Behaviors of nitrogen, iron and sulfur compounds in contaminated marine sediment

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ABSTRACT

The marine sediment sustains from the anoxic condition due to increased nutrients of external sources. The nutrients are liberated from the sediment, which acts as an internal source. In hypoxic environments, anaerobic respiration results in the formation of several reduced matters, such as N₂, NH₄⁺, NO₃⁻, Fe²⁺, H₂S, etc. The experimental results have shown that nitrogen and sulfur played an influential, notable role in this biogeochemical cycle with expected chemical reductions and a ‘diffusive’ release of present nutrient components trapped in pore water inside sediment toward the bulk water. Nitrate/ammonium, sulfate/sulfides, and ferrous/ferric iron are found to be the key players in these sediment-waters mutual interactions. Organonitrogen and nitrate in the sediment were likely to be converted to a form of ammonium. Reductive nitrogen is called dissimilatory nitrate reduction to ammonium and denitrification. The steady accumulation in the sediment and surplus increases in the overlying waters of ammonium strongly support this hypothesis as well as a diffusive action of the involved chemical species. Sulfate would serve as an essential electron acceptor so as to form acid volatile sulfides in present of Fe³⁺, which ended up as the Fe²⁺ positively with an aid of the residential microbial community.

Keywords: Denitrification, Eutrophication, Hypoxia, Nitrogen release, Nutrient

1. Introduction

The explosive growth of resource uses and related population over the world lets us focus on marine resources and the oceanic environment [1, 2]. Subsequently, those growths have accelerated water and terrestrial pollution. Especially, marine eutrophication has been a big concern in this context due to the rises of industrial wastewater, agricultural/livestock waste, aquaculture activities (e.g., fish and oyster farm) [3, 4]. As a result, input nutrients containing phosphorus, nitrogen and all the organic matter accumulate in the sediment of coastal areas ultimately to result in serious algal blooms in the marine environment [5, 6]. Nitrogen is one of the most crucial factors of marine eutrophication as a major component for most of the aquatic lives. In general, the coastal area in Korea has a lot of fish and oyster farms, therefore, may confront eutrophication problems due to the direct supply of fish food and effective microbial activation in the sediment. Several coastal regions in South Korea have been suffered from coastal hypoxia caused by eutrophication, in addition to the effects of the artificial structures, such as cages [7, 8]. These cages are generally located from 100 m to 1.5 km offshore. In most of open sea cage system in the coast, high nutrients loading generated from feed waste and biotic excretion is directly discharged into the environment. As a result, coastal eutrophication and the presence of artificial structures have involved severe deoxygenation in the coastal areas. In addition, coastal eutrophication is regarded as a serious environmental and social problem that needs to be resolved.

Most often the increase of nutrients loads to coastal waters and sediment are the main cause of eutrophication-associated hypoxia. The consequent hypoxia can demolish the benthos and converted the flow of energy in the food chain downward instead of upward, thus feeding microbes in sediment [9]. Simultaneously, the pursuant hypoxia-induced release of nutrients such as phosphorus and nitrogen from deposited organic matter can be substantial and hold

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down the tainted consequences of external loading [10, 11]. Thermodynamically, oxygen is the most favorable electron acceptor, but the oxygen depletion in the sediment may contribute to liberate nitrogen from sediment into the water [12]. So increased nitrogen concentration and algal blooms conduct to more intense anoxia and there is a mutual prolonged effect between these processes [13]. Hypoxia can also enhance the release of nutrients from organic compounds in the sediment as ammonium is released from organic compounds by bacterial degradation [14-16]. Under anaerobic and reducing conditions undesirable greenhouse or malodorous gases are produced such as methane (CH4) and hydrogen sulfide (H2S) [17]. Moreover, H2S is highly toxic to living organisms and when it is oxidized, oxygen is used up. Generally speaking, acid volatile sulfide (e.g., H2S and FeS) and ferrous iron (Fe2+) are produced such as methane (CH4) and hydrogen sulfide (H2S) [18]. H2S is highly toxic to living organisms and when it is oxidized, oxygen is used up. Generally speaking, acid volatile sulfide (AVS; not only H2S but also including different sulfur compounds), the eutrophication matter suggests that the excess nutrients input enshrouded the self-purify ability of water bodies, thereby changing the characteristics of the ecosystem and leading to phytoplankton blooms [19-21]. Over time, these nutrients could also augment themselves in the sediment and make it possible that an internal load is recycled back into the overlying waters under different environmental conditions [22].

The processes of nutrients across the sediment-water interface are of consideration in understanding the impacts of the chemical composition and the trophic level of aquatic systems, particularly, in coastal marine environments [23]. The nutrients and organic matter concentration in the overlying water of marine environments, which originates from sediment, are regarded as a major component of the internal source. Such releases from bottom sediment may have a significant impact on water quality and may result in continued eutrophication, hence the degree of eutrophication should be determined, and the causation of eutrophication should be diagnosed in the process of eutrophication management, which will be helpful to acquire an apt plan and management [24].

The main purpose of this study was to investigate mutual interactions between sulfate and Fe(III) reduction as well as the production of acid volatile sulfide (e.g., H2S and FeS) and ferrous iron (Fe2+) in the sediment, served as electron donors for dissimilatory nitrate reduction to ammonium (DNRA). Another goal is to find the roles of the electron donors in nitrogen release from organically-enriched sediment into the water body under a certain environmental condition. Experiments were conducted in a sediment-water basin, simulating the aquatic environment that we are interested in. This study will provide helpful information for the practice of nitrogen release estimation and determine the direction of future studies of coastal eutrophication.

2. Materials and Methods

2.1. Sample Collection and Study Area

Marine water and sediment samples were collected in the city of Tongyeong (34°50′28.5″N128°28′16. 4″E), in the southeast coast of South Korea. The sampling site was characterized by odoriferous sediment and water due to external pollution sources such as waste dumping through a pipeline and fishing activities particularly by aquaculture activities (e.g., fish and oyster farm). Sediment samples were collected from around 10 m to 12 m below of water level using a boat through a stainless steel grab sampler at a depth of 0-20 cm. And then they were quickly packed in airtight cleaned polythene bags and were transported to the laboratory for storage at -20°C until analyses. The sampler was cleaned with distilled water before use to eschew unnecessary contamination. A sufficient amount of seawater was collected from the same site as samples at a depth of 0.5 m to 1.0 m by a water sampler. All samples were homogenized before their quantification/analyses.

2.2. Laboratory Setup for Incubation

For experiments, a sediment sample of 300 g was prepared in a 2-L graduated basin. One liter of filtered seawater was added carefully into the basin in order to avoid disturbing the sediment. Five replicate basins were established for the experiments of the 20 d incubation period. All basins were covered with aluminum foil and were placed in the incubator at 22°C. The temperature was fixed as the same condition with situ areas that might ensure steady microbial activity. A time interval of 12 h light and 12 h darkness in a day was maintained through the entire incubation period. Samples were taken from each individual basin for analysis on the days of 0, 5, 10, 15 and 20.

2.3. Analyses of Physicochemical Characteristics and Chemical Analysis

Before measuring the physicochemical parameters, the overlying water & sediment were separated from the basin and the sediment was homogenized. The parameters of seawater and sediment, including oxidation-reduction potential (ORP) and pH were measured at the basin using the multi-parameter meter (Orion 3 star, USA), additionally DO with temperature in the overlying water was measured by DO meter (YSI 550A, USA). The AVS was measured by the sulfide detection tube (Detector Tube No. 201H; measuring range 0.02-0.20 mg, GASTEC, Japan) as follows: 2 g of a sediment sample was mixed with 2 mL concentrated sulfuric acid, which was continuously pumped into the tube until the tube color changed [25].

The water samples were carefully withdrawn from the basins and were filtered through a glass microfiber filter paper (GF/C, What man, UK) before sampling. The sediment samples were collected to three centrifuge tube on an average 65-70 gm from basin then centrifuged at 2,000 rpm for 20 min to collect around 10 mL of supernatant pore water. This pore water was used as the diluted sample within the definite range. The chemical oxygen demand (COD) was determined by the oxidizing agent of potassium permangenate followed by the iodometric titration method which denoted the standardized analytic procedure. The concentration of ammonium nitrogen (NH4+-N) was determined by the indophenol blue method, total nitrogen (T-N) was measured by oxidizing sample with potassium persulfate, nitrate (NO3-N) and nitrite (NO2-N) concentration was measured by through a cadmium-copper(Cd-Cu) column reduction N-(1-naphthyl)- ethylenediamine adsorption spectrophotometry respectively according to standard methods for the examination of marine environmental pollution [25]. Sulfate
was determined by spectrophotometry turbidimetric method using barium sulfate. Fe was determined spectrophotometrically using reducing ferrozine reagent assay after extraction [26, 27]. The concentration of extractable Fe\(^{3+}\) was determined by the difference between total extractable Fe and Fe\(^{2+}\). The concentration of all spectroscopic analyses was done by UV Mini- 1,240 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 Experiments

Nutrients releases at the sediment and water interface in the basin were investigated in terms of those rates. Nutrients release rates were determined according to the method of Hieltjes and Lijklema [28] proposed. The rates were calculated under the assumption that the concentrations of species \(i\) depend only on flow-out, flow-in and horizontal surface area over the sediment and with the material balance over the reactor [29]. In order to achieve the nutrients release rate, the calculation was done by the following equation:

\[
\frac{dC}{dt} = \frac{\sum V_n C_n - V_n C_0}{A t} + \frac{V_n (C_n - C_{n+1})}{A t} + \frac{V_n C_0}{A t}
\]

Where,
\(r\) is release rate (mg/m\(^2\)/d).
\(V\) is the volume of overlying water (0.001 m\(^3\) in this study).
\(C_n\) is the concentration of nutrient got the \(n\)th time (mg/L).
\(C_0\) is the initial concentration of nutrients (mg/L).
\(V_n\) is the sampling water volume each time (m\(^3\)).
\(n\) is the number of sampling.
\(A\) is the water interfacing area of the sediment (0.00785 m\(^2\) in this study).
\(t\) is the averaged sampling interval (day).

3. Results and Discussion

3.1. Changes of pH, DO and COD

The physical and chemical characteristics of sea sediment and water were measured during the 20 d incubation period (Table 1). It was observed that the pH of overlying water increased from 7.99 to 8.21 meanwhile sediment pH decreased from 7.58 to 6.9. The change of pH seemed to be due to the migration of some chemical species, that ammonium might be released from the sediment pores into the overlying water. This natural migration of that species turned pH lower in the slurry phase while overlying water pH value slightly increased. The DO concentration of the overlying water has decreased from 5.7 mg/L to 4.1 mg/L, which means the oxygen depletion originating from the anaerobic sediment. The COD can be regarded as an important indicator of pollution level, indicating a full degree of chemical oxidation of organic matter involved in the sediment and water. It also represents the substance including organic compounds prohibiting biodegradation. The COD value slightly increased from 21.7 mg/g to 24.4 mg/g,ds in sediment while overlying water COD value increased significantly from 2.2 mg/L to 7.2 mg/L. Organic compounds including nitrogen species (may be ammonium) could transport across the sediment/water interface so as to contribute to rise of COD, which might be depending on the migration rate as will be mentioned later.

3.2. Change of Sulfur and Iron Concentration in the Sediment

Sulfur is widespread in the marine environment and is present in many different forms: sulfides (S\(^-\)), elemental sulfur (S\(_0\)), polysulfides (S\(_n\)), sulfite (SO\(_3\)), sulfate (SO\(_4\)), thiosulfate (S\(_2O_3\)) and different organic sulfur compounds. It is very common that polluted sediment along with overlying water contains a high concentration of organic matter. That tells how COD is considerably high and ORP value is so negative like for instance, -215.3 mV in this case. This surroundings condition would become anoxic, thus resulting in the reduction of the oxidized forms of sulfur to H\(_2\)S or sulfides that are a measure of the reduced (anoxic) state of the sediment. H\(_2\)S is regarded as a predominant form generated out of sulfate by anaerobic respiration in the marine environment [30]. Furthermore, H\(_2\)S can react with Fe\(^{2+}\) and produce mineral FeS as well. AVS (H\(_2\)S and FeS), the most common form of reduced sulfur is often used as a key index for sediment characterization [29]. The overall reaction can be represented by the equation:

\[
\text{CH}_2\text{O} + 1/2\text{SO}_4^{2-} + \text{H}^+ \rightarrow 1/2\text{H}_2\text{S} + \text{CO}_2 + \text{H}_2\text{O} \quad (2)
\]

\[
\text{SO}_4^{2-} + 4\text{H}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O} \quad (3)
\]

\[
\text{Fe}^{2+} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{H}^+ \quad (4)
\]

Where \(\text{CH}_2\text{O}\) represents a generic form of organic matter as carbohydrate.

As shown in (Fig. 1), AVS concentration kept increasing from 0.088 mg/g,ds to 0.12 mg/g,ds, 35% increase in total. Accordingly,
Fig. 1. Time evolution of acid volatile sulfide (AVS) and sulfate in the sediment.

Fig. 2. Time evolution of Fe\(^{2+}/Fe^{3+}\) concentrations in the sediment.

sulfate dropped to 7.8 mM from 10.1 mM (23% decrease). The graph obviously dictates sulfate reduction through a complicated bio & chemical pathway. Raise of acid volatile sulfide accelerated until the end of the experiment.

In an individual experiment, Fe\(^{3+}\) was determined as the difference between total extractable Fe and Fe\(^{2+}\). At the beginning concentrations of Fe\(^{3+}\) and Fe\(^{2+}\) were 0.56 mM and 0.40 mM in the sediment, respectively, which meant to be comparable with each other. The ferrous compound was reduced via electron acceptance to a ferric form as seen clearly in the plots of (Fig. 2). Note that despite of some error in mole numbers (0.56 mM to 0.39 mM for Fe\(^{3+}\); 0.40 mM to 0.66 mM for Fe\(^{2+}\)) the rise and fall of the two species match fairly. The reduction of iron by sulfide leads to a release of Fe\(^{2+}\) into the sediment, which reflects the close mutual interaction between the sedimentary Fe and S cycle.

3.3. Transition and Exchange among T-N, NH\(_4^+\)-N and NO\(_3^-\)-N in the Sediment-Water System

Nitrogen is one of the major parts of aquatic life in the marine environment. Reactive inorganic nitrogen like nitrate, nitrite, and ammonium are a dominant species in the marine environment where particulate matter accumulates in the sediment and is re-mineralized, oxidized and eventually denitrified by a variety of microorganism. Nitrogen in the form of nitrate or ammonium, as a main moderating nutrient can be released from sediment into overlying water, which may have a serious impact on water quality and result in continuous eutrophication under certain environmental condition. The nitrogen and nitrogenous compounds in seawater and sediment are known to be controlled by many factors, for example, sediment type, the rate of sedimentation, redox condition, amount and type of organic matter, the intensity of mineralization of organic matter [31].

The transition and change of T-N, NH\(_4^+\)-N, and NO\(_3^-\)-N concentrations in the whole system were monitored (Fig. 3-5). In spite of a little disturbance, T-N was measured as decreasing with time in the sediment whilst it soared (Fig. 3) up to 0.8 mg/L, more than as twice as that of the starting value in the overlying waters. By comparing (Fig. 3 and 4), it was shown that half of the T-N may be organo-nitrogen. That indicates organic nitrogenous compounds were degrading over time in aid of existing microorganism, thus showing the decline of T-N concentration in the sediment. A part of T-N could migrate across the sediment-water interface to the bulk water to increase the T-N content in the water column. Migration can be explained with that simple Fick's law where the transport at large counts on concentration gradient, but it is complicated in fact since the diffusional process should occur through so many bent, narrow, porous channels inside the sediment.

Likewise in (Fig. 3), the behavior of NH\(_4^+\)-N in the sediment and water were very similar as expected (Fig. 4). Sole difference in this plot is surplus production of NH\(_4^+\)-N in the sediment pores possibly with the DNRA process, an anaerobic respiration, where nitrate is reduced to nitrite and then ammonium. Ammonium overproduction would not be possible without DNRA because ammonia or ammonium in a highly reductive state could be denitrified easily by abundant denitrifying bacteria or so. The NH\(_4^+\)-N concentration in the sediment decreased from 1.67 mg/g to 1.29 mg/g while overlying water changed from 0.14 mg/L to 0.52 mg/L.

Compared to T-N and NH\(_4^+\)-N, NO\(_3^-\)-N concentrations in the system are not significant. However, the trend was totally different from the previous plots in that nitrate kept diminishing with time. In this case, we presume the oxidized form of nitrogen could be
Fig. 4. Time evolution of NH$_4$$^+$-N in the sediment and overlying water.

Fig. 5. Time evolution of NO$_3$$^-$-N of the sediment and overlying water.

Fig. 6. Calculated release rates of (a) T-N, (b) NH$_4$$^+$-N and (c) NO$_3$$^-$-N from sediments toward water.

Nitrogen is a predominant compound in terms of its impact on biological activity and its migration between the bottom and water column. Nitrogen is more easily degraded than other compounds, thus the importance of the accumulation of organic matter, reflecting intense biological activity, with organic decomposition and nitrogen release into the overlying water predomination [24].

3.4. Evaluation of Release Rates from Sediments to Water

Nitrogen is a predominant compound in terms of its impact on biological activity and its migration between the bottom and water column. Nitrogen is more easily degraded than other compounds, thus the importance of the accumulation of organic matter, reflecting intense biological activity, with organic decomposition and nitrogen release into the overlying water predomination [24].

Experimental data suggests that oxidants like nitrate and sulfate greatly affect states of the interested species, particularly in the overlying waters by donating necessary electrons in the related redox reactions. DNRA is known to be activated in a carbon-rich environment by strictly anaerobic bacteria, i.e. sulfate-reducing bacteria [34, 35] which may be located close to the surface sediment under much-reduced conditions. DNRA and denitrification could be stimulated with the provision of those electrons while nitrate and sulfate are converted to ammonium and sulfides (or AVS) in the presence of ferric ions. The carbon source is essential to the activation of DNRA or denitrification but the limited amount of organic substance in this experiment (COD) might drive those metabolisms to be working somehow [36, 37]. In the further work, we try to propose a mechanistic model comprising diffusion theory and effects of governing environmental parameters in order to precisely describe nutrients distribution and migration. In reality, exchanges or migration of nutrients between water and sediment are highly complex, involving physical, biological and interrelated chemical processes [38, 39].
compounds can be released through the pore paths inside sediment toward water column by simple diffusion (depicted by Fick's law; flux is proportional to a concentration gradient) and microbial activation depending on the local environmental condition such as pH, reduction state and temperature. Presuming a steady reduction state and a mild temperature and close-neutral pH for the microbial organism, diffusion, and physical hindrance could be a major limitation against releases of nitrogenous species. A simple calculation suggests about 50% of T-N may be NH$_4^+$-N. It was assume that, the rest would be organonitrogen which might keep being degraded under the current reductive condition. As shown in (Fig. 6), almost identical release rate around 3.8 mg/m$^2$/d for both of T-N and NH$_4^+$-N initially. After that, the rate of NH$_4^+$-N turned out to be lower than T-N probably because of surplus production of ammonium on the sediment side through DNRA. The final release rate for both nitrogenous species was close to 2.8 mg/m$^2$/d. On the other hand, release rate for nitrate was found to be negative, which implied oxidation would prevail in the water phase rather than in the anaerobic sediment where reduction would dominate preferably.

4. Conclusions

Eutrophication in the marine environment has been a longtime issue in southern coastal areas of Korea. This study investigated the physicochemical characteristics and behavior of chemical substances, and related environmental variables using a lab-scale setup so as to simulate a system of sediment-overlying waters in a typical eutrophic region. Nitrogenous and sulfur species such as ammonium, nitrate, sulfate, and sulfide as key substance were analyzed along with basic environmental parameters such as pH, ORP, and COD on the two phases. As a result, it was found that the T-N and nitrate concentrations in the sediment decreased sufficiently for DNRA to take place. The high concentration of ammonium in the sediment-water column exists used by sulfide as an electron donor in DNRA. Consequently, excess ammonium could be found in the sediment as well as in the overlying waters along with a consequence of diffusional release through prevailing pore water in the sediment. In addition, AVS (mostly H$_2$S and FeS) increased more with increasing time, which thus confirmed the reduction of sulfate into sulfides under the highly anaerobic condition. T-N and NH$_4^+$-N showed a considerable rate of releases from the sediment to the water phase, around 4.5 mg/m$^2$/d at maximum on $10^3$ d and then reduced to less than 2.8 mg/m$^2$/d on 20 d later, meanwhile nitrate seemed to diffuse back to the sediment from the subsurface of overlying waters, which might happen in a mild, oxic mood. This work can be progress in evaluating the inner eutrophication in terms of nitrogen, iron and sulfur compounds.

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