



Ph.D. Dissertation of Xiaoyu Chen

# Behaviors of trace elements and rare earth elements in the coastal oceans

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# Behaviors of trace elements and rare earth elements in the coastal oceans

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## Abstract

Many trace elements, such as Fe, Ni, and Zn, act as essential micronutrients for marine phytoplankton growth and influence marine primary production. The inventory of trace elements in the ocean is largely regulated by the boundary inputs from atmospheric deposition, benthic diffusion, and from coastal oceans through riverine runoff and submarine groundwater discharge. In this study, the concentrations of trace elements and rare earth elements (REEs) in coastal waters were measured to investigate their behaviors in the coastal interface zone.

The behaviors of trace elements (Mn, Fe, Ni, Cu, and Zn) and REEs were investigated in a coastal embayment off the southern coast of Korea, which features a long water residence time. The results showed intense depletion of inorganic nutrients throughout the bay relative to the fresh and open-ocean water mixing curve. Moreover, REE fractionation revealed notable particle scavenging with a significant removal of Ce. However, trace elements showed higher concentrations in lower salinity waters and significant positive correlations with humic dissolved organic matter ( $DOM_H$ ), indicating the conservative behavior of trace elements associated with terrestrial  $DOM_H$  in the coastal mixing zone. Thus, further studies

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were carried out in two coastal regions in Korea (Jinhae Bay [JH] and offshore Tongyeong [TY]) to investigate the influence of different origins of DOM<sub>H</sub> on the behaviors of dissolved trace elements (Mn, Fe, Ni, Cu, Zn, and Cd) in coastal oceans. Both regions displayed intensive scavenging and settling of the particle-reactive Ce and radioactive  $^{234}$ Th tracers. However, in JH, where DOM<sub>H</sub> is mainly terrestrial-derived, the concentrations of trace elements (Fe, Ni, and Cu) were negatively correlated with salinity and positively correlated with  $DOM_{H}$ . This indicates that terrestrial  $DOM_{H}$  could complex with trace elements, and this complexation likely deters the adsorptive removal of trace elements by settling particles. In TY, similar interactions between trace elements (Mn, Fe, and Cu) and DOM<sub>H</sub>, which mainly originated from marine primary production, were also discovered. These results reveal that both terrestrial and marine DOM<sub>H</sub> would associate with dissolved trace elements, stabilizing them in the dissolved phase in coastal waters. This DOM<sub>H</sub>-trace element complexation in coastal waters could play a key role in regulating the cycling and transport of trace elements in the ocean.

In recent decades, the increasing aquaculture activities in the coastal regions have greatly influenced the coastal ocean environment by releasing pollutants (e.g., fertilizers) into the water columns. In this study, the influence of fish-farm activities on the inventory of trace elements (Mn, Fe, Co, Ni, and Cu) in the coastal waters off the fish-farm plants on Jeju Island was investigated. NH<sub>4</sub><sup>+</sup> and REEs were used as tracers to examine the production and removal processes in both coastal and fish-farm waters. Relatively higher concentrations of trace elements were observed in the coastal waters and significantly correlated with the concentrations of  $NH_4^+$ . These results suggest that the excess dissolved trace elements in the coastal waters could be mainly produced inside fish farms, together with  $NH_4^+$  and light-REEs (La to Nd). Although dissolved trace elements were found to be partially scavenged onto particles in the fish-farm rearing waters as indicated by the significant removal of particle-reactive Ce, these particles would be eventually discharged into the coastal ocean and release the dissolved trace elements back into the water columns. Overall, these results reveal that, although dissolved trace elements in fish farms are commonly considered to be removed onto sinking particles, the influence of fish farm activities on the trace element distributions in the coastal oceans has been largely underestimated.

**Keyword:** Trace elements; Rare earth elements; Dissolved organic matters; Humic substances; Scavenging; Coastal ocean

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#### Chapter 1. Introduction

#### 1.1. Trace elements in the coastal ocean

Trace elements (e.g., Mn, Fe, Co, Ni, Cu, and Zn) are present in seawater at very low concentrations, which range down to a level of nanomole per liter (nM) of even lower (Charette et al., 2016; Ellwood, 2008; Fitzwater et al., 2000; Janssen et al., 2020). In ocean waters, trace elements play an important role in regulating the growth of phytoplankton by either directly or indirectly involving in several key enzyme reactions within marine phytoplankton cells (Bruland et al., 2006; Ellwood et al., 2015; Ellwood et al., 2020; Morel et al., 2020; Sunda, 1989).

The boundary inputs of trace elements (e.g., Fe, Cu, Zn, etc.), from the atmosphere or from the coastal to the open ocean, regulate their inventory influencing marine primary production levels in the euphotic zone (Bruland et al., 2006; Ellwood et al., 2014; Ellwood et al., 2020; Hunter and Boyd, 1999; Janssen et al., 2020; Morel and Price, 2003). Nevertheless, the main sources and behaviors of trace elements in continental shelf water are poorly understood as they are influenced by various input sources, such as rivers, submarine groundwater discharge (SGD), and atmosphere, as well as subsequent biogeochemical cycles through biota, sediments, and water columns (Charette et al., 2016). Due to the rapid growth of industrialization and agriculture worldwide in coastal regions during recent decades, the input of trace elements from anthropogenic activities has greatly increased in the coastal ocean (Gao et al., 2016; Mitra et al., 2018; Pavoni et al., 2021). Although trace elements in the coastal ocean originate from various sources, most of the trace elements in the coastal ocean are known to be rapidly removed by biological consumption as well as settling to the seafloor, before they can reach the open ocean (Charette et al., 2016; Charette and Sholkovitz, 2002; Jeong et al., 2012; Wen et al., 1999).

#### 1.2. Rare earth elements in seawater

Rare earth elements (REEs; La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu) are a coherent group of elements with similar chemical and physical properties that exist in seawater at trivalent oxidation state (Elderfield, 1988). The behaviors of REEs have been increasingly applied to trace various geochemical processes in the ocean waters. REEs in seawater mainly originate from lithogenic sources, like riverine runoff, dust deposition, and submarine groundwater discharge (Byrne and Kim, 1990; Chevis et al., 2015; Elderfield, 1988; Kim and Kim, 2014; Kim et al., 2020; Sholkovitz, 1995). When normalized to the Post-Archaean Australian Shale (PAAS) (Taylor and McLennan, 1985), the fractionation of REEs can highlight the supply and removal of REEs away from their lithogenic origins (Byrne and Kim, 1990; Cantrell and Byrne, 1987; Elderfield, 1988). REEs are normally divided into three groups, light-REEs (LREEs; La to Nd), middle-REEs (MREEs; Sm to Dy), and heavy-REEs (HREEs; Ho to Lu) based on their masses. Generally, in seawater, LREEs are more preferentially scavenged onto particle surfaces compared to MREEs and HREEs (Byrne and Kim, 1990; Cantrell and Byrne, 1987). This would result in an enrichment of HREEs relative to LREEs in the ocean waters, which is the typical distribution pattern of REEs normalized to those in shale. Among all REEs, cerium (Ce) showed relatively different chemical properties, as the soluble Ce<sup>3+</sup> tends to be very particle-reactive under oxic conditions and oxidized to the insoluble Ce(IV), resulting in the effective removal of Ce in the water columns (de Baar et al., 2018; Moffett, 1990; Sholkovitz, 1995). Overall, the interpretation of the relative changes in REE concentrations makes REE a powerful tool to investigate advection, cycling, and inputs of trace metals, especially in the coastal mixing area. However, in the coastal waters, REE behaviors are normally more complicated compared with that in the open ocean due to the complex biogeochemical cycles and various sources of input.

#### 1.3. Study aims

This study mainly aims to understand the distributions and behaviors of trace elements and REEs in the coastal waters. The concentrations of trace elements, REEs, and radioactive <sup>234</sup>Th were investigated with the following objectives.

(1) to investigate the interactions between trace elements and humic dissolved organic matters in the coastal ocean

(2) to examine the influence of humic dissolved organic matter on the behaviors of trace elements in the coastal ocean

(3) to evaluate the influence of anthropogenic fish-farm activities on the distributions of trace elements in the coastal ocean

(4) to examine the behaviors of REEs in the coastal waters and utilize the REE fractionations to trace the production and removal processes in the water columns

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#### Chapter 2. Materials and methods

#### 2.1. Sample collection

Seawater samples for the analyses of trace elements and REEs were collected using acid-washed, trace metal-clean 1.7 L Tefloncoated Niskin-X bottles (General Oceanics, INC, USA) when depth profiles are needed. The collected seawater samples were gravityfiltered directly from the Niskin-X bottles into 125 mL lowdensity polyethylene (LDPE) bottles (Nalgene/Thermo Fisher) precleaned with acid. Acid-cleaned, 0.2 µm pore size Supor EKV membrane capsule filters (AcroPak, Pall) were used for filtration. The LDPE bottles were rinsed three times with the filtered sample water before collecting samples; then the samples were acidified instantly with concentrated, ultra-high pure grade HCl (ODLAB) to pH < 2. When only surface investigation is required, seawater samples for the analyses of trace elements and REEs were collected using an acid-cleaned high-density polyethylene (HDPE) beaker and transferred into acid-cleaned 125 mL low-density polyethylene (LDPE) bottles on the front side of a small ship while it slowly moved forward. The samples were stored in an ice-box and transferred to the laboratory within 5 h. Then the samples were defrosted at room temperature and filtered through 0.45  $\mu$ m pore size membrane filters using acid-cleaned filter sets in a laminar flow hood. The samples were acidified to a pH of < 2 using concentrated ultrahigh-purity HCl (ODLAB) and left to stand at room temperature for more than five months to allow the complete desorption of any trace elements from the bottle walls (Conway and John, 2014a; Jensen et al., 2020a; Jensen et al., 2020b). Seawater samples (10 L) for total <sup>234</sup>Th analysis were collected in acid-cleaned HDPE bottles with a submersible pump and acidified (pH < 1) in-situ using 8 M ultra-high-purity HNO<sub>3</sub>.

#### 2.2. Sample analyses

#### 2.2.1. Trace elements and REEs analyses

Acidified seawater samples were transferred to acid-cleaned 30 mL LDPE vials for measurements. Trace elements (<sup>55</sup>Mn, <sup>56</sup>Fe, <sup>59</sup>Co, <sup>60</sup>Ni, <sup>63</sup>Cu, <sup>66</sup>Zn, and <sup>111</sup>Cd) and REEs in seawater samples were analyzed using the seaFAST (Elemental Scientific Inc.) automated sample introduction system in online pre-concentration mode that was directly coupled to the Element-2 HR-ICP-MS system (Thermo Fisher Scientific), as described by Wuttig et al. (2019). The samples (10 mL) were preconcentrated automatically with seaFAST using Nobias PA1 resin and buffered with optima grade 4M NH<sub>4</sub>Ac. The column was then rinsed with Milli-Q water and NH<sub>4</sub>Ac to remove the seawater matrix. The target elements were then eluted with 0.3 mL of 1.6 M HNO<sub>3</sub>. The 10 ppb <sup>103</sup>Rh internal standard was measured automatically between every sample to calibrate the instrument sensitivity shifts for all measurements. The concentrations of trace elements and REEs were determined using the external standard curve created by diluting the multi-element standards for the measurement of trace elements and REEs. The isobaric interference of MoO<sup>+</sup> on <sup>111</sup>Cd was corrected by comparing the measured Mo

intensities to that of MoO and Mo in the Mo standard solution. Although it has been reported that UV-irradiation is required for the measurement of "total" dissolved Co concentrations (Biller and Bruland, 2012; Milne et al., 2010), Wuttig et al. (2019) suggested that the UV-oxidation process is not preferred when measuring multiple elements because of the possibility of inducing unnecessary contaminations. In addition, Zheng et al. (2019) suggested that the conduction of UV-irradiation using PFA jar would reduce Fe concentrations. Therefore, here the concentrations of Co reported in this study only represent the fractions that can be extracted by Nobias PA-1 resin, instead of the "total" dissolved Co concentration. Furthermore, excess thulium (Tm) was added to each sample to examine the recovery of REEs throughout the measurement process following the method described by Seo and Kim (2020). The recovery of Tm was more than 90% and was also applied to all REEs. To validate the accuracy of our analysis, certified reference materials (CRM) CASS-5, CASS-6, NASS-6, and NASS-7 (National Research Council of Canada) were measured between the samples. The analytical uncertainties for trace elements and REEs were within the error margins of CRMs. The measured values agreed well within 10% of the certified and previously published values of CRMs for both trace elements and REEs.

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### 2.2.2. <sup>234</sup>Th analyses

The collected samples (10 L) were transferred to acid-cleaned HDPE buckets in the lab, then 6.5 dpm  $^{230}$ Th spike and 70 mg Fe $^{3+}$ carrier were added to each sample. After isotopic equilibration, 7 % NH<sub>4</sub>OH was added to each sample to adjust pH to around 8 for the precipitation of Fe(OH)<sub>3</sub>. After settling, the supernatant was siphoned off, and the precipitates in the residual samples were collected with 22  $\mu$  m pore size filters (diameter: 142 mm; Whatman). The collected precipitates were dissolved in 20 mL of 8 M HNO<sub>3</sub> and adjusted to ~ 4 M HNO<sub>3</sub> solution in a Teflon acid-cycle digestion vessel (ODLAB). Samples were then heated on a hotplate (230° C) for one hour. The samples were then purified with UTEVA resin and prepared for the alpha counting for <sup>230</sup>Th and beta counting for <sup>234</sup>Th by co-precipitating Th with CeF<sub>3</sub>. The measurement of <sup>234</sup>Th was conducted multiple times to verify the purity and to reduce the errors.

## Chapter 3. Conservative behavior of terrestrial trace elements associated with humic substances in the coastal ocean

#### 3.1. Introduction

The long-range transport of trace elements through the atmosphere exerts a considerable effect on their inventory in remote oceans. For example, 71 - 87% of the dissolved Fe in the Northern Atlantic Ocean originates from atmospheric dust (Buck et al., 2019; Conway and John, 2014b; Jickells et al., 2016; Kadko et al., 2020), and the input of dissolved Fe from aerosols to the global surface ocean was estimated to be  $2 - 12 \times 10^9$  mol y<sup>-1</sup> (Elrod et al., 2004). Inputs of trace elements from continental shelf water to the open ocean are also considered critical in regulating the inventories of trace elements basin-wide. Compared with dust which contributes the dominant input of dissolved Fe, shelf inputs also contribute a considerable portion of trace element fluxes into the global euphotic zone, with an estimated minimum dissolved Fe flux of 2.2  $\times$  10<sup>9</sup> mol  $y^{-1}$  (Elrod et al., 2004; Severmann et al., 2010).

Nevertheless, the behaviors of trace elements in river estuaries and subterranean estuaries are better understood than that in the coastal ocean. River estuaries are known to be important sinks for trace elements. Approximately 75 - 90% of Fe and 90 - 100% of Mn are removed by flocculation or oxidation processes during estuarine mixing processes in Scotland and on the east coast of the United States, respectively (Boyle et al., 1977; Charette et al., 2016; Sholkovitz, 1976). Furthermore, the scavenging of trace elements in the mixing zone of oxic subterranean estuaries (STE), where oxidation processes such as the formation of "iron curtain" would cause the scavenging of trace metals before the water is discharged into the coastal ocean (Charette and Sholkovitz, 2002; Moore, 2010). was also found to be significant. Thus, colloids in STE play a vital role in transporting trace elements through SGD, enabling longer residence times for trace elements in STE (Jeong et al., 2012; Kim and Kim, 2015). In the coastal ocean, radionuclide tracers (i.e., <sup>234</sup>Th, <sup>210</sup>Po, and <sup>210</sup>Pb) have revealed more vigorous scavenging of particle-reactive elements than those in the productive areas of the open ocean (Bacon, 1988; Church, 2016; Cochran and Masque, 2003; Feng et al., 1999; Ip et al., 2007; Marsan et al., 2014). Although the behaviors of bio-essential trace elements are poorly understood, a widely held assumption is that most of the particle-reactive trace elements are removed in coastal waters before reaching the open ocean. Therefore, this study aimed to examine the behaviors of

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terrestrial trace elements in coastal waters. In this study, it is hypothesized that although there are intensive removals of inorganic substances, the binding of humic substances with trace elements (i.e., Mn, Fe) renders them less susceptible to scavenging and biogeochemical removal processes, as shown in estuarine and freshwater aquatic systems (Eastman and Church, 1984; Hiraide, 1992; Ilina et al., 2016b; Mostofa et al., 2013; Oldham et al., 2019; Pedrot et al., 2008; Raspor et al., 1984; Rose and Waite, 2003; Sholkovitz and Copland, 1981; Sposito, 1986). Rare earth elements (REEs; here defined as lanthanide group of elements) fractionations were utilized to determine the relative scavenging processes in the study region, owing to their particle-reactive characteristics as shown in other previous studies (Byrne and Kim, 1990; Chevis et al., 2015; Elderfield, 1988; Hathorne et al., 2015). This study was carried out in a coastal bay area (Jinhae Bay), which has a long water residence time, to examine the extreme differences in the behaviors of rare earth elements and trace elements in the coastal ocean.

#### 3.2. Study region and sampling methods

Jinhae Bay is the largest semi-enclosed bay in South Korea, with an approximate area of 640 km<sup>2</sup>. It is relatively shallow with water depths ranging from 5 to 25 m and has weak semi-diurnal tidal current velocities from 0.1 to 1  $ms^{-1}$ . The water residence time of this bay is over 85 days in the inner bay (Kim et al., 2016; Kwon et al., 2020a; Park et al., 2020; Yoon et al., 2019), whereas the amount of stream water discharge is approximately 2.4  $\times$  10<sup>8</sup> m<sup>3</sup> yr<sup>-1</sup> with large seasonal variations (Lee et al., 2009). This area is known to receive significant anthropogenic wastewater and domestic sewage from industrial complexes and adjacent streams (Kim et al., 2014; Kim et al., 2013). In addition, the river waters in the inner bay discharge considerably high concentrations of trace elements (e.g., 184 - 536 nM for Zn) into this area (Park et al., 2020). Owing to the heavy loading of nutrients and other terrestrial materials, the inner bay has experienced severe eutrophication and large phytoplankton blooms almost every spring (Cho, 1991; Kim et al., 2013; Kwon et al., 2020a; Lee et al., 2009; Park et al., 2020).

Sampling in Jinhae Bay was conducted from March 25 to 27, 2019 with R/V NARA of Pukyong National University, Korea. The samples

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were collected along three transects (Transects A, B, and C) at 14 stations (0 - 60 m) throughout the bay (Fig. 3.1). Hydrological parameters, including salinity and temperature, were collected with an onboard conductivity temperature and depth probe (CTD, SBE 911+).

Seawater samples (n = 46) for trace element analysis were collected using 6 trace metal-clean 1.7 L Niskin-X bottles (General Oceanics, INC, USA) at target depths and were filtered directly through acid-cleaned  $\mu$ m pore size Supor EKV membrane capsule filters (AcroPak, Pall) into pre-cleaned 125 mL low-density polyethylene (LDPE) bottles (Nalgene/Thermo Fisher). The LDPE bottles were rinsed three times with the filtered sample water before collecting samples.



**Figure 3.1** Sampling sites in Jinhae Bay, on the southeastern coast of Korea. The color gradient indicates the surface salinity distribution throughout the study area.

#### 3.3. Results

Salinity in the study area ranged from 33.1 to 34.4 (Fig. 3.1), and water temperatures ranged from 10 to 14 ° C (Fig. 3.2). While both salinity and temperature values increased from the inner bay to the outer bay, they were relatively constant with depth at each site (Fig. 3.3a, b). Dissolved oxygen ranged from 205 to 344 µmol/kg, showing a slightly decreasing trend from the inner bay to the outer bay. Dissolved inorganic nutrients (DIN  $(NO_3^- + NO_2^- + NH_4^+)$ , DSi  $(Si(OH)_4)$ , and DIP  $(PO_4^{3-})$  concentrations were significantly lower at the innermost bay stations and gradually increased toward the outer bay. The concentration ranges were from 0.02 to 10  $\mu$ M for DIN, from below the detection limit to 8  $\mu$  M for DSi, and from 0.04 to 0.4  $\mu$  M for DIP (Fig. 3.2c, d). Meanwhile, the distribution pattern of DOC concentrations was opposite to that of salinity and temperature, with the highest value (100  $\mu$  M) in the inner bay and the lowest value (56  $\mu$  M) in the outer bay (Fig. 3.3f). The fluorescence intensity C peak and M peak also showed higher values in the inner bay and decreased toward the outer area (0.23 - 1.59)R.U. for C peak and 0.02 - 1.89 R.U. for M peak) (Fig. 3.3g, h). The concentrations of DOC and C peak were consistent with those observed in other coastal waters in Korea (Kim et al., 2018; Kwon et

al., 2018b). However, dissolved inorganic nutrient concentrations exhibited relatively lower values, which were more similar to those observed in the remote open ocean of the Southern Sea of Korea (Kwon et al., 2019; Kwon et al., 2018a).

The concentrations of dissolved trace elements (Mn, Fe, Ni, Cu, and Zn) exhibited a trend opposite to those for dissolved inorganic nutrients, decreasing from the inner bay toward the outer bay (Fig. 3.3i-m). For example, dissolved Mn concentrations showed the highest value of 170 nM at station B1 and decreased to 3 nM at station B8. Here, the acidification of samples for trace element analysis (to pH < 2) described in Chapter 2 may lead to an underestimation of the dissolved total Mn concentration (Oldham et al., 2017a). A similar decreasing trend toward the outer bay was also observed for REEs, except for the innermost bay stations (stations A1, A2, and B1), which showed relatively lower concentrations. For example, Nd concentrations were relatively lower at station B1 (30 pM), increased to the highest concentration at station B2 (50 pM), and then decreased to the lowest concentration at the outermost bay station (15 pM) (Fig. 3.4). The observed trace element (Mn, Ni, Cu, and Zn) concentrations fell within the range that had been reported previously in this bay (Park et al., 2020).

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Potential Temperature θ [degC]



**Figure 3.2** Temperature-salinity (T-S) diagram of sampling sites. Different colors indicate different sites.

#### 3.4. Discussion

# 3.4.1. Depletion of dissolved inorganic nutrients and particle scavenging processes of REEs in the inner bay

The concentrations of dissolved inorganic nutrients showed positive relationships with salinity (Fig. 3.5a, b), with extremely low values (below the detection limit) in the inner bay. Previous studies have demonstrated the significant inputs of nutrients through adjacent stream waters (salinity = 0) with high concentrations  $(133 - 256 \ \mu \text{ M} \text{ for DIN}, 4 - 11 \ \mu \text{ M} \text{ for DIP}, \text{ and } 54 - 267 \ \mu \text{ M} \text{ for}$ DSi) in Jinhae Bay (Lee et al., 2009). Thus, unlike the typical distribution pattern exhibiting a negative relationship between nutrient concentrations and salinity in different seasons in Jinhae bay and nearby coastal areas (Hwang et al., 2005; Kwon et al., 2020b), our results indicate the depletion of nutrients in the inner bay (Fig. 3.5a, b). Previous studies have demonstrated notable spring blooms during the same season in the study area (Lee et al., 2009; Yoon et al., 2019). Indeed, the satellite-based surface chlorophyll data showed a considerably higher concentration in the inner bay, decreasing toward the outer bay (Fig. 3.6). These results suggest that the depletion of nutrients is likely due to biological uptake.

Dissolved REEs also showed non-conservative behavior throughout the bay (Fig. 3.4a-c). In general, light-REEs (LREEs; La to Nd) are preferentially scavenged onto particle surfaces compared to middle-REEs (MREEs; Sm to Dy) and heavy-REEs (HREEs; Ho to Lu) (Byrne and Kim, 1990; Cantrell and Byrne, 1987). This fractionation of REEs would be informative for the interactions between the solid and dissolved phases of trace elements (Byrne and Kim, 1990). Thus, the lower (Nd/Er)<sub>PAAS</sub> (as a proxy of LREE/HREE) ratio in the very inner bay compared with that in the outer bay (Fig. 3.5j) suggests intensive scavenging of more particle-reactive LREEs in the inner bay. In addition, the depletion of Ce traces scavenging processes as Ce tends to be very particle-reactive under oxic conditions (de Baar et al., 2018; Moffett, 1990; Sholkovitz, 1995). The relative removal of Ce is often denoted as Ce/Ce\* [calculated as Ce/Ce\* =  $3 \times Ce_{PAAS} / [2 \times La_{PAAS} + Nd_{PAAS}]$ (Sholkovitz, 1995). Here, REE concentrations were normalized with the Post Archean Australian Shale (PAAS) to eliminate the effect of the Oddo - Harkins rule (Taylor and McLennan, 1985). The plot of Ce/Ce\* values against salinity showed consistent depletion in the inner bay, with relatively lower values (Fig. 3.5i). The overall trends clearly indicate vigorous inorganic scavenging in the inner bay area.

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**Figure 3.3** Depth profiles of salinity, temperature, dissolved inorganic nutrients, and dissolved trace elements in transect B from the innermost to the outermost bay. (a) salinity, (b) temperature, (c)

dissolved inorganic nitrogen (DIN =  $NO_2^- + NO_3^- + NH_4^+$ ), (d) dissolved inorganic silicate (DSi =  $Si(OH)_4$ ), (e) Ce/Ce\*, (f) dissolved organic carbon (DOC), (g) C peak, (h) M peak, (i) Mn, (j) Fe, (k) Ni, (l) Cu, and (m) Zn. The dots in the figures are the sampling sites at certain depths.



Figure 3.4 Plots of salinity versus REEs and C peak. (a) Nd, (b) Dy,

(c) Er, and (d) C peak.



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**Figure 3.5** Plots of salinity versus other chemical components: (a) Dissolved inorganic nitrogen, (b) Dissolved inorganic silicate, (c) DOC, (d) Mn, (e) Fe (f) Cu, (g) Zn, (h) Ni, (i) Ce/Ce\*, and (j) (Nd/Er)<sub>PAAS</sub>. Red, blue, and green dots indicate transects A, B, and C, respectively. Similarly, cyan dots indicate dissolved inorganic nutrient concentrations in the adjacent stream water in 2006 (Lee et al., 2009), whereas orange dashed lines and arrows indicate the consumption of nutrients in the coastal mixing zone. The concentration ranges of Cu, Zn, and Ni from river endmember values (Park et al., 2020) are presented with pink lines. Certain data points are given with stations and depth information in plot i.

# 3.4.2. Complexation of trace elements with terrestrial humic substances and protection from removal

Significant correlations were observed between the concentrations of dissolved trace elements (Mn, Fe, Ni, Cu, and Zn) and salinity (Fig. 3.5d-h), suggesting an insignificant influence of and consumption processes on trace scavenging element distributions. Among the trace elements observed, dissolved Ni concentrations against salinity showed lower values in transect A relative to the regression line for both transects B and C (Fig. 3.5h). This may be due to the mixing of different water masses, as indicated in the T-S diagram (Fig. 3.2). The riverine inputs, with high concentrations of trace elements (94 - 426 nM for Ni, 53 - 200 nM for Cu, and 184 - 536 nM for Zn), were found to be the major sources of dissolved trace elements in Jinhae Bay (Park et al., 2020). If the concentrations of trace elements (Ni, Cu, and Zn) in our study are extrapolated to salinity = 0 according to the conservative mixing linear regression, the extrapolated concentration ranges match well with the endmembers of riverine trace elements reported by Park et al. (2020) (Fig. 3.5f-h). This pattern indicates the conservative mixing of terrestrial trace elements from river sources with the open-ocean water in the entire bay.

DOC concentrations also showed a similar significant negative correlation with salinity (Fig. 3.5c), indicating high terrestrial inputs and subsequent conservative mixing patterns. To examine the shuttling effect of trace elements complexing with humic substances that are commonly observed in freshwater systems (Hiraide, 1992; Ilina et al., 2016b; Mostofa et al., 2013; Pedrot et al., 2008; Raspor et al., 1984; Sholkovitz and Copland, 1981; Sposito, 1986), the relationship between trace element concentrations and the C peak of FDOM, a proxy for terrestrial humic substances were investigated. The higher C peak and M peak values in the inner bay along the B transect (maximum at station B1: 1.59 R.U. for C peak and 0.71 R.U. for M peak) clearly indicate a notable input of terrestrial humic substance into the bay (Fig. 3.3). Significant positive linear correlations (n = 46,  $r^2$  ranging from 0.62 to 0.91) were observed between trace elements (Mn, Fe, Ni, Cu, and Zn) and the C peak throughout the bay (Fig. 3.7; Fig. 3.4d). Notably, the correlation with the C peak was more significant than with salinity or DOC (Fig. 3.8) for all trace elements.

The lack of studies from other coastal ocean areas on this issue limits our ability to draw firm conclusions. Even though the complexation between humic substances and metals (Mn, Ni, Cu, Zn, and Fe) has been found to be significant in previous studies (Boggs Jr et al., 1985; Mantoura et al., 1978; Mostofa et al., 2013), only Mn and Fe have been predominantly studied in ocean waters (Batchelli et al., 2010; Eastman and Church, 1984; Krachler et al., 2015; Misumi et al., 2013; Oldham et al., 2017a; Oldham et al., 2017b; Oldham et al., 2019; Rose and Waite, 2003). Batchelli et al. (2010) reported higher humic-bound Fe concentrations at lower salinity, which decreased with increasing salinity in the NE Atlantic coastal waters, similar to our findings. The quite refractory characteristics of terrestrial humic substances (Gledhill and Buck, 2012) and the stabilization effect of Fe - humic complexes during mixing (Batchelli et al., 2010) appear to shield Fe from intensive scavenging and biological uptake. Similar stability has been found with Mn, in which the formation of stabilized soluble Mn(III)-humic compounds was presumed to be important in the transportation of Mn to the ocean (Oldham et al., 2017a; Oldham et al., 2017b). In addition, Mn showed strong competence against Fe when binding with the same humic species (Oldham et al., 2017a; Oldham et al., 2017b).

Although the complexation of humic substances with Ni, Cu, and Zn has been observed and investigated in a few studies (Alberts and Filip, 1998; Boiteau et al., 2016; Bruland, 1989; John and Conway, 2014; Ruacho et al., 2020; Whitby and van den Berg, 2015), the shuttling effect of these elements by humic substances has seldom been discussed. In this study, the positive linear correlations of dissolved Ni, Cu, and Zn concentrations with the C peak ( $r^2 = 0.88$ , 0.87, and 0.85, respectively; transect A was excluded from the regression of Ni) indicate that these elements may also bind with humic substances and survive biological uptake and scavenging processes in the same way as Mn and Fe. The correlation between Ni concentrations against the C peak showed a deviation in transect A, consistent with that against salinity (Fig. 3.7e). This may be due to the relatively older water mass in the area of transect A (Kim et al., 2013; Lee et al., 2018; Yoon et al., 2019). As Ni<sup>2+</sup> has weak binding strength with humic substances compared with other elements (e.g., Fe, Cu) (Boggs Jr et al., 1985), the outcompetition of Ni by other elements when binding with humic substances may lead to the depletion of Ni in transect A. These differences in binding strength may also result in a slight deviation of Fe concentrations against the C peak because of the relatively weaker binding strength compared with Mn and Cu (Boggs Jr et al., 1985; Boiteau et al., 2016; Irving and Williams, 1953) (Fig. 3.7b). Overall, it can be hypothesized that trace elements (Mn, Fe, Ni, Cu, and Zn) associated with terrestrial humic substances are discharged into the bay and transported conservatively to the open ocean.

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Figure 3.6 Surface Chlorophyll-a concentration in the study area. Figure data were provided by NOAA's Center for Satellite Applications & Research (STAR) and the CoastWatch program and distributed by NOAA/NMFS/SWFSC/ERD.\. (https://coastwatch.pfeg.noaa.gov/erddap/griddap/nesdisVHNSQchla Daily.graph?chlor\_a%5B(2019-03-26T12:00:00Z)%5D%5B(0.0)%5D%5B(35.272):(34.70625)%5D%5 B(128.4938):(129.1)%5D&.draw=surface&.vars=longitude%7Clatit ude%7Cchlor\_a&.colorBar=%7C%7C%7C%7C%7C&.bgColor=0xffc cccff)



**Figure 3.7** Plots of C peak versus dissolved trace element concentrations: (a) Mn, (b) Fe, (c) Cu, (d) Zn, and (e) Ni. Dissolved Ni concentrations for transect A are circled with red ovals and excluded from the regression.



**Figure 3.8** Plots of DOC versus trace element concentrations. (a) Mn, (b) Fe, (c) Cu, (d) Zn, and (e) Ni. Dissolved Ni concentrations for transect A are circled with red ovals and excluded from the regression in plot c.

### 3.5. Conclusion

This study investigated the conservative behavior of trace elements (Mn, Fe, Ni, Cu, and Zn) in a coastal embayment. Our study discovered a notable depletion of inorganic nutrients (DIN, DIP, and DSi) in the inner bay, where the concentrations of these nutrients retained extremely low values in the innermost area. This depletion could largely be resulted by biological uptake. In addition, the particle scavenging process was also observed with lower values of (Nd/Er)<sub>PAAS</sub> and Ce/Ce\* in the innermost bay, suggesting vigorous removal of the more particle-reactive LREEs. Unlike the conventional understanding of the removal of trace elements in coastal oceans (Boyle et al., 1977; Charette et al., 2016; Sholkovitz, 1976), the findings of this study support the hypothesis that terrestrial trace elements (Mn, Fe, Ni, Cu, and Zn) associated with humic substances could survive either particle scavenging or biological uptake, and thereby would be transported conservatively to the open ocean. In light of this, our findings supplement the lack of studies on the shuttling effect of terrestrial trace elements by humic substances in coastal oceans, where trace elements are commonly thought to be intensively removed. In addition to previous studies on Fe and Mn behaviors (Batchelli et al., 2010; Oldham et al., 2020), our

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study shows the same shuttling effect of Ni, Cu, and Zn by complexing with humic substances in the coastal ocean, remote from the low-salinity estuarine mixing zone. This study reveals an important pathway for terrestrial trace metal input into the open ocean via coastal oceans. However, further studies on the speciation of trace elements are necessary to validate this hypothesis.

### Chapter 4. Role of terrestrial versus marine sources of humic dissolved organic matter on the behaviors of trace elements in seawater

### 4.1. Introduction

The coastal ocean plays an important role in regulating the transfer of trace elements from land to the open ocean, through various biogeochemical processes. Trace elements in the coastal oceans originate from various sources, including riverine runoff, submarine groundwater discharge (SGD), atmospheric deposition, and sedimentary diffusion (Charette et al., 2016; Elrod et al., 2004; Felix–Bermudez et al., 2017; Kim et al., 2020; Severmann et al., 2010). However, most of the trace elements in the coastal ocean are known to be rapidly removed by biological consumption as well as settling to the seafloor, before they can reach the open ocean (Charette et al., 2016; Charette and Sholkovitz, 2002; Jeong et al., 2012; Joung and Shiller, 2016; Sanders et al., 2015).

Despite the effective removal of dissolved trace elements in coastal oceans, some portions of these elements can reside in water columns for a longer period through complexation with dissolved organic matter (DOM); such complexation would make trace

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elements less susceptible to scavenging processes (Dai et al., 1995; Kim and Kim, 2015; Moran and Buesseler, 1993; Mostofa et al., 2013; Rose and Waite, 2003; Wen et al., 1999). The gross chemical composition of marine (Aluwihare et al., 1997; Benner et al., 1992) and riverine (Lam et al., 2007) DOM mainly consist of polysaccharides, lipids, and alicyclic organic molecules, with minor contributions from proteins and humics. In particular, the humic component of dissolved organic matter  $(DOM_H)$  plays the primary role in stabilizing dissolved trace elements in estuarine areas and other freshwater aquatic systems (Eastman and Church, 1984; Ilina et al., 2016a; Oldham et al., 2017a; Oldham et al., 2019; Sposito, 1986). However, only a few studies have investigated the stabilizing effect of  $DOM_H$  on dissolved trace elements (Mn and Fe) in coastal areas beyond the estuarine mixing zone (Batchelli et al., 2010; Chen et al., 2021; Oldham et al., 2020). Batchelli et al. (2010) reported that nearly 100 % of the riverine Fe that survived flocculation in a coastal bay was associated with  $DOM_{H}$ .

While terrestrial inputs, such as riverine runoff, are known to be the major supplier of  $DOM_H$  to the coastal ocean (Burns et al., 2008; Dai et al., 2012; Lee and Kim, 2018), the biological production by marine phytoplankton may become a significant source of  $DOM_H$ when terrestrial inputs are limited (Fukuzaki et al., 2014; Kwon et al.,

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2018b; Romera-Castillo et al., 2010). However, whether marinederived  $DOM_H$  forms complexes with trace elements as terrestrialderived  $DOM_H$  does and whether these different origins of  $DOM_H$  have different impacts on trace element distributions are still unclear.

Thus, in this study, the distributions of trace elements (Mn, Fe, Ni, Cu, Zn, and Cd) together with DOM components in two coastal areas of Korea were investigated, where either terrestrial input or marine biological production of DOM<sub>H</sub> was found to be dominant (Kwon et al., 2018b; Lee et al., 2020b). In this study, rare earth elements (REEs; here defined as the lanthanide group of elements) and <sup>234</sup>Th (half-life: 24.1 days) were used to examine the particlereactive characteristics of trace elements (Bacon and Rutgers van der Loeff, 1989; Black et al., 2018; Charette et al., 2016; Chevis et al., 2015; Elderfield, 1988). In seawater, <sup>234</sup>Th is known to be very particle-reactive and is constantly produced by its conservative parent  $^{238}$ U (half-life: 4.5  $\times$  10<sup>9</sup> years). Thus, the disequilibrium between <sup>234</sup>Th and <sup>238</sup>U has been widely observed and utilized to trace particle scavenging (Bacon and Rutgers van der Loeff, 1989; Black et al., 2018; Black et al., 2019; Buesseler et al., 1992). As such, the relative removal of Ce and light-REEs (LREEs; La to Nd), which are preferentially scavenged onto particle surfaces amongst REEs (Byrne and Kim, 1990; Cantrell and Byrne, 1987), is often used to

examine the seawater scavenging conditions.

#### 4.2. Study region and sampling methods

The study regions, Jinhae Bay (JH) and the coastal area off Tongyeong (TY), are located off the southern coast of the Korean Peninsula (Fig. 4.1). JH has shallow water depths varying from 5 to 25 m with weak semi-diurnal tidal current velocities varying from 0.1 to 1 ms<sup>-1</sup>. This area receives significant freshwater input from local streams with a discharge rate of 2.4  $\times$  10<sup>8</sup> m<sup>3</sup> yr<sup>-1</sup> (Lee et al., 2009). Owing to the anthropogenic inputs from industrial complexes, the trace element concentrations in the stream waters are elevated (e.g., 53–200 nM for Cu), which could account for the heavy loading of trace elements in adjacent coastal oceanic waters (e.g., 6.6-16.0 nM for Cu) (Kim et al., 2014; Kim et al., 2013; Kwon et al., 2019; Lee et al., 2010; Park et al., 2020). In this study, two JH subregions (i.e., JH-A and JH-B) were defined, of which JH-A is close to the main streams of this region and JH-B is a semi-enclosed area with a long water residence time of more than 85 days (Fig. 4.1a) (Kim et al., 2016; Lee et al., 2020a; Park et al., 2020).

In TY, the water depths range from 10 m nearshore to 50 m offshore (Kwon et al., 2019; Kwon et al., 2018b). In general, the open-ocean seawater in this region belongs to the Tsushima Current. However, during summer and autumn, a mixture of the Tsushima

Current, Yellow Sea seawater, and low-salinity Changjiang diluted water may pass through this region (Kwon et al., 2019; Lee et al., 2010). This region is known for the frequent outbreaks of dinoflagellate red tides (*Margalefidinium polykrikoides* [formerly *Cochlodinium polykrikoides*]) under conditions of low inorganic nutrients levels and high organic nutrients levels (Kwon et al., 2018b; Lee and Kim, 2007; Lee, 2006). During the study period, a red tide outbreak was first observed on August 23, 2019 and disappeared on September 24, 2019 (http://www.nifs.go.kr/).

Surface seawater samples from JH were collected at six stations in JH-A (JH1 to JH6) and four stations in JH-B (JH7 to JH10) from May 27 to 28, 2021. During the red tide outbreak in TY, surface water samples were collected on September 17, 2019 at five stations (TY1 to TY5) in the red tide patch area and four stations (TY6 to TY9) in the non-patch area. Samples for the analyses of dissolved trace elements, dissolved REEs, dissolved organic carbon (DOC), fluorescent dissolved organic matter (FDOM), and phytoplankton pigments were collected from both study regions. Moreover, samples for <sup>234</sup>Th were additionally collected in JH. Salinity was measured insitu at each sampling station using a portable multimeter (Orion Star A329; Thermo Fisher Scientific).

For trace element and REE analysis, seawater samples were

collected using an acid-cleaned high-density polyethylene (HDPE) beaker and transferred into acid-cleaned 125 mL low-density polyethylene (LDPE) bottles on the front side of a small ship while it slowly moved forward. The samples were stored in an ice-box and transferred to the laboratory within 5 h. Seawater samples (10 L) for total <sup>234</sup>Th analysis were collected in acid-cleaned HDPE bottles with a submersible pump and acidified (pH < 1) using 8 M ultra-high-purity HNO<sub>3</sub>.



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**Figure 4.1** Map of study sites in the southern Korean coastal regions, JH (a) and TY (b). The color gradient indicates surface water salinity. In plot (a), the dots outlined in red indicate the sampling sites in this study (JH1 to JH10). The dots with black outlines indicate the sampling sites in a previous study by Chen et al. (2021). In plot (b), the sampling sites in the red tide patch area in TY are labeled with red letters (TY1 to TY5). The sampling sites in the non-patch area are labeled with black letters (TY6 to TY9).

### 4.3. Results

## 4.3.1. The distributions of trace elements, REEs, and DOM components in Jinhae Bay

Salinity in JH ranged from 32.8 to 34.0, exhibiting an increasing trend from station JH1 to JH10 (Fig. 4.1; Fig. 4.2a). Chlorophyll a concentrations ranged from 0.1 to 1.1  $\mu$ g L<sup>-1</sup>, with higher values in JH-A (0.7  $\pm$  0.2 µg L<sup>-1</sup>, n = 6) than those in JH-B (0.2  $\pm$  0.1 µg  $L^{-1}$ , n = 4) (Fig. 4.2a). DOC concentrations in JH-A showed a decreasing trend from station JH1 (125  $\mu$ M) to station JH6 (93  $\mu$ M), with an anomalously high value at station JH4 (174  $\mu$ M). DOC concentrations in JH-B showed a slight increasing trend from JH7  $(88 \ \mu\text{M})$  to JH10 (101  $\mu\text{M}$ ) (Fig. 4.2b). The T peak (protein-like) of the FDOM components showed a distribution pattern similar to that of DOC, with an anomalously high value at JH4 (3.0 R.U.). The C peak (humic-like) of FDOM showed a decreasing trend from JH1 (2.5 R.U.) to JH6 (1.5 R.U.) in JH-A and a slight increasing trend from JH7 (1.4 R.U.) to JH10 (1.5 R.U.) in JH-B (Fig. 4.2b).

In general, the concentrations of dissolved trace elements (Mn, Fe, Ni, Cu, and Zn) in JH-A decreased from the inner study area to the outer edges (Fig. 4.3). For example, dissolved Mn concentrations showed a maximum value of 411 nM at station JH1 and decreased to 21 nM at station JH5. Trace element concentrations in JH-B showed relatively constant values, which were generally lower than those in JH-A. For instance, dissolved Fe concentrations yielded an average value of 4.5  $\pm$  2.1 nM (n = 4) in JH-B and 7.3  $\pm$  3.5 nM (n = 6) in JH-A. Cd concentrations showed relatively constant values throughout the entire study area, with an average value of 0.17  $\pm$ 0.02 nM (n = 10). REE concentrations showed lower values in the inner part of JH-A and increased towards the outlying area. In JH-B, a decreasing trend from the outer to the inner area was observed for REEs. For example, Nd concentrations in JH-A ranged from 22 pM at station JH2 to 43 pM at station JH6, whereas in JH-B Nd concentrations decreased from 38 pM at station JH7 to 26 pM at station JH10.



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**Figure 4.2** Spatial variations of (a) salinity, chlorophyll a, (b) DOC, C peak, and T peak in JH, and (c) salinity, chlorophyll a, peridinin, fucoxanthin, (d) DOC, C peak, and T peak in TY.

# 4.3.2. The distributions of trace elements, REEs, and DOM components in the coastal waters off Tongyeong

Salinity in TY ranged from 31.0 to 32.5, with lower values in the red tide patch area compared with the non-patch area (Fig. 4.1; Fig. 4.2c). The chlorophyll concentrations showed higher values in the red tide patch area (1.6  $\pm$  0.5 µg L<sup>-1</sup>, n = 5) compared with the non-patch area  $(0.3 \pm 0.2 \ \mu g \ L^{-1}, n = 4)$  (Fig. 4.2c). The concentrations of peridinin, the marker pigment for dinoflagellate, increased from station TY1 (2.1  $\mu$ g L<sup>-1</sup>) to TY3 (3.3  $\mu$ g L<sup>-1</sup>) and then decreased towards TY5 (1.2  $\mu$ g L<sup>-1</sup>) in the red tide patch area. Peridinin concentrations in the patch area were similar to those observed in the same area during a red tide outbreak in 2014 (2.5  $\pm$ 1.8  $\mu$ g L<sup>-1</sup>) (Kwon et al., 2019). In the non-patch area, peridinin concentrations showed relatively lower values with an average of 0.3  $\pm$  0.2 µg L<sup>-1</sup> (n = 4). The concentrations of fucoxanthin, the marker pigment for diatoms, exhibited a distribution pattern opposite to that of peridinin, with lower values in the red tide patch area (0.3  $\pm$  0.2  $\mu$ g L<sup>-1</sup>, n = 5) and higher values in the non-patch area (0.6 ± 0.6  $\mu g L^{-1}$ , n = 4).

DOC concentrations ranged from 97  $\mu$ M to 115  $\mu$ M, decreasing from station TY1 to the outermost station TY9 (Fig. 4.2d). The C and

T peaks of FDOM all showed higher fluorescence intensities in the red tide patch area compared with the non-patch area (Fig. 4.2d). The average intensities of C peak and T peak in the red tide patch area were 1.76  $\pm$  0.04 R.U. (n = 5) and 1.96  $\pm$  0.02 R.U. (n = 5), and those in the non-patch area were 0.95  $\pm$  0.12 R.U. (n = 4) and 1.47  $\pm$  0.05 R.U. (n = 4), respectively.

The distributions of trace elements varied for different elements. The concentrations of dissolved Mn, Fe, and Cu were higher in the red tide patch area than in the non-patch area, whereas dissolved Ni and Zn concentrations were lower in the patch area than in the nonpatch area (Fig. 4.4). For instance, dissolved Fe concentrations ranged from 2.7 to 4.7 nM in the patch area and 1.3 to 2.0 nM in the non-patch area, while dissolved Ni concentrations ranged from 3.9 to 4.2 nM in the patch area and 4.2 to 5.4 nM in the non-patch area. Cd concentrations remained fairly constant in both the patch and non-patch areas, ranging from 0.23 to 0.28 nM, with an exceptionally high value of 0.40 nM at station TY8. The REE concentrations in the red tide patch area showed slightly lower values and larger variations than those in the non-patch area. For example, Nd concentrations ranged from 28.8 to 55.6 pM (avg:  $38.9 \pm 9.0$  pM) in the patch area and 35.2 to 43.8 pM (avg: 40.5  $\pm$  3.2 pM) in the non-patch area.



**Figure 4.3** Plots of salinity versus (a) Fe, (b) Cu, (c) Ni, (d) C peak, (e) (Nd/Er)<sub>PAAS</sub>, and (f) Ce/Ce\* in JH. The red triangles and green diamonds indicate the results from JH-A and JH-B, respectively.

The results from a previous study by Chen et al. (2021) in the Jinhae Bay area are indicated by yellow hexagons. The grey dashed lines in plots (a) – (d) are also from Chen et al. (2021).

### 4.4. Discussion

### 4.4.1. Particle scavenging of <sup>234</sup>Th and REEs

To examine the scavenging characteristics of the study areas, the fractionation of dissolved REEs were investigated. In the ocean, LREEs are preferentially scavenged onto particle surfaces compared to middle-REEs (MREEs; Sm to Dy) and heavy-REEs (HREEs; Ho to Lu) (Byrne and Kim, 1990; Cantrell and Byrne, 1987). The concentrations of REEs in this study were normalized by the Post Archean Australian Shale (PAAS) to eliminate the effect of the Oddo-Harkins rule (Taylor and McLennan, 1985). In JH, the (Nd/Er)<sub>PAAS</sub> ratio (as a proxy of the LREE/HREE ratio) showed lower values in JH-A compared with those in JH-B (Fig. 4.3e), indicating more vigorous scavenging of LREEs in JH-A. This may be attributed to the high degree of biological activity and a large amount of suspended particles in JH-A, which is located closer to streams (Chen et al., 2021). In addition, the (Nd/Er)<sub>PAAS</sub> ratio in this study showed considerably lower values than those found in a previous study (2019) in the same area (Chen et al., 2021). This trend indicates a more vigorous scavenging of LREEs in the innermost JH, as suggested by Chen et al. (2021). In addition, the relative removal of Ce compared with the other REEs can be utilized to trace

scavenging processes. The relative removal of Ce is denoted as Ce/Ce\* ratio, which is often calculated as

$$Ce/Ce^* = 3 \cdot \frac{Ce_{PAAS}}{2 \times La_{PAAS} + Nd_{PAAS}}$$
(1)

where Ce<sub>PAAS</sub>, La<sub>PAAS</sub>, and Nd<sub>PAAS</sub> are the PAAS-normalized concentrations of each REE (Sholkovitz, 1995). Similar to the distribution of (Nd/Er)<sub>PAAS</sub>, the Ce/Ce\* ratios in this study showed much lower values than those obtained from the higher salinity waters of the outer JH in a previous study (Chen et al., 2021). Although negative Ce anomalies could also be influenced by the oxidation of Ce (de Baar et al., 2018; Moffett, 1990) or the intrusion of freshwater with a pre-existing Ce deficit, the lower (Nd/Er)<sub>PAAS</sub> values in the study area indicate that these negative Ce anomalies could be mainly due to the intensive scavenging process in the inner area of JH (Fig. 4.3f).

To further demonstrate and investigate the scavenging rates relative to the water residence times, radioactive <sup>234</sup>Th and <sup>223</sup>Ra/<sup>226</sup>Ra ratios were analyzed. The water residence time was calculated using the <sup>223</sup>Ra and <sup>226</sup>Ra pair, with the method adapted from Lee et al. (2020b) and Moore (2000). The water residence time t can be calculated using the following equation:

$$\begin{bmatrix} \frac{2^{23} \text{ Ra}}{2^{26} \text{ Ra}} \end{bmatrix}_{\text{obs}} = \begin{bmatrix} \frac{2^{23} \text{ Ra}}{2^{26} \text{ Ra}} \end{bmatrix}_{i} \cdot \frac{e^{-\lambda_{223} t}}{e^{-\lambda_{226} t}}$$
(2)

where Ra<sub>obs</sub> indicates the measured Ra activity of each isotope subtracted from the lowest activity at the outermost station, Rai indicates the initial activity of each isotope (the maximum activity at the innermost station subtracted from the lowest activity at the outermost station), and  $\lambda_{223}$  (0.0608 days<sup>-1</sup>) and  $\lambda_{226}$  (0.1187 ×  $10^{-5}$  days<sup>-1</sup>) indicate the decay constants of <sup>223</sup>Ra and <sup>226</sup>Ra, respectively. This model assumes negligible addition and removal of Ra, with the exception of radioactive decay. The water residence times of JH ranged from 15 to 70 days (Fig. 4.5b), similar to that (~ 85 days) obtained through modelling results (Jung et al., 2016; Kim et al., 2016).

In JH, the activities of <sup>234</sup>Th (0.14 to 0.39 dpm L-1) were much lower than the activities of <sup>238</sup>U (2.25 to 2.33 dpm L-1), suggesting an effective removal of <sup>234</sup>Th via scavenging (Fig. 4.5a). Here, <sup>238</sup>U activity (A<sup>238</sup>U) was calculated using an equation (A<sup>238</sup>U = 0.06856  $\times$  salinity) suggested by Buesseler et al. (2001). The <sup>234</sup>Th activities showed relatively lower values in JH-A (0.19 ± 0.04 dpm/L, n = 6) compared with those in JH-B (0.26 ± 0.09 dpm/L, n = 4), indicating more intensive removal of <sup>234</sup>Th in JH-A than in JH-B (Fig. 4.5a). The removal rate of total <sup>234</sup>Th was calculated as

$$\mathbf{k} = \lambda_{234} \cdot \frac{1 - A_{\mathrm{Th}} / A_{\mathrm{U}}}{A_{\mathrm{Th}} / A_{\mathrm{U}}} \tag{3}$$

where k is the scavenging rate and  $\lambda_{234}$  (0.0289 days<sup>-1</sup>) is the decay constant of <sup>234</sup>Th; A<sub>Th</sub> and A<sub>U</sub> represent the activities of Th and U, respectively (Swarzenski et al., 2003). Thus, the residence time of total <sup>234</sup>Th is calculated as  $\tau = 1/k_{Th}$ . Here, it is assumed that both vertical and horizontal water mixing were negligible compared with the scavenging rates of <sup>234</sup>Th. In JH, the estimated residence times of total <sup>234</sup>Th ranged from 2.2 to 7.1 days (Fig. 4.5b). At all sampling stations, the residence times of <sup>234</sup>Th were much shorter than the water residence times (Fig. 4.5b). Thus, our assumption for the calculation of <sup>234</sup>Th scavenging rate seems to be valid in this study region. This result also suggests that the effective scavenging of REEs and <sup>234</sup>Th occurred before the coastal waters were mixed with the open ocean waters.

In TY, the Ce/Ce\* ratios in the red tide patch area (0.24-0.26) were lower than those in the non-patch area (0.25-0.31), suggesting effective particle scavenging in the red tide patch area (Fig. 4.4f). Given that the sample collection in TY was conducted towards the end of the red tide period, it is probable that a large fraction of dinoflagellate cells would have died off and settled to the seafloor. Consequently, the lower Ce/Ce\* values in the red tide patch area, relative to the non-patch area, could be attributed to the intensive particle scavenging associated with dinoflagellate cells.

However, the (Nd/Er)<sub>PAAS</sub> ratios in TY showed higher values in the red tide patch area compared with those in the non-patch area (Fig. 4.4e). This suggests that there was an enrichment of LREEs (except for Ce) in the red tide patch area instead of the removal of LREEs via intensive particle scavenging. This may be due to the influence of intensive biological activities in this region, which is discussed in Section 4.4.3.



Figure 4.4 Plots of salinity versus (a) Mn, (b) Fe, (c) Cu, (d) C peak,

(e) (Nd/Er)  $_{\text{PAAS}},$  and (f) Ce/Ce\* in TY.



**Figure 4.5** Spatial variations of (a) <sup>234</sup>Th activities, <sup>238</sup>U activities, (b) Th residence times, and Ra ages (water residence times) in JH.

# 4.4.2. Complexation of trace elements with terrestrial $\text{DOM}_{\text{H}}$

Notable negative relationships between salinity and trace element (Fe, Ni, and Cu) concentrations were observed in JH (Fig. 4.3a-c), indicating the input of trace elements from freshwater and the limited influence of particle scavenging on the distributions of these elements. Similarly, the negative relationship between salinity and C peak also indicates the terrestrial input of  $DOM_H$  from freshwaters (Fig. 4.3d). A significant positive relationship was observed between trace element concentrations and C peak (Fig. 4.8a-c), indicating that the terrestrial DOM<sub>H</sub> would associate with dissolved trace elements in the study region where stream water discharges into the coastal area. Similarly, Chen et al. (2021) observed a conservative behavior of trace elements associated with DOM<sub>H</sub> in high-salinity waters from JH. Since the particle-reactive  $^{234}$ Th was removed rapidly with a short residence time of 4  $\pm$  1 days relative to the long water residence time of 47  $\pm$  16 days in JH, it is likely that the complexation of trace elements (Fe, Ni, and Cu) with DOM<sub>H</sub> may stabilize dissolved trace elements and protect these elements from being removed by particle scavenging over a long period of transport time in JH.
However, dissolved Mn showed exceedingly large inputs of terrestrial sources from station JH1 to JH3 and a drastic decrease from JH4 to JH10, without showing a significant correlation with  $DOM_{H}$  (Fig. 4.6; Fig. 4.7). This behavior of Mn could be largely affected by the redox conditions of the discharged stream waters, which are often found to be suboxic (Park et al., 2020). Although Mn(III) is considered to have a strong binding strength with DOM (Oldham et al., 2017a), the binding strength between  $DOM_H$  and Mn(II)is relatively weak (Boggs Jr et al., 1985). This could eventually result in the effective scavenging of dissolved Mn onto particles rather than complexing with  $DOM_H$  in JH-A where the waters become fully oxic (Chen et al., 2021). This deduction is also supported by the much lower  $(Nd/Er)_{PAAS}$  and Ce/Ce\* values in this study than those found in 2019 in JH (Fig. 4.3e, f). In addition, the relatively older water mass in JH-B (Fig. 4.5b) would also result in other elements outcompeting Mn in terms of association with DOMH. Similarly, this process would also lead to the outcompetition and depletion of Ni in JH-B, which is consistent with the previous study in 2019 (Chen et al., 2021).

Similarly, dissolved Zn also exhibited rapid removal patterns in both JH-A and JH-B (Fig. 4.6; Fig. 4.7). This could largely be influenced by the much weaker binding strength of Zn<sup>2+</sup> with humic

components compared with that of other elements such as Fe and Cu (Boggs Jr et al., 1985). This weaker binding strength may result in the outcompetence of Zn when associating with  $DOM_H$ , resulting in a certain degree of Zn depletion. The Cd concentrations showed no obvious correlation with either salinity or  $DOM_H$  (Fig. 4.6; Fig. 4.7). This suggests that terrestrial  $DOM_H$  has a limited influence on dissolved Cd, which may result from the weaker binding strength of Cd<sup>2+</sup> with humic substances and the low affinity of Cd for complexation with colloidal organic matter (Boggs Jr et al., 1985; Neff, 2002).



**Figure 4.6** Plots of salinity versus dissolved trace element concentrations in both JH and TY. Results for JH are shown from plot

(a) to (c): (a) Mn, (b) Zn, and (c) Cd. Results for TY are shown from plot (d) to plot (f): (d) Ni, (e) Zn, and (f) Cd.



Figure 4.7 Plots of C peak versus dissolved trace element concentrations in both JH and TY. Results for JH are shown from plot

(a) to (c): (a) Mn, (b) Zn, and (c) Cd. Results for TY are shown from plot (d) to plot (f): (d) Ni, (e) Zn, and (f) Cd.

# 4.4.3. Interactions between trace elements and marine $\text{DOM}_{\text{H}}$

In TY, no obvious correlations were observed between salinity and the concentrations of DOC, the C peak, or the T peak (Fig. 4.2c, d). Instead, the plot of C peak against salinity showed a significant excess of C peak in the red tide patch area (Fig. 4.4d). A previous study in TY also found an enrichment of FDOM (C and T peaks) in surface seawater and demonstrated that the enriched  $DOM_H$  was produced from dinoflagellates during a red tide bloom (Kwon et al., 2018b). Meanwhile, higher concentrations of peridinin and chlorophyll a were also observed in the red tide patch area (Fig. 4.2c). The concentrations of fucoxanthin, however, showed relatively low values throughout the entire study area (Fig. 4.2c). Therefore, the similar distribution between C peak and the concentrations of phytoplankton pigments (peridinin and chlorophyll a) in this study indicates that marine biological production, instead of terrestrial sources, is likely to be the main controlling factor of  $DOM_H$  in TY (Fig. 4.2d).

This production process can be further indicated by REE fractionations. Strady et al. (2015) demonstrated that the LREE/HREE ratios in the surface seawater could be lower than those

in the deeper water due to the preferential uptake of LREEs by planktons in the surface water. In light of this, the higher values of (Nd/Er)<sub>PAAS</sub> in the red tide patch area are likely related to the potential release of LREEs by the decomposing of phytoplankton cells, together with DOM (Fig. 4.4e). As such, the higher concentrations of Mn, Fe, and Cu in the patch area could be attributed to this regeneration process (Boyd and Ellwood, 2010; Fisher and Wente, 1993; Hollister et al., 2020). Considering that intensive particle scavenging occurred in the red tide patch area, as indicated by the low Ce/Ce\* ratios, it can be assumed that the regeneration process was the dominant factor influencing the fractionation of LREEs and HREEs in this study.

Although the sources of  $DOM_H$  in TY were different from those in JH, positive correlations were also observed between C peak and the concentrations of Mn, Fe, and Cu (r<sup>2</sup> ranging from 0.71 to 0.84) (Fig. 4.8d-f). This result shows that the marine-derived  $DOM_H$ would associate with trace elements, similar to the terrestrial  $DOM_H$ , which prevents these elements from being removed by particle scavenging. A similar association between marine-derived  $DOM_H$ and Fe was observed in the coastal area of the NE Atlantic, where the chemical characteristic of the DOM that bound with Fe shifted from land-derived  $DOM_H$  to compounds released by biological

production or decomposition as Fe was transported from the coastal to the open ocean (Batchelli et al., 2010).

Ni and Zn, however, behaved differently with Mn, Fe, and Cu, exhibiting a depletion pattern in the red tide patch area (Fig. 4.6). Unlike that in JH, where the concentrations of trace elements and DOM<sub>H</sub> are considerably high in stream waters (Lee et al., 2020a; Park et al., 2020), the concentrations of  $DOM_H$  and trace elements in TY were much lower than those in the freshwaters of JH. Moreover, the biological activities in the red tide patch area would result in a more intensive scavenging process than that in the non-patch area. Therefore, the scavenging of Ni and Zn could be dominating over the stabilization effect by DOM<sub>H</sub> in the red tide patch area. This deduction can be further supported by the relatively weaker binding strengths of Ni and Zn with DOM<sub>H</sub> compared with Mn, Fe, and Cu (Boggs Jr et al., 1985; Boiteau et al., 2016; Irving and Williams, 1953; Whitby et al., 2020). This result suggests that the stabilization of trace elements by different sources of DOM<sub>H</sub> could be variable depending on the biogeochemical processes. Cd concentrations in TY also showed no obvious relationship with either salinity or  $DOM_H$  (Fig. 4.6; Fig. 4.7), similar to the case in JH. This indicates the limited influence marine-derived of both terrestrialand  $DOM_{H}$ on the biogeochemistry of Cd in seawater.



**Figure 4.8** Plots of C peak versus (a) Fe, (b) Cu, and (c) Ni in JH, and (d) Mn, (e) Fe, and (f) Cu in TY. The red triangles and green diamonds indicate the results from JH-A and JH-B, respectively.

The results from a previous study in JH by Chen et al. (2021) are plotted in yellow hexagons. The grey dashed lines in plots (a) – (c) are also from Chen et al. (2021). The pink circles and cyan squares indicate the results from the red tide patch area and non-patch area in TY, respectively.

### 4.5. Conclusion

This study investigated the different roles of terrestrial and marine DOM<sub>H</sub> influencing the behaviors of dissolved trace elements in two coastal areas of South Korea. In JH, DOM<sub>H</sub> was mainly derived from freshwater input. In TY, excess DOM<sub>H</sub> was found to be produced by marine microorganisms during a red tide. Intensive particle scavenging processes were observed in both regions with rapid removal of particle-reactive <sup>234</sup>Th and Ce. Despite these intensive scavenging processes, in JH, dissolved trace elements (Fe, Ni, and Cu) behaved relatively conservatively throughout the study area and showed strong positive correlations with DOM<sub>H</sub>. Similar strong positive correlations were also identified between the concentrations of dissolved trace elements (Mn, Fe, and Cu) and  $DOM_H$  in TY. These results suggest that both terrestrial – and marine – derived DOM<sub>H</sub> can associate with trace elements, stabilizing them in the water column and limiting the effective removal of these elements by particle scavenging processes. However, this complexation and stabilization of trace elements by different sources of DOM<sub>H</sub> could be variable depending on the biogeochemical conditions.

Overall, our study reveals that both terrestrial and marine  $\mathrm{DOM}_{\mathrm{H}}$  can complex with dissolved trace elements and enable these

elements to reside for a longer time in seawater. This complexation of trace elements with  $DOM_H$  could be critical in shuttling the trace elements from coastal to open oceans and supporting the oceanic primary production by supplying the bio-essential trace elements. However, further investigations on the extraction of trace element- $DOM_H$  compound are necessary to solidify this conclusion.

### Chapter 5. Significant contribution of coastal fish-farm activities to the inventory of trace elements in coastal waters: Traced by ammonia and rare earth elements

### 5.1. Introduction

Dissolved trace elements in coastal oceans can largely influence coastal ecosystems as bio-essential elements (Boyd and Ellwood, 2010; Charette et al., 2016; Chen et al., 2022; Morel and Price, 2003; Sunda, 1989). They originate from various natural sources (e.g., discharge of lithogenic trace elements) and anthropogenic sources (e.g., wastewater discharge) (Charette et al., 2016; Flegal et al., 1991; Gunther et al., 1987; Richir and Gobert, 2016; Worakhunpiset, 2018; Yunginger et al., 2018). Due to the rapid growth of industrialization and agriculture activities worldwide in coastal regions during recent decades, the input of trace elements to the coastal ocean from anthropogenic activities has greatly increased (Gao et al., 2016; Mitra et al., 2018; Pavoni et al., 2021).

More recently, aquaculture activities have been found to release pollutant chemicals, such as fertilizers, inorganic and organic nutrients, and toxic heavy metals into the coastal ocean (Kalantzi et al., 2021; Lenzi et al., 2003; Liu et al., 2011; Oh et al., 2021; Pan et al., 2014; Salem et al., 2014). However, dissolved trace elements within the farm waters are found to be largely scavenged onto the sinking particles and accumulated in animal tissues (Kanda et al., 2020; Olaifa et al., 2004; Oliveira et al., 2017; Osman et al., 2010; Salem et al., 2014). Thus, trace elements are not commonly considered as typical pollutants in the fish-farm effluent waters (Oliveira et al., 2017). Overall, the cycling of trace elements within the farm and the output fluxes to the ocean as well as their effects on coastal waters are poorly understood.

The construction of land-based aquaculture fish farms along the coast of Jeju Island, Korea, has sharply increased in recent years (http://www.data.go.kr). Previous studies have found that the farm effluent waters act as the major source of dissolved inorganic nutrients as well as dissolved organic matters (DOMs) in the coastal areas of Jeju Island (Kwon et al., 2022; Lee et al., 2020c; Oh et al., 2021). However, the influence of fish-farm effluent waters on the trace element distributions in the coastal waters off Jeju Island has received little attention and has seldom been studied. Instead, a previous study in Bangdu Bay on Jeju Island discovered 3- to 70- fold higher concentrations of trace elements (Al, Mn, Fe, Co, Ni, and Cu) in the submarine groundwater than those in the seawater of the

bay, suggesting that submarine groundwater discharge (SGD) could be the dominant source of trace elements in the coastal waters off Jeju Island (Jeong et al., 2012).

Therefore, the purpose of this study was to investigate the behavior of dissolved trace elements inside fish farms and to assess impact of fish-farm effluent waters on trace element the distributions in the coastal ocean of Jeju Island. For this purpose, trace element (Mn, Fe, Co, Ni, and Cu) concentrations inside fish farms and in the coastal waters off the fish-farm plants were measured. In addition, the behaviors of rare earth elements (REEs; here defined as the lanthanide group of elements) were investigated to examine the redox-related removal and regeneration processes. Owing to the particle-reactive characteristic under oxic conditions, the relative removal of Ce is often used to assess the redox and scavenging conditions in the seawater (de Baar et al., 2018; Moffett, 1990; Sholkovitz, 1995). As such, the fractionation between light-REEs (LREEs; La to Nd) and heavy-REEs (HREEs; Ho to Lu) is also employed to examine the removal and regeneration processes in the water columns, due to the preferential scavenging of LREEs onto particle surfaces compared with HREEs (Byrne and Kim, 1990; Cantrell and Byrne, 1987; Chen et al., 2022; Sholkovitz, 1995; Strady et al., 2015).

#### 5.2. Study region and sampling methods

Jeju Island is a volcanic island located in the southern sea of Korea. With an area of approximately 1830 km<sup>2</sup>, porous basaltic rocks cover nearly 90% of the island (Jeong et al., 2012; Kim and Kim, 2011). Owing to the high permeability of volcanic rocks, the seepage rates along the sandy coast of Jeju Island are much higher than those in typical coastal areas, ranging from 50 to 300 m yr<sup>-1</sup> (Jeong et al., 2012; Taniguchi et al., 2002). The high permeability of the underlying basaltic layers in Jeju also causes this coastal region to be highly susceptible to surface contaminations (Koh et al., 2006; Won et al., 2006). The study regions, Pyosun (PS) and Sagye (SG), are located in the eastern and western parts of Jeju Island, respectively (Fig. 5.1). Approximately, 21 fish farms are being operated along the coast of PS. The fish farms utilize a mixture of local groundwater and adjacent coastal seawater as rearing water and discharge them to the coastal area. There was no operation of fish farms along the coast of SG.

Samples of coastal seawater were collected in PS and SG in May 2021, and additional sampling was conducted in PS, which is influenced by fish farms, during the heavy-precipitation period in August 2021 to explore the influence of seasonal variations. Surface

seawater samples were collected from 16 sites in the coastal waters of both locations, PS (P1–P16; n = 16) and SG (S1–S16; n = 16). Bottom samples at 2 m depth were collected at 11 ~ 12 sites for both PS (P5–P16; n = 11) and SG (S5–S16; n = 12) in August and at 10 sites for PS (P6–P15; n = 10) in May.

Surface seawater samples for the analysis of trace elements, REEs, and  $NH_4^+$  were collected on the front side of a small ship while slowly moving forward with 1 L acid-cleaned low-density polyethylene (LDPE) bottles. The bottom seawater samples were collected by scuba divers using 1 L acid-cleaned LDPE bottles at each site. Additionally, for both sampling periods in PS, fresh groundwater (FGW) samples were collected from local groundwater wells (May: one site; August: two sites), and water samples from fish farms (influent water and rearing water) were collected at each site (May: one site; August: four sites). The salinity data were collected in situ for each sample with a portable multimeter (Orion Star A329; Thermo Fisher Scientific). The collected samples were kept frozen in ice-boxes before they were transferred to the laboratory within 5 h. Although it has been reported that UV-irradiation is required for the measurement of "total" dissolved Co concentrations (Biller and Bruland, 2012; Milne et al., 2010), Wuttig et al. (2019) suggested that the UV-oxidation process is not preferred when measuring multiple elements because of the possibility of inducing unnecessary contaminations. In addition, Zheng et al. (2019) suggested that the conduction of UV-irradiation using PFA jar would reduce Fe concentrations. Therefore, worth to note that the concentrations of Co reported in this study only represent the fractions that can be extracted by Nobias PA-1 resin, instead of the "total" dissolved Co concentration.



**Figure 5.1** Map of study sites of fresh groundwater, fish-farm water, and coastal seawater in Sagye (a) and Pyosun (b), Jeju Island, Korea. The blue filled areas indicate the land-based fish farm plants along the coastal line of Pyosun.

# 5.3.1. The distributions of trace elements and REEs in Pyosun

Salinity of the coastal seawater in PS ranged from 23 to 35 in May and 23 to 31 in August, both exhibiting an increasing trend from the inner shore to the outer shore areas (Fig. 5.2). The salinity of the fish-farm influent and rearing water in May showed similar values of 27. Similarly, the salinity of the influent and rearing water in August also showed similar values, ranging from 15 to 30 (23.0  $\pm$ 6.5; n = 4) and 14 to 30 (23.0  $\pm$  6.6; n = 4), respectively.

In general, the surface concentrations of dissolved trace elements (Mn, Fe, Co, Ni, and Cu) in both sampling periods showed a decreasing trend from the inner shore to the outer shore areas (Fig. 5.2). Any results that were more or less than three times the standard deviations from the average values of each period were identified as statistical outliers for these stations and were excluded from discussion (e.g., surface Mn concentration in PS in August at station P5: 147 nM). Mn, Fe, and Cu concentrations showed a decreasing trend from the innermost stations to the outer ocean region in May, while Co and Ni showed lower concentrations at the innermost stations (P1 - P4) (Fig. 5.2). Similarly, in August, the

concentrations of dissolved trace elements showed much lower values at the innermost stations (P1 - P4) than at the adjacent outer stations (P5 - P8) (Fig. 5.2). For example, dissolved Mn concentrations in May showed high values of 12 nM and 13 nM at stations P3 and P5, respectively, and decreased to a minimum value of 7 nM at station P13 (Fig. 5.2). In August, dissolved Mn concentrations showed lower values from stations P1 to P4, with an average of  $17 \pm 10$  nM, and higher values of  $47 \pm 20$  nM from stations P5 to P8 (Fig. 5.2) and decreased to a value of 24 nM at station P12.

The concentrations of dissolved trace elements showed lower values in the bottom waters compared with those in the surface waters during both sampling periods (Fig. 5.2; Fig. 5.3). For instance, dissolved Fe showed an average concentration of  $20 \pm 11$  nM (n = 16) in the surface waters in May and an average concentration of 13  $\pm 4$  nM (n = 10) in the bottom waters. Similarly, in August, dissolved Fe concentrations showed an average value of  $8 \pm 6$  nM (n = 16) in the surface waters and an average value of  $2 \pm 2$  nM (n = 12) in the bottom waters.

Most trace element concentrations in the fish-farm rearing waters showed higher values than those in the influent waters, except for Ni, which showed higher concentrations in the influent waters (Fig. 5.3). Generally, the concentrations of trace elements in the FGW in both sampling periods, except for Ni in August, showed lower values than those at the nearshore stations (Fig. 5.3).

During both sampling periods, dissolved REE concentrations in the surface waters showed an increasing trend from the inner shore to the outer shore. However, the distribution pattern of LREEs differed slightly from that of middle-REEs (MREEs; Sm to Dy) and HREEs, where higher concentrations of LREEs appeared at the innermost stations (P1 - P4), compared with the adjacent outer stations (P5 - P8). For instance, Nd concentrations in May, decreased from 9 pM at station P1 to the lowest value of 3 pM at station P5 and increased to a maximum of 11 pM at station P13 (Fig. 5.2). This distribution pattern of LREEs was also exhibited in August. REE concentrations in both sampling periods all showed higher values in the surface waters compared with those in the bottom waters (Fig. 5.2). For example, Nd concentrations showed average values of 7  $\pm$ 2 pM (May) and 4  $\pm$  5 pM (August) in the surface waters and average values of 5  $\pm$  1 pM (May) and 2  $\pm$  1 pM (August) in the bottom waters. The concentrations of LREEs in the influent and rearing waters of fish farms showed higher concentrations than those in the coastal ocean waters, while the concentrations of MREEs and HREEs showed similar values between those in the fish-farm influent and rearing water and coastal waters (Fig. 5.4).

# 5.3.2. The distributions of trace elements, REEs, and $NH_4^+$ in Sagye

Salinity of the coastal seawater in SG ranged from 31 to 35, with the lowest value at the innermost station S2 and increased sharply towards the outer area. Dissolved trace elements showed scattering distribution patterns in both surface and bottom waters in SG (Fig. 5.2). In addition, the concentrations of trace elements showed similar values between the surface and bottom waters. For example, dissolved Fe showed an average concentration of  $8 \pm 5$  nM (n = 16) in the surface waters and an average of  $9 \pm 3$  nM (n = 12) in the bottom waters (Fig. 5.2).

All REE concentrations in SG showed an increasing trend from the upper inner shore (station S2 to S4) to the lower outer area (Fig. 5.2). Similar to the distribution patterns of trace elements, REE concentrations also showed similar values between the surface and bottom waters. For example, dissolved Nd concentrations ranged from 3 to 12 pM (8 ± 3 pM; n = 16) for the surface waters and 3 to 12 pM (8 ± 2 pM; n = 12) for the bottom waters. NH<sub>4</sub><sup>+</sup> concentrations in SG ranged from 0.5 to 1.3  $\mu$ M, showing relatively scattering distribution with higher concentrations observed at station S1 (1.33  $\mu$ M) and S4 (1.21  $\mu$ M) and decreased towards the outer ocean. Slightly higher concentrations of  $NH_4^+$  were observed in the surface waters (0.8 ± 0.3 µM; n = 16) compared with those in the bottom waters (0.6 ± 0.1 µM; n = 12) in SG (Fig. 5.2).



**Figure 5.2** Contours of salinity, and concentrations of  $NH_4^+$ , Mn, Fe, Co, Ni, Cu, Nd, Dy, and Er in both surface and bottom waters in Pyosun and Sagye. The surface data of salinity and  $NH_4^+$  concentrations in Pyosun are from Kwon et al. (2022).



Figure 5.2 (Continued)

#### 5.4. Discussion

### 5.4.1. Source of the excess trace elements in the coastal waters off Jeju Island

In the coastal waters off PS, the concentrations of dissolved trace elements (Mn, Fe, Co, Ni, and Cu) in May showed higher values in the low salinity waters than those in the high salinity waters (Fig. 5.3). In August, except for the innermost stations (P1 - P4), the concentrations of trace elements also showed generally higher values in the lower salinity waters (Fig. 5.3). To examine the sources of dissolved trace elements in PS, the influence of FGW on the distribution of trace elements in the coastal waters was investigated, because there were no main streams or local rivers in PS (Kwon et al., 2022). Although previous studies discovered significant attribution of trace elements to the coastal waters off Jeju by SGD (Jeong et al., 2012; Kim and Kim, 2015), the concentrations of trace elements in the FGW in this study showed relatively lower values than those in the nearshore ocean waters (Fig. 5.3). Assuming a conservative mixing between FGW and seawater, the plot of salinity against trace element concentrations showed significant excesses in the coastal waters in PS (Fig. 5.3). These results indicate that SGD input may not act as the dominant source of trace elements in the

coastal waters off PS.

Furthermore, the substantially lower concentrations of trace elements in bottom waters than those in the surface waters in both sampling periods in PS also indicate a negligible influence of benthic inputs on the surface trace element distributions. In SG, however, the concentrations of trace elements (except for Co) showed much lower values than those found in PS and exhibited no obvious relationship with salinity (Fig. 5.3). Unlike that in PS, the concentrations of Mn and Ni in SG showed similar values between the surface and bottom waters. Moreover, the concentrations of Fe and Cu in the bottom waters in SG showed higher values than those in the surface waters at certain stations (Fig. 5.2; Fig. 5.3), indicating considerable influence from benthic inputs on the trace element distributions in the seawater of SG.

Therefore, since both FGW and benthic input have limited influence on the distribution of trace elements in the surface water of PS, it is likely that the input of trace elements in the coastal waters of PS is mainly regulated by the aquaculture activities in the fish farms. The influence of fish-farm effluent waters on the coastal seawater was studied by Kwon et al. (2022). Based on a threeendmember mixing model, Kwon et al. (2022) demonstrated that fish-farm effluent waters can contribute to  $95 \pm 7\%$  of the total

NH<sub>4</sub><sup>+</sup> input to the coastal ocean, compared with the contribution from FGW and coastal seawater. The high levels of NH<sub>4</sub><sup>+</sup> in the fish-farm rearing water were considered to be mainly produced by the decomposition of particles and organic matters, such as fish food and fish feces (Herbeck et al., 2013; Ip and Chew, 2010; Kwon et al., 2022). In comparison, the concentrations of NH<sub>4</sub><sup>+</sup> in the coastal waters off SG (0.69  $\pm$  0.22  $\mu$ M; n = 28), where no fish farm plant is being operated along the coastline, showed much lower values than those in the coastal waters off PS (May: 3.95  $\pm$  4.47  $\mu$ M, n = 27; August: 4.82  $\pm$  5.94, n = 28), supporting the argument by Kwon et al. (2022) that the high levels of NH<sub>4</sub><sup>+</sup> in PS originated from fish farms.

Thus, to evaluate the influence of fish-farm activities on the coastal trace element distributions, the relationship between  $NH_4^+$  and trace element concentrations was investigated in both study areas. In PS,  $NH_4^+$  concentrations showed good positive correlations ( $r^2$  ranging from 0.32 to 0.87 in May and 0.62 to 0.82 in August) with trace element concentrations during both sampling periods (Fig. 5.5). However, trace element concentrations in SG showed no consistent positive relationship with  $NH_4^+$  (Fig. 5.5), except for Mn and Cu. In SG, the positive relationships between the concentrations of  $NH_4^+$  and the concentrations of Mn and Cu could be resulted by the benthic

inputs of these components because (1)  $NH_4^+$  concentrations were much lower than those in PS and (2) the concentrations of these components were similarly higher in both surface and bottom waters (Fig. 5.5).

Moreover, the excess concentrations of trace elements relative to the theoretically conservative mixing curve for each station of PS were calculated using the following equation:

$$[TE_{Excess}] = [TE_{Obs}] - [TE_{Mixing}]$$
(1)

where  $[TE_{Excess}]$  denotes the excess concentration of each element, [TE<sub>Obs</sub>] denotes the measured concentration of each element, and [TE<sub>Mixing</sub>] denotes the concentration of each trace element calculated from the theoretically mixing curve (Fig. 5.3). Good positive correlations (r $^2$  ranging from 0.42 to 0.87 in May and 0.56 to 0.82 in August) were also observed between the excess trace element concentrations and the  $NH_4^+$  concentrations (Fig. 5.6). In summary, our findings indicate that the elevated amounts of dissolved trace elements in the coastal waters off PS could mainly originate from fish farms. However, unlike that with NH4<sup>+</sup>, the concentrations of trace elements in the fish-farm rearing waters showed lower values than those in the coastal waters (Fig. 5.3). This could be due to the removal of dissolved trace elements inside the farm waters, which is discussed in the following section.



**Figure 5.3** Plots of salinity versus the concentrations of Mn, Fe, Co, Ni, and Cu in the coastal waters off Pyosun and Sagye. The hollow pink circles and grey circles indicate the surface seawater and bottom seawater, respectively. The cyan diamonds and yellow squares indicate the fish-farm influent waters and rearing waters, respectively. The dark red triangles indicate the fresh groundwater in Pyosun. The grey dashed lines indicate the theoretically conservative mixing line of fresh groundwater and seawater.



**Figure 5.4** Plots of salinity versus REE (Nd, Dy, and Er) concentrations and (Nd/Er)<sub>PAAS</sub> values in Pyosun and Sagye.


**Figure 5.5** Plots of NH<sub>4</sub><sup>+</sup> concentrations versus the concentrations of Mn, Fe, Co, Ni, and Cu in the seawater off Pyosun and Sagye. The hollow pink circles and grey circles indicate the surface seawater and bottom seawater, respectively. The innermost stations (P1 to P4) are circled with dashed light pink ovals and excluded from linear regression.

# 5.4.2. Biogeochemical cycles of trace elements within the fish farms

To examine the behaviors of trace elements inside fish-farm waters, the behaviors and fractionations of REEs were investigated. Owing to the more particle-reactive characteristics of LREEs than HREEs, the fractionation between LREEs and HREEs has always been commonly utilized to evaluate the scavenging or regeneration processes in the water columns (Byrne and Kim, 1990; Cantrell and Byrne, 1987; Chen et al., 2022; Chen et al., 2021). Here, the concentrations of REEs were normalized using the Post Archean Australian Shale (PAAS) to eliminate the effect of the Oddo - Harkins rule (Taylor and McLennan, 1985). In PS, the (Nd/Er)<sub>PAAS</sub> ratio (as a proxy for LREEs/HREEs) showed negative relationships with salinity in the coastal waters of both sampling periods, with much higher values inside the farm waters (Fig. 5.4). In addition, higher values of (Nd/Er)<sub>PAAS</sub> ratio were observed in the fish-farm influent and rearing waters than those found in coastal waters (Fig. 5.4). These higher values of (Nd/Er)PAAS inside fish-farm waters (especially in the rearing waters) could be due to the preferential release of LREEs during the decomposition of particles and organic matters inside the farm waters. Similarly, high values of (Nd/Er)<sub>PAAS</sub>

ratios were resulted by the decomposition of particulate and organic matters during red tide outbreaks in the coastal areas of Korea (Chen et al., 2022). In addition, good positive correlations between (Nd/Er)<sub>PAAS</sub> ratios and NH<sub>4</sub><sup>+</sup> concentrations were observed in the seawater samples from both sampling periods in PS (Fig. 5.7). These patterns, together with the strong correlation between  $NH_4^+$  and trace element concentrations (Fig. 5.5), indicate that dissolved trace elements were produced inside the farm waters through vigorous regeneration processes (e.g., the decomposition of particles and organic matter), alongside the production of LREEs and NH<sub>4</sub><sup>+</sup> (Kwon et al., 2022) (Fig. 5.8). Unlike that in PS, the (Nd/Er)<sub>PAAS</sub> ratios in SG showed no obvious relationship with either salinity or the concentrations of NH4<sup>+</sup>, further demonstrating that the production procedures inside fish farms can have a major impact on the chemical compositions (i.e., trace elements and  $NH_4^+$ ) in the coastal waters off PS (Fig. 5.4; Fig. 5.7).

However, concerning the lower concentrations of dissolved trace elements in the fish-farm rearing waters in PS, it can be postulated that dissolved trace elements generated in fish farms were partially absorbed onto particle surfaces during discharge operations before being discharged and released into coastal seawater. This deduction can be supported by the relative removal of Ce, since Ce tends to be

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very particle-reactive under oxic conditions (the oxidation of Ce<sup>3+</sup> to Ce (IV)) (de Baar et al., 2018; Moffett, 1990; Sholkovitz, 1995). The removal of Ce relative to other REEs is denoted as the ratio of Ce/Ce\* and is often calculated as

$$Ce/Ce^* = 3 \cdot \frac{Ce_{PAAS}}{2 \times La_{PAAS} + Nd_{PAAS}}$$
(2)

where  $Ce_{PAAS}$ ,  $La_{PAAS}$ , and  $Nd_{PAAS}$  are the PAAS-normalized concentrations of each REE (Sholkovitz, 1995).

During both sampling periods in PS, much lower values of Ce/Ce\* ratio were observed in the fish-farm waters (0.04 to 0.68) compared with those in the coastal seawater (0.05 to 0.91) and FGW (0.12 to 0.91)1.09), indicating a vigorous removal of dissolved Ce to particulate Ce through oxidation and particulate scavenging processes (Fig. 5.7). In light of this, the lower concentrations of dissolved trace elements in the fish-farm waters that were mentioned in the previous section could also be due to from the oxidation and scavenging processes within the farm waters. In addition, the lower Ce/Ce\* values in the innermost stations (P1 - P4) in PS in August further suggest that the lower trace element concentrations at these stations were removed via scavenging processes (Fig. 5.7). These trace elements, which were scavenged onto particles within the farm waters, could be discharged into the seawater through the fish-farm effluent waters and eventually released to a dissolved phase in the water columns, where the concentrations were much lower (Charette et al., 2016; Lenstra et al., 2021) (Fig. 5.8). This is also evidenced by higher Ce/Ce\* values in coastal waters compared with those in the farm waters, indicating the desorption and release of dissolved phase Ce in the coastal seawater (Fig. 5.7; Fig. 5.8). Ce/Ce\* ratios in SG, like that with (Nd/Er)<sub>PAAS</sub>, show no obvious relationship with salinity, with higher values in the bottom waters compared with those in the surface waters. This indicates the release of dissolved Ce from the particulate phase, which further supports our deduction that the trace element distribution in SG could be primarily regulated by benthic inputs (Charette et al., 2016) (Fig. 5.7).



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**Figure 5.6** Plots of  $NH_4^+$  concentrations versus the excess trace element concentrations in Pyosun and Sagye. The innermost stations (P1 to P4) are circled with dashed light pink ovals and excluded from linear regression.



**Figure 5.7** Plots of salinity versus Ce/Ce\* and (Nd/Er)<sub>PAAS</sub> values in Pyosun and Sagye. The hollow pink circles and grey circles indicate the surface seawater and bottom seawater, respectively. The cyan

diamonds and yellow squares indicate the fish-farm influent waters and rearing waters, respectively. The dark red triangles indicate the fresh groundwater in Pyosun.



**Figure 5.8** Schematic overview of the biogeochemical cycles of dissolved trace elements ( $TE_{Diss}$ ), REEs, and  $NH_4^+$  in the land-based fish farm and the coastal waters off the fish farm plant in PS.

### 5.5. Conclusion

This study evaluated the contributions of land-based fish-farm activities on the dissolved trace element (Mn, Fe, Co, Ni, and Cu) distributions in the coastal area of Jeju Island, Korea. Significant excess trace elements were observed in the coastal waters off PS, where land-based fish farms are being operated along the coastline. In addition, regeneration processes inside fish-farm waters were observed with higher NH4<sup>+</sup> concentrations and higher (Nd/Er)PAAS ratios in the fish-farm rearing waters in PS. The concentrations of trace elements in the coastal waters off PS showed strong positive correlations with NH<sub>4</sub><sup>+</sup>, which suggests that these excess dissolved trace elements could be mainly produced in the fish-farm rearing waters, along with the production of  $NH_4^+$  and LREEs. The lower concentrations of trace elements in the rearing waters, on the other hand, suggest that the produced dissolved trace elements were partially scavenged onto particles, as shown by the intensive removal of Ce in the rearing waters. These particulate trace elements were eventually discharged into the coastal ocean through the effluent waters and the dissolved trace elements were released into the coastal water columns. Typical distribution patterns of trace elements were observed in coastal waters off SG, a region with no aquaculture activity. Overall, this study reveals that, although dissolved trace elements in fish farms are commonly considered to be removed onto sinking particles, the influence of fish farm activities on the trace element distributions in the coastal oceans has been largely underestimated. This increase of trace element inventories in coastal waters by fish-farm activities could influence the biological production of the coastal ocean. However, a long-term monitoring study on both coastal waters and fish-farm waters is required to further solidify this conclusion.

## Chapter 6. Summary and conclusion

The behaviors of trace elements and rare earth elements (REEs) in the coastal ocean play essential roles in marine biogeochemical cycles. However, it is challenging to fully understand the cycling and transport of trace elements and REEs in the coastal water columns due to complex biogeochemical processes and various inputs. Thus, additional studies are required to investigate the key processes impacting the biogeochemical cycles of trace elements and REEs in the coastal mixing zone.

In chapter 3, the behaviors of trace elements (Mn, Fe, Ni, Cu, and Zn) and REEs were investigated in Jinhae Bay, the largest semienclosed bay in South Korea. Despite the occurrence of a significant scavenging activity revealed by the REE fractionations and intensive biological removal processes revealed by dissolved inorganic nutrients depletion, dissolved trace elements showed a conservative mixing pattern and significant positive correlations with terrestrial humic dissolved organic matter (DOM<sub>H</sub>). These results led to the hypothesis that when associated with terrestrial DOM<sub>H</sub>, trace elements would survive particle scavenging and biological consumption in the coastal mixing zone. This association processs would enable these particle–reactive trace elements to transport

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conservatively to the open ocean. This study supplements the lack of studies on the shuttling effect of terrestrial trace elements by humic substances in coastal oceans, where trace elements are commonly thought to be intensively removed.

In chapter 4, the influence of different sources of  $DOM_H$ (terrestrial and marine  $DOM_H$ ) on the behaviors of dissolved trace elements (Mn, Fe, Ni, Cu, Zn, and Cd) were examined in two coastal areas of South Korea (Jinhae Bay [JH] and offshore Tongyeong [TY]). Although intensive particle scavenging processes were revealed with rapid removal of <sup>234</sup>Th and Ce in the study areas, dissolved trace elements showed conservative mixing patterns in JH and notable excesses in the red tide patch area in TY. The significant positive correlations between trace element concentrations and DOM<sub>H</sub> indicate that the association of trace elements with DOM<sub>H</sub> would prevent these elements from being removed, hence residing longer time in the water columns. These results show that both terrestrial and marine  $DOM_H$  would associate with dissolved trace elements (Mn, Fe, and Cu) in seawater. Meanwhile, although Ni and Zn also showed association with terrestrial  $DOM_H$  in JH, they were more effectively removed without being stabilized by marine DOM<sub>H</sub> in TY. This reveals that the stabilization of trace elements by different sources of DOM<sub>H</sub> could be variable depending on the

biogeochemical processes.

In chapter 5, the influence of aquaculture activities on the behaviors of trace elements (Mn, Fe, Co, Ni, and Cu) and REEs in coastal waters has been studied. Although dissolved trace elements are mostly known to be removed onto sinking particles inside fish farms and are not commonly considered as main pollutants, this study observed excess dissolved trace elements (Mn, Fe, Co, Ni, and Cu) in the coastal waters off the land-based fish farms. These excess trace elements were found to be produced within the fish-farm rearing waters, alongside the production of ammonia  $(NH_4^+)$  and light-rare earth elements (LREEs). Although intensive particle scavenging processes were revealed with the removal of Ce within the rearing waters, the excess trace elements in the coastal waters indicates that these elements which were scavenged onto particles would eventually be discharged into the coastal ocean and released back into the water columns. These findings reveal that the influence of fish-farm activities on the trace element inventories in coastal oceans has been largely underestimated.

# Bibliography

Alberts J. J. and Filip Z. (1998) Metal binding in estuarine humic and fulvic acids: FTIR analysis of humic acid-metal complexes. *Environmental Technology* **19**, 923-931.

Aluwihare L. I., Repeta D. J. and Chen R. F. (1997) A major biopolymeric component to dissolved organic carbon in surface sea water. *Nature* **387**, 166–169.

Bacon M. P. (1988) Tracers of Chemical Scavenging in the Ocean – Boundary Effects and Large-Scale Chemical Fractionation. *Philos. Trans. R. Soc. A.* **325**, 147–160.

Bacon M. P. and Rutgers van der Loeff M. M. (1989) Removal of thorium– 234 by scavenging in the bottom nepheloid layer of the ocean. *Earth Planet. Sci. Lett.* **92**, 157–164.

Batchelli S., Muller F. L. L., Chang K. C. and Lee C. L. (2010) Evidence for strong but dynamic iron-humic colloidal associations in humic-rich coastal waters. *Environ. Sci. Technol.* **44**, 8485–8490.

Benner R., Pakulski J. D., Mccarthy M., Hedges J. I. and Hatcher P. G. (1992) Bulk Chemical Characteristics of Dissolved Organic-Matter in the Ocean. *Science* **255**, 1561–1564.

Biller D. V. and Bruland K. W. (2012) Analysis of Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in seawater using the Nobias-chelate PA1 resin and magnetic sector inductively coupled plasma mass spectrometry (ICP-MS). *Mar. Chem.* **130**, 12–20.

Black E. E., Buesseler K. O., Pike S. M. and Lam P. J. (2018) 234Th as a tracer of particulate export and remineralization in the southeastern tropical Pacific. *Mar. Chem.* **201**, 35–50.

Black E. E., Lam P. J., Lee J.-M. and Buesseler K. O. (2019) Insights From the 238U-234Th Method Into the Coupling of Biological Export and the Cycling of Cadmium, Cobalt, and Manganese in the Southeast Pacific Ocean. *Global Biogeochem. Cycles* **33**, 15-36.

Boggs Jr S., Livermore D. and Seitz M. G. (1985) Humic substances in natural waters and their complexation with trace metals and radionuclides: a review.[129 references]. Argonne National Lab., IL (USA).

Boiteau R. M., Till C. P., Ruacho A., Bundy R. M., Hawco N. J., McKenna A. M., Barbeau K. A., Bruland K. W., Saito M. A. and Repeta D. J. (2016) Structural Characterization of Natural Nickel and Copper Binding Ligands along the US GEOTRACES Eastern Pacific Zonal Transect. *Front. Mar. Sci.* **3**.

Boyd P. W. and Ellwood M. J. (2010) The biogeochemical cycle of iron in the ocean. *Nat Geosci* **3**, 675-682.

Boyle E., Edmond J. and Sholkovitz E. (1977) The mechanism of iron

removal in estuaries. *Geochim. Cosmochim. Acta* **41**, 1313-1324.

Bruland K., Lohan M. J. T. o. and geochemistry m. (2006) Controls of trace metals in seawater. **6**, 23–47.

Bruland K. W. (1989) Complexation of Zinc by Natural Organic-Ligands in the Central North Pacific. *Limno.l Oceanogr.* **34**, 269-285.

Buck C. S., Aguilar–Islas A., Marsay C., Kadko D. and Landing W. M. (2019) Trace element concentrations, elemental ratios, and enrichment factors observed in aerosol samples collected during the US GEOTRACES eastern Pacific Ocean transect (GP16). *Chem. Geol.* **511**, 212–224.

Buesseler K. O., Bacon M. P., Kirk Cochran J. and Livingston H. D. (1992) Carbon and nitrogen export during the JGOFS North Atlantic Bloom experiment estimated from 234Th: 238U disequilibria. *Deep Sea Res. Part A. Oceanographic Research Papers* **39**, 1115–1137.

Buesseler K. O., Benitez-Nelson C., van der Loeff M. R., Andrews J., Ball L., Crossin G. and Charette M. A. (2001) An intercomparison of small- and large-volume techniques for thorium-234 in seawater. *Mar. Chem.* **74**, 15-28.

Burns K. A., Brunskill G., Brinkman D. and Zagorskis I. (2008) Organic carbon and nutrient fluxes to the coastal zone from the Sepik River outflow. *Cont. Shelf Res.* **28**, 283–301.

Byrne R. H. and Kim K. H. (1990) Rare-Earth Element Scavenging in Seawater. *Geochim. Cosmochim. Acta* **54**, 2645-2656.

Cantrell K. J. and Byrne R. H. (1987) Rare–Earth Element Complexation by Carbonate and Oxalate Ions. *Geochim. Cosmochim. Acta* **51**, 597–605.

Charette M. A., Lam P. J., Lohan M. C., Kwon E. Y., Hatje V., Jeandel C., Shiller A. M., Cutter G. A., Thomas A., Boyd P. W., Homoky W. B., Milne A., Thomas H., Andersson P. S., Porcelli D., Tanaka T., Geibert W., Dehairs F. and Garcia–Orellana J. (2016) Coastal ocean and shelf–sea biogeochemical cycling of trace elements and isotopes: lessons learned from GEOTRACES. *Philos. Trans. R. Soc. A.* **374**.

Charette M. A. and Sholkovitz E. R. (2002) Oxidative precipitation of groundwater-derived ferrous iron in the subterranean estuary of a coastal bay. *Geophys. Res. Lett.* **29**.

Chen X., Kwon H. K., Joung D., Baek C., Park T. G., Son M. and Kim G. (2022) Role of terrestrial versus marine sources of humic dissolved organic matter on the behaviors of trace elements in seawater. *Geochim. Cosmochim. Acta* **333**, 333–346.

Chen X., Seo H., Han H., Seo J., Kim T. and Kim G. (2021) Conservative behavior of terrestrial trace elements associated with humic substances in the coastal ocean. *Geochim. Cosmochim. Acta* **308**, 373–383.

Chevis D. A., Johannesson K. H., Burdige D. J., Cable J. E., Martin J. B. and Roy M. (2015) Rare earth element cycling in a sandy subterranean estuary in Florida, USA. Mar. Chem. 176, 34-50.

Cho C.-H. (1991) Mariculture and eutrophication in Jinhae Bay, Korea. *Mar. Pollut. Bull.* **23**, 275-279.

Church T. M. (2016) Marine Chemistry in the Coastal Environment: Principles, Perspective and Prospectus. *Aquat. Geochem.* **22**, 375-389.

Cochran J. K. and Masque P. (2003) Short-lived U/Th series radionuclides in the ocean: Tracers for scavenging rates, export fluxes and particle dynamics. *Uranium-Series Geochemistry* **52**, 461-492.

Conway T. M. and John S. G. (2014a) The biogeochemical cycling of zinc and zinc isotopes in the North Atlantic Ocean. *Global Biogeochem. Cycles* **28**, 1111-1128.

Conway T. M. and John S. G. (2014b) Quantification of dissolved iron sources to the North Atlantic Ocean. *Nature* **511**, 212-+.

Dai M., Martin J. M. and Cauwet G. (1995) The significant role of colloids in the transport and transformation of organic-carbon and associated tracemetals (Cd, Cu and Ni) in the Rhone delta (France). *Mar. Chem.* **51**, 159– 175.

Dai M. H., Yin Z. Q., Meng F. F., Liu Q. and Cai W. J. (2012) Spatial distribution of riverine DOC inputs to the ocean: an updated global synthesis. *Curr. Opin. Environ. Sustain.* **4**, 170–178.

de Baar H. J. W., Bruland K. W., Schijf J., van Heuven S. M. A. C. and Behrens M. K. (2018) Low cerium among the dissolved rare earth elements in the central North Pacific Ocean. *Geochim. Cosmochim. Acta* **236**, 5–40.

Eastman K. W. and Church T. M. (1984) Behaviour of iron, manganese, phosphate and humic acid during mixing in a Delaware salt marsh creek. *Estuarine, Coastal and Shelf Science* **18**, 447–458.

Elderfield H. (1988) The Oceanic Chemistry of the Rare-Earth Elements. *Philos. Trans. R. Soc. A.* **325**, 105–126.

Ellwood M. J. (2008) Wintertime trace metal (Zn, Cu, Ni, Cd, Pb and Co) and nutrient distributions in the Subantarctic Zone between 40-52 degrees S; 155-160 degrees E. *Mar. Chem.* **112**, 107-117.

Ellwood M. J., Hutchins D. A., Lohan M. C., Milne A., Nasemann P., Nodder S. D., Sander S. G., Strzepek R., Wilhelm S. W. and Boyd P. W. (2015) Iron stable isotopes track pelagic iron cycling during a subtropical phytoplankton bloom. *P Natl Acad Sci USA* **112**, E15–E20.

Ellwood M. J., Nodder S. D., King A. L., Hutchins D. A., Wilhelm S. W. and Boyd P. W. (2014) Pelagic iron cycling during the subtropical spring bloom, east of New Zealand. *Mar. Chem.* **160**, 18–33.

Ellwood M. J., Strzepek R., Chen X. Y., Trull T. W. and Boyd P. W. (2020) Some observations on the biogeochemical cycling of zinc in the Australian sector of the Southern Ocean: a dedication to Keith Hunter. *Mar. Freshw.*  Res. 71, 355-373.

Elrod V. A., Berelson W. M., Coale K. H. and Johnson K. S. (2004) The flux of iron from continental shelf sediments: A missing source for global budgets. *Geophys. Res. Lett.* **31**.

Felix-Bermudez A., Delgadillo-Hinojosa F., Huerta-Diaz M. A., Camacho-Ibar V. and Torres-Delgado E. V. (2017) Atmospheric Inputs of Iron and Manganese to Coastal Waters of the Southern California Current System: Seasonality, Santa Ana Winds, and Biogeochemical Implications. *J Geophys Res-Oceans* **122**, 9230-9254.

Feng H., Cochran J. K. and Hirschberg D. J. (1999) 234Th and 7Be as tracers for the transport and dynamics of suspended particles in a partially mixed estuary. *Geochim. Cosmochim. Acta* **63**, 2487–2505.

Fisher N. S. and Wente M. (1993) The Release of Trace-Elements by Dying Marine-Phytoplankton. *Deep-Sea Res Pt I* **40**, 671-694.

Fitzwater S. E., Johnson K. S., Gordon R. M., Coale K. H. and Smith W. O. (2000) Trace metal concentrations in the Ross Sea and their relationship with nutrients and phytoplankton growth. *Deep-Sea Res Pt Ii* **47**, 3159–3179.

Flegal A. R., Smith G. J., Gill G. A., Sanudowilhelmy S. and Anderson L. C. D. (1991) Dissolved Trace-Element Cycles in the San-Francisco Bay Estuary. *Mar. Chem.* **36**, 329-363.

Fukuzaki K., Imai I., Fukushima K., Ishii K. I., Sawayama S. and Yoshioka T. (2014) Fluorescent characteristics of dissolved organic matter produced by bloom-forming coastal phytoplankton. *J. Plankton Res.* **36**, 685–694.

Gao Q., Li Y., Cheng Q. Y., Yu M. X., Hu B., Wang Z. G. and Yu Z. Q. (2016) Analysis and assessment of the nutrients, biochemical indexes and heavy metals in the Three Gorges Reservoir, China, from 2008 to 2013. *Water Res* **92**, 262–274.

Gledhill M. and Buck K. N. (2012) The organic complexation of iron in the marine environment: a review. *Front. Microbiol.* **3**, 69.

Gunther A. J., Davis J. A. and Phillips D. J. (1987) An Assessment of the Loading of Toxic Contaminants to the San Francisco Bay-Delta: Executive Summary. Aquatic Habitat Institute.

Hathorne E. C., Stichel T., Bruck B. and Frank M. (2015) Rare earth element distribution in the Atlantic sector of the Southern Ocean: The balance between particle scavenging and vertical supply. *Mar. Chem.* **177**, 157–171.

Herbeck L. S., Unger D., Wu Y. and Jennerjahn T. C. (2013) Effluent, nutrient and organic matter export from shrimp and fish ponds causing eutrophication in coastal and back-reef waters of NE Hainan, tropical China. *Cont. Shelf Res.* **57**, 92–104.

Hiraide M. (1992) Heavy-metals complexed with humic substances in fresh-water. *Anal. Sci.* **8**, 453-459.

Hollister A. P., Kerr M., Malki K., Muhlbach E., Robert M., Tilney C. L., Breitbart M., Hubbard K. A. and Buck K. N. (2020) Regeneration of macronutrients and trace metals during phytoplankton decay: An experimental study. *Limno.l Oceanogr.* **65**, 1936–1960.

Hunter K. A. and Boyd P. (1999) Biogeochemistry of trace metals in the ocean. *Mar. Freshw. Res.* **50**, 739-753.

Hwang D. W., Kim G. B., Lee Y. W. and Yang H. S. (2005) Estimating submarine inputs of groundwater and nutrients to a coastal bay using radium isotopes. *Mar. Chem.* **96**, 61–71.

Ilina S. M., Lapitskiy S. A., Alekhin Y. V., Viers J., Benedetti M. and Pokrovsky O. S. (2016a) Speciation, Size Fractionation and Transport of Trace Elements in the Continuum Soil Water - Mire - Humic Lake - River -Large Oligotrophic Lake of a Subarctic Watershed. *Aquat. Geochem.* **22**, 65– 95.

Ilina S. M., Lapitskiy S. A., Alekhin Y. V., Viers J., Benedetti M. and Pokrovsky O. S. (2016b) Speciation, size fractionation and transport of trace tlements in the continuum soil water-mire-humic lake-river-large oligotrophic lake of a subarctic watershed. *Aquat. Geochem.* **22**, 65–95.

Ip C. C. M., Li X. D., Zhang G., Wai O. W. H. and Li Y. S. (2007) Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China. *Environ. Pollut.* **147**, 311–323.

Ip Y. K. and Chew S. F. (2010) Ammonia production, excretion, toxicity, and defense in fish: a review. *Frontiers in physiology* **1**, 134.

Irving H. and Williams R. J. P. (1953) The Stability of Transition-Metal Complexes. *J. Chem. Soc.*, 3192-3210.

Janssen D. J., Sieber M., Ellwood M. J., Conway T. M., Barrett P. M., Chen X., de Souza G. F., Hassler C. S. and Jaccard S. L. (2020) Trace metal and nutrient dynamics across broad biogeochemical gradients in the Indian and Pacific sectors of the Southern Ocean. *Mar. Chem.* **221**, 103773.

Jensen L. T., Morton P., Twining B. S., Heller M. I., Hatta M., Measures C. I., John S., Zhang R., Pinedo-Gonzalez P., Sherrell R. M. and Fitzsimmons J. N. (2020a) A comparison of marine Fe and Mn cycling: U.S. GEOTRACES GN01 Western Arctic case study. *Geochim. Cosmochim. Acta* **288**, 138-160.

Jensen L. T., Wyatt N. J., Landing W. M. and Fitzsimmons J. N. (2020b) Assessment of the stability, sorption, and exchangeability of marine dissolved and colloidal metals. *Mar. Chem.* **220**.

Jeong J., Kim G. and Han S. (2012) Influence of trace element fluxes from submarine groundwater discharge (SGD) on their inventories in coastal waters off volcanic island, Jeju, Korea. *Appl. Geochem.* **27**, 37–43.

Jickells T. D., Baker A. R. and Chance R. (2016) Atmospheric transport of trace elements and nutrients to the oceans. *Philos. Trans. R. Soc. A.* **374**.

John S. G. and Conway T. M. (2014) A role for scavenging in the marine  $% \left( {\left[ {{{\rm{A}}} \right]_{{\rm{A}}}} \right)$ 

biogeochemical cycling of zinc and zinc isotopes. *Earth Planet. Sci. Lett.* **394**, 159–167.

Joung D. and Shiller A. M. (2016) Temporal and spatial variations of dissolved and colloidal trace elements in Louisiana Shelf waters. *Mar. Chem.* **181**, 25–43.

Jung W.-S., Hong S.-J., Lee W.-C., Kim H.-C., Kim J.-h. and Kim D.-M. (2016) Modeling for pollution contribution rate of land based load in Masan Bay. *Journal of the Korean Society of Marine Environment & Safety* **22**, 59–66.

Kadko D., Aguilar-Islas A., Buck C. S., Fitzsimmons J. N., Landing W. M., Shiller A., Till C. P., Bruland K. W., Boyle E. A. and Anderson R. F. (2020) Sources, fluxes and residence times of trace elements measured during the US GEOTRACES East Pacific Zonal Transect. *Mar. Chem.* **222**.

Kalantzi I., Rico A., Mylona K., Pergantis S. A. and Tsapakis M. (2021) Fish farming, metals and antibiotics in the eastern Mediterranean Sea: Is there a threat to sediment wildlife? *Sci. Total Environ.* **764**, 142843.

Kanda A., Ncube F., Mabote R. R., Mudzamiri T., Kunaka K. and Dhliwayo M. (2020) Trace elements in water, sediment and commonly consumed fish from a fish farm (NE Zimbabwe) and risk assessments. *Sn Appl Sci* **2**.

Kim D., Baek S. H., Yoon D. Y., Kim K. H., Jeong J. H., Jang P. G. and Kim Y. O. (2014) Water quality assessment at Jinhae Bay and Gwangyang Bay, South Korea. *Ocean Sci. J.* **49**, 251–264.

Kim D., Choi H. W., Choi S. H., Baek S. H., Kim K. H., Jeong J. H. and Kim Y. O. (2013) Spatial and seasonal variations in the water quality of Jinhae Bay, Korea. *N. Z. J. Mar. Freshw. Res.* **47**, 192–207.

Kim I. and Kim G. (2011) Large fluxes of rare earth elements through submarine groundwater discharge (SGD) from a volcanic island, Jeju, Korea. *Mar. Chem.* **127**, 12–19.

Kim I. and Kim G. (2014) Submarine groundwater discharge as a main source of rare earth elements in coastal waters. *Mar. Chem.* **160**, 11-17.

Kim I. and Kim G. (2015) Role of colloids in the discharge of trace elements and rare earth elements from coastal groundwater to the ocean. *Mar. Chem.* **176**, 126–132.

Kim J., Cho H. M. and Kim G. (2018) Significant production of humic fluorescent dissolved organic matter in the continental shelf waters of the northwestern Pacific Ocean. *Sci. Rep.* **8**.

Kim N. S., Kang H., Kwon M.-S., Jang H.-S. and Kim J. G. (2016) Comparison of seawater exchange rate of small scale inner bays within Jinhae Bay. *J. Korean Soc. Mar. Environ. Energy* **19**, 74-85.

Kim T., Kim H. and Kim G. (2020) Tracing river water versus wastewater sources of trace elements using rare earth elements in the Nakdong River estuarine waters. *Mar. Pollut. Bull.* **160**, 111589.

Koh D. C., Plummer L. N., Solomon D. K., Busenberg E., Kim Y. J. and Chang H. W. (2006) Application of environmental tracers to mixing, evolution, and nitrate contamination of ground water in Jeju Island, Korea. *J Hydrol* **327**, 258–275.

Krachler R., Krachler R. F., Wallner G., Hann S., Laux M., Recalde M. F. C., Jirsa F., Neubauer E., von der Kammer F., Hofmann T. and Keppler B. K. (2015) River-derived humic substances as iron chelators in seawater. *Mar. Chem.* **174**, 85–93.

Kwon H. K., Kim G., Han Y., Seo J., Lim W. A., Park J. W., Park T. G. and Han I. S. (2019) Tracing the sources of nutrients fueling dinoflagellate red tides occurring along the coast of Korea using radium isotopes. *Sci. Rep.* **9**.

Kwon H. K., Kim G., Hwang J., Lim W. A., Park J. W. and Kim T. H. (2018a) Significant and conservative long-range transport of dissolved organic nutrients in the Changjiang diluted water. *Sci. Rep.* **8**.

Kwon H. K., Kim G., Kim T.-H., Park S.-E. and Lee W. C. (2022) Quantification of groundwater versus fish-farm sources of nutrients in the coastal water off Jeju Island, Korea, using fluorescent dissolved organic matter as a tracer. *Journal of Sea Research* **188**, 102270.

Kwon H. K., Kim G., Lim W. A. and Park J. W. (2018b) In-situ production of humic-like fluorescent dissolved organic matter during Cochlodinium polykrikoides blooms. *Estuar. Coast. Shelf Sci.* **203**, 119–126.

Kwon H. K., Kim G., Lim W. A., Park J. W. and Park T. G. (2020a) Conditions of nutrients and dissolved organic matter for the outbreaks of Paralytic Shellfish Poisoning (PSP) in Jinhae Bay, Korea. *Mar. Pollut. Bull.* **158**, 111381.

Kwon H. K., Seo J., Cho H. M. and Kim G. (2020b) Tracing Different Freshwater Sources for Nutrients and Dissolved Organic Matter in Coastal Waters off Jeju Island Using Radon. *Estuar. Coast.* **43**, 487–495.

Lam B., Baer A., Alaee M., Lefebvre B., Moser A., Williams A. and Simpson A. J. (2007) Major structural components in freshwater dissolved organic matter. *Environ. Sci. Technol.* **41**, 8240–8247.

Lee J., Park K.-T., Lim J.-H., Yoon J.-E. and Kim I.-N. (2018) Hypoxia in Korean coastal waters: a case study of the natural Jinhae Bay and artificial Shihwa bay. *Front. Mar. Sci.* **5**.

Lee S. A. and Kim G. (2018) Sources, fluxes, and behaviors of fluorescent dissolved organic matter (FDOM) in the Nakdong River Estuary, Korea. *Biogeosciences* **15**, 1115–1122.

Lee S. A., Kim T. H. and Kim G. (2020a) Tracing terrestrial versus marine sources of dissolved organic carbon in a coastal bay using stable carbon isotopes. *Biogeosciences* **17**, 135–144.

Lee S. A., Lee J., Han Y. J. and Kim G. (2020b) Biogeochemical alteration and fluxes of dissolved organic matter and nutrients in coastal bays. *Estuar.* 

Coast. Shelf Sci. 245.

Lee T., Moon J. H., Jung S. K., Park G., Kwon S., Min S. H. and Son Y. B. (2020c) Changes in the nutrient budget due to physiochemical factors in the coastal area of Jeju, Korea. *J Coastal Res*, 57–61.

Lee Y.-W. and Kim G. (2007) Linking groundwater-borne nutrients and dinoflagellate red-tide outbreaks in the southern sea of Korea using a Ra tracer. *Estuarine, Coastal and Shelf Science* **71**, 309-317.

Lee Y. S. (2006) Factors affecting outbreaks of high-density Cochlodinium polykrikoides red tides in the coastal seawaters around Yeosu and Tongyeong, Korea. *Mar. Pollut. Bull.* **52**, 1249–1259.

Lee Y. W., Hwang D. W., Kim G., Lee W. C. and Oh H. T. (2009) Nutrient inputs from submarine groundwater discharge (SGD) in Masan Bay, an embayment surrounded by heavily industrialized cities, Korea. *Sci. Total Environ.* **407**, 3181-3188.

Lee Y. W., Kim G., Lim W. A. and Hwang D. W. (2010) A relationship between submarine groundwater-borne nutrients traced by Ra isotopes and the intensity of dinoflagellate red-tides occurring in the southern sea of Korea. *Limno.l Oceanogr.* **55**, 1–10.

Lenstra W. K., Hermans M., Séguret M. J. M., Witbaard R., Severmann S., Behrends T. and Slomp C. P. (2021) Coastal hypoxia and eutrophication as key controls on benthic release and water column dynamics of iron and manganese. *Limno.l Oceanogr.* **66**, 807–826.

Lenzi M., Palmieri R. and Porrello S. (2003) Restoration of the eutrophic Orbetello lagoon (Tyrrhenian Sea, Italy): water quality management. *Mar. Pollut. Bull.* **46**, 1540–1548.

Liu S. M., Li R. H., Zhang G. L., Wang D. R., Du J. Z., Herbeck L. S., Zhang J. and Ren J. L. (2011) The impact of anthropogenic: activities on nutrient dynamics in the tropical Wenchanghe and Wenjiaohe Estuary and Lagoon system in East Hainan, China. *Mar. Chem.* **125**, 49–68.

Mantoura R. F. C., Dickson A. and Riley J. P. (1978) The complexation of metals with humic materials in natural waters. *Est. Coast. Mar. Sci.* **6**, 387–408.

Marsan D., Rigaud S. and Church T. (2014) Natural radionuclides 210Po and 210Pb in the Delaware and Chesapeake Estuaries: modeling scavenging rates and residence times. *J. Environ. Radioact.* **138**, 447–455.

Milne A., Landing W., Bizimis M. and Morton P. (2010) Determination of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in seawater using high resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS). *Anal Chim Acta* **665**, 200–207.

Misumi K., Lindsay K., Moore J. K., Doney S. C., Tsumune D. and Yoshida Y. (2013) Humic substances may control dissolved iron distributions in the global ocean: Implications from numerical simulations. *Global Biogeochem.* 

*Cycles* **27**, 450–462.

Mitra S., Sarkar S. K., Raja P., Biswas J. K. and Murugan K. (2018) Dissolved trace elements in Hooghly (Ganges) River Estuary, India: Risk assessment and implications for management. *Mar. Pollut. Bull.* **133**, 402– 414.

Moffett J. W. (1990) Microbially mediated Cerium oxidation in sea water. *Nature* **345**, 421-423.

Moore W. S. (2000) Determining coastal mixing rates using radium isotopes. *Cont. Shelf Res.* **20**, 1993–2007.

Moore W. S. (2010) The Effect of Submarine Groundwater Discharge on the Ocean. *Annu. Rev. Mar. Sci.* **2**, 59–88.

Moran S. B. and Buesseler K. O. (1993) Size-Fractionated Th-234 in Continental-Shelf Waters Off New-England – Implications for the Role of Colloids in Oceanic Trace-Metal Scavenging. *J Mar Res* **51**, 893-922.

Morel F. M. M., Lam P. J. and Saito M. A. (2020) Trace Metal Substitution in Marine Phytoplankton. *Annu Rev Earth Pl Sc* **48**, 491–517.

Morel F. M. M. and Price N. M. (2003) The biogeochemical cycles of trace metals in the oceans. *Science* **300**, 944–947.

Mostofa K. M., Liu C.-q., Feng X., Yoshioka T., Vione D., Pan X. and Wu F. (2013) *Complexation of dissolved organic matter with trace metal ions in natural waters, Photobiogeochemistry of organic matter*. Springer, pp. 769–849.

Neff J. M. (2002) *Chapter 5 – Cadmium in the Ocean*, in: Neff, J.M. (Ed.), *Bioaccumulation in Marine Organisms*. Elsevier, Oxford, pp. 89–102.

Oh Y. H., Kim Y., Park S. R., Lee T., Son Y. B., Park S. E., Lee W. C., Im D. H. and Kim T. H. (2021) Spatiotemporal change in coastal waters caused by land-based fish farm wastewater-borne nutrients: Results from Jeju Island, Korea. *Mar. Pollut. Bull.* **170**.

Olaifa F., Olaifa A., Adelaja A. and Owolabi A. (2004) Heavy metal contamination of Clarias gariepinus from a lake and fish farm in Ibadan, Nigeria. *African Journal of Biomedical Research* **7**.

Oldham V. E., Lamborg C. H. and Hansel C. M. (2020) The Spatial and Temporal Variability of Mn Speciation in the Coastal Northwest Atlantic Ocean. *J Geophys Res-Oceans* **125**.

Oldham V. E., Miller M. T., Jensen L. T. and Luther G. W. (2017a) Revisiting Mn and Fe removal in humic rich estuaries. *Geochim. Cosmochim. Acta* **209**, 267–283.

Oldham V. E., Mucci A., Tebo B. M. and Luther G. W. (2017b) Soluble Mn(III)-L complexes are abundant in oxygenated waters and stabilized by humic ligands. *Geochim. Cosmochim. Acta* **199**, 238-246.

Oldham V. E., Siebecker M. G., Jones M. R., Mucci A., Tebo B. M. and Luther

G. W. (2019) The Speciation and Mobility of Mn and Fe in Estuarine Sediments. *Aquat. Geochem.* **25**, 3–26.

Oliveira K. F., Lacerda L. D., Peres T. F., Marins R. V. and Santos J. A. (2017) The Fate of Cu, Zn and Mn in an Intensive Fish Aquaculture (Tilapia – Oreochromis niloticus) in an Artificial Reservoir in Northeastern Brazil. *Environ Process* **4**, 107–121.

Osman M., Mohamed M., Ali M. and Al-Afify A. (2010) Assessment of agriculture drainage water quality to be used for fish farm irrigation. *Nature and Science*  $\mathbf{8}$ , 60–74.

Pan J. J., Pan J. F. and Wang M. (2014) Trace elements distribution and ecological risk assessment of seawater and sediments from Dingzi Bay, Shandong Peninsula, North China. *Mar. Pollut. Bull.* **89**, 427-434.

Park S., Choi M., Jang D., Joe D. and Park K. (2020) Distribution and sources of dissolved and particulate heavy metals (Mn, Co, Ni, Cu, Zn, Cd, Pb) in Masan Bay, Korea. *Ocean Sci. J.* 

Pavoni E., Crosera M., Petranich E., Faganeli J., Klun K., Oliveri P., Covelli S. and Adami G. (2021) Distribution, Mobility and Fate of Trace Elements in an Estuarine System Under Anthropogenic Pressure: the Case of the Karstic Timavo River (Northern Adriatic Sea, Italy). *Estuar. Coast.* **44**, 1831–1847.

Pedrot M., Dia A., Davranche M., Bouhnik-Le Coz M., Henin O. and Gruau G. (2008) Insights into colloid-mediated trace element release at the soil/water interface. *J. Colloid Interface Sci.* **325**, 187-197.

Raspor B., Nürnberg H., Valenta P. and Branica M. (1984) Studies in seawater and lake water on interactions of trace metals with humic substances isolated from marine and estuarine sediments: II. Voltammetric investigations on trace metal complex formation in the dissolved phase. *Mar. Chem.* **15**, 231–249.

Richir J. and Gobert S. (2016) Trace elements in marine environments: occurrence, threats and monitoring with special focus on the Costal Mediterranean. *Journal of environmental and analytical toxicology* **6**.

Romera-Castillo C., Sarmento H., Alvarez-Salgado X. A., Gasol J. M. and Marrase C. (2010) Production of chromophoric dissolved organic matter by marine phytoplankton. *Limno.l Oceanogr.* **55**, 446–454.

Rose A. L. and Waite T. D. (2003) Kinetics of iron complexation by dissolved natural organic matter in coastal waters. *Mar. Chem.* **84**, 85–103.

Ruacho A., Bundy R. M., Till C. P., Roshan S., Wu J. and Barbeau K. A. (2020) Organic dissolved copper speciation across the U.S. GEOTRACES equatorial Pacific zonal transect GP16. *Mar. Chem.* **225**, 103841.

Salem D. M. S. A., Khaled A., El Nemr A. and El–Sikaily A. (2014) Comprehensive risk assessment of heavy metals in surface sediments along the Egyptian Red Sea coast. *The Egyptian Journal of Aquatic Research* **40**, 349-362.

Sanders C. J., Santos I. R., Maher D. T., Sadat-Noori M., Schnetger B. and Brumsack H. J. (2015) Dissolved iron exports from an estuary surrounded by coastal wetlands: Can small estuaries be a significant source of Fe to the ocean? *Mar. Chem.* **176**, 75–82.

Seo H. and Kim G. (2020) Rare earth elements in the East Sea (Japan Sea): Distributions, behaviors, and applications. *Geochim. Cosmochim. Acta* **286**, 19–28.

Severmann S., McManus J., Berelson W. M. and Hammond D. E. (2010) The continental shelf benthic iron flux and its isotope composition. *Geochim. Cosmochim. Acta* **74**, 3984–4004.

Sholkovitz E. R. (1976) Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. *Geochim. Cosmochim. Acta* **40**, 831–845.

Sholkovitz E. R. (1995) The Aquatic Chemistry of Rare Earth Elements in Rivers and Estuaries. Aquat. Geochem. 1, 1-34.

Sholkovitz E. R. and Copland D. (1981) The coagulation, solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in a river water. *Geochim. Cosmochim. Acta* **45**, 181–189.

Sposito G. (1986) Sorption of trace-metals by humic materials in soils and natural-waters. *CRC Crit. Rev. Environ. Ctrl.* **16**, 193–229.

Strady E., Kim I., Radakovitch O. and Kim G. (2015) Rare earth element distributions and fractionation in plankton from the northwestern Mediterranean Sea. *Chemosphere* **119**, 72–82.

Sunda W. G. (1989) Trace metal interactions with marine phytoplankton. *Biological Oceanography* **6**, 411-442.

Swarzenski P. W., Porcelli D., Andersson P. S. and Smoak J. M. (2003) The behavior of U- and Th-series nuclides in the estuarine environment. *Uranium-Series Geochemistry* **52**, 577–606.

Taniguchi M., Burnett W. C., Cable J. E. and Turner J. V. (2002) Investigation of submarine groundwater discharge. *Hydrol Process* 16, 2115-2129.

Taylor S. R. and McLennan S. M. (1985) The continental crust: its composition and evolution.

Wen L. S., Santschi P., Gill G. and Paternostro C. (1999) Estuarine trace metal distributions in Galveston Bay: importance of colloidal forms in the speciation of the dissolved phase. *Mar. Chem.* **63**, 185–212.

Whitby H., Planquette H., Cassar N., Bucciarelli E., Osburn C. L., Janssen D. J., Cullen J. T., Gonzalez A. G., Volker C. and Sarthou G. (2020) A call for refining the role of humic-like substances in the oceanic iron cycle. *Sci. Rep.* **10**.

Whitby H. and van den Berg C. M. G. (2015) Evidence for copper-binding humic substances in seawater. *Mar. Chem.* **173**, 282-290.

Won J. H., Lee J. Y., Kim J. W. and Koh G. W. (2006) Groundwater occurrence on Jeju Island, korea. *Hydrogeol J* **14**, 532–547.

Worakhunpiset S. (2018) Trace Elements in Marine Sediment and Organisms in the Gulf of Thailand. *Int J Env Res Pub He* **15**.

Wuttig K., Townsend A. T., van der Merwe P., Gault-Ringold M., Holmes T., Schallenberg C., Latour P., Tonnard M., Rijkenberg M. J. A., Lannuzel D. and Bowie A. R. (2019) Critical evaluation of a seaFAST system for the analysis of trace metals in marine samples. *Talanta* **197**, 653–668.

Yoon J. E., Lim J. H., Son S., Youn S. H., Oh H. J., Hwang J. D., Kwon J. I., Kim S. S. and Kim I. N. (2019) Assessment of satellite-based chlorophylla algorithms in eutrophic Korean coastal waters: Jinhae Bay case study. *Front. Mar. Sci.* **6**.

Yunginger R., Bijaksana S., Dahrin D., Zulaikah S., Hafidz A., Kirana K. H., Sudarningsih S., Mariyanto M. and Fajar S. J. (2018) Lithogenic and Anthropogenic Components in Surface Sediments from Lake Limboto as Shown by Magnetic Mineral Characteristics, Trace Metals, and REE Geochemistry. *Geosciences* **8**.

Zheng L. J., Minami T., Konagaya W., Chan C. Y., Tsujisaka M., Takano S., Norisuye K. and Sohrin Y. (2019) Distinct basin-scale-distributions of aluminum, manganese, cobalt, and lead in the North Pacific Ocean. *Geochim. Cosmochim. Acta* **254**, 102-121.

### Abstract (in Korean)

Fe, Ni, Zn와 같은 미량원소는 해양의 식물 플랑크톤의 성장에 있어 필수 미량성분으로서 해양의 일차 생산에 영향을 미친다. 해양의 미량원소 인벤토리는 주로 대기 유입, 해저 확산, 그리고 하천과 해저 지하수를 통한 연안 바다로부터의 경계면 유입량에 의해 조절된다. 본 연구에서는 연안 경계면에서 미량원소와 희토류 원소(REE)의 거동을 알아보기 위해 연안 해수 중 미량원소와 (REE)의 농도를 측정하였다.

미량원소(Mn, Fe, Ni, Cu, and Zn)와 REE의 거동을 파악하고자 비교적 긴 체류시간을 보이는 남해 연안의 내만 지역에서수행 되었다. 무기 영양염은 만 전체에서 담수와 해수의 혼합 곡선에 비해 고갈된 농도 분포를 보였다. 또한, REE의 분획과 Ce의 제거를 통해서 강한 스캐빈징이 일어나는 것을 보였다. 그러나, 미량원소는 염분이 낮은 물에서 더 높은 농도를 보였고 휴믹한 용존 유기물(DOM<sub>H</sub>)과 유의한 양의 상관관계를 보였으며, 이는 연안 혼합 구역에서 미량원소들이 휴믹한 유기물과 결합하여 보존적으로 거동함을 나타낸다. 따라서, 연안 해수 중 다양한 기원의 휴믹한 용존 유기물이 미량원소의 거동에 미치는 영향을 조사하기 위해 국내 두 곳의 연안지역(진해만 및 통영)에서 추가 연구를 수행하였다. 두 지역 모두 입자 반응성 Ce과 방사성 Th-234의 강한 스캐빈징과 침전을 보였다. 하지만, 육상 기원의 DOM<sub>H</sub> 공급이 많은 진해에서 미량원소(Fe, Ni, and Cu)는 염분에 대하여 음의 상관관계를 보였으며, DOM<sub>H</sub>에 대하여 양의 상관관계를 보였다. 이는 육상 기원의 DOM<sub>H</sub>가 미량원소와 강한 결합물을 형성하여 미량원소의 입자에 의한 제거를 억제할 수 있음을 나타낸다. 해양 생물 생산에 의한 DOM<sub>H</sub> 공급이 많은 통영에서도 진해와 유사한 결과를 보였으며, 이러한 결과는 연안에서 육상과 해양 기원의 DOM<sub>H</sub>과 연관된 용존 미량원소는 안정화된 용존 상태로 존재함을 나타낸다. 연안에서 DOM<sub>H</sub>와 미량원소의 결합물은 해양 내 미량원소의 순환과 수송을 조절하는 데 주요한 역할을 할 수 있다.

최근 수십 년 동안, 양식 활동이 증가하면서 해양으로 방출되는 오염원은 연안 환경에 큰 영향을 미치고 있다. 본 연구는 제주도 연안에서 양식 활동이 미량원소 인벤토리에 미치는 영향을 파악하고자 하였으며, 연안과 양식장의 생성 및 제거 기작을 이해하기 위해 NH4<sup>+</sup>와 REE 농도를 측정하였다. 연안에서 상대적으로 높은 미량원소의 농도 분포를 보였으며, NH4<sup>+</sup>에 대하여 유의미한 상관관계를 보였다. 이는 연안에서의 과잉 용존 미량원소가 NH4<sup>+</sup>와 가벼운 REE와 함께 양식장 내부에서 생성될 수 있음을 시사한다. 양식장 내에서 입자 반응성이 있는 Ce의 제거되는 것을 통해 용존 미량워소가 입자에 의해 부분적으로 스캐비징 되는 것으로 나타났지만, 결국에는 이 입자들이 연안으로 방출되기에, 미량원소가 용존 형태로 다시 수층으로 유입될 것이다. 따라서 본 연구결과, 비록 양식장의 용존 미량원소 들이 침강 입자에 의해서 제거되는 것으로 간주되지만, 양식 활동이 연안의 미량원소의 분포에 미치는 영향은 크게 과소평가 된 것으로 보여진다.

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