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# Transport of trace metals (Mn, Fe, Ni, Zn and Cd) in the western Arctic Ocean (Chukchi Sea and Canada Basin) in late summer 2012

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## ABSTRACT

Distributions of trace metals (Mn, Fe, Ni, Zn and Cd) in the western Arctic Ocean (Chukchi Sea and Canada Basin) in September 2012 were investigated to elucidate the mechanisms behind the transport of these metals from the Chukchi Shelf to the Canada Basin. Filtered ($<0.22\ \mu$m) and unfiltered seawater samples were analyzed to determine dissolved (D) and total dissolvable (TD) trace metal concentrations, respectively. We identified maxima in vertical profiles for the concentrations of D-Fe and TD-Fe, as well as for the other four analyzed trace metals, which occurred in the halocline and/or near-bottom waters. Concentration profiles of all trace metals except for Cd also tended to show peaks near the surface, which suggest that the inflow of low-salinity Pacific-origin water from the Bering Strait, as well as local fresh water inputs such as river water and melting sea-ice, influenced trace metal concentrations. The distribution patterns and concentration ranges were generally similar between the D and TD fractions for Ni, Zn and Cd, which indicate that Ni, Zn and Cd were present mainly in their dissolved forms, whereas the concentrations of TD-Fe and TD-Mn were generally higher than those of D-Fe and D-Mn, respectively. These results are consistent with the results of previous studies of this region. For both Fe and Mn, labile particulate (LP) concentrations (the difference between the TD and D fractions, which is acid-leachable fraction in the particles during storage at pH 1.5–1.6) were highest in the near-bottom waters of the Chukchi Shelf region. The relationships between the distance from the shelf break and the concentrations of trace metals revealed that Fe and Mn concentrations in halocline waters tended to decrease logarithmically with distance, whereas changes in the concentrations of Ni, Zn, Cd and phosphate with distance were small. These results suggest that the distributions of Fe and Mn were controlled mainly by input from shelf sediment and removal through scavenging processes. Based on the phase distributions of Fe and Mn, which were calculated as ratios between the LP and D fractions, different behaviors between Fe and Mn were expressed during lateral transportation. The concentration of TD-Fe declined rapidly via removal of LP-Fe from the water column, whereas the concentration of TD-Mn declined more slowly through the transformation of D-Mn into LP-Mn. In contrast, the concentrations of D-Cd, D-Zn and D-Ni were more strongly correlated with phosphate levels, which suggest that, like phosphate, the distributions of Cd, Zn and Ni were generally controlled by the internal biogeochemical cycles of the ocean interior. Based on the findings of studies that have previously evaluated the concentration maxima of Ni, Zn and Cd within the halocline layer in the Canada Basin near the Canadian Arctic Archipelago, the elevated Ni, Zn and Cd concentrations in the halocline layer may extend across the Canada Basin from the Chukchi Sea shelf-break area. The determination coefficients for correlations with phosphate concentration varied between the concentrations of Ni, Zn and Cd, which suggest that the sources of these trace metals, such as sediments and sea-ice melting, affected their patterns of distributions differently. Our findings reveal the importance and impact of the halocline layer for the transport of trace metals in the western Arctic Ocean during the late summer. The existence of rich and various sources likely sustained the high concentrations of trace metals and their unique profiles in this region.

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## 1. Introduction

Although the Arctic Ocean constitutes only about 3% of the world's oceans by area, it includes approximately 20% of the world's continental shelf area (Chang and Devol, 2009). The Chukchi Sea, located in the western Arctic Ocean, is a highly productive region during times of ice-edge retreat (Hill and Cota, 2005). Physical, chemical and biological characteristics of the Chukchi Sea are strongly influenced by currents that flow northward through the Bering Strait (Springer and McRoy, 1993). The mean annual transport through the Bering Strait into the Chukchi Sea is about 0.8 Sv, which has strong seasonal variability between a summer maximum and a winter minimum, and supports the high productivity of this region through the transport of nutrients (Coachman and Aagaard, 1988). It has been reported that a large fraction of the organic matter that forms in surface waters in the shelf areas of the Chukchi Sea sinks to the seafloor, which fuels productive benthic communities and causes high rates of sedimentary denitrification (Chang and Devol, 2009; Brown et al., 2015). The Pacific-origin water from the Bering Strait is already depleted in nitrate ($NO_3-$) relative to phosphate ($PO_4^{3-}$), and $NO_3^-$ is further depleted relative to $PO_4^{3-}$ in the Chukchi Sea via the effect of sedimentary denitrification (Yamamoto-Kawai et al., 2006). A unique feature of the upper surface water in the western Arctic Ocean is the dominance of a strong, cold halocline that separates the Pacific-origin surface waters from the underlying Atlantic-origin waters (Aagaard et al., 1981). Cold and dense brine is produced in the fall and winter as sea ice forms, and the halocline is maintained by large-scale lateral advection from the adjoining continental shelves (Aagaard et al., 1981; Jones and Anderson, 1986). The water of this halocline is therefore associated with prominent maxima of nutrients and dissolved organic matter (Anderson et al., 2013). In the Canada Basin, mixtures of Pacific-origin and Atlantic-origin waters are only found below the nutrient maxima (Yamamoto-Kawai et al., 2008). Pacific-origin water that enters through the Bering Strait can be highly modified throughout transport on the shelves by runoff, interaction between sediment and near-bottom water, and sea-ice formation (Cooper et al., 1997). The Canada Basin is separated from the Makarov Basin by the Mendeleev–Alpha Ridge with a sill depth of $\sim$2000 m, and is fairly isolated from ventilation by the dense shelf waters of the Makarov, Barents, Kara and Laptev seas (Swift et al., 1997). In the Canada Basin, freshening of surface seawater began in the 1990s and has been attributed to increased river runoff and sea ice melting (Morison et al. (2012) and references therein).

Trace metals such as iron (Fe), manganese (Mn), nickel (Ni), zinc (Zn) and cadmium (Cd) are involved in numerous processes in the metabolisms of phytoplankton and can be toxic at high concentration (Twining and Baines, 2013 and references therein). Iron is required for many processes including photosynthesis, chlorophyll synthesis and nitrogen metabolic pathways such as nitrogen fixation and $NO_3^-$ and nitrite ($NO_2^-$) reduction. It is well established that Fe often limits phytoplankton growth in environments where subsurface nutrients are replete, which include high-nutrient, low-chlorophyll areas such as the upwelling regions of the Southern Ocean and the eastern equatorial Pacific (e.g., Moore et al., 2013). Zinc also plays a role in many metalloproteins such as alkaline phosphatase, carbonic anhydrase and the Zn form of superoxide dismutase (Zn-SOD). Cadmium is also known to be a cofactor in carbonic anhydrase, and can substitute for Zn in diatom growth pathways (Lane and Morel, 2000); it has been suggested that phytoplankton mistakenly import Cd through a non-specific divalent metal transporter in this process (Horner et al., 2013). Sunda and Huntsman (2000) demonstrated that Cd drawdown was accelerated under Fe-limited conditions. Nickel is associated primarily with urease and the Ni form of superoxide dismutase (Ni-SOD) (Dupont et al., 2008a, 2008b). Manganese is an essential trace metal for phytoplankton growth because it is prominently involved in the oxygen-evolving complex of photosystem II and the Mn form of superoxide dismutase (Mn-SOD) (Wolfe-Simon et al., 2005). However, limitation of Mn for phytoplankton growth has not yet been observed in the ocean.

In the open ocean, vertical distributions of Ni, Zn and Cd in dissolved fractions ($<0.2$–$0.4\ \mu$m) are generally characterized by surface minima, rapid increases to maximum concentrations in the thermocline, and then relatively constant concentrations in deep water, similar to the distribution patterns of nutrients (e.g., Bruland et al., 1991). However, the vertical distributions of dissolved Mn and Fe differ from those of the above “nutrient-type” trace metals. Maximum Mn occurs in the surface water and decreases with depth, which is why Mn is called a “scavenging-type” trace metal (e.g., Bruland et al., 1991). Vertical profiles of Fe are often reported as nutrient-type or a combination of nutrient-type and scavenging-type elements; therefore, Fe is called as “hybrid-type” trace metal. Both Fe and Mn have short residence times relative to Ni, Zn and Cd (Chester and Jickells, 2012). In oxygenated seawater, the thermodynamically favored form of Fe is Fe(III), which is strongly hydrolyzed, and its removal is mainly constrained by complexation with natural organic ligands such as humic substances (Laglera et al., 2011).

Recent studies have gradually revealed the distribution of Fe in the western Arctic Ocean (Chukchi Sea and Canada Basin). The reported ranges for the concentrations of dissolved Fe and total dissolvable Fe (i.e., the concentration of leachable Fe in acidified unfiltered sample, see Section 2) have been extremely broad (0.36–33.1 nM and 0.8–89,000 nM, respectively), but the maxima of dissolved Fe concentration occurred consistently within the halocline layer (HL) with high concentrations of nutrients and dissolved organic matter (Nakayama et al., 2011; Cid et al., 2012; Nishimura et al., 2012; Aguilar-Islas et al., 2013; Hioki et al., 2014). Because high concentrations of trace metals have been observed in near-bottom water in the shelf region, it has been suggested that sedimentary input is an important source of trace metals in the western Arctic Ocean. However, few studies of trace metals (especially Mn and Fe) in Chukchi Sea sediments have been performed (Naidu et al., 1997; Trefry et al., 2014). Naidu et al. (1997) investigated metal concentrations (Al, Fe, Mn, Cu, Cr, Co, Zn, Ni and V) in the seafloor muds of the Chukchi Sea in 1986, and found that the concentrations of these metals were low relative to those of Arctic shelves of Russia, East Greenland and the Beaufort Sea. A more recent study also investigated concentrations of Fe, Al and selected trace metals (including Mn, Cd, Ni, Zn) in surface sediments from the Chukchi Sea collected in 2009 and 2010; although concentrations of each trace metal varied considerably with sediment texture (i.e., grain size), these metals were found to exist at natural background levels in most samples when normalized for Al concentration (Trefry et al., 2014). These studies suggest that Chukchi Shelf sediment is unlikely to have been significantly influenced by anthropogenic pollution. In addition to continental shelf sediments and remineralization of biogenic and/or mineral particles, river discharge and melting sea ice are also potential sources of trace metals (Nakayama et al., 2011; Nishimura et al., 2012; Cid et al., 2012; Hioki et al., 2014). The presence of these diverse sources is likely to influence the lateral transport of Fe in this region. Compared to Fe, there are relatively few data for distributions of Zn, Cd, Ni and Mn in the western Arctic Ocean (Yeats, 1988; Yeats and Westerlund, 1991; Cid et al., 2012). Yeats (1988) and Yeats and Westerlund (1991) investigated the distributions of total dissolvable Mn, Co, Ni, Cu, Zn and Cd and dissolved Mn in the Canada Basin near the Canadian Arctic Archipelago, and found that Ni, Zn and Cd concentrations tended to peak around the nutrient maximum in the halocline. More recently, Cid et al. (2012) investigated distributions of trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb) from samples collected in September 2000 and found that roughly all of these trace metals had concentration