論文の内容の要旨

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論文題目　Dynamics of trace metal biogeochemistry in the estuary and open ocean: Studies from Ariake Sea, Bay of Bengal and Eastern Indian Ocean
(有明海、ベンガル湾、東部インド洋における微量金属元素の生物地球化学ダイナミクス)

In marine environments, trace metals are involved in many enzymatic reactions, which showed either synergetic or antagonistic interactions. Therefore, trace metals in seawater play vital roles for growth of marine microorganisms. In addition, trace metals are also proxies for oceanic processes including water mass movement and anthropogenic disturbance into the marine environment. Trace metals like dissolved iron, manganese, cadmium, cobalt, copper, and zinc (hereafter refer to as dFe, dMn, dCd, dCo, dCu, and dZn, respectively) are known as essential micronutrients for growth of marine phytoplankton. In addition dissolved lead (dPb) is an excellent tracer for anthropogenic perturbance to the marine environments. Distributions of trace metals are controlled by complex biogeochemical processes such as their sources, interaction with particles, and removal processes. This thesis aims to reveal trace metal distributions in different marine environments and elucidate the factors that govern their distributions. I studied trace metal biogeochemistry in three different marine environments including Ariake Sea, eastern Indian Ocean, and Bay of Bengal.

In Chapter III, I studied trace metal biogeochemistry in Ariake Sea. Ariake Sea is a shallow (20 m on average) semi-enclosed bay that covers roughly 1.700 square kilometers of area located near Kyushu Island, Japan. A narrow strait (approximately 6.5 km) located in the southwest of the bay, restricts the water mass exchange between this bay and the East China Sea (ECS). The rivers surrounding Ariake Sea transported large amounts of trace metals and macronutrients from the Kyushu Island into the marine ecosystem. A simple mixing diagram between two end-members was used to study the biogeochemical dynamics of trace metals in seawater. In the simple mixing diagrams, all trace metals behaved differently during estuarine mixing. Non-conservative patterns were observed for dFe, dMn, and dCu. Their distributions were not simply controlled by physical mixing between rivers and ECS waters. On the other hand, dCo exhibited a conservative pattern.

The deviations of trace metal concentrations relative to the mixing line suggested either removal or addition during the estuarine mixing. Removal was pronounced for dFe and dMn due to the internal processes in the water column. Moreover, the well-oxygenated condition during the sampling period promoted the formation of particulate Fe and Mn oxyhydroxides and their deposition onto the surface sediment. Contrary to dFe and dMn, an upward deviation was observed relative to the mixing line for dCu. The internal estimated flux (I_E) of dCu (1.6 x 10^{13} nmol/month) was slightly larger than the estimated fluvial flux (1.1 x 10^{13} nmol/kg). This indicates the internal input of dCu within the embayment system was responsible for the upward curvature of dCu relative to the mixing line. To elucidate the additional source of dCu unrelated to the fluvial discharge, I estimated the dCu fluxes from several possible sources including groundwater discharge, atmospheric deposition, photodissolution of resuspended sediment, and benthic input from sediment. Based on my estimation, sediment possibly serves as an important source of dCu considering its estimated flux was at the same order with the I_E. The estimated dCu flux from sediment was ranged from 2.1 x 10^{11} – 1.8 x10^{13} nmol/kg. At the high end, the sediment flux may be overestimated given that they were calculated from the highest sedimentary phosphate flux that occurred in August. In comparison, other sources contributed lower dCu fluxes and can be neglected.

Previous studies have indicated a similar behavior between dCu and dCo in estuarine and coastal waters. Both metals can also complex with organic ligands which hider their removals from the water column. However, in Ariake Sea, they behaved differently. While dCu exhibited a non-conservative pattern, dCo behaved conservatively during the mixing between river water and marginal seawater. Therefore, I contrasted those metals to gain insight into the dCo behavior. Assuming that sediment also supplied dCo, I estimated dCo flux from sediment similarly to dCu. DCo flux was calculated as 1.1 x 10^{10} – 1.6 x 10^{12} nmol/month. The highest possible benthic flux was one magnitude higher than the riverine flux (7.9 x 10^{11} nmol/month), which is not case for dCo in Ariake Sea. The conservative pattern of dCo, therefore, suggests that different processes may be controlling the distributions of these metals. Different pathways of remobilization from marine sediment were due to the different carrier phases. In Ariake Sea, Co in surface sediment correlated with Mn and Fe while Cu did not. This suggests that Co binds tightly with Fe/Mn oxyhydroxide in surface sediment, while organic phase is the main carrier of Cu. During early diagenesis of sediment, both dCu and dCo may release from biogenic particles but only Co was incorporated in the Fe/Mn oxyhydroxide and removed from the water column. The conservative behavior of dCo thus reflected the balance between input and removal from the sediments.

In Chapter IV, I revealed distributions of trace metals in the eastern Indian Ocean. The samples were collected during R/V Hakuho Maru KH-18-6 cruise crossing the transect from Bay of Bengal (16.5ºN) to South Indian Ocean (20ºS). The eastern Indian Ocean lies in the third largest oceanic region but remained under-sampled, particularly for trace metal studies. Therefore, increasing the basin-scale trace metal dataset obviously will enhance the understanding of trace metal sources, sink, and internal cycling. Previous studies highlighted the gradients of physical and chemical properties in the eastern Indian Ocean. In the northern part, the surface ocean is strongly affected by monsoonal winds. Those monsoonal winds that flow in the reverse direction through the year bring aerosols from different sources to the Bay of Bengal. In addition, at the surface of Bay of Bengal, low salinity waters occupied due to the riverine input from the surrounding rivers. In the equator, a current reverses the direction flowing eastward during transition between two monsoons. Further to the south, the westward flowing South Equatorial Current (SEC) near 15ºS carries fresh water from the Pacific through Indonesian Archipelago, which is called as Indonesian Throughflow (ITF) across the upper 300 m of the eastern Indian Ocean. Thus it is an area with a variable dynamic current system over the annual cycle.

My data indicated that the river waters transported large amounts of trace metals including dFe, dMn, dPb, dCd, dCu, and dZn into the surface layers of northern Bay of Bengal. Moreover, across the transect, a macronutrient, dissolved inorganic nitrogen (DIN), was consistently below the detection limit, while dFe concentrations were higher than 0.01 nmol/kg. DFe fluxes by vertical diffusion (12.1 – 138 nmol/m^2/day) and atmospheric deposition (27 – 274 nmol/m^2/day) were hypothesized as the vital sources of dFe to the surface mixed layer. An adequate supply of dFe from those sources lead to the higher dFeflux/dNflux (0.01 – 0.1 nmol/µmol) relative to the Fe/N demand in phytoplankton of 0.02 – 0.04 nmol/µmol, and was further responsible for the repleted iron condition across the transect.

Below the surface mixed layer, a unique feature of the eastern Indian Ocean was a gradient of dissolved oxygen condition in the thermocline, extending from Bay of Bengal to the southern-end station. In the thermocline, all trace metals except dPb and dMn were correlated with phosphate, suggesting that the same regeneration process regulated their cycles. However, additional input unrelated to the remineralization and particle scavenging led to the decoupling of dFe, dMn, and dCu with phosphate. The dFe data in the thermocline indicated elevated concentrations associated with the oxygen minimum zone (OMZ). I used an index called as Fe* to evaluate the contribution of external sources into the dFe pool along the transect. The positive values of Fe* in the Bay of Bengal thermocline revealed that other than remineralization processes supplied dFe into the water column. Since other trace metals were not enriched in the oxygen minimum zone, the high Fe* was caused by the release of dFe from the continental shelf at oxic conditions.

The thermocline of Bay of Bengal was occupied by the North Indian Central Water (NICW) that is characterized by the dissolved oxygen-deficiency. Unlike dFe that showed elevation in NICW, distributions of other metals were not affected by the extreme DO condition in NICW. However, dCd to phosphate ratio in NICW showed deviations from the global trend. This indicates that low dissolved oxygen concentrations in Bay of Bengal may alter the biogeochemical processes of dCd and phosphate in the water column. In the deep water, dCd, dCu, and dZn concentrations showed gradual increases with the depth due to the remineralization and continued supply from bottom sediment. Contrary, scavenging of dFe, dMn, and dPb was likely the important sink of those metals in the deep water. However, dFe and dMn showed high concentrations in coastal bottom waters where Fe* also showed positive values, indicating the supply of those metals from external sources.

In Chapter V, I focused on the Bay of Bengal. The spatial and temporal variations of trace metal distributions in the Bay of Bengal were studied previously, to a certain extent. However, among those previous studies, the report of trace metal biogeochemical processes during southwest monsoon was limited only at two stations in the central part of the Bay of Bengal. Therefore, the available data during southwest monsoon are still limited. In addition, all previous studies also highlighted the high dFe concentrations associated with OMZ in the thermocline. However, the source of dFe remained unclear. This study succeeded in obtaining new data of trace metals including dFe, dMn, dPb, dCd, dCu, and dZn during southwest monsoon and provided insight on the role of continental margin as sources of trace metals particularly dFe and dMn.

In surface waters, a high concentration of dFe up to 1.35 nmol/kg was found in the station BA-5 located close to the coast. Lateral input from coastal area might enrich dFe at that station. Pronounced elevation of dFe and dMn up to 13.4 and 22 nmol/kg were observed at 200 m depth in station MY-11 characterized by the OMZ. Judging from the location of station MY-11 at the edge of continental margin, input from the marginal sediment might be responsible for supplying dFe and dMn into the water column. Intermediate water movements might also affect dFe distributions at stations MY-9 and MY-7. Furthermore, exploring the relationship between trace metals and micronutrients in Bay of Bengal provided insight into the role of local processes in shaping the trace metal distributions. For instance, continuous supply from the margin and bottom sediment, as well as reverse scavenging processes, might increase dCu concentsrations in the water column and cause the higher dCu to phosphate ratios in NICW and IDW compared to those obtained in the eastern Indian Ocean. In addition, in NICW, the deviation of dCd and phosphate ratio from the global trend was consistently observed. Moreover, dPb concentrations (up to 120 pmol/kg) observed in surface waters of Bay of Bengal was the highest reported elsewhere. These new dPb data collected during this study are important to gain better understanding on the impact of anthropogenic Pb to the global-scale environment because (i) profoundly limited data of dPb in the eastern Indian Ocean, (ii) limited environmental regulation, and (iii) large-scale economic development and later phase out of leaded gasoline resulted in very high fluxes of Pb from the southern Asia and Oceania into the Indian Ocean.

In summary, complex processes governed trace metal distributions in those three different marine environments. In all study areas, rivers played a vital role in transporting trace metals into marine environments. While atmospheric input was negligible in Ariake Sea, the atmospheric deposition (together with vertical diffusion) was responsible for supplying dFe in the surface mixed layer of the eastern Indian Ocean and provided an adequate supply for the phytoplankton growth. The sediment also served as sources of trace metals particularly for dCu, dFe, and dMn.