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Processes controlling the distribution and cycling of dissolved manganese in the northern South China Sea

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ABSTRACT

The Northern South China Sea (NSCS) is one of the most important marginal seas in the northwest Pacific Ocean. It receives large amounts of terrestrial inputs, and is affected by intrusion of Kuroshio Water. Dissolved manganese (Mn) can be used as a chemical tracer, facilitating study of fluxes and processes at ocean interfaces. To investigate the behavior and transport of dissolved Mn in the NSCS, we measured the concentrations of dissolved Mn in samples collected in summer 2011 and 2015, during field survey voyages supported by the National Science Foundation of China. The concentration of dissolved Mn ranged from 0.5 to 29.9 nM, with an average of 3.7 nM. Elevated concentrations (> 15 nM) of dissolved Mn were found in coastal waters, while low concentrations (< 3 nM) were found in areas affected by Kuroshio Water intrusion. There was no significant interannual variation in the dissolved Mn concentrations in the study region. Vertical profiles of dissolved Mn in the NSCS were similar to those found in open ocean conditions, with maxima occurring in surface waters and a decrease with depth. Large inputs of dissolved Mn occurred from terrestrial sources to the NSCS coastal areas via the Pearl River. Variations in the distribution of dissolved Mn resulting from intrusion of Kuroshio Water and its interactions with NSCS water were associated with Shelf Water transport. Data on dissolved Mn concentrations across the NSCS slope indicated that the offshore transport of Shelf Water in the upper water layer plays an important role in regulating the distribution of dissolved Mn. A preliminary box model was established to develop a dissolved Mn budget for the NSCS. The flux of dissolved Mn was dominated by exchanges between the NSCS and the northwest Pacific Ocean, with > 60% of the material transport flux occurring in the Luzon Strait.

1. Introduction

Manganese (Mn) is designated as a key parameter in the GEOTRACES program, and all GEOTRACES cruises should study the biogeochemical behavior of dissolved Mn in the ocean focusing on its sources, sinks and key processes controlling its internal cycling (www.geotraces.org). Dissolved Mn occurs in a very low concentration range (0.1 to 25 nM) in the global ocean (Shiller, 1997). Vertical profiles of dissolved Mn show higher concentrations in surface waters, and low and quite uniform concentrations in the deep ocean (van Hulten et al., 2017). Processes controlling the behavior of dissolved Mn include dust deposition (Baker et al., 2006), river inputs (Aguilar – Islas and Bruland, 2006), biological interactions (Raven, 1990), photo-dissolution of particulate Mn (Sunda and Huntsman, 1994), remobilization from sediments (Burdige, 1993), and mixing processes (Delgadillo-Hinojosa et al., 2006). Mn is a biogeochemically active element in marine environments because it can be used in biological processes and transformed between dissolved and particulate phases (Middag et al., 2013; van Hulten et al., 2017). However, in the open ocean the removal rates of dissolved Mn can be slow because of the relatively low levels of biological activity and particulate scavenging. Therefore, Mn can persist and serve as a chemical tracer to improve understanding of processes in the ocean, including water mass mixing (Statham et al., 1998), lateral transport (Slemons et al., 2010), hydrothermal inputs (Resing et al., 2015), etc. Studying the fundamental factors driving the distribution and fluxes of dissolved Mn in the ocean is of vital importance because it can clarify some poorly understood processes in the marine ecosystem.

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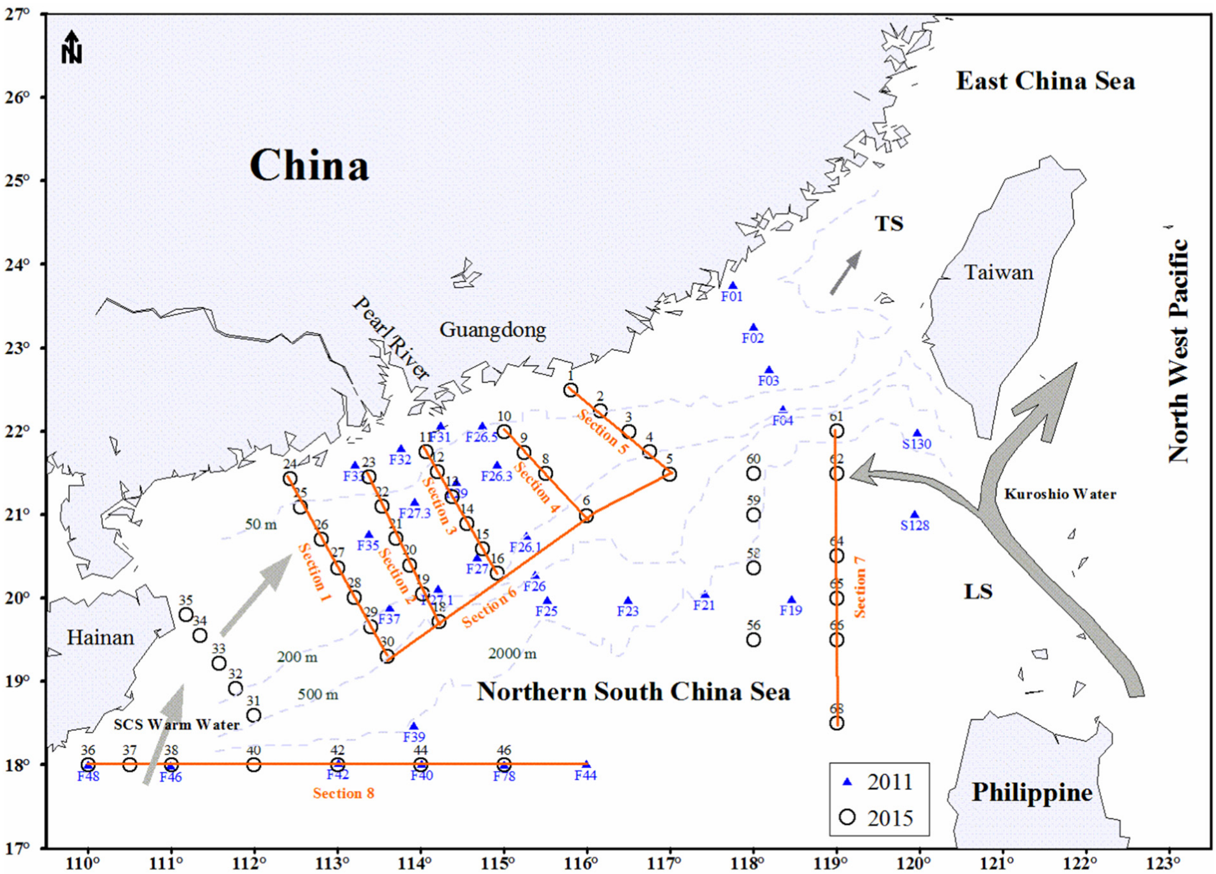

Fig. 1. Sampling locations in the Northern South China Sea ("▲": summer 2011; "○": summer 2015; orange solid lines: sections 1–5 Section 6–8). Abbreviations in the map, TS: Taiwan Strait; LS: Luzon Strait; Gray arrows: the Kuroshio Water and South China Sea Warm Water intrusion.

The South China Sea (SCS) is the largest marginal sea in the northwest Pacific Ocean. Southwesterly winds of approximately 6 m/s dominate over most parts of the SCS in summer (Hu et al., 2000). Under the effect of monsoonal winds, the northern SCS (NSCS) circulation is affected by riverine inputs (e.g., the Pearl River), water exchanges between the SCS and the East China Sea through the Taiwan Strait and between the SCS and the northwest Pacific Ocean through the Luzon Strait (Chen et al., 2001). The NSCS is advantageous for study of the biogeochemical behavior of dissolved Mn because it receives coastal inputs from the Pearl River, and is also affected by the intrusion of Kuroshio Water through the Luzon Strait. Coastal waters in this region are often Mn-replete because of high levels of Mn input from the Pearl River (Wang et al., 2012). However, data on trace metals in the NSCS are limited, and this has hampered our understanding of key processes controlling the supply of trace metals and other nutrients to the water column in this area. Therefore, identifying and quantifying the Mn sources to this region is of fundamental ecological importance.

In this report, we present data on the summer concentrations of dissolved Mn in the NSCS, from the Pearl River estuary, across the continental shelf, and to the open ocean areas (Fig. 1). We also report the behavior, possible controlling factors, and transport processes for dissolved Mn in the NSCS. Much of the emphasis is on the northern shelf regions and the adjacent areas of the Luzon Strait, because it sets the stage for studying behavior of dissolved Mn under the influence of Shelf Water and Kuroshio Water mixing. Finally, the observation data and published data were used to develop a preliminary dissolved Mn budget for the NSCS. This paper helps to improve our understanding of dissolved Mn supply to the NSCS and transport offshore, which can also provide important information on the levels and roles of global oceanic Mn.

2. Materials and methods

2.1. Field observation and sampling

Sampling was carried out in the NSCS from June to July 2011 aboard the R/V "*Dongfanghong 2*", and in June 2015 aboard the R/V "*ShiYan 3*" (Fig. 1). Seawater samples were collected using 12 L acid-rinsed Niskin bottles (Model: Sea-Bird 911^{plus}). The internal black rubber springs were also replaced with silicon springs before the cruise. A CTD-rosette assembly with the Niskin bottles was used to measure the profiles of temperature and salinity in the water column at grid stations. We have conducted inter-calibration of different water sampling systems (MITESS from MIT, newly designed X-Vane and normal acid-rinsed Niskin bottle) in the Okinawa Trough of the East China Sea (28 °N, 127 °E) before with samples ranged from 1.0 to 10 nM, the results from Niskin bottles have no significant difference with those from MITESS sampler and are believed to be suitalbe for the collection of Mn samples after rigorous cleaning in marginal seas (Zhang et al., 2015). Following collection, each sample was filtered through a pre-cleaned Whatman polycarbonate filter (pore size: 0.4 μm) in a class-100 clean bench. Prior to use, the filters were immersed in an ultrapure HCl solution (pH = 2; Merck) for 24 h, and then rinsed with Milli-Q water until a neutral pH was obtained. All samples were stored double-bagged in acid-cleaned Nalgene low-density polyethylene bottles and acidified to pH 1.8 in the clean bench with ultrapure HCl within 1 day of collection, then stored for > 1 month prior to analysis. Blanks were carefully prepared at sea by filtering a known volume of Milli-Q water with methods identical to the bulk sample sets.