Diffusive Fluxes across Sediment–Water Interface in the Seto Inland Sea, Japan

Sarawut Srithongouthai\textsuperscript{1*} and Kuninao Tada\textsuperscript{2}

Department of Environmental Science, Faculty of Science, Chulalongkorn University, Bangkok, Thailand \textsuperscript{1}
Department of Life Sciences, Faculty of Agriculture, Kagawa University, Miki, Kagawa, 761-0795, Japan \textsuperscript{2}
* Corresponding author, Tel: +66-2-218-5194, Fax: +66-2-218-5180, E-mail: sarawut.sr@chula.ac.th

Abstract: Spatial investigations of pore water nutrient concentrations and their theoretical fluxes were carried out in six different sediment types within a coastal environment (Shido Bay, the Seto Inland Sea, Japan). Nutrient concentrations in pore waters reached maximum values of 711 µM-NH\textsubscript{4}+, 20.1 µM-PO\textsubscript{4}\textsuperscript{3-} and 195 µM-Si(OH)\textsubscript{4} at depth in cores. Diffusive fluxes of NH\textsubscript{4}+, PO\textsubscript{4}\textsuperscript{3-} and Si(OH)\textsubscript{4} were estimated using a modification of a Fick’s first law from concentration gradients. Fluxes were positive at all stations, ranging from 0.29 to 4.15 mmol m\textsuperscript{-2} d\textsuperscript{-1} for NH\textsubscript{4}+, 0.01 to 0.08 mmol m\textsuperscript{-2} d\textsuperscript{-1} for PO\textsubscript{4}\textsuperscript{3-}, and 0.11 to 0.72 mmol m\textsuperscript{-2} d\textsuperscript{-1} for Si(OH)\textsubscript{4}. These fluxes from the bottom to the overlying water are related to the type of sediment and its biogeochemical compositions. Spatial variations of NH\textsubscript{4}+, PO\textsubscript{4}\textsuperscript{3-} fluxes were found to be linearly correlated with the organic matter content of surface sediments. Also, NH\textsubscript{4}+ and PO\textsubscript{4}\textsuperscript{3-} fluxes increased with the C:N ratio of sedimentary organic matter. Differently, the highest Si(OH)\textsubscript{4} fluxes were related with the relative high pheo-pigments and biogenic silica (Bio-Si) contents in the surface sediment, which are affected by fecal matter from the oyster culture. As a result, organic matter availability was found to be an important factor in regulating spatial variability of NH\textsubscript{4}+ and PO\textsubscript{4}\textsuperscript{3-} fluxes, whereas significant contents of sedimentary pheo-pigments and Bio-Si characterise the sites where Si(OH)\textsubscript{4} is available.

Keywords: Nutrients, Porewater, Diffusive fluxes, Sediment-water interface, the Seto Inland Sea

I. INTRODUCTION

The concentrations of nutrient (N, P and Si) in the surface, near-bottom and porewater are good indicators of water pollution and intensity of mineralization processes of organic matter in the sediment and water. They can also be an indicator of the rate of primary production, due to the bio-limiting character of these nutrients. Particularly in shallow coastal ecosystems, the nutrient demand of pelagic primary producers is apparently satisfied to a large extent by benthic remineralization processes [1], [2], [3]. The importance of the recycling of organic material at the sediment-water interface and within the surficial sediments can be estimated by measuring sediment-water nutrient fluxes [2], [3], [4]. However, quality and quantity of nutrient regeneration at sediment-water interface depend very much on sediment characteristic and biogeochemical compositions of sediment. In the present study, we calculated nutrient fluxes based on measurements of nutrient concentration gradients close to the sediment-water interface to assess the role of sediments from a coastal environment in nutrient regeneration. Porewater nutrient concentrations and theoretical diffusive fluxes, in addition to biogeochemical properties of six typical sediment types taken in Shido Bay (the Seto Inland Sea, Japan) were also compared.

II. MATERIALS AND METHODS

A. Study area

Shido Bay is located at eastern part of the Seto Inland Sea, Japan (Fig. 1) and this bay can be divided in Tamaura Bay and Nagahama Bay, where is a shallow-water coastal ecosystem. The main freshwater input is from the Kabe River. The hydrodynamics of this area is very complex, and results in the presence of a wide variety of sedimentary environments in spite of the bay’s relatively small area (ca. 20 km\textsuperscript{2}). This Bay is connected with the enclosed eutrophic embayment of Harima-Nada (the Seto Inland Sea), where the productivity is high (218 g-C m\textsuperscript{-2} y\textsuperscript{-1}) [5]. The area is characterized by a macrotidal regime (ca. 2 m), and the current velocity at the mouth varies from 15 to 20 cm s\textsuperscript{-1}, which is higher than in the inner part (less than 10 cm s\textsuperscript{-1}) [6]. The annual temperature ranges from 9.6 to 26.7 °C, and salinity varies between 30.5 and 32.4 psu [3]. The bottom sediments of Shido Bay have a variability of diverse: sands of various particle sizes, fine sand, silts, mud, sludge and organic matter. Moreover, the characteristics of the bay have permitted the exploitation of the biomass by means of different types of aquaculture (Fig. 1). The yellowtail (\textit{Seriola quinquergiata}) cage farms are established from the middle toward the mouth of the Bay with 38,745 m\textsuperscript{2} of the total area. In the inner part of Tamaura Bay, the oyster (\textit{Crassostrea gigas}) farms are established, covering 39,704 m\textsuperscript{2} of the total area. During December to March of each year, the seaweed (\textit{Porphyra tenera}) farms are established at the mount of the Bay, whose total area is 422,924 m\textsuperscript{2}.

B. Sampling site

The present study was carried out at six sites (Fig. 1). Stn.S is located in the centre of Tamaura Bay (6.7 m mean depth) with silt clay sediment. Stn.T4 is located in the oyster culture (5.2 m mean depth) and the bottom is predominantly gray-black mud. Stn.T6 is the shallowest (4.5 m mean depth), is affected by urban sewage from the
town of Shido and the bottom is made of black sludge. Stn.N (7.4 m mean depth) was chosen because it is close to fish cage farm, the bottom being largely composed by clay. Stn.T18 (10.5 m mean depth) is located at the mount of the Bay; the bottom is fine sands. Moreover, Stn.N and Stn.T18 are affected by strong tidal currents. Finally, Stn.N25 (8.2 m mean depth) is located in the middle of Kabe river estuary (Nagahama Bay) with a muddy bottom.

C. Sampling procedure and chemical analysis

Duplicate undisturbed sediments were collected using a gravity core sampler with 50 cm long acrylic tube, 4 cm in diameter. Sediments were immediately sliced on board at 1 cm intervals to a depth of 10 cm. Samples were stored on ice in the darkness and brought to a coastal laboratory. Each slice was weighed and divided into 2 subsamples. The first was analyzed for porosity and phytopigments (chlorophylla and pheo-pigments) on the same day. The other sub-sample was centrifuged (3000 rpm, 15 min at 4 °C) to extract the pore water, which was immediately passed through nucleopore filters (0.40 µm) for nutrient analyses. The same sediment samples were used to determine total organic carbon (TOC), total organic nitrogen (TON), total phosphorus (TP) and biogenic silica (Bio-Si). Sediment porosity was calculated by measuring the weight loss of sediment dried overnight at 105 °C to constant weight [7]. The sediment content of Chlα and pheo-pigments were determined according to the method of Lorenzen [8] as described by Parsons [9]. TOC and TON were analyzed using a CHNS Elemental Analyzer (Fison, NA-1500NC). TP determination consisted of initial ashing of dry samples with 50% (w/v) Mg (NO₃)₂ as an oxidant at 550 °C followed by extraction with 1 N HCl at room temperature [10], [11]. The Bio-Si content was extracted by 5% of Na₂CO₃ [12] as described by Parsons [9]. Porewater was analyzed for NH₄⁺, PO₄³⁻ and Si(OH)₄ using a Technicon AutoAnalyzer II, according to Strickland and Parsons [13].

D. Sampling procedure and chemical analysis

Diffusional NH₄⁺, PO₄³⁻ and Si(OH)₄ fluxes from interface concentration gradients were estimated using a modification of the Fick’s first law of diffusion appropriate for sediments [14]:

$$F_D = \phi D_S \left[ \frac{\partial C}{\partial Z}\right]_{Z=0}$$

where $F_D$ is the diffusive flux, $\phi$ is the porosity of the surface sediment layer, $D_S$ is the effective diffusion coefficient of the solute in the sediment, $\left[ \frac{\partial C}{\partial Z}\right]_{Z=0}$ is the estimated concentration gradient of dissolved nutrients across the sediment-water interface and $z$ is the depth within the sediment. Accurate assessment of diffusive exchange across the sediment-water interface required several corrections to the diffusion coefficient measured at infinite solution before it could be used for sediments [15]. The diffusion coefficient of a solute in the sediment was calculated as described in Li and Gregory’s expression [16]:

$$D_S = \phi D^o$$

where $D^o$ is the coefficient of diffusion in water at infinite dilution. Diffusion appropriate for these sediments must correct for differences in temperature and porosity. $D^o$ for NH₄⁺ and PO₄³⁻ were obtained by taking into account the dependence of diffusion on temperature [15], [16]. $D^o$ used for Si(OH)₄ was 10⁻⁵ cm² s⁻¹ [17]. The in situ temperature used for this correction was 22 °C of the bottom water temperature. Calculated sediment diffusion coefficients ranged from 9.66 to 14.2×10⁻⁵ cm² s⁻¹ for NH₄⁺, from 4.22 to 6.08×10⁻⁵ cm² s⁻¹ for PO₄³⁻ and from 5.35 to 7.1×10⁻⁵ cm² s⁻¹ for Si(OH)₄ (Table I). The concentration gradient ($\left[ \frac{\partial C}{\partial Z}\right]_{Z=0}$) was calculated by means of linear fitting of concentration against $z$ for the superficial layer of the sediment. A significant linear gradient over the upper 10 cm of the sediment was considered and used in this study to estimate the gradient close to the sediment-water interface. Diffusion coefficients ($D_S$) and concentration gradient ($\left[ \frac{\partial C}{\partial Z}\right]_{Z=0}$) values were used to calculate diffusive fluxes ($F_D$).

<table>
<thead>
<tr>
<th>Station</th>
<th>Porosity</th>
<th>NH₄⁺ (x10⁻⁵ cm² s⁻¹)</th>
<th>PO₄³⁻ (µM m⁻¹)</th>
<th>Si(OH)₄ (µM m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0.82</td>
<td>12.4</td>
<td>5.24</td>
<td>6.64</td>
</tr>
<tr>
<td>T4</td>
<td>0.83</td>
<td>12.5</td>
<td>5.32</td>
<td>6.97</td>
</tr>
<tr>
<td>T6</td>
<td>0.88</td>
<td>14.3</td>
<td>6.08</td>
<td>7.71</td>
</tr>
<tr>
<td>T18</td>
<td>0.73</td>
<td>9.96</td>
<td>5.03</td>
<td>6.37</td>
</tr>
<tr>
<td>N</td>
<td>0.80</td>
<td>11.9</td>
<td>5.03</td>
<td>6.37</td>
</tr>
<tr>
<td>N25</td>
<td>0.82</td>
<td>12.6</td>
<td>5.37</td>
<td>6.80</td>
</tr>
</tbody>
</table>

III. RESULTS

A. Spatial distributions of surface sediment

Values of C, N, stoichiometric C:N ratios, P, Si, Chlα and pheo-pigments in the surface sediment are given in Table II. In the surface sediment layers, TOC ranged from 8.04 to 33.7 mg-C g⁻¹, with lower content at the mount of the bay (Stn.T18). Highest TOC was measured at the inner part of the bay at Stn.T6. The spatial distributions of TON (1.28 to 3.12 mg-N g⁻¹) were in agreement with TOC data ($r=0.980, p<0.01$, Table III), with lowest content for Stn.T18, and highest content at Stn.T6. The C:N ratio is usually used as an indication of organic matter type and source. The values of C:N reported here were in range of 7.85 up to 13.5. The C:N ratio of organic matter in the surface sediment is high at Stn.T6 when compared to the value proposed by Redfield ratio for the average
composition of marine phytoplankton [18]. Although Redfield ratio may exhibit significant local variations, the present result (13.5) suggests a prevailingly anthropogenic origin for the superficial organic matter in this station. The TP varied within a narrow range (0.41 to 0.76 mg-P g⁻¹), however the highest contents recorded at Stn.T6, and lowest contents at Stn.T18. The Bio-Si ranged from 19.0 to 39.5 mg-Si g⁻¹, with lowest content at Stn.T18, and highest at Stn. T4 (39.5 mg-Si g⁻¹) and Stn.T6 (35.1 mg-Si g⁻¹). Chla varied from 2.96 to 24.1 µg g⁻¹, with lowest content found at Stn.T18, and highest again at Stn.T6. Pheo-pigments varied greatly, ranging from 22.8 to 135 µg g⁻¹, and showed a spatial pattern similar to that for Bio-Si, with higher values at Stn.T4 (135 µg g⁻¹) and T6 (104 µg g⁻¹), while lowest value also observed at Stn.T18. There was a significant positive relationship between pheo-pigments and Bio-Si in the surface sediment (r=0.850, p<0.05, Table III).

TABLE II

<table>
<thead>
<tr>
<th>Station</th>
<th>TOC (mg g⁻¹)</th>
<th>TON (mg g⁻¹)</th>
<th>C:N</th>
<th>TP (mg g⁻¹)</th>
<th>Bio-Si (mg g⁻¹)</th>
<th>Chla (µg g⁻¹)</th>
<th>Pheo (µg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>17.04</td>
<td>2.15</td>
<td>9.91</td>
<td>0.53</td>
<td>24.6</td>
<td>6.43</td>
<td>73.7</td>
</tr>
<tr>
<td>T4</td>
<td>16.82</td>
<td>2.19</td>
<td>9.60</td>
<td>0.57</td>
<td>39.5</td>
<td>16.50</td>
<td>134.6</td>
</tr>
<tr>
<td>T6</td>
<td>33.72</td>
<td>3.12</td>
<td>13.51</td>
<td>0.76</td>
<td>35.1</td>
<td>24.07</td>
<td>103.7</td>
</tr>
<tr>
<td>T18</td>
<td>8.04</td>
<td>1.28</td>
<td>7.85</td>
<td>0.41</td>
<td>19.0</td>
<td>2.96</td>
<td>22.8</td>
</tr>
<tr>
<td>N</td>
<td>14.00</td>
<td>1.95</td>
<td>8.97</td>
<td>0.67</td>
<td>24.2</td>
<td>4.72</td>
<td>34.9</td>
</tr>
<tr>
<td>N25</td>
<td>12.60</td>
<td>1.83</td>
<td>8.61</td>
<td>0.59</td>
<td>29.8</td>
<td>3.41</td>
<td>30.1</td>
</tr>
</tbody>
</table>

TABLE III

<table>
<thead>
<tr>
<th>Porosity</th>
<th>TOC (mg g⁻¹)</th>
<th>TON (mg g⁻¹)</th>
<th>C:N</th>
<th>TP (mg g⁻¹)</th>
<th>Bio-Si (mg g⁻¹)</th>
<th>Chla (µg g⁻¹)</th>
<th>Pheo (µg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>0.864*</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.928**</td>
<td>0.980**</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.841*</td>
<td>0.988**</td>
<td>0.971**</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.755</td>
<td>0.920**</td>
<td>0.843*</td>
<td>0.765</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.799*</td>
<td>0.900**</td>
<td>0.839*</td>
<td>0.887*</td>
<td>0.834*</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.850*</td>
<td>0.822*</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B. Vertical distributions of porewater and their fluxes

NH₄⁺ concentrations showed a significant increase with depth (Fig. 2) with linear profiles (r=0.93 to 0.99, p<0.01, data not shown). At Stn.S, T4, T18, N and N25, lowest concentration found at the surface and either slightly increased or remained relatively constant with depth in the sediments. However, the vertical gradient was stronger for Stn.T6, where a maximal NH₄⁺ concentration was reached to 711 µM at depth of 7 to 8 cm. These profiles resulted in predicted NH₄⁺ fluxes directed from the sediment toward the overlying water. Diffusive fluxes of NH₄⁺ varied over a large range, from 0.29 mmol m⁻² d⁻¹ at Stn.T18 up to 4.15 mmol m⁻² d⁻¹ at Stn.T6 (Fig. 3a). As a result, NH₄⁺ fluxes among stations varied 93%. The PO₄³⁻ profiles exhibited an increasing concentrations from the surface layer to a depth of 10 cm at all stations. A particularly high concentration was observed at Stn.T6 (up to 20.1µM at 9 to 10 cm of the sediment profile) (Fig. 2). Diffusive fluxes of PO₄³⁻ also showed great variability, with highest flux of 0.08 mmol m⁻² d⁻¹ at Stn.6 and minimal value of 0.01 mmol m⁻² d⁻¹ for Stn.T18 (Fig. 3b). As a result, PO₄³⁻ fluxes among stations varied 90%. At each station, it can be noticed that Si(OH)₄ concentration increased along the whole of the analyzed cores, but mostly in deeper layers (Fig. 2). The vertical gradient was strongest for Stn.T4, and reached to 177 µM at depth of 9 to 10 cm. As a consequence, diffusive fluxes of Si(OH)₄ varied in the range of 0.11 to 0.72 mmol m⁻² d⁻¹. The highest flux was recorded at Stn.T4 and lowest at Stn.T18 (Fig. 3c). As a result, Si(OH)₄ fluxes among stations varied 84%.

![Fig. 2](image-url) Vertical distributions of NH₄⁺, PO₄³⁻ and Si(OH)₄ concentration in the pore water of the sediments at Stn.S (●), T4 (▲), T6 (▲), T18 (●), N (□) and N25 (□).

![Fig. 3](image-url) Nutrient fluxes calculated using pore water concentration gradients; (a) NH₄⁺, (b) PO₄³⁻ and (c) Si(OH)₄.

Calculated fluxes are shown and compared in Fig. 3. All of them are directed from sediments to the overlying waters. The lowest NH₄⁺, PO₄³⁻ and Si(OH)₄ were characterise Stn.T18, where was the deepest and the sediment was characterised by low porosity and organic matter content, thus suggesting that this site is exposed to resuspension events due to strong the tidal current at the mount of the bay [6]. Mid-bay stations (S and N25) showed moderate fluxes of all species. Surprisingly, fluxes of NH₄⁺ and PO₄³⁻ at Stn.N close to the fish cage farm
IV. DISCUSSION

The six sampling stations considered in this study described spatial distributions which are in good agreement with sediment biogeochemistry. The highest concentrations of TOC (33.7 mg g⁻¹), N (3.12 mg g⁻¹) and P (0.76 mg g⁻¹) were found in the inner part of the bay, the represented by Stn.T6, due to the influence of the urbanized regions. This is also confirmed by the high C:N ratio (13.5) that clearly accounts for a terrestrial source. Moreover, the pore water NH₄⁺ concentration was as high as 294 µM in the surface sediment. Bickford [19] clearly explained that the anthropogenic input of organic matter to the coastal zone can cause the enrichment of nutrients in sediment pore waters. With these characteristics, Stn.T6 had the highest sediment nutrient concentrations and the highest sediment-water fluxes of NH₄⁺ and PO₄³⁻. The station is also characterised by autotrophic conditions, testified by the high Chla concentrations. The NH₄⁺ and PO₄³⁻ fluxes appear to have a significant relationship with TOC in the upper 1 cm of sediment ($r^2 = 0.960$, $p < 0.01$ and $r^2 = 0.768$, $p < 0.05$ Fig. 4a and b, respectively). The explanation is organic matter degradation which, in turn, produces pore water nutrients which generate diffusive fluxes. Furthermore, organic matter degradation follows a first-order kinetics with respect to organic matter content. In this regard, many authors have stated that organic matter degradation in marine sediments is the main process responsible for the effluxes through the sediment-water interface [20], [21], [22]. On the other hand, TOC availability was not found to be an important factor in regulating spatial variability of Si(OH)₄ fluxes ($r^2 = 0.459$, $p > 0.1$; Fig. 4c). We observed a significant relationship between the fluxes of NH₄⁺ ($r^2 = 0.941$, $p < 0.01$; Fig. 4d) and PO₄³⁻ ($r^2 = 0.714$, $p < 0.05$; Fig. 4e) and the C:N ratio in organic matter from the surface sediment, suggesting that the dependence of NH₄⁺ and PO₄³⁻ regeneration on the quality of organic matter in the sediment. In contrast, the C:N ratio did not exist for Si(OH)₄ fluxes ($r^2 = 0.444$, $p > 0.1$; Fig. 4f). At Stn.T4 located in oyster farms, the surface sediment showed enrichment of Chla (16.5 µg g⁻¹), together with the highest concentrations of pheopigments (134.6 µg g⁻¹) and Bio-Si (39.5 mg-Si g⁻¹). These high values are probably due to an increased preservation of microphytobenthos in the shallow areas, in addition to marked increases in bio-deposition from the oyster farming in the surface sediments. The work of Hayakawa [23] suggested that the sedimentation rate at the site has significantly increased and that the material supplied consists mainly of bio-deposits from oyster (Crassostrea gigas) farms. Furthermore, Pietsro and Rice reported that oysters (Crassostrea virginica) affected phytoplankton species composition and increased rates of sedimentation [24].

Due to the benthic-pelagic characteristics, diatoms show a great spatial variation in Shido Bay. Therefore, Si(OH)₄ fluxes should be related to sediment concentrations of Bio-Si because the source of Si(OH)₄ released from the sediments is largely from remineralization of diatom tests [3], [25]. The magnitude of spatial variations of Si(OH)₄ fluxes found in this study might be related to irregular diatom production and accumulation in the area. In this study, highest Si(OH)₄ fluxes were observed at Stn.T4, where phytopigments and Bio-Si contents in the surface sediment are relative high (16.5 µg-Chla g⁻¹, 134.6 µg-pheo-pigments g⁻¹ and 39.5 mg-Si g⁻¹; Table II). Moreover, Si(OH)₄ fluxes are related to Bio-Si availability in the surface sediments ($r^2 = 0.709$, $p < 0.05$; Fig. 5a). Additionally, an excellent correlation was found between sediment pheo-pigments and Si(OH)₄ fluxes ($r^2 = 0.959$, $p < 0.1$; Fig. 5b). It strongly suggested that the upward Si flux came from the decomposition of diatom cells at surface sediment layer. This (among the highest reported) may cause steeper overlying water to pore water Si(OH)₄ concentration gradients due to rapidly decomposed faecal matter from oyster culture.
V. CONCLUSION
The sediments of Shido Bay are sources of N (0.28 to 2.84 mmol-NH$_4^+$ m$^{-2}$ d$^{-1}$), P (0.02 to 0.12 mmol-PO$_4^{3-}$ m$^{-2}$ d$^{-1}$) and Si (0.18 to 0.89 mmol-Si(OH)$_4$ m$^{-2}$ d$^{-1}$) to the water column based on the diagenesis through their concentration gradients. Fluxes of N, P and Si liberate at interface of sediment and water are related to sediment types and their different biogeochemical compositions. One interesting aspect of our data analysis is that its show the highest flux of N and P where the concentration of organic matter in sediments is high, under eutrophic conditions. When sedimentary pheo-pigments and Bio-Si contents are high, Si release rates are correspondently high, thus indicating a control by the accumulation of diatoms.

ACKNOWLEDGMENT
Prof. Dr. S. Montani is gratefully acknowledged for his invaluable suggestions, both from a scientific and technical point of view. The authors wish also to thank Prof. Dr. H. Tsutsumi, Prefectural University of Kumamoto, for his help in sediment analysis, and Mr. T. Hamagaki for ensuring successful field operation.

REFERENCES