Variability of trace metal distributions (Cd, Pb, Mn, Cu and Zn) and their biogeochemical cycles in the East China Sea and coastal areas, Japan

Sep.2017 Marine Biogeochemical Cycles 47156785 Ronald Muhammad

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Keyword: trace metals, East China Sea, Ariake Sea, Tachibana Bay, Otsuchi Bay, hydrothermal vent,

I. Introduction

It has been widely known that trace elements and their isotopes (TEIs) are important to understand the marine ecosystem. In seawater at low concentrations, some trace metals like cadmium (Cd), manganese (Mn), copper (Cu) and zinc (Zn) can act as micronutrients for phytoplankton growth (Morel et al., 2004). However, at high concentrations, some metals can be toxic and harmful for microorganism (Viarengo, 1985; Magdeleno et al., 1997; Hodson, 1988). Their vertical profiles, such as nutrient type profiles for Cd, Cu and Zn, are indicative of biologically related processes (Boyle and Edmond, 1975; Boyle, 1988). Copper is an important cofactor in the last step of denitrification process (Granger and Ward, 2003); Cd and Zn can replace each other as a metal center in carbonic anhydrate that catalyzes inorganic carbon acquisition in respiration process for diatoms (Morel et al., 2004). Meanwhile, according to Bruland and Lohan (2003), Mn at high latitudes can be considered as a hybrid-type metal, whose distribution is controlled by both biological uptake and scavenging processes. Mn can substitute for iron in superoxide dismutase (SOD) in diatom (Morel et al., 2004). Lead (Pb), widely known as a toxic element, has a scavenged-type profile (Flegal and Patterson, 1983), and could act as a tracer for atmospheric derived contaminant in the ocean.

It is important to reveal the distribution of those elements (Cd, Pb, Mn, Cu & Zn) in seawater and their biogeochemical cycles to enhance our understanding of their bioaccumulation and sources. In particular, at coastal region such as Ariake Sea, Tachibana Bay and Otsuchi Bay as well as marginal sea such as East China Sea, anthropogenic effect might affect the distributions of these metals. Here, I will reveal their distributions and their internal biogeochemical cycling.

II. Sampling and methods

Acid-cleaned Teflon-coated Niskin-X samplers, mounted on conductivity-temperature-depth carousel multi-sampling system (CTD-CMS) attached to Vectran armored cable wire, were used to collect the seawater samples in the East China Sea (KH-15-3). In Ariake Sea and Tachibana Bay, acid-cleaned Teflon-coated X-type Niskin samplers, mounted on conductivity-temperature-depth carousel multi-sampling system (CTD-CMS), were used to collect the seawater samples. Acid-cleaned Niskin-X sampler, triggered by a stainless-steel messenger, was used to collect the seawater samples in the Otsuchi Bay. Seawater was filtered through 0.2 μm filter (Acropak) into acid-cleaned 500 mL of LDPE bottles onboard the ship. Samples were acidified to pH less than 1.8 using ultrapure HCl (Tamapure AA-100, Tama Chemicals), and stored at room temperature.

Samples used for total dissolved trace metals analysis were placed under UV radiation for 60 minutes to destroy all organic ligands prior to analysis. A resin column was made by packing 0.6 grams of chelating resin into a column. Before introducing the sample, the column should be washed by 15 ml of 2 M HNO_3 two times followed by 15 ml of MQW, and 15 ml of acetic buffer at pH 6. 30 ml of seawater at pH 2 was adjusted to pH 6.2-6.3 with acetic acid and ammonium acetate buffer. Hereafter, the sample was introduced to the column by peristaltic pump. Immediately after all the samples were passed through the column, the column was washed by acetic buffer in order to remove the sea-salt remaining in the column. In the final step, the metals of interest that were bonded in column were eluted by using 5 ml of 2 M HNO_3 introduced into the column using Teflon syringe from the opposite direction. All the conditioning steps and sample loading were performed at a flow rate of 2 ml/min, and the elution rate was about 1 ml/min. The concentration factor of the sample was about 6 times. Concentrations of Cd, Mn, Pb, Cu and Zn were determined using a high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS).

III. Results and discussion

In the East China Sea, the higest concentration of total dissolved Cu was found at the surface (10 m) in AND-26, where [Cu] = 2.6 nM. Salinity of surface water at this station was relatively low when compared to those of other stations, and this can be attributed to the freshwater discharge from Yangtze River, which is likely a major source of copper into the East China Sea (Koshikawa et al., 2007; Abe et al., 2003). Vertical profiles of Cu, Zn, and Cd, were nutrient-type. Meanwhile, Pb and Mn showed scavenging-type profile in these areas. High concentrations of Mn were found at the bottom layer of AND-31. Mn concentrations increased from 1.4 nM to 3.6 nM at the bottom layer. This could be caused by remineralization at bottom sediment (Minakawa et al., 1996).

In Tachibana Bay, station T1 which is located near the hot spring area, showed slight decrease of total dissolved metal concentrations (0.23nM to 0.13nM for Cd; 0.061nM to 0.039nM for Pb; 2.7nM to 2.1nM for Cu and 7.3nM to 5.8nM for Zn). This result could be attributed to the presence of hydrothermal activities in this area because of sulfide formation and precipitations (Edmond et al., 1982; Godfrey et al., 1994; James and Elderfield, 1996; Trocine and Trofrey, 1988).

Negative correlation between salinity and Cu was found (R^2=0.86) in Ariake Sea, suggesting the most important sources of Cu was freshwater discharge. High concentrations of Cu were also observed in the rivers of Otsuchi Bay, ranging from 3.5 nM to 6.2 nM, suggesting riverine sources of Cu in this bay. Concentrations of Pb Otsuchi Bay were higher concentrations (~0.102 nM) compared to those Ariake Sea (~0.048 nM). These high Pb concentrations were found in bottom waters probably derived from sediments transported from terrestrial area after the huge tsunami in 2011. Meanwhile, the trace elements could be controlled the some factors, such as scavenging process, water residence time, atmospheric deposition and the water circulation.

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東シナ海及び日本沿岸域における微量金属元素 (Cd, Pb, Mn, Cu, Zn)の分布の変動とその生物地球化学的物質循環

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I. はじめに

海水中の微量金属元素は海洋生態系を理解する上で重要である。例えば、海水中のカドミウム (Cd)、マンガン (Mn)、銅 (Cu)、亜鉛 (Zn)といった微量金属元素は植物プランクトンの成長にとって不可欠な元素である (Morel et al., 2004)。一方、海水中の濃度が高くなっていくと、ある金属が微生物にとって有害となる金属元素もある (Viarengo, 1985; Magdeleno et al., 1997; Hudson et al., 1988)。カドミウム、銅と亜鉛は栄養塩型の鉛直分布を示し、その循環過程は、生物活動と密接に関わっていると考えられる (Boyle & Edmond, 1975; Boyle, 1988)。銅は海水中の脱窒反応の重要な補因子(cofactor)と考えられる (Granger & Ward, 2003)。カドミウムと亜鉛は珪素細胞内の炭酸脱水酵素中で重要な役割を負っている (Morel et al., 2004)。高緯度海域においては、マンガンはハイブリッド型の鉛直分布を示し、その分布は生物の活動と粒子による除去プロセスにより大きな影響を受けている(Bruland &Lohan, 2003)。また、マンガンは superoxide dismutase 中の鉄と置き換わっている可能性も指摘されている (Morel et al., 2004)。有毒な元素とよく知られている鉛は、除去型を示し、大気経由で海洋に輸送される物質のトレーサーとして広く使われている (Flegal & Patterson, 1983)。上記の元素の海水中の分布を調べ、その物質循環を理解することはこれらの元素の海洋生態系への関わりや海洋への供給源を解明するために非常に重要である。特に、沿岸地域では、人為的に放出されたこれらの元素がどのような挙動を示すかを明らかにする必要がある。本研究では日本の沿岸域である有明海、橘湾、大槌湾における海水中の微量金属元素の分布を調べ、その循環過程を研究した。また、人為的な影響を受けやすい縁辺海である東シナ海においても海水中の 微量金属元素の分布と循環の解明を目的した。

II. 試料採取と分析法

東シナ海での海水サンプルの採取は、白鳳丸 KH-15-3 次研究航海において 、テフロンでコーティングされ、洗浄された Niskin-X 採水器を使用して行った。Niskin-X 採水器は、Vectran ケーブルに接続した CTD カロセル多層採取装置(CTD-CMS)に搭載され、採水に用いられた。有明海と橘湾では、2015 年の長崎大学水産学部鶴洋丸航海において CTD-CMS に搭載した Nishkin-X 採水器を使用して海水を採取した。大槌湾では、東京大学大気海洋研究所国際沿岸研究センターの調査船弥生により テフロンでコーティングされ、洗浄された Nishkin-X 採水器により海水を採取した。採取した海水は船上で 0.2 μm のフィルターをろ過し、酸洗浄した 500 mL の低密度ポリエチレン瓶に採集した。その後、サンプルは超高純度塩酸 (Tamapure AA-100, Tama Chemicals) を使って pH 1.8 に調整し、室温で保存した。全溶存態金属分析用のサンプルは分析前に 60 分間紫外線を照射した。前濃縮用のカラムは 0.6 g のキレート樹脂をカラムに充填し作成した。カラムに導入する前にカラムは 15 mL の 2M HNO_3 二回、 15 mL の超純水(MQW)、15 mL の酢酸緩衝溶液 (pH 6)で洗浄した。海水は酢酸と酢酸アンモニウム溶液により、pH 6.2 – 6.3 に調整した。その後、サンプルはペリスタポンプでカラムに導入した後、酢酸緩衝溶液によって、カラムで捕集された金属元素は 2M HNO_3 で溶離し、採集した。サンプル導入及びカラム洗浄は流速 2

mL/min で行われ、カラムからの溶離は 1 mL/min で行った。最終に海水中の金属は六倍に濃縮し、高分解能 ICP 質量分析計で測定した。

III. 結果

東シナ海では、全溶存態銅の濃度は低塩分の海水中では 2.6 nM であり、最も高い値となった揚子江からの河川水の流入により高濃度になったと考えられる(Koshikawa et al., 2007; Abe et al., 2003)。海水中の銅、亜鉛、カドミウムの鉛直分布は栄養塩型を示した。一方、鉛とマンガンは除去型の分布を示した。全溶存態マンガンは大陸棚上の深層水では濃度が 1.4 nM から 3.6 nM までに上昇した。海底堆積物から供給による濃度の上昇と考えられる (Minakawa et al., 1996)。

橘湾では、熱水活動が観測されている観測点において、全溶存態の金属の濃度が減少する傾向が見られた (Cd: 0.23 nM - 0.13 nM; Pb: 0.061 nM – 0.039 nM; Cu: 2.7 nM – 2.1 nM; Zn: 7.3 nM – 5.8 nM)。これは熱水活動に伴って放出された硫化物により金属が海水中から除去されたためと考えられる (Edmond et al., 1982; Godfrey et al., 1994; James & Elderfield, 1996)。

有明海と大槌湾では、銅は河川水の流入により海水中の濃度が上昇した。大槌湾内への流入河川中でも高濃度の銅が検出されている (3.5 nM – 6.2 nM)。鉛については、有明海 (0.048 nM)より大槌湾 (0.102 nM) のほうが高濃度であった。陸上に存在していた鉛が 2011 年の津波により大槌湾内に輸送され、堆積物から溶出されている可能性が考えられる。

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