of dissolved oxygen (DO) in the overlying water and material flux into the water body. In the present study, a mathematical model was developed to describe the DO dynamics and related organic transformation in the sediment after a pulsed load of rich organic, sediment. The model includes DO diffusion at the sediment–water interface and inside the sediment, diagenetic reactions of particulate organic to soluble organic, substances, biodegradation of soluble organic, and related DO consumption. The model can simulate sediment oxygen demand (SOD) in a dynamic system after a sudden organic load on the sediment and the flux of both biodegradable and non-biodegradable organic can be predicted. In addition, laboratory experiments were conducted using SOD chambers to investigate the SOD dynamics and sediment material fluxes. The sediment of the batch SOD tests was loaded with fish food at various rates for the sudden organic input. Numerical simulations for SOD and organic fluxes compared well with the experimental measurements. The results demonstrate that the model can be used to predict the effect of sediment pollutants on the water quality of surface waters.

Keywords Boundary layer; pollutant transport; sediment oxygen demand; sediment pollution; water quality modelling

Introduction

Sediments are an important feature of the natural water environment. The physical, chemical, and biological processes that take place in the sediment have a profound influence on the quality of the water body (DiToro, 2001). A primary interaction is the exchange of substances between the sediment and the overlying water. The consumption of dissolved oxygen (DO) by the organic matter accumulated in the sediment is one of the main causes of summertime oxygen depletion in lakes and estuaries (Floderus and Hakanson, 1989; McComb, 1995; DiToro, 2001). Dissolved organic matter and nutrients produced by diagenesis in the sediment also can be returned to the water column where they are reused by the biological community, resulting in bacteriological contamination or eutrophication. Therefore, material exchange and DO consumption at the sediment–water interface are crucial to the water quality problem of surface waters, which need to be included in water quality modelling (Thomann and Mueller, 1987; Lee *et al.*, 2000; DiToro, 2001).

Organic transformation in sediment is a complex process that is closely related to the background situation (Lung, 1993; McComb, 1995; DiToro, 2001). The parameterization of the current sediment diagenetic model is based primarily on a few major studies in temperate waters with clean or slight polluted natural sediment (Thomann and Mueller, 1987; Lung, 1993; DiToro, 2001). In the warm tropical and sub-tropical coastal regions, a sudden load of rich particulate organic on the sediment would increase significantly sediment biological activity and associated material fluxes. This rapid load may come from the suspended matter brought about by a major surface runoff, fish food fed in mariculture, and settled biomass after a massive algal bloom (Zhang *et al.*, 2002). However,

DO dynamics and biodegradation in the sediment after a sudden load of rich organic have not been well addressed. In the present study, a mathematical model was developed to describe the sediment oxygen demand (SOD) and the organic flux after a pulsed sediment input. Laboratory experiments were carried out with batch SOD chambers to validate the results of modelling simulations.

Methods

Model formulation

DO transport in the sediment. Biochemical reactions in the sediment result in a gradient of DO decrease with the sediment depth. Based on the DO level, the sediment can be divided into an aerobic layer with a thickness of H_1 and an anaerobic layer with a thickness of H_2 (Figure 1). There is a diffusive boundary layer (δ_D) in the overlying water adjacent to the sediment–water interface where molecular diffusion dominates overall mass transport (Levich, 1962). The one-dimensional (y -axis) mass balance equations for the rate of DO change in the diffusive boundary layer and inside the sediment can be written (DiToro, 2001) as

$$\frac{\partial O}{\partial t} = D_w \frac{\partial^2 O}{\partial y^2} \quad (\text{overlying water}) \quad (1)$$

$$\frac{\partial O}{\partial t} = D_s \frac{\partial^2 O}{\partial y^2} - r_o \quad (\text{inside the sediment}) \quad (2)$$

where D_w and D_s are the oxygen molecular diffusion coefficients in water and sediment, respectively, O signifies the DO concentration, and r_o is the DO consumption rate in the sediment, while DO consumption in the water boundary layer is neglected. The diffusion coefficient of oxygen in the sediment may be estimated from the correlation of $D_s = D_w / (1 - 2 \ln \phi)$, where ϕ is the porosity of the sediment (Boudreau, 1997).

DO consumption. DO consumption is the result of biological and chemical oxidation reactions (DiToro, 2001). For a pulsed input of rich particulate organics into the sediment, biological carbonaceous oxidation by heterotrophs is more important than nitrification and chemical oxidation to DO consumption in the early phase of diagenesis. According to Bailey and Ollis (1986), DO consumption is caused by microbial assimilation and growth as well as maintenance, and the DO consumption rate can be written as

$$r_o = \frac{1}{Y_O} \left(\frac{dX}{dt} \right)_G + mX \quad (3)$$

where Y_O is the effective yield for the microbial utilization of oxygen, X is the biomass concentration of aerobic heterotrophs, and m is the first order maintenance coefficient of oxygen for the biomass.

In the aerobic sediment, the limiting substrates for biomass growth are the organic carbon source and DO. The biomass growth rate may be described by a Monod dependence on each of the limiting substrates (Bailey and Ollis, 1986) in

$$\left(\frac{dX}{dt} \right)_G = \mu_{\max} \frac{O}{K_O + O} \frac{S}{K_S + S} X \quad (4)$$

where μ_{\max} is the maximum specific growth rate of the microbes, S is the organic carbon concentration in pore water, K_O and K_S are the half-saturation coefficients for oxygen and

carbon utilization, respectively, by the microbes. Hence, the DO consumption rate becomes

$$r_O = \frac{\mu_{\max}}{Y_O} \frac{O}{K_O + O} \frac{S}{K_S + S} X + mX \quad (5)$$

In addition, the net biomass growth in the sediment can be written as

$$\frac{dX}{dt} = \left(\mu_{\max} \frac{O}{K_O + O} \frac{S}{K_S + S} - k_d \right) X \quad (6)$$

where k_d is the first-order biomass decay coefficient.

According to Equation (2), the overall change in DO concentration with time in the sediment is the result of DO transport, or SOD, minus the total DO consumption in the aerobic sediment layer. Hence, the SOD can be calculated by

$$SOD = \int_0^{H_1} \frac{\partial O}{\partial t} dy + \int_0^{H_1} \left(\frac{1}{Y_O} \mu_{\max} \frac{O}{K_O + O} \frac{S}{K_S + S} X + mX \right) dy \quad (7)$$

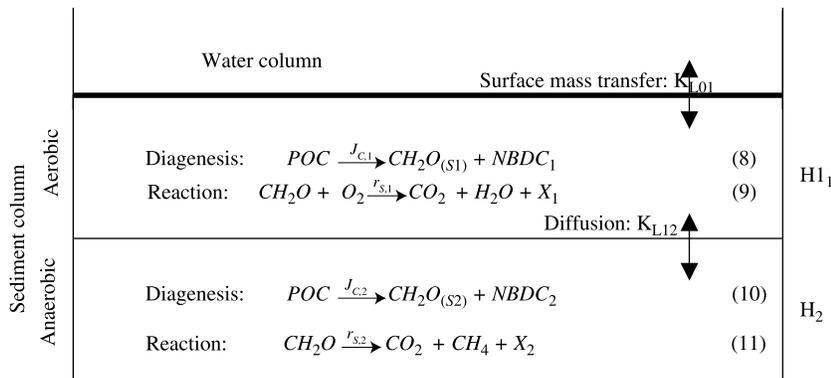


Figure 1 Schematic diagram of the total organic carbon transformation and DO consumption model. POC means particulate organic carbon

Flux of organic carbon from the sediment into water. Particulate organic matter (POM) initially is mineralized rather rapidly but then the reaction slows down (DiToro, 2001). This has been modelled successfully by assigning a fraction of the POM to each of various reactivity classes called ‘G classes’. Following this approach (DiToro, 2001), the POM used in the present experimental study, fish food, is divided into four parts with four different scales of diagenesis reactivity: G1 the fastest POC pool, G2 the fast part, G3 the slow one, and G4 the slowest fraction. The diagenesis product is assumed to consist of two types of soluble organic carbon, one is the biodegradable organic carbon (BDC) accounting for 90% of the diagenesis product, and the other is non-biodegradable organic carbon (NBDC) accounting for the remaining 10%. Thus, the diagenesis fluxes of soluble organic carbon into the two sediment layers are

$$J_{C,1} = \sum_{i=1}^4 k_i f_i C_s H_1 \quad (12)$$

$$J_{C,2} = \sum_{i=1}^4 k_i f_i C_s H_2 \quad (13)$$

where f_i specifies the mass fraction of the G1 class in the POM (fish food), k_i is its first order diagenesis constant, and C_s is the POM concentration in the sediment. The rate of organic degradation in the aerobic layer can be written as

$$r_{S,1} = \frac{1}{Y_{C,O}} \mu_{\max,O} \frac{O}{K_O + O} \frac{S_1}{K_S + S_1} X_1 \quad (14)$$

where $Y_{C,O}$ is the effective yield for the microbial utilization of biodegradable organic carbon, S_1 , in layer 1. Similarly, in the anaerobic layer,

$$r_{S,2} = \frac{1}{Y_{C,A}} \mu_{\max,A} \frac{S_2}{K_{S,A} + S_2} X_2 \quad (15)$$

where S_2 is the concentration of biodegradable organic carbon in layer 2, and $\mu_{\max,A}$ and K_A are the coefficients for anaerobic growth.

The mass balance for the change of soluble biodegradable organic carbon in the aerobic layer in relation to biodegradation and mass transport is

$$\frac{dS_1}{dt} H_1 = 0.9J_{C,1} - r_{S,1}H_1 + K_{L12}(S_2 - S_1) - K_{L01}(S_1 - S_0) \quad (16)$$

and the change of soluble biodegradable organic carbon in the anaerobic layer is

$$\frac{dS_2}{dt} H_2 = 0.9J_{C,2} - r_{S,2}H_2 - K_{L12}(S_2 - S_1) \quad (17)$$

where K_{L01} is the mass transport coefficient between the aerobic layer and the water column and K_{L12} is the mass transport coefficient between two sediment layers. K_{L01} and K_{L12} can be estimated (DiToro, 2001) by

$$K_{L12} = \frac{D_{TOC,S}}{(H_1 + H_2)/2} \quad (18)$$

$$K_{L01} = \frac{D_{TOC,S}}{H_1} \quad (19)$$

where $D_{TOC,S}$ is the molecular diffusion coefficient for soluble organic carbon measured as TOC in the sediment. In addition, for the total soluble organic, including both biodegradable carbon and non-biodegradable carbon, the mass balance equations are

$$\frac{d[TOC]_1}{dt} H_1 = J_{C,1} - r_{S,1}H_1 + K_{L12}([TOC]_2 - [TOC]_1) - K_{L01}([TOC]_1 - [TOC]_0) \quad (20)$$

$$\frac{d[TOC]_2}{dt} H_2 = J_{C,2} - r_{S,2}H_2 - K_{L12}([TOC]_2 - [TOC]_1) \quad (21)$$

As the TOC concentration in water is much lower than that in pore water, let $[TOC]_0 = 0$. Thus, the TOC flux from the sediment to water is

$$J_{TOC} = K_{L01}([TOC]_1 - [TOC]_0) = K_{L01}[TOC]_1 \quad (22)$$

SOD and sediment flux experiments

SOD apparatus. Batch experiments with SOD chambers were used to measure the SOD and organic flux from the sediment. The SOD chambers were fabricated from a Perspex cylinder with an internal diameter of 14.2 cm and a height of 14 cm (Lee et al., 2000). To establish a hydraulic flow field over the sediment in the chamber, water was recirculated by pumping at a rate of 4 L/h (Lee et al., 2000). The water was sampled from the

chamber once a day or every two days for various measurements; thereafter, the water was replaced by flushing with DO saturated fresh seawater.

Sediment flux tests. For each batch test, 300 g of natural marine sediment collected from the surface sediment of the Mai Po Natural Reserve, Hong Kong, was placed in the SOD chamber to form a sediment layer around 3 cm in thickness. Artificial salt water with a salinity of 2‰ and DO saturation was used as marine water to fill and flush the chamber. The sediment–water system inside the chamber was stabilized by continuous water flushing at 4 L/l for 3–5 days. A pre-determined amount of fish food (Kamihata Fish Ind. Ltd., Japan), 0.5, 1.0, or 2.0 g, was then gently placed inside the sediment to simulate a sudden input of rich organic load into the sediment. The fish food organic contained 43% carbon, 8.1% nitrogen, 1.3% phosphorous, and other elements. The fish food granules about 2 mm in diameter were crushed into smaller pieces before placing in the sediment, while the fines were discarded.

Measurements. Prior to each water exchange and replacement, the water was withdrawn from the chamber after one to two days of recirculation. The sample was analysed for various parameters, including DO, TOC, pH, NH_4^+ -N, NO_3^- -N, PO_4^{3-} -P, acidity, and alkalinity. The SOD value may be calculated using

$$SOD = \frac{(O_{initial} - O_{end})V}{A\theta} \quad (23)$$

where $O_{initial}$ and O_{end} are the DO concentrations in the water at the beginning and the end of a sampling period, θ , during the SOD test, V is the water volume (2.3 L), and A is the area of the sediment surface (0.016 m²). Similarly, the organic flux measured as TOC can be determined by

$$J_{TOC} = \frac{([TOC]_{end} - [TOC]_{initial})V}{A\theta} \quad (24)$$

where $[TOC]_{initial}$ and $[TOC]_{end}$ are the TOC concentrations at the beginning and the end of a sampling period.

Kinetic rate coefficients and model parameters. The bioreaction kinetic coefficients and other parameters used in the model and simulations are given in Table 1. The thickness of the diffusive boundary layer is estimated based on the simulation result of Lee et al. (2000) for the same SOD apparatus. The $D_{TOC,S}$ for the soluble organic of a high molecular weight in the sediment is slightly lower than the value used by Rittmann et al. (2002). The initial biomass in the sediment is assumed to be 100 mg/L according to the measurement of Higashino and Stefan (2005).

Results and discussion

Simulation and experiment results

The SOD and the sediment organic flux obtained from the laboratory tests and numerical simulations for three different fish food loadings into the sediment are given in Figure 2 and Figure 3. A sudden organic input resulted in a higher SOD, and the initial SOD value increased significantly with the amount of fish food loaded. The SOD for 2 g of fish food could be as high as 1.1 g O₂/m²-d according to the measurement, in comparison to the initial SOD of less than 0.6 g O₂/m²-d for the case of 0.5 g fish food. The differences in SOD were about 0.35–0.4 g O₂/m²-d between the chambers of 2 g and 1 g fish food, and about 0.25–0.3 g O₂/m²-d between the chambers of 1 g and 0.5 g fish food. The SOD

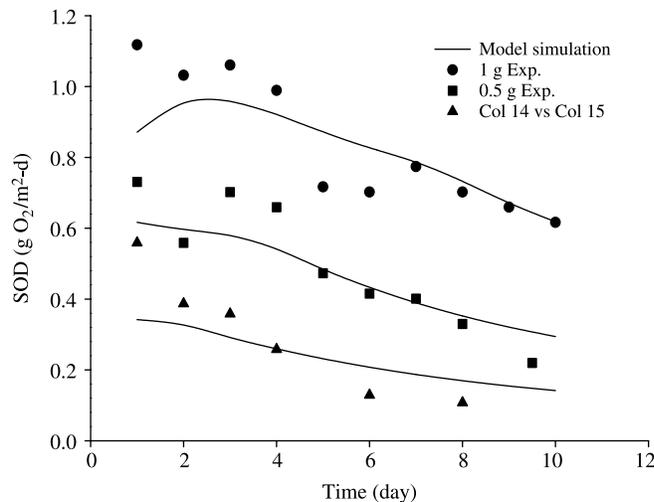
Table 1 Coefficients and parameter values used in the model and simulations

Parameter	Value	Reference
δ_D (mm)	0.5	Lee <i>et al.</i> (2000)
$D_{O_2,W}$ (cm ² /d)	2.0	
$D_{TOC,S}$ (cm ² /d)	0.4	
ϕ	0.8	
X_O (mg/L)	100	Higashino and Stefan (2005)
K_{O_2} (mg/L)	0.1	Rittmann and McCarty (2001)
m (1/d)	0.05	Rittmann <i>et al.</i> (2002), Bailey and Ollis (1986)
K_S (mg/L)	30	Tchobanoglous <i>et al.</i> (2004)
$K_{S,A}$ (mg/L)	60	Tchobanoglous <i>et al.</i> (2004)
k_d (1/d)	0.1	Rittmann <i>et al.</i> (2002)
Y_O	0.5	Bailey and Ollis (1986)
$Y_{C,O}$	0.5	Bailey and Ollis (1986)
$Y_{C,A}$	0.1	Bailey and Ollis (1986)
μ_{max} (1/d)	10	Rittmann and McCarty (2001)
$\mu_{max,A}$ (1/d)	0.5	Rittmann and McCarty (2001)
f_1, f_2, f_3, f_4	0.2, 0.4, 0.3, 0.1	DiToro (2001)
k_1, k_2, k_3, k_4	0.2, 0.02, 0.002, 0.0002	DiToro (2001)

values decreased with time during the batch experiments for all loading rates. For the low input of 0.5 g, the SOD appeared to be stabilized at a level of around 0.1 g O₂/m²-d after 6 days. However, for higher loadings of 1 and 2 g, the SOD showed continuous decrease after 10 days.

The SOD simulation results compared fairly well with the SOD measurements for three different sediment loadings (Figure 2). The model results had a better fitting with the experimental data for the later phase of the SOD tests than that for the early phase. Nonetheless, the model developed in this study is adequate for describing the magnitude of SOD and its trend of change for the SOD dynamics after a sudden sediment load. The discrepancy between the modelling and experimental results could come mainly from the non-uniform distribution of the fish food in the sediment, which was encountered only in the experiment and was not considered by the simulation.

Diagenesis in the sediment converted particulate organic matter into soluble organic molecules, which diffused into the overlaying water. The laboratory observations for the

**Figure 2** Experimental SOD results in comparison with the simulations

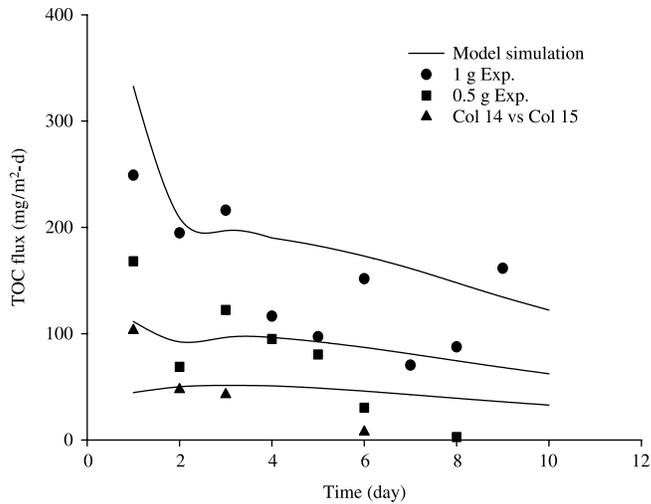


Figure 3 Experimental organic flux results in comparison with the simulations

sediment TOC flux were similar to those for the SOD (Figure 3). The chamber with 2 g fish food in the sediment had a higher organic flux into water than the chambers with 1 and 0.5 g fish food. For the load of 2 g fish food, the TOC flux was 250 mg/m²-d on the first day. It decreased to below 150 mg/m²-d after 4 days and fluctuated at a level of 100–150 mg/m²-d in following days. The chamber having 0.5 g fish food in the sediment released a TOC flux of 100 mg/m²-d at the beginning, which reduced to almost zero after 6 days.

The model also was able to simulate the trend and variation of TOC flux after a pulsed sediment organic input (Figure 3). The simulation results were in general agreement with the experimental data for the lower loading cases. For the input of 2 g fish food, the simulated TOC flux was somewhat higher than the measurements, particularly for the first two days. The reason may be due partially to the non-uniform distribution of the fish food in the sediment. Moreover, the values of some coefficients and parameters used in the model may need to be determined more specifically through laboratory calibrations.

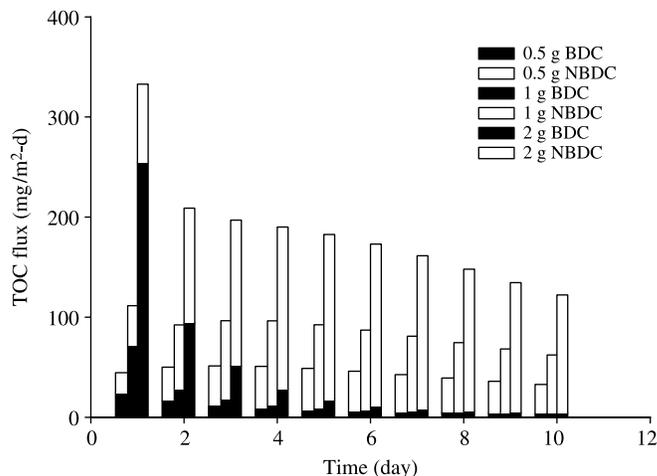


Figure 4 Flux of biodegradable carbon (BDC) and non-biodegradable carbon (NBDC) based on the model simulations

The fluxes of biodegradable and non-biodegradable organic into the overlaying water also can be simulated with the new model (Figure 4). After a sudden load on the sediment, more than 50% of the TOC released was biodegradable organic, which would increase the BOD in the water phase. However, after a few days of organic biodegradation in the sediment, TOC flux from the sediment gradually decreased. More importantly, the biodegradable fraction in the TOC flux reduced to 10% or lower. The sediments with different initial organic loadings had a similar trend of reduction in both the TOC flux and the biodegradable fraction in the TOC released.

Conclusions

A mathematical model was developed to simulate the DO dynamics and related sediment organic transport after a pulsed load of rich organic on the sediment. The model includes DO diffusion at the sediment–water interface and inside the sediment, diagenesis of particulate organic to soluble organic, biodegradation of soluble organic substrate, and related DO consumption. The model can simulate the SOD in a dynamic system after a sudden organic load, and the flux of both biodegradable and non-biodegradable organic into the water column can be predicted. The numerical simulation results for SOD and organic fluxes compared well with the experimental results obtained from the laboratory batch SOD tests for which fish food was loaded into natural sediment at various loading rates. The results demonstrate that the model developed in this study can be used to predict the effect of organic pollutants in sediment on the water quality of surface waters.

Acknowledgements

This research was supported by grants HKU7120/03E from the Research Grants Council (RGC) and AoE/P-04/2004 from the University Grants Committee (UGC) of the Hong Kong SAR Government, China. The technical assistance of Mr Keith C. H. Wong is highly appreciated.

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