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# PROCESS OF DISSOLVED SUBSTANCE RELEASE FROM BOTTOM SEDIMENT TO FLOWING WATER

by

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## SYNOPSIS

The influence of flow velocity, water content of sediment, and the amount of dissolved substances contained in sediment on a diffusional mass transfer from bottom sediment to flowing water was investigated experimentally in a laboratory. On the other hand, the model of diffusional mass transfer across the sediment-water interface was formulated by applying the analysis of heat transfer.

The experimental results show that the vertical flux of a dissolved substance increases as the flow velocity increases, and that the release flux is also influenced by the water content of sediment and the amount of dissolved substance contained in sediment. It was found that the adsorption process between methylene blue and kaolinite can be expressed by a Langmuir isotherm equation, and that the solute concentration at the sediment-water interface can be estimated using that equation. The release flux of dissolved substance estimated by the proposed model is in fairly good agreement with that observed in the experiments.

## INTRODUCTION

The sediment in the bottom of rivers, lakes or reservoirs consumes dissolved oxygen (DO) in the water near the bottom, causing oxygen depletion and resulting in some nutrients and heavy metals being released from the bottom sediment. The nutrients released and transported to the upper water layer cause phytoplankton to proliferate so that water-quality problems such as red tide or bloom occur. Hence, it is of great importance to clarify the mechanism of diffusional mass transfer across the sediment-water interface relating to phenomena such as DO consumption by bottom sediment and the release of dissolved substances from the sediment.

Although studies concerning the mass transfer between sediment and the water column have been performed from various viewpoints, reports on the diffusional mass transfer across the interface of sediment and flowing water have been very few. Moreover, those reports are chiefly concerned with DO consumption by sediment [1)~3)], and hardly any research concerning the release of dissolved substance from sediment has been done until now [4),5)]. In this paper, assuming the case of dissolved organic compounds released from sediment being transported to the upper water layer to consume DO in the water, fundamental studies were conducted concerning the influence of water flow and the physical properties of sediment such as water content and the amount of dissolved substances contained in sediment on the release of those dissolved substances.

The influence of water flow on the exertion of diffusional mass transfer across the sediment-water interface can be considered as follows. The vertical flux of diffusional scalar

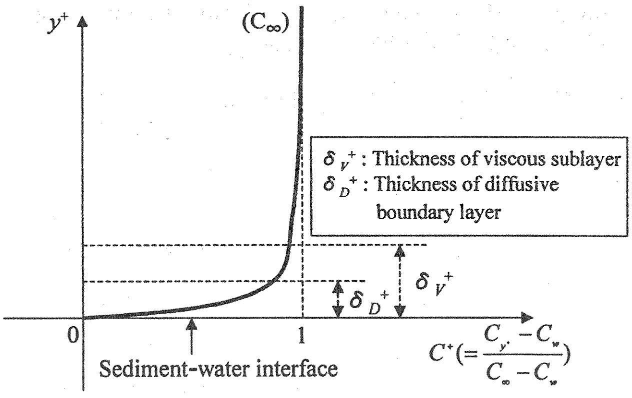

Fig. 1 Schematic distribution of solute concentration on the sediment-water interface.

across the interface is determined by molecular diffusion in the diffusive boundary layer just above the sediment. When flow velocity increases, the concentration gradient of solute increases because the boundary layer thickness decreases, resulting in an increase in release flux. In addition, it is thought that solute concentration at the interface is related to the water content of sediment and the amount of dissolved substance contained in sediment. Therefore, as a method of estimating the release flux of dissolved substances from sediment to flowing water, the process of diffusional mass transfer in the boundary layer and the relation among solute concentrations at the interface, the water content of sediment, and the amount of dissolved substances contained in that sediment should be clarified. Only then can a model be formulated which will enable us to express the release flux as a function of water flow and the physical properties of sediment.

Laboratory experiments which use kaolinite as the sediment and methylene blue as the dissolved substance were performed in order to investigate the influential factors on dissolved substance release. Mass transfer in the diffusive boundary layer is formulated by referring to the analysis of heat transfer. Moreover, solute concentration at the interface is formulated as a function of the physical properties of sediment such as water content and the amount of dissolved substance contained in the sediment, which is incorporated in the model to estimate the release flux of dissolved substance from the sediment to flowing water. In addition, the validity of the model is verified by comparing the estimation by the model with the experimental results.

## FORMULATION OF DIFFUSIONAL MASS TRANSFER ACROSS SEDIMENT-WATER INTERFACE

### Mass Transfer through the Diffusive Boundary Layer

The release flux of dissolved substance from sediment to flowing water can be formulated by applying the analysis of heat transfer to the diffusional mass transfer across the sediment-water interface. The assumed condition is steady state, and any chemical reaction, microorganism metabolization or other phenomena except for physical mass transfer are not considered. In order to formulate a model in the fully developed turbulent boundary layer, the following assumptions are made:

1) The sediment surface is hydraulically smooth, and the erosion of sediment particles is not considered.
2) The flow velocity and solute concentration are uniform in the flow direction and nonuniform in the vertical direction.
3) Shear stress and the vertical flux of diffusional scalar in the diffusive boundary layer are equal to shear stress and the flux at the sediment-water interface, respectively, and are spatially invariant.

The typical distribution of a solute concentration in a boundary layer overlying a smooth surface is shown in Fig. 1. The conservation equation of diffusional scalar (mass) is written as follows:

$$J=-(D+D_t)\frac{\mathrm{d}C}{\mathrm{d}y} \tag{1}$$

where $J$ and $C$ are the vertical flux of diffusional scalar (positive into the water column) and solute concentration, $D$ and $D_t$ are molecular and turbulent diffusivities, respectively, and $y$ is the vertical coordinate from the sediment-water interface (positive upward).

The boundary conditions are

$$C=C_w \quad \text{at} \quad y=0$$

$$C=C_\infty \quad \text{at} \quad y=\infty$$

where $C_w$ is solute concentration at the interface and $C_\infty$ is bulk concentration of solute.

When the Schmidt number and the turbulent Schmidt number are defined respectively as

$$Sc=\frac{\nu}{D} \quad , \quad Sc_t=\frac{\nu_t}{D_t} \tag{2}$$

then, the distribution of solute concentration is rewritten as follows: where $\nu$ and $\nu_t$ are kinematic and eddy viscosities, respectively,

$$\mathrm{d}C=-\frac{J}{U_*}\frac{\mathrm{d}y^+}{\dfrac{1}{Sc}+\dfrac{\nu_t^+}{Sc_t}} \tag{3}$$

In the above equation, $y^+$ and $\nu_t^+$ are non-dimensionalized with respect to the friction velocity $U_*$ and kinematic viscosity $\nu$ as:

$$y^+=\frac{U_* y}{\nu} \quad , \quad \nu_t^+=\frac{\nu_t}{\nu} \tag{4}$$

The release flux is obtained by integrating Eq. (3) of $y^+$ as described later. In Eq. (3), for mass transfer with a large $Sc$ number, assuming $Sc_t=1$, $\nu_t^+$ must be evaluated precisely down to $1/Sc$ or less even in the viscous sublayer, because intermittent turbulence exists in the layer. In addition, molecular diffusivity of the solute is extremely small compared with kinematic viscosity (i.e., $Sc$ number is large) in the diffusional mass transfer in this study. Therefore, the values of $\nu_t^+$ near the interface must be estimated precisely, because the diffusive boundary layer, in which the concentration varies steeply, is very thin. The following formulas have been proposed as a function of $\nu_t^+$ near the wall.

$$\nu_t^+=(ny^+)^4 \quad (n=0.124) \quad \text{(Deissler)}^{6)} \tag{5}$$

$$\nu_t^+=\left(\frac{y^+}{14.5}\right)^3 \quad (y^+\leqq 5) \quad \text{(Lin)}^{7)} \tag{6}$$

$$\nu_t^+=\left(\frac{y^+}{10}\right)^3 \quad (y^+\leqq 10) \quad \text{(Dade)}^{8)} \tag{7}$$

Recent investigations suggest that the eddy viscosity is proportional to $y^3$ ($\nu_t \propto y^3$) in regard to the limiting behavior of turbulence near a wall. Moreover, Eqs. (5) and (6) are empirical formulas. On the other hand, Eq. (7) is formulated based on an analysis of the turbulent kinetic energy balance. Therefore, Eq. (7) is used as the distribution of eddy viscosity near the sediment-water interface in this study.

Substituting Eq. (7) into Eq. (3), and integrating Eq. (3) from 0 to $\delta_D^+$ (thickness of the diffusive boundary layer), we obtain a difference of solute in the diffusive boundary layer ($C_{\delta D+}-C_w$). The concentration of solute is almost uniform outside the diffusive boundary layer ($C_{\delta D+} \fallingdotseq C_\infty$) because of turbulence there. Assuming $Sc_t=1$ ($\nu_t=D_t$), we obtain the following equation for the vertical flux of diffusional scalar ($\delta_D^+ \to \infty$).

$$J=-\frac{3\sqrt{3}}{2\pi}nSc^{-\frac{2}{3}}U_*(C_\infty-C_w)=-\frac{3\sqrt{6}}{8\pi}n\sqrt{f}Sc^{-\frac{2}{3}}U(C_\infty-C_w) \tag{8}$$

where $n(=0.1)$, $f(=8\tau_0/\rho U^2)$, $\rho$, $\tau_0$ and $U$ are the numerical constant, friction factor, fluid density, boundary shear stress and mean velocity, respectively.

### Solute Concentration at the Interface

When the release flux of a dissolved substance from sediment to flowing water is estimated from Eq. (8), a method to evaluate the solute concentration at the interface $C_w$ is investigated by the following procedure. In diffusional mass transfer near the interface, there are important features that the diffusive boundary layer thickness decreases when flow velocity increases, as shown in Fig. 2; in addition, the solute concentration at the interface $C_w$ varies with the water content of sediment and the amount of dissolved substance contained in sediment. That is, the diffusive boundary layer thickness is dominated by flow velocity, and the solute concentration at the interface is dominated by physical properties of the sediment. The solute concentration at the interface $C_w$ is then formulated as a function of the water content of sediment and the amount of dissolved substance contained in sediment as follows:

$$C_w = func(w, C_0) \tag{9}$$

where $w$ is the water content of sediment and $C_0$ is the initial concentration of methylene blue before mixing with kaolinite.

In the above equation, if the solute concentration at the interface can be approximated to the solute concentration in the pore water, $C_w$ is formulated as a function of $w$ and $C_0$ by modeling the adsorption process between the solute in pore water and the particle of sediment.

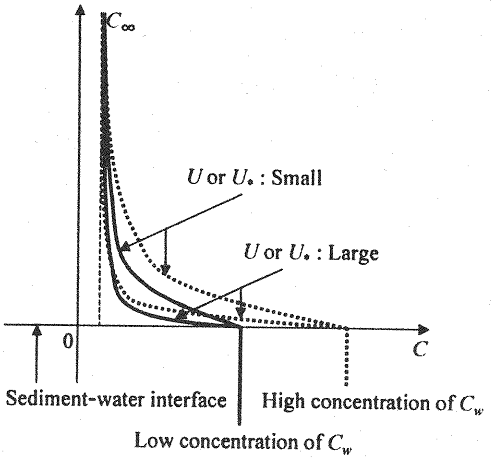

Fig. 2 Diffusional mass transfer across sediment-water interface.

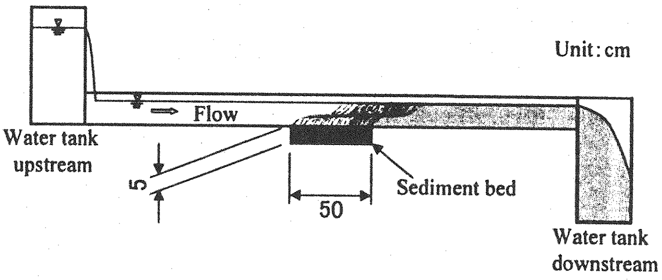

Fig. 3 Schematic diagram of flow system.

## LABORATORY EXPERIMENTS

Laboratory experiments concerning a dissolved substance released from sediment to flowing water were performed in an open channel of acrylic resin 650 cm long, 20 cm wide and 20 cm deep. A sediment bed was installed at about 4 m from the upstream edge of this channel. Using kaolinite and methylene blue solution, the sediment bed was set to a fixed ratio of water content. Water samples were collected on the downstream end of the channel for each flow velocity, and absorbance was measured with a spectrophotometer. The concentration of methylene blue in each sample was calculated from the relation between concentration and absorbance calibrated before the experiments. Substituting methylene blue concentration into the following equation, the release flux of dissolved

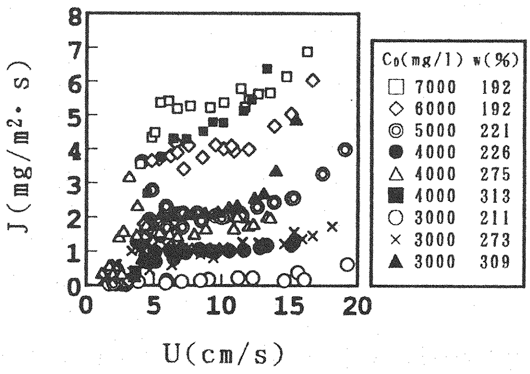

Fig. 4 Relation between release flux of dissolved substance $J$ and mean velocity $U$.

substance is obtained.

$$J = QC/A \tag{10}$$

where $J$ is the release flux of dissolved substance, $Q$ the flow discharge, $C$ the methylene blue concentration in each sample, and $A$ the area of sediment bed.

In order to investigate how the dissolved substance release is influenced by the flow velocity and physical properties of sediment, experiments were performed with various methylene blue concentrations and different amounts of kaolinite, and the release flux for various flow velocities was obtained at each experiment.

Figure 4 shows the relation between the release flux $J$ and mean velocity $U$. The release flux was found to increase as flow velocity increased in almost all experiments. These results suggest that the release flux increases because the diffusive boundary layer thickness decreases as flow velocity increases, so that the concentration gradient of methylene blue increases.

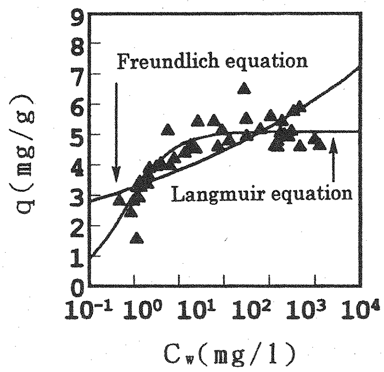

Fig. 5 Adsorption rate $q$ vs. solute concentration in the pore water $C_w$.

As for the influence of sediment properties, the release flux increased as the water content of sediment (kaolinite) $w$ increased if the initial methylene blue concentration $C_0$ was the same. Moreover, the release flux increased as $C_0$ increased if $w$ was the same.

## SOLUTE CONCENTRATION AT THE SEDIMENT-WATER INTERFACE

The solute concentration at the interface can be expressed by Eq. (9) by assuming that it can approximate the solute concentration in the pore water as explained above. The relation of solute concentration in the pore water to both the initial methylene blue concentration $C_0$ and the water content of sediment $w$ was investigated as follows:

Figure 5 shows the relation at an equilibrium state between solute concentration in the pore water $C_w$ and the solid phase concentration for solute (adsorption rate) $q$ evaluated from the following mass conservation equation.

$$C_w = C_0 - \frac{100}{w} q \gamma_w \tag{11}$$

where $C_w$ is the solute concentration in the pore water, $C_0$ the initial methylene blue concentration, $q$ the adsorption rate, $\gamma_w$ the unit weight of water (=$1.0\times10^3 g/l$ ($9.8\times10^{-3}$N/$l$)), and $w$ the water content of sediment.

The adsorption rate $q$ increases as solute concentration $C_w$ increases, and it approaches a certain constant value in the high concentration region in Fig. 5. In Fig. 5, the Langmuir isotherm equation (12) is drawn with a solid line.

$$q = \frac{10.72C_w}{1+2.11C_w} \tag{12}$$

From Fig. 5, the Langmuir isotherm equation expresses quite well the variation in the adsorption rate approaching a constant value in the high concentration region. Then, if Eq. (12) is substituted into Eq. (11), the following equation is obtained for the estimation of the solute concentration in the pore water (i.e., solute concentration at the interface) from the initial methylene blue concentration and the water content of sediment.

$$C_w = \frac{-g(w,C_0)+\sqrt{\{g(w,C_0)\}^2+4.22C_0}}{4.22} \tag{13}$$

where

$$g(w,C_0)=1+\frac{1.072\times10^6}{w}-2.11C_0$$

Solid lines in Fig. 6 show the relation between $C_w$ and $C_0$ for various $w$ calculated by Eq. (13). The agreement of the calculated with observed values is quite satisfactory, and Eq. (13) using the Langmuir equation is found to be applicable to the estimation of $C_w$.

## ESTIMATION OF RELEASE FLUX

### Equation to Estimate Release Flux - Application of Analysis of Heat Transfer-

When the analysis of heat transfer is applied to the diffusional mass transfer across the sediment-water interface, the release flux $J$ is given by Eq. (8) as described above. When Eq. (8) is non-dimensionalized, the Sherwood number $Sh$ (i.e., non-dimensional release flux) is given as the function of the Reynolds number $Re$ and the Schmidt number $Sc$ as follows:

$$Sh=\frac{3\sqrt{6}}{8\pi}nSc^{\frac{1}{3}}\sqrt{f}Re \tag{14}$$

where

$$Sh=\frac{h_D\cdot R_H}{D} \tag{15}$$

$$h_D=\frac{J}{C_w-C_\infty} \tag{16}$$

$$Re=\frac{UR_H}{\nu} \tag{17}$$

In the above equations, $h_D$ and $R_H$ are the mass transfer coefficient and the hydraulic radius, respectively. The friction factor $f$ is given by the following equation as a function of $Re$.

$$\frac{1}{\sqrt{f}}=2.0\log_{10}(4Re\sqrt{f})-0.8 \tag{18}$$

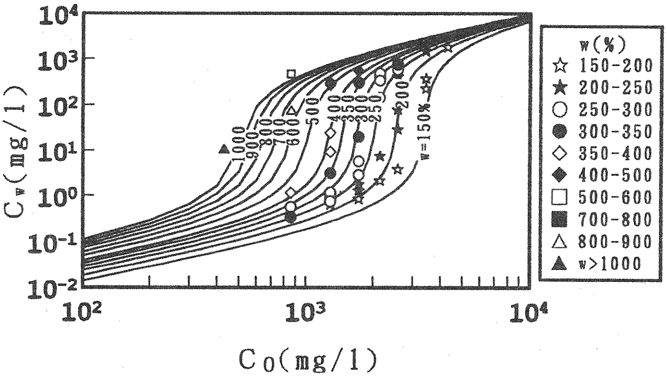

Fig. 6 Observed and calculated results for relation between $C_w$ and $C_0$.

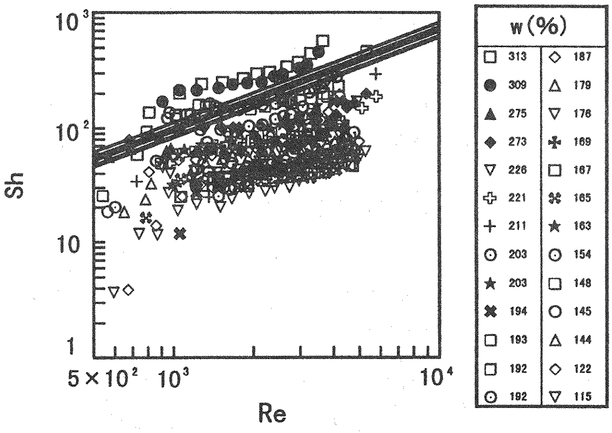

Fig. 7 Comparison of observed and calculated results for $Sh$ vs. $Re$.

To verify the validity of Eq. (14), the estimation by the model is compared with the experimental results. Concerning the evaluation of $Sh$ in the experiments, $C_w$ is calculated from Eq. (13), and $C_\infty$ is measured for each sample. Moreover, $Sh$ is calculated with Eqs. (15) and (16) by using the hydraulic radius $R_H$ and the molecular diffusivity $D$ in the experiments.

Figure 7 shows the plots of experimental values obtained by the above procedure and the curves of the $Sh\sim Re$ relation calculated from Eq. (14) when $Sc$ are regarded as the experimental values. Although the values estimated by the model roughly corresponded to the experimental values, it was also found that the experimental values with a high water content of sediment were larger than the values estimated by the model, and that the experimental values with a lower water content became smaller than the values estimated by the model.

As mentioned above, the release flux calculated by the model does not show much variation. By contrast, the release flux in the experiments was greatly influenced by the water content of sediment. The reason can be explained as follows; a phenomenon different from heat transfer at the wall should be considered to occur at the sediment-water interface. The influence of the adsorption of the dissolved substance (i.e., methylene blue) into the sediment particles (i.e., kaolinite) near the interface seemed to cause this difference. Therefore, an improvement of the model was attempted by the following analysis.

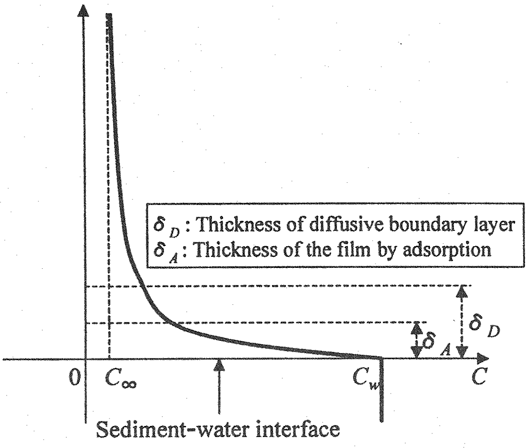

Fig. 8 Modeling of diffusional mass transfer at the sediment-water interface.

## Modeling the Mechanism of Diffusional Mass Transfer, and Improvement of the Model

When a dissolved substance in sediment travels to a water column across the interface, it is adsorbed on the surface of sediment particles at the interface, which results in a decrease in diffusional scalar flux across the interface. The adsorption process of a dissolved substance at the interface is closely related to the spatial concentration of the adsorbent (i.e., particles of sediment). The water content of sediment is considered as a parameter that indicates the spatial concentration of the particles of sediment at the interface, i.e., low water content, compared with high water content, includes many particles of sediment in the unit surface area. Therefore, the diffusional mass transfer is controlled by the adsorbing action. This action is thought to weaken as the water content of sediment increases.

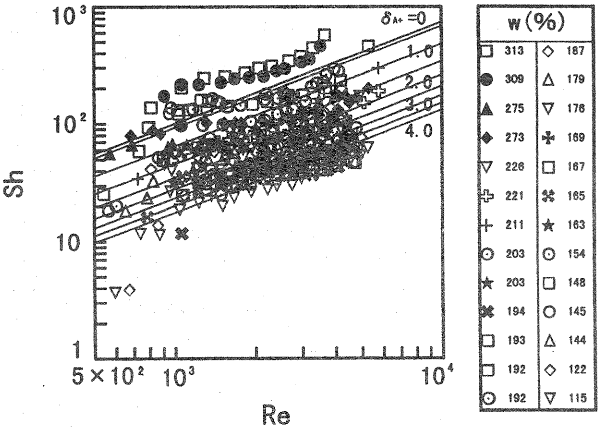

Fig. 9 Comparison of experimental results and estimated values calculated by Eq. (19) for *Sh* vs. *Re*.

To evaluate the effect of the control of diffusional mass transfer by adsorption at the interface, the mechanism of diffusional mass transfer is modeled as shown in Fig. 8, where we assume the existence of a film through which a dissolved substance travels only by molecular diffusion (the turbulent diffusivity for solute $D_t(=\nu_t)=0$) in the diffusive boundary layer; this film thickness is also assumed to vary with the water content of sediment. Similar to the formulation of Eq. (8), the following equation for release flux can be obtained if the solute concentration is considered to be uniform outside the diffusive boundary layer due to turbulent mixing.

$$Sh=\frac{1}{2\sqrt{2}F(Sc,\delta_A{}^+)}\sqrt{f}ReSc \tag{19}$$

where

$$F(Sc, \delta_A{}^+) = Sc\,\delta_A{}^+ + \frac{Sc^{\frac{2}{3}}}{\sqrt{3}n}[\frac{\pi}{2} - \frac{1}{2\sqrt{3}}\ln\frac{(n\,\delta_A{}^+ + Sc^{-\frac{1}{3}})^2}{n^2\,\delta_A{}^{+2} - n\,\delta_A{}^+ Sc^{-\frac{1}{3}} + Sc^{-\frac{2}{3}}} - \mathrm{Tan}^{-1}\{\frac{Sc^{\frac{1}{3}}}{\sqrt{3}}(2n\delta_A{}^+ - Sc^{-\frac{1}{3}})\}] \qquad (20)$$

In the above equation, $\delta_A{}^+ (= U_* \delta_A / \nu)$ is the film thickness by adsorption.

The values of *Sh* estimated by Eq. (19), varying $\delta_A{}^+$ from 0 to 4.0, are shown together with experimental values in Fig. 9. This figure shows that estimated values, when $\delta_A{}^+$ is small, agree comparatively with experimental values for higher water content of sediment and, when $\delta_A{}^+$ is increased, the estimated values come to agree with the experimental values for lower water content. These results suggest that because the film thickness $\delta_A{}^+$ corresponding to an impedance of mass transfer is thick when water content is low, diffusional mass transfer is controlled by adsorption. On the other hand, the higher the water content of sediment becomes, the thinner the film becomes , so that the release flux increases.

## CONCLUSION

Some important conclusions in this study are as follows:

1) The release flux of a dissolved substance varies with the velocity of water flow above the sediment and with the physical properties of the sediment such as water content and the amount of dissolved substance contained in the sediment.
2) The adsorption process between methylene blue and kaolinite is expressed by a Langmuir isotherm equation, which enables us to estimate the concentration of dissolved substance at the sediment-water interface.
3) Diffusional mass transfer at the sediment-water interface has been modeled in consideration of the adsorption process of the dissolved substance at the interface. By combining this modeling with the estimation equation of solute concentration at the interface, an equation for estimating the release flux has been formulated in this study.

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## APPENDIX-NOTATION

The following symbols are used in this paper:

$J$ = vertical flux of diffusional scalar ;
$C$ = solute concentration ;
$y$ = vertical coordinate ;
$D$ = molecular diffusivity ;
$D_t$ = turbulent diffusivity ;
$\nu$ = kinematic viscosity ;
$\nu_t$ = eddy viscosity ;
$C_w$ = solute concentration at the sediment-water interface ;
$C_\infty$ = bulk solute concentration ;
$Sc$ = Schmidt number ;
$Sc_t$ = turbulent Schmidt number ;
$U_*$ = friction velocity ;
$f$ = friction factor ;
$U$ = mean velocity ;
$w$ = water content of sediment ;
$C_0$ = initial concentration of methylene blue ;
$Q$ = flow discharge ;
$A$ = area of sediment bed ;
$q$ = solid phase concentration for solute (adsorption rate) ;
$\gamma_w$ = unit weight of water ;
$Sh$ = Sherwood number ;
$Re$ = Reynolds number ;
$h_D$ = mass transfer coefficient ;
$\delta_A$ = film thickness by adsorption ; and
$\delta_A^+$ = nondimensional film thickness by adsorption.

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