

ORIGINAL ARTICLE

## Distribution of Vital, Environmental Components and Nutrients Migration Over Sedimentary Water Layers

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### Abstract

Contaminated marine sediment is a secondary pollution source in the coastal areas, which can result in increased nutrients concentrations in the overlying water. We analyzed the nutrients release characteristics into overlying water from sediments and the interaction among benthic circulation of nitrogen, phosphorus, iron, and sulfur were investigated in a preset sediment/water column. Profiles of pH, ORP, sulfur, iron, nitrogen, phosphorus pools were determined in the sediment and three different layers of overlying water. Variety types of sulfur in the sediments plays a significant role on nutrients transfer into overlying water. Dissimilatory nitrate reduction and various sulfur species interaction are predominantly embodied by the enhancing effects of sulfide on nitrogen reduction. Contaminant sediment take on high organic matter, which is decomposed by bacteria, as a result promote bacterial sulfate reduction and generate sulfide in the sediment. The sulfur and iron interactions had also influence on phosphorus cycling and released from sediment into overlying water may ensue over the dissolution of ferric iron intercede by iron-reducing bacteria. The nutrients release rate was calculated followed by release rate equation. The results showed that the sediments released large-scale quantity of ammonium nitrogen and phosphate, which are main inner source of overlying water pollution. A mechanical migration of key nutrients such as ammonia and inorganic phosphate was depicted numerically with Fick's diffusion law, which showed a fair agreement to most of the experimental data.

**Key words** : Eutrophication, Denitrification, Ammonification, Nutrients release, Fick's diffusion mechanics

### 1. Introduction

Nutrients exchange in the overlying water from sediments is an important factor affecting nutrient equality in the water bodies, such as estuaries and coastal marine environment (Ignatieva, 1999). Sediments are an internal pollution source, so excessive nutrients could be

released from the contaminated sediments to the overlying water through mass transfer, bioturbation and particle resuspension, which can result in increased nutrients concentrations in the overlying water (Mu et al., 2017). In this problem of the coastal area due to the deposition of different waste from industrial wastewater, agricultural intensive aquaculture activities resulting in

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coastal eutrophication (Khirul et al., 2020).

In recent decades, the coastal area of South Korea has been suffered from coastal hypoxia caused by eutrophication, in addition to the effects of fish cages and oyster longline farm (Bashkin et al., 2002; Lim et al., 2006). Day by day increasing seafood demand, massive marine aquaculture has been developed in the coastal area. Therefore, eutrophication problems enhance caused by the direct supply of fish food and dominant microbial activation in the sediment. Marine floating cages system, high nutrients, and organic loading enhance from feed wastage and excretion productions are directly discharged into the environment. The process and augment of the nutrient's diffusion, as well as the eutrophication of the water body, leads from augmentation of pollution.

The high loading of organic matter associate with anoxia enhanced bacterial sulfate reduction and production of sulfides (Lovely and Phillips, 1987). Sulfides are highly toxic, which are impacts on marine ecosystems. Ferric and ferrous iron are present in the sediment, particularly iron (hydr)oxides which can be reduced by iron-reducing bacteria and by chemical reaction, e.g. reacting with sulfides (Azzoni et al., 2005). The iron (hydr)oxides minerals are the main reservoir of phosphate and its release from sediments into the water due to the dissolution of the iron (hydr)oxide-mediated by the biotic process (Lentini et al., 2012). Under anoxic condition, phosphorus bounds to iron (III) oxides and it is released from sediments when iron (III) oxides are reduced. Anaerobic metabolism takes place successively, at the beginning microorganisms use nitrate nitrogen, then iron oxide and sulfate as an electron acceptor compound (Frenchel et al., 2007). The dissolved inorganic nutrients accumulate in the sediment by the organic decomposition, which is gradually separated from the water (Miller et al., 2015). Consequently, nutrients release into overlying water from sediments by molecular diffusion. Therefore, the release rate calculation into the water from the sediment

depending on the nutrients and deposited organic matter movement (Nowlin et al., 2005).

The purpose of this study was to the behavior of iron and sulfur components served as electron donors on nutrients transformation and release from sediments to overlying water. Therefore, the results of this study can be used for proper management and improvement of sediments-water quality in the coastal area.

## 2. Materials and Methods

### 2.1. Sample collection and study area

The sediment and seawater samples were collected from Tongyeong bay located at the southeast coast of South Korea. The sampling site is affected by high land-based nutrient load from external pollution sources such as waste dumping through a pipeline and fishing activities especially by aquaculture activities (e.g. oyster and fish farm). Sediment samples were collected from around 10 to 12 meters below of water level using a stainless-steel ponar grab sampler at a depth of 0-20 cm. The collected marine sediments were quickly sealed in airtight cleaned polyethylene bags and were transported to the laboratory for storage at  $-20^{\circ}\text{C}$  until analyses. Before use, the debris and pebbles were manually removed from the sediments. The overlying seawater was collected as samples at 0.5 to 1.0 meter below the water surface by a water sampler from the same contaminated site. The sediments and water samples were homogenized before quantification/analyses.

### 2.2. Experimental setting

In the experimental column, 300 g of sediment samples were injected into the bottom of the 3-L graduated column (100 cm in height  $\times$  6 cm in diameter) and two liters of filtered seawater was added carefully into the column in order to avoid disturbing the sediment. The column was covered with aluminum foil and was placed at a room temperature of  $22^{\circ}\text{C} \pm 2^{\circ}\text{C}$  in the laboratory for a period of 15 days. Sediment samples

were analyzed at day zero and at the last sampling day. Overlying water samples were taken from the top, middle and bottom layers of the water column for analysis on the days of 0, 3, 9, 12 and 15. The experimental columns were marked as a top, middle and bottom from the surface by the distance of 20, 37, and 55 cm, respectively. The sediment-water column experiment was conducted in triplicates.

### 2.3. Analytical parameters

The parameters of sediment and overlying water, pH, and Oxidation-Reduction Potential (ORP) were measured at the column using the multi-parameter meter (Orion 3 star, USA). The Dissolved Oxygen (DO) concentration with temperature in the overlying water was measured by DO meter (YSI 550A, USA). The Acid Volatile Sulfide (AVS) was measured by the sulfide detection tube (Detector Tube No. 201H; measuring range 0.02-0.20 mg, GASTEC, Japan).

The overlying water samples were carefully collected from three different sampling points from the column and were filtered through a glass microfiber filter paper (GF/C, What man, UK) before analysis. The sediment samples were collected to three centrifuge tubes on an average 65~70 gm from the column then centrifuged at 2000 rpm for 20 min to collect around 10 ml of supernatant pore water. This pore water was used as the diluted sample within the detective range. The Chemical Oxygen Demand (COD) was determined by the potassium permanganate followed by the iodometric titration method. The Concentration of ammonium nitrogen ( $\text{NH}_4^+\text{-N}$ ) was determined by the indophenol blue method, nitrate ( $\text{NO}_3^-\text{-N}$ ) and nitrite ( $\text{NO}_2^-\text{-N}$ ) concentration was measured by through a cadmium-copper(Cd-Cu) column reduction N-(1-naphthyl)-ethylenediamine adsorption spectrophotometry respectively, phosphate phosphorus ( $\text{PO}_4^{3-}\text{-P}$ ) was analyzed by the ascorbic acid reduction method. Sulfate was determined by spectrophotometry turbidimetric method using barium sulfate. For the examination of

seawater and sediments were analyzed by standard methods of the Ministry of Oceans and Fisheries, South Korea, 2013. Iron concentrations were determined spectrophotometrically using reducing ferrozine reagent assay after extraction (Stookey, 1970; Viollier et al., 2000). The concentration of extractable iron (III) was determined by the difference between total extractable iron and iron (II). The concentration of all spectroscopic analyses was done by UV Mini- 1240 spectrophotometer (Shimadzu Corporation, Kyoto, Japan). For all samples, sediment and overlying water were analyzed three times and the data were used on average.

### 2.4. Nutrients release analysis

The release of nutrients at the sediment-water column affect by the different environmental conditions. Physical, chemical and biological process, such as the composition of sediments, temperature, DO, ORP, amount of deposited organic matter, depth of water etc. are involved in the migration of nutrients between the sediment and water column (Lee and Oh, 2018). In this experiment, we used laboratory incubation technique at the sediment water column for 15 days. The concentration of nutrients was measured each 3 days and release rates were calculated according to the following equation (Lee and Oh, 2018).

$$r = \frac{[V(C_n - C_0) + \sum V_n(C_{n-1} - C_a)]}{At} \quad (1)$$

where  $r$  is releases rate ( $\text{mg/m}^2/\text{day}$ ),  $V$  is the overlying water volume ( $\text{m}^3$ ),  $C_n$  is the concentration of nutrient got the  $n^{\text{th}}$  time ( $\text{mg/L}$ ),  $C_0$  is the initial concentration of nutrients ( $\text{mg/L}$ ),  $V_n$  is the volume of sampling water each time ( $\text{m}^3$ ),  $C_a$  is the concentration of nutrients after replenishing overlying water,  $n$  is the sampling number,  $A$  is the sediment water interfacing area ( $\text{m}^2$ ), and  $t$  is the sampling interval day.

### 3. Results and Discussion

#### 3.1. Physico-chemical characteristics of sediments and water

The physical and chemical characteristics of overlying water and sediment at initial day are presented in Table 1. It was observed that the sediment pH decreased from 7.54 to 6.91 meanwhile overlying water pH slightly increased in all layers. The pH change indicated due to the exchange of nutrient concentration, such as phosphates, ammonium released into overlying water from the sediment. This nutrient exchange slightly

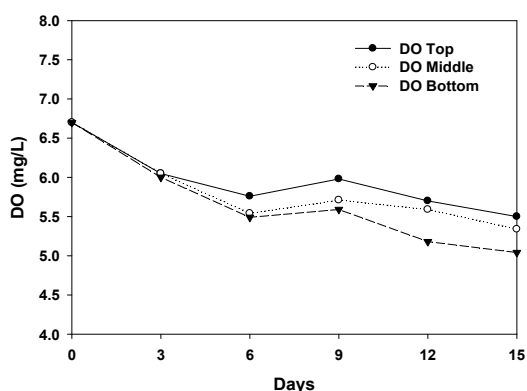


Fig. 1. Change of DO in the overlying water for 15 days.

Table 1. Physico-chemical characteristics of the sediments and water at initial day

Parameters	Sediment	water
pH	7.54	7.66
DO (mg/L)	--	6.7
ORP (mV)	-211.9	+260.3
NH <sub>4</sub> <sup>+</sup> -N (mg/L)	2.50*	0.085
NO <sub>3</sub> <sup>-</sup> -N (mg/L)	0.022*	0.278
PO <sub>4</sub> <sup>3-</sup> -P (mg/L)	0.29*	0.035
COD (mg/L)	22.0*	2.0
AVS (mg/g)	0.166	--
SO <sub>4</sub> <sup>2-</sup> (mM)	20.05	--
Fe <sup>2+</sup> (mM)	0.66	--
Fe <sup>3+</sup> (mM)	0.61	--

\*sediment unit mg/g

increased pH value in the overlying water while the slurry phase pH value decreased. As shown in Fig. 1, the concentration of Dissolved Oxygen (DO) of the overlying water has decreased from 6.7 to 5.5 mg/L in the top, 6.7 to 5.34 mg/L in the middle, and 6.7 to 5.04 mg/L in the bottom layer, which means the depletion of oxygen become from the anaerobic sediment. It was observed that the DO concentration in the bottom layer was lowest than other layers in the experimental column. The Chemical Oxygen Demand (COD) is a significant indicator of the pollution level. The Chemical Oxygen Demand (COD) value slightly increased from 22.0 to 23.8 mg/g. ds in sediment.

#### 3.2. Sulfur characteristics in the sediment

Sulfur is ubiquitously distributed in the sediments and its presence in various forms: sulfate, sulfide, metal sulfide, elemental sulfur, polysulfide, thiosulfate, sulfite, and other organic sulfur compounds. The sulfur cycle is interceded by a combination of oxidation and reduction process, including sulfate reduction and sulfur oxidation (Wu et al., 2013; Purcell et al., 2014). Sulfate is a dominant species and thermodynamically stable in the marine environment. Under the anoxic condition, sulfate reduced to sulfide and its reduced product are known to be corrosive, toxic and malodorous to aquatic organisms. The AVS pools accounted for the reduced inorganic sulfur species. Sulfide is originated by sulfate reduction, which is a form of anaerobic respiration in the marine environment (Canfield et al., 1993). In the experimental column, the SO<sub>4</sub><sup>2-</sup> concentration in the sediment decreased to 9.98 mM from 20.05 mM while Acid Volatile Sulfide (AVS) increased to 0.367 mg/L from 0.166 mg/L. The AVS concentration indicates that the simultaneous formation of FeS is more stable in the anaerobic sediment. Acid volatile sulfide increased, which is associated with a reduction of iron, indicated that the iron reduction by sulfides can play role in phosphorus cycling (Rozan et al., 2002). The interconnection between iron species and sulfide

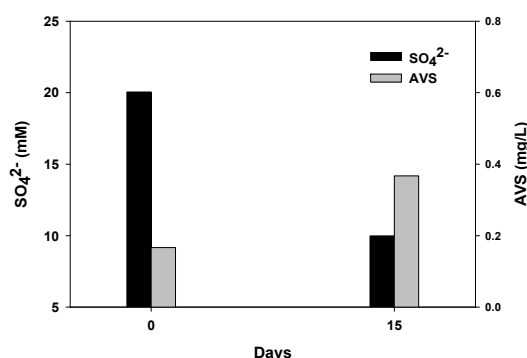


Fig. 2. Change of SO<sub>4</sub><sup>2-</sup> and AVS in the sediments.

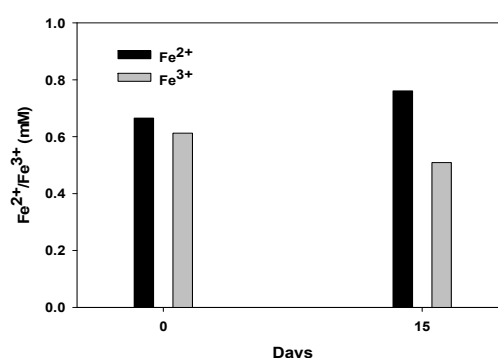


Fig. 3. Change of Fe<sup>2+</sup> and Fe<sup>3+</sup> in the sediments.

indicates to the control of both phosphorus and iron availability to primary producers, with a possible impact on the eutrophication process.

Sulfate reduction may interface with both denitrification (Fossing et al., 1995) and dissimilatory nitrate reduction to ammonia (Sayama et al., 2005). High sulfide concentration can suppress nitrification-denitrification and may prolong DNRA by providing an electron donor (An and Gardner, 2002). In this study, the AVS concentration might stimulate the DNRA process with the nitrate reduced and release ammonia from sediment into the water. Availability of sulfide in the anoxic condition which is consumed by oxygen by sulfur-oxidizing bacteria like *Thiomicrospira*, *Sulfuriferula*, *Sulfolobus* and *Thiobacillus* whereas a large group of bacteria such as *Beggiatoa*, *Aeromonas*, *Thioploca* and *Klebsiella* reductively converts enormous sulfate to sulfide in the sulfur cycle of marine areas (Stolp, 1988). It was found that, *Thioploca*, *Beggiatoa*, *Klebsiella*, and *Aeromonas* bacteria species involved in the sulfate reduction and sulfide production in the experimental sediments.

### 3.3. Iron reduction and P cycling

Fe (hydro)oxides in the sedimentary process, reduction of iron (III) can have an influence on carbon degradation. The iron (III) reduction mechanism is an indirect consequence of microbial respiration or

fermentation, in which organisms couple the carbon oxidation to the reduction of iron (III) by iron-reducing bacteria. In particular, microbial iron (III) reduction with low sulfate concentrations in the sediment is an important system of anaerobic degradation (Lovely et al., 2004). In addition, in the presence of heavy metal, iron-reducing bacteria are also connected in the bioremediation of contaminated sediments (Petrie et al., 2003). The phosphorus dissolution contributing processes in the sediment pore water, which is involved in the dissimilatory iron (III) reduction (Azzoni et al., 2005). In the experimental result observed that the decrease of iron (III) concentration from 0.613 to 0.509 mM and increased sulfide concentration from 0.16 to 0.36 mg/L. In sea sediments, high sulfate concentration resulting from sulfate reduction by sulfate-reducing bacteria, reduced iron (III) and the released iron (II) precipitated as iron sulfide that slightly adsorbs phosphorus at neutral pH. As a result, the phosphorus concentration was decreased and gradually released into overlying water from sediments.

Iron (III) reduction is widely in nature being iron-reducing bacteria (IRB) represented by various types of Archaea and Bacteria (Lovely et al., 2004). However, most of the research about the ecological importance and mechanisms of microbial iron (III) reduction focusing on *Shewanella* and *Geobacter* genera (Klueglein et al., 2013). *Geobacter* associate with

the *Geobacteraceae* family in the Delta subdivision of Proteobacteria which contains energy from the organic compound oxidation with iron (III) as an electron acceptor compound in the sediments. *Shewanella* belonging in the Gamma-subdivision of Proteobacteria which are capable to reduce iron (III) in the sediments (Lovely et al., 2004). Another iron-reducing bacteria was found in the sediments named is *Ferrimonas*, *Ferribacterium*, which can also reduce iron (III) under anoxic conditions.

#### 3.4. Concentration variations of nutrients in the sediment and overlying

The inorganic nutrients in the sediments and overlying were analyzed and presented in Table 1.  $\text{NH}_4^+$ -N and  $\text{NO}_3^-$ -N were the dominant species of dissolved inorganic nitrogen in the sediment and water. Dissolved inorganic nitrogen concentration was higher than phosphate concentrations. The molar ratios of N/P in the top, middle, and bottom varied from 7.83 to 10.75, 7.29 to 10.94, and 7.43 to 11.42, respectively.

Similar to the sediment pore water, the dissolved inorganic nitrogen concentration was also dominated by  $\text{NH}_4^+$ -N compound with the low  $\text{NO}_3^-$ -N and high  $\text{NH}_4^+$ -N concentration. The experimental results compared between sediments and overlying water, the concentrations of  $\text{NO}_3^-$ -N found initially high in the overlying water and decreased gradually until 15 days experimental period in the three experimental layers. It could be attributed to the different layers of the water column, initially oxygen in the overlying water layer was abundant and then gradually decreased until the end of the experiment. It was observed that denitrification was executed and its balance with the dissolved oxygen concentration varied conversely among three different layers in the overlying water (Fig. 1). Although, the  $\text{NO}_3^-$ -N concentration decreased with depth while the  $\text{NH}_4^+$ -N concentration increased with depth (Fig. 4). The ratio of  $\text{NO}_3^-$ -N vs.  $\text{NH}_4^+$ -N decreased with depth, which showed the associated with degradation of organic

matter in the sediments, increased DNRA and decreased nitrification down the core.

The  $\text{NO}_3^-$ -N concentrations decreased sharply after 3 days. The concentration of  $\text{NO}_3^-$ -N decreased rate in the bottom layer was higher than the top layer. Although the  $\text{NO}_3^-$ -N concentration at the sediment was relatively low (from 0.022 to 0.12 mg/g).

Due to the diagenetic reactions, the  $\text{NH}_4^+$ -N concentration profiles showed a mirror image of  $\text{NO}_3^-$ -N concentration in the overlying water. The concentration kept increasing until 15 days experimental period and it reached 1.37 from 0.085 mg/L in the bottom water while top water concentration changed 1.10 from 0.085 mg/L. It was interesting that different layers displayed same pattern and the maximum concentration was found in the bottom layer. The maximum concentration of 1.37 mg/L (highest concentration in the column) was reached at bottom layer water and top layer concentration was 1.10 mg/L (highest concentration). The  $\text{NH}_4^+$ -N concentration peaked at the bottom water layer, whereas  $\text{NO}_3^-$ -N concentration was low at the bottom layer, compared with the top layer, implying active DNRA activity. The differences could be related to various redox conditions, sediment properties, and disturbances. It was observed that the concentration of organic matter was also high which might be indicated more organic matter degradation.

The concentration  $\text{PO}_4^{3-}$ -P was high in the sediment and low concentration in the overlying water, which might be oxidizing condition of the sediment. The concentration kept increasing from 0 to 6 days, and change was steady after day 6 to 15 days. Under oxidizing condition, phosphorus tends to be absorbed by iron (III) (Jensen et al., 1995). The phosphate concentration increased down core as the decreased dissolved oxygen concentration with depth and increased remineralization with depth. These reactions also depend on microorganism activities.

In the overlying water, different depth from  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N and  $\text{PO}_4^{3-}$ -P profiles down the cores exhibit fast

change rate with linearity. The production of sulfide and iron (II) concentrations are moderately sensitive to sorption in the sediment which depends on dissolution rate mineralization. However, sulfide and iron (II) concentration increased due to the organic matter dissolution diagenesis in the sediment. According to the experimental results, the nutrient flux exchange depends on molecular diffusion, bio irrigations and reaction mechanisms.

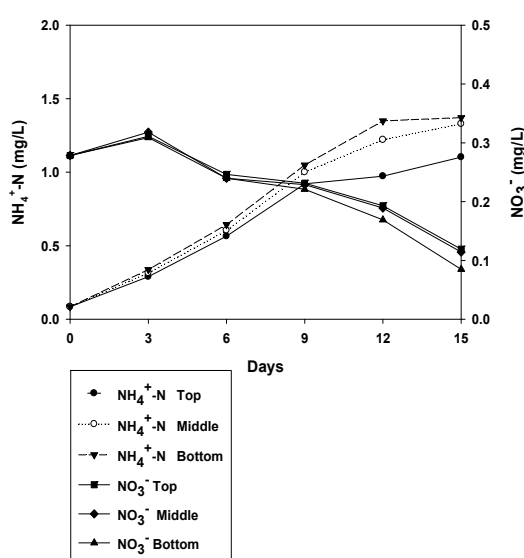


Fig. 4. Change of  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  in the overlying water for 15 days.

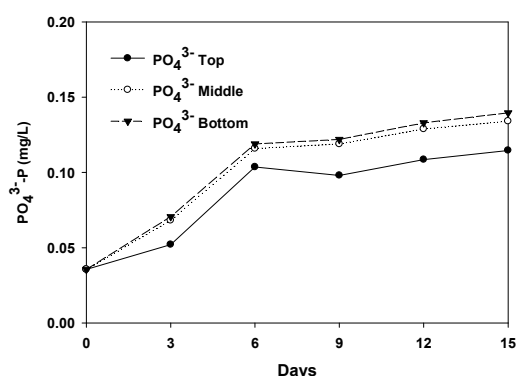


Fig. 5. Change of  $\text{PO}_4^{3-}\text{-P}$  in the overlying water for 15 days.

### 3.5. Nutrient release rate analysis

Nutrient release through the sediment-water interface was calculated based on nutrient concentration (Lee and Oh, 2018). Nutrients exchange between sediment and water are highly complex, it depends on physical, chemical, and biological processes (Gao et al., 2009). The release rate of  $\text{NO}_3^-\text{-N}$ ,  $\text{NH}_4^+\text{-N}$ , and  $\text{PO}_4^{3-}\text{-P}$  for the three layers were given in Fig. 6. In terms of column height, the calculated release rates were observed clear differences among the three layers. The  $\text{NH}_4^+\text{-N}$  was released into overlying water from sediment, where the sediment acted as an internal source. The highest value of  $\text{NH}_4^+\text{-N}$  was found at 3 days in the bottom layer ( $59.50 \text{ mg/m}^2/\text{day}$ ) and lowest value was found at 15 day in bottom layer ( $1.20 \text{ mg/m}^2/\text{day}$ ). Opposite patterns were observed in  $\text{NO}_3^-\text{-N}$  release rate among these water layer. The  $\text{NO}_3^-\text{-N}$  release rates of top, middle and bottom water were ( $-7.26$  to  $8.37 \text{ mg/m}^2/\text{day}$ ), ( $-8.85$  to  $10.05 \text{ mg/m}^2/\text{day}$ ), ( $-7.75$  to  $7.83 \text{ mg/m}^2/\text{day}$ ), respectively. The production of  $\text{NH}_4^+\text{-N}$  in the overlying water occurred by DNRA process, where nitrate is reduced condition. It was observed  $\text{PO}_4^{3-}\text{-P}$  concentration was released into overlying water from sediment, where sediment acted as an internal source. The highest value of the  $\text{PO}_4^{3-}\text{-P}$  released rates was observed on 3 days in the bottom layer ( $8.30 \text{ mg/m}^2/\text{day}$ ) and lowest was found on 9 days in the top layer ( $-0.40 \text{ mg/m}^2/\text{day}$ ). The nutrients fluxes considered by Fick's diffusion law from the sediments pore water profiles are led by molecular diffusion, bioturbation and remineralization which are significant effect in coastal area (Way et al., 1994). Therefore, the molecular diffusion was not only the nutrient exchange across the sediment water among three layers but also involved other process like bioturbation, bio irrigations, and reaction mechanisms are also responsible for the exchange of nutrients fluxes (Mu et al., 2017).

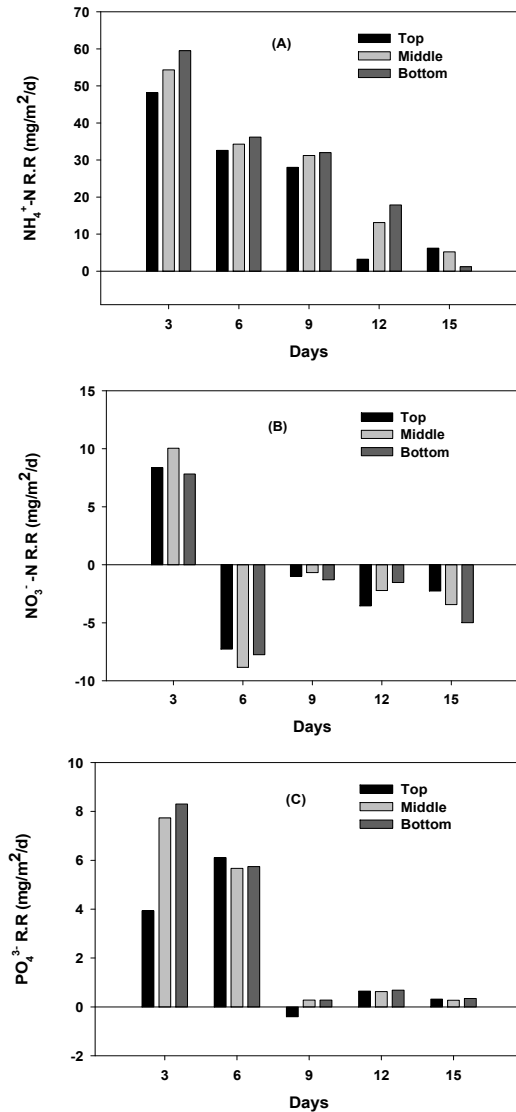


Fig. 6. Calculated release rates of (A)  $\text{NH}_4^+\text{-N}$  (B)  $\text{NO}_3^-\text{-N}$  and (C)  $\text{PO}_4^{3-}\text{-P}$  from sediment toward water.

### 3.6. Effect of redox condition

As shown in Fig. 4, the  $\text{NO}_3^-\text{-N}$  decreased while  $\text{NH}_4^+\text{-N}$  increased in the overlying water due to the organic matter decomposition. The transition and transportation of nitrogen in the sediment-water interface are complicated. Nitrification, denitrification, ammonification, and DNRA play significant roles in the nitrogen transition processes. The concentration of

dissolved oxygen reflects the redox potential (Jiang et al., 2008) and therefore affect the reciprocal transformation of  $\text{NO}_3^-\text{-N}$  and  $\text{NH}_4^+\text{-N}$ . Initial oxidation-reduction potential (ORP) was -211.9 mV in the sediment, which indicates sediments become anoxic condition. Under this condition, the concentration of  $\text{NH}_4^+\text{-N}$  converted to  $\text{NO}_3^-\text{-N}$  was inhibited but the DNRA occurred. The concentration of  $\text{NH}_4^+\text{-N}$  is generated while the  $\text{NO}_3^-\text{-N}$  is reduced in the DNRA process. The concentration of  $\text{NH}_4^+\text{-N}$  adsorption in the sediments also affects by the redox condition (Morse and Morin, 2005). Under anoxic conditions, the desorption rate increased and released of  $\text{NH}_4^+\text{-N}$  occurred to overlying water (Brezonik, 1972).

Under the anoxic condition, the  $\text{PO}_4^{3-}\text{-P}$  concentration exchange flux was high. This result is showed a negative correlation between DO concentration and the transition rate of phosphorus. oxic condition, phosphorus can bind with iron (III) and prolong the sediment adsorption (Jiang et al., 2008) and phosphorus can easily release into overlying water from the sediments under anoxic conditions (Gomez et al., 1999).

### 3.7. Nutrients migration via molecular diffusion

To describe the migration between sediment and overlying water, we adopted a diffusion mechanics, called Fick's 2<sup>nd</sup> law. The proposed system is diagrammed in Fig. 7. As schemed in that figure, a nutrient component is assumed to diffuse out at the sediment-water interface where the component fully resides. Initially the component exists as a constant bulk concentration throughout the overlying layer. When a one-dimensional, transient diffusion applies, we have:

$$\frac{\partial c_i}{\partial t} = D_{w,i} \frac{\partial^2 c}{\partial z^2} + R_i \quad (2)$$

With boundary conditions as

$$c_i(o,t) = c_{0,i} \quad @ \quad z = 0$$

$$c_i(z,0) = c_{b,i} \quad @ \quad t = 0$$



$$R_i = k_{i,j} f(c_i, c_j)$$

Where  $c_i(z,t)$  is the concentration of component  $i$ ,  $D_{w,i}$  stands for diffusion coefficient of solute  $i$  in water phase,  $R_i$  denotes disappearance rate of  $i$  via a homogeneous chemical reaction, and  $k_{ij}$  is a reaction rate constant for component  $i$  and  $j$  involved. For  $R_i$ , the component  $i$  would be supposed to convert to another species through an oxidation or reduction depending on the surrounding condition. In this case, we suppose ammonia would turn to nitrite/nitrate aerobically or gaseous nitrogen through denitrification under anoxic environment. Without any chemical reactions involved ( $R_i = 0$ ), the Equation 2 would be simply a conventional partial differential equation in which an analytical solution should exist as follows:

$$c_i^*(z,t) = 1 - \operatorname{erf}\left(\frac{z}{2\sqrt{D_{w,i}t}}\right) \quad (3)$$

$$\text{Where } c_i^*(z,t) = \frac{(c_i - c_{b,i})}{(c_{o,i} - c_{b,i})}$$

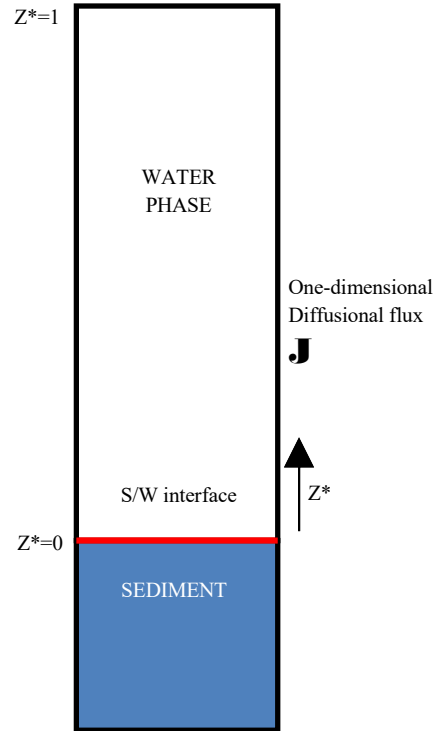
With some chemical reactions, Equation 1 was solved numerically using Maple IV (*routine solve*). Table 2 shows all parameters and constants used in this computation. As described earlier, nitrate in the water phase should decrease because of effect of DNRA. Ammonia-N would experience one chemical reaction, i.e., disappearance due to nitrification as stated clearly with a highly positive ORP value. Inorganic phosphate would appear in the overlying water only because of

**Table 2.** Parameters and constants used in calculations based on Fick's diffusion law

Parameters	Values
$D_{w,a}$ (ammonia/water)	$1.76 \times 10^{-5} \text{ cm}^2/\text{s}^b$
$D_{w,p}$ (ammonia/phosphorus)	$0.7 \times 10^{-5} \text{ cm}^2/\text{s}^b$
$k_d : R_a = -k_d c_a$ , rate constant for ammonia	$0.2 \text{ s}^{-1,c}$

<sup>b</sup> (Ullman and Aller, 1982), <sup>c</sup> arbitrary

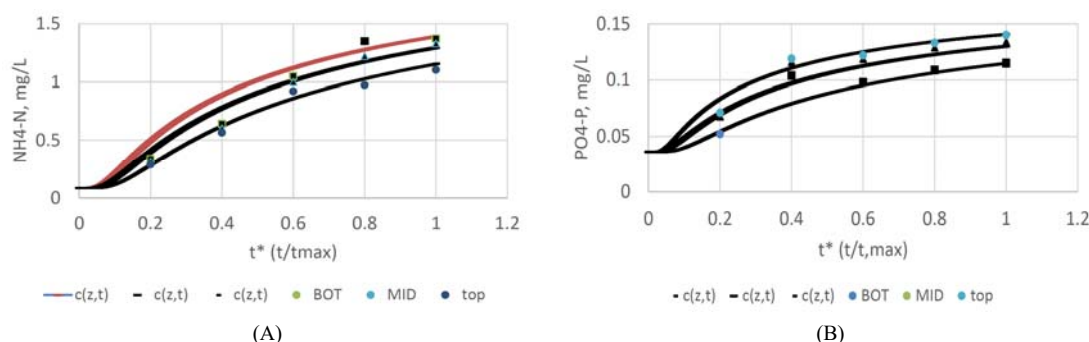
diffusional migration from the sediment. Some comparative data between simulation and experiment for species like ammonia and phosphorus are shown in Fig. 8. Overall, the comparison agrees with each other in a reasonable range.



**Fig. 7.** Schematic of the simulation setup via Fick's molecular diffusion (1-D) to solve concentration of nutrient species over time and space.

#### 4. Conclusions

Sediment plays an internal source of nitrogen and phosphorus into the overlying water, thus contributing to eutrophication. According to the experimental result of the collected three-layers overlying water and sediment in the column experiments, the conclusions on nutrients exchange are summarized as follows. It was observed the pH, ORP, and COD as base environmental parameters, and analyzed nitrogenous, iron and sulfur species such as nitrate, ammonium, sulfide, and sulfate on the two phases. These results indicate that sediments



**Fig. 8.** Ammonia distribution in overlying water for (A)  $\text{NH}_4^+\text{-N}$  and (B)  $\text{PO}_4^{3-}\text{-P}$  simulated as line curves. Symbols denote experimental points at specified positions over time. The positions of  $z^*=1.0$ , 0.64, and 0.27 were located as top, middle, and bottom, respectively.

release a lot of ammonium and phosphate contents to the overlying water in the experimental column and it has become an effective source of inner pollution. It was estimated that the nutrients released into the bottom layer from sediment hardly influenced the water quality. As a result, the nitrate concentrations decreased enough to DNRA to take place. Additionally, DO decreased in the overlying water were considered to have an impact on water quality specially at the bottom layer of the column. Nutrients released from sediment could thus worsen water pollution as an internal source. In the experimental column, high concentration of ammonium was used of sulfide as an electron donor in dissimilatory nitrate reduction to ammonia. Under the highly anaerobic condition, acid volatile sulfide (mostly  $\text{H}_2\text{S}$  and  $\text{FeS}$ ) increased with time, which confirmed the sulfate reduction and produced sulfides. Fick's molecular diffusion with some plausible reactions depending on local environmental conditions may explain fairly the distribution of nutrient species such as ammonia and phosphorus in the water phase through a numerical simulation. This work was progress in order to obtain comprehensive knowledge of inner eutrophication and nutrients release pathways coupled with iron and sulfur compounds.

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