Marine Chemistry 166 (2014) 9–24

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

The distribution of dissolved manganese in the tropical–subtropical North Atlantic during US GEOTRACES 2010 and 2011 cruises

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ARTICLE INFO

Article history:
Received 29 January 2014
Received in revised form 11 August 2014
Accepted 15 August 2014
Available online 2 September 2014

Keywords:
Dissolved manganese
Trace metal
North Atlantic
GEOTRACES

ABSTRACT

Dissolved manganese (Mn) concentration was determined in seawater samples collected along a section across the North Atlantic between 17°N and 40°N during US GEOTRACES North Atlantic 2010 and 2011 cruises (GT GA03). Dissolved Mn exhibits elevated concentrations in the surface, at the mid-ocean ridge and near oceanic boundaries, and low concentrations in the deep water of the gyre center. At both western and eastern boundaries, dissolved Mn concentration in the surface mixed layer (30–40 m) and at depths below 200 m decreases with increasing distance from shore, in contrast to the seaward increase of dissolved Mn concentration at depth between 80 and 120 m. Simple model calculation suggests that in the North Atlantic gyre center, dissolved Mn concentration is controlled primarily by eolian Mn(II) deposition and in-situ photochemical reduction of MnO_2 in the surface mixed layer (0–40 m), and by the intensity of sunlight available for in-situ MnO_2 photochemical reduction in the euphotic zone below the mixed layer (40–200 m). At depth between 200 and 700 m, dissolved Mn concentration is determined by regeneration, preformed Mn in the source water and lateral inputs from hydrothermal and sedimentary sources. Below 700 m, dissolved Mn concentration is controlled predominantly by lateral inputs from hydrothermal and sedimentary sources. Accounting for the observed dissolved Mn concentration by lateral mixing at this depth range requires low rates of Mn(II) oxidation.

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1. Introduction

Manganese (Mn) is one of the first trace metals in oceanic waters measured reliably since early 1980s (Landing and Bruland, 1980, 1987; Klinkhammer and Bender, 1980; Yeats and Bewers, 1985; Statham and Burton, 1986). Mn is an essential nutrient for biological growth (Raven, 1990) and has been used as a tracer for inputs of elements from hydrothermal vents (Klinkhammer et al., 1985; Klinkhammer and Hudson, 1986; Hydes et al., 1986) and reducing sediments (Klinkhammer and Bender, 1980; Heggie et al., 1987). The lack of basin scale high quality dissolved Mn data has constrained our ability to unravel the detailed mechanism controlling dissolved Mn distribution in the ocean.

The vertical profile of dissolved Mn that exhibits elevated surface and low deep water concentrations with maxima in oxygen minimum zone (OMZ) (Klinkhammer and Bender, 1980; Landing and Bruland, 1980, 1987) has been attributed to a source from eolian deposition of Mn to the surface (Klinkhammer and Bender, 1980; Shiller, 1997) and a sink via Mn(II) oxidation by dissolved O_2 in the deep water (Klinkhammer and Bender, 1980; Landing and Bruland, 1980, 1987; Johnson et al., 1996; Morgan, 2005). However, it is not clear if the elevated dissolved Mn in the euphotic zone of the open ocean results from lateral input of dissolved Mn from continental margin, eolian deposition of Mn(II) (Shiller, 1997; Statham et al., 1998) or in-situ MnO_2 photoreduction (Sunda et al., 1983; Sunda and Huntsman, 1994). It is also not known if the constant background concentration of dissolved Mn observed in the deep waters of the global ocean (~0.1 nM, Statham et al., 1998; Landing and Bruland, 1987; Middag et al., 2011a) results primarily from regeneration from sinking organic matter (Johnson et al., 1996), dissolution of manganese oxyhydroxide (Klinkhammer and Bender, 1980; Landing and Bruland, 1987), preformed Mn in the source water (Statham et al., 1998), or lateral inputs of dissolved Mn from hydrothermal and slope sedimentary sources (Landing and Bruland, 1980; Martin and Knauer, 1984, 1985). The GEOTRACES program may answer these questions by measuring dissolved Mn sections in a systematic fashion across the major ocean basins.

In this paper, we report the distribution of dissolved Mn measured along a section across the tropical–subtropical North Atlantic between 17°N and 40°N during US GEOTRACES North Atlantic 2010 and 2011 cruises (GT GA03). The measured data are combined with simple models to infer processes controlling dissolved Mn distribution in the surface and deep oceans.

2. Sampling and analytical methods

Seawater samples were collected during the US North Atlantic GEOTRACES 2010 cruise (November–December 2010) along a transect (GT GA03) beginning at a station near the Strait of Gibraltar (38.3°N,

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http://dx.doi.org/10.1016/j.marchem.2014.08.007
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9.7°W) extending southward to a station (17.4°N, 24.5°W) at the oxygen minimum zone of the tropical eastern North Atlantic off northwest Africa, and during the US North Atlantic GEOTRACES 2011 cruise (November–December 2011) along a transect (GT GA03) beginning at station USGT11-01 (39.7°N, 69.8°W) in the continental slope of the western North Atlantic extending eastward across the oligotrophic Atlantic basin to station USGT11-24 at 17.4°N, 24.5°W that was also occupied in the 2010 cruise (station USGT10-12, Fig. 1). One station in the eastern North Pacific at 30°N, 140°W (SAFe station) was occupied in the 2009 GEOTRACES North Pacific Inter-comparison Cruise.

Water samples were collected with the 12 L internal Teflon coated GO-FLO (General Oceanics®) bottles mounted on the US GEOTRACES carousel attached to plastic coated cable (Cutter and Bruland, 2012). Seawater samples were passed through 0.2 μm pore Acropak® capsule filter within 12 h after the sample collection. The sample filtrates were acidified to pH 1.7–2.0 using 2.8 ml Q-HCl (~9 N, sub-boiling distilled in Savillex® all-Teflon still, Mn blank is less than 10 pM/L HCl) per liter of seawater within 12 h of sample filtration. The acidified samples were stored in narrow mouth low-density polyethylene bottles at room temperature for more than 6 months before analysis. Dissolved manganese concentrations were measured with a newly modified procedure of $Mg(OH)_2$ co-precipitation isotope dilution (Wu and Boyle, 1997) using a multiple collector high resolution ICPMS (Finnigan Neptune®) at the University of Miami. In this procedure, dMn is quantified by the addition of ^{57}Fe, ^{52}Cr and ^{59}Co to the sample followed by $Mg(OH)_2$ coprecipitation and the detection of $^{55}Mn/^{57}Fe$, $^{55}Mn/^{52}Cr$ and $^{55}Mn/^{59}Co$ using ICPMS. The detection limit of the method was ~0.006 nM Mn. The average precision for the entire data set reported in this manuscript is ~4%. All sample handling and analyses were carried out using trace metal clean procedures. Table 1 lists concentrations of the reference samples measured in this study compared with the most recent consensus values. Both Atlantic and Pacific samples were measured with these reference samples in each analytical session to ensure consistency and accuracy. Inter-comparison with data determined by Bruland's laboratory at several stations shows an excellent agreement. The comparison data as well as other North Atlantic Mn data are available in the GEOTRACES Intermediate Data Product at BCO-DMO (http://www.bco-dmo.org/dataset/3843/data; http://www.bco-dmo.org/dataset/3822/data).

Table 1
Comparison of reference samples measured in this study with the most recent consensus values.

Dissolved Mn reference samples		SAFe S		SAFe D2	
		Average	Stdev	Average	Stdev
This work	Concentration (nM)	0.807	0.012	0.374	0.011
	Concentration (nmol/kg)	0.786	0.011	0.364	0.011
			n = 24		n = 28
Consensus value (May 2013)	Concentration (nmol/kg)	0.790	0.060	0.350	0.050

3. Results and discussion

Dissolved Mn distribution is plotted in Fig. 2 and the data are listed in Tables 2a and 2b. Fig. 3 plots the dissolved Mn concentration, AOU, fluorescence, particle beam attenuation coefficient (as an index of particle concentration) and percentage of sunlight intensity (with respect to the sunlight above sea-surface) in the upper 200 m of the water column. Dissolved Mn has low concentrations in the deep water of the central gyre and high concentrations in the surface water, at the mid-ocean ridge and near oceanic boundaries, reflecting sources from eolian deposition, hydrothermal vents and reducing sediments at the oceanic boundaries. Except at stations USGT11-16 and USGT11-14 where hydrothermal input results in a dissolved Mn maximum at depths, the general pattern of dissolved Mn vertical distribution showing decreasing concentration with depth from the surface maximum to low values in deep waters is similar to previous reports (Klinkhammer and Bender, 1980; Landing and Bruland, 1987; Statham and Burton, 1986; Statham et al., 1998). However, there are previously unreported horizontal gradients in dissolved Mn concentration that differ substantially between the surface mixed layer (at 30–40 m), below the surface mixed layer at the base of euphotic zone (80–120 m) and subsurface water below 200 m at both western and eastern boundaries (Figs. 2, 3, 4 and 5). While dissolved Mn concentration in the surface mixed layer and at depths below 200 m decreases with increasing distance from shore, dissolved Mn concentration at depth between 80 and 120 m at the base of euphotic zone increases with increasing distance from shore (Figs. 2, 3, 4 and 5). These gradients imply fundamentally different mechanisms controlling dissolved Mn concentration in the surface and deep oceans.

3.1. Dissolved Mn in the surface mixer layer

The steady state concentration of dissolved Mn measured at 30–40 m (Figs. 3a and 4) in the surface mixed layer reflects a balance between the input and the removal. As Mn^{2+} is not effectively removed

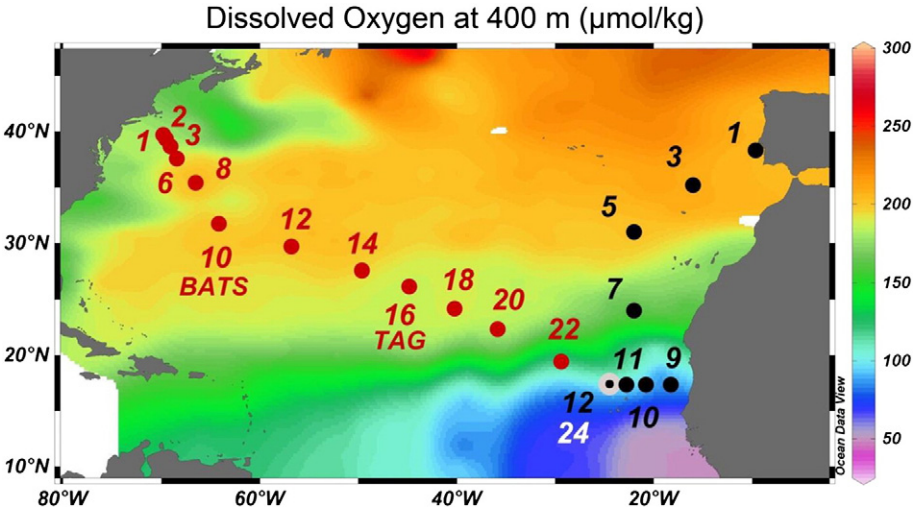

Fig. 1. Dissolved O_2 distribution at 400 m depth from the WOCE dataset with sampling station locations shown as USGT10-# in black circles for GEOTRACES 2010 cruise and USGT11-# in red filled circles for GEOTRACES 2011 cruise.

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