TAO, Vol. 9, No. 1, 119-125, March 1998

NOTE AND CORRESPONDENCE

A Persistent Mid-Depth Dissolved Manganese Maximum in the Southern Okinawa Trough

Tung-Ming Hsiung[1], Gwo-Ching Gong[2] and Su-Cheng Pai[3]

(Manuscript received 3 July 1997, in final form 11 December 1997)

ABSTRACT

The vertical distributions of manganese at a station in the southern Okinawa Trough were investigated bi-monthly by analyzing the dissolved manganese in filtered seawaters. The analysis of every survey showed the elevated concentrations of dissolved manganese between depths of 600 and 900 m, with the peak at about 800 m and a maximum concentration of 5-8 nM. Repeated observations showed that the dissolved manganese maximum always appeared within a narrow range of σ_θ between 27.1 and 27.2. The results not only confirmed the previous report of a mid-depth Mn maximum, but also revealed that the dissolved manganese is one of the major forms in the mid-depth manganese maximum. In this study, we conclude that a persistent mid-depth maximum of dissolved manganese exits in the southern Okinawa Trough off northeastern Taiwan.

(Key words: Dissolved manganese, Mid-depth maximum, Southern Okinawa trough)

1. INTRODUCTION

Variation of manganese in the oceans is a complex issue of great interest because of its key role in geochemical (Glasby, 1984) and biological (Sunda *et al.*, 1981) processes. Generally speaking, dissolved Mn (DMn) concentrations are higher along continental margins than in the open ocean (Martin and Knauer, 1985; Jones and Murray, 1985). Due to the low oxidation rate of Mn(II) in the open ocean (Yeats and Strain, 1990), the DMn is considered as a useful tracer in the study of continental margin-ocean interior exchange (Martin and Knauer, 1980). The vertical structure of DMn distribution in the open ocean often shows a surface maximum as well as a mid-depth maximum (Bender *et al.*, 1977; Landing and Bruland, 1980; Martin and Knauer, 1980 and 1984).

The conception of the mid-depth DMn maximum is a controversial issue. The Mn(IV)

[1]Institute of Marine Biotechnology, National Taiwan Ocean University, Keelung, Taiwan, ROC
[2]Department of Oceanography, National Taiwan Ocean University, Keelung, Taiwan, ROC
[3]Institute of Oceanography, National Taiwan University, Taipei, Taiwan, ROC

reduction in the continental slope has been considered as the origin of the mid-depth Mn. Release of Mn(II) from sediment to the water column has been incorporated with the low oxygen and pH, as well as the organic matter consumption processes (Klinkhammer and Bender, 1980). Thus, Martin and Knauer (1985) suggested that lateral transport of DMn released from the continental slope produced the mid-depth Mn maximum. With benthic flux measurements, Johnson *et al.* (1996) opposed the hypothesis that the source of Mn was the continental slope because the oxygen minimum layer was also a region of minimal Mn(II) flux from the sediments. Johnson *et al.* believed that mid-depth DMn was produced by Mn(II) release during particulate organic matter oxidation, where Mn(II) was incorporated into organic matter in the mixing layer and sank into the deep water associated with particulate organic matter.

In the southern Okinawa Trough, the mid-depth maximum distribution of Mn has been reported by Wei and Sun (1991) based on a single survey. In addition, the mid-depth Mn maximum was observed as corresponding to low beam transmission (i.e., an indicator of suspended particulate matter, Wei, 1995). The Mn maximum observed by Wei and Sun (1991) was based on unfiltered seawaters, which is termed the "total dissolvable manganese" (TDMn) (Jones and Murray, 1985). However, which form of manganese is responsible for the mid-depth maximum is not clear. This study reports the vertical distribution of truly dissolved manganese (DMn) collected from five cruises to a station in the southern Okinawa Trough off northeastern Taiwan, where the Kuroshio Edge Exchange Processes (KEEP) project has been conducted. If the dominant form of mid-depth Mn were DMn, the mechanism responsible for the origin of the mid-depth Mn maximum could be the lateral transport of Mn from the continental slope. However, we measured the DMn as supporting about half of the Mn in the mid-depth maximum. Thus, other processes acting within the water column must be responsible for the mid-depth Mn maximum.

2. MATERIALS AND METHODS

The station used for the study was the KEEP-KEY Station 17, located in the southern Okinawa Trough with a water depth of about 1700 m. Five cruises on board R/V Ocean Researcher I and II were undertaken between March 1995 and January 1996 (Table 1). Seawater samples were collected using 5-liter Go-Flo bottles (Type#1080, General Oceanic, USA)

Tab;e 1. Cruise information

Cruise no.	Date	Longitude (E)	Latitude (N)	Depth (m)
OR1-414	03-27, 1995	123 10.07	25 10.56	1718
OR2-111	05-02, 1995	123 13.02	25 06.57	1686
OR2-131	07-04, 1995	123 17.33	25 06.77	1825
OR2-149	09-02, 1995	123 12.55	25 06.77	1681
OR2-184	01-06, 1995	123 19.17	25 06.10	1860

* The stations recorded were the casting turn for our samples. During retrieval free-floating mooring experiments by another research group were in progress.

mounted on a Rosette sampler, which was assembled with a SeaBird SBE 9/11 CTD system. Upon retrieving the samples, clean compressed air was connected to an inlet connector on each Go-Flo bottle, and the outlet of the bottle was led to a filter holder with a 0.4 μm Nucleopore filter. The filtrates were collected in acid washed 1 L polypropylene (PP) bottles, and the dissolved manganese was pre-concentrated shortly after filtration with the Chelex-100 chelating ion-exchange resin (Pai *et al.*, 1990). The sample contained in the PP bottle was connected to a column set. The column set consisted of a BioRad Econo column (bed dimension 1x5 cm), pre-packed with 2 g of Chelex-100 resin (100-200 mesh, in ammonium form). The bottle was hung upside down to allow the seawater to flow at a rate of about 4 mL/min. The columns containing the manganese were brought back to a land-based laboratory for elution analysis.

Each column was eluted with 5 portions of 2 mL 2 N nitric acid to yield a final volume of 10 mL which resulted in a 100-fold concentration factor. Manganese in the final yield was detected by a Hitachi Z-8000 graphite furnace atomic absorption spectrometer. The injection size was 20 μL, which provided an instrumental detection limit of 0.3 μg/L. By dividing by the concentration factor, the actual detection limit for the seawater sample was 0.05 nM. A recovery test was made by spiking seawater sample with 5 nM of Mn standard, and the recovery range of 92-104% (n=7) was obtained. The differences between duplicate analyses of samples with 2-5 nM concentrations were in the range of 3-8 % (n=7).

3. RESULTS AND DISCUSSION

Figure 1(a) shows the profiles of DMn concentration observed on five cruises. All profiles exhibit a surface maximum of 2-5 nM. Below the surface, DMn concentration decreases

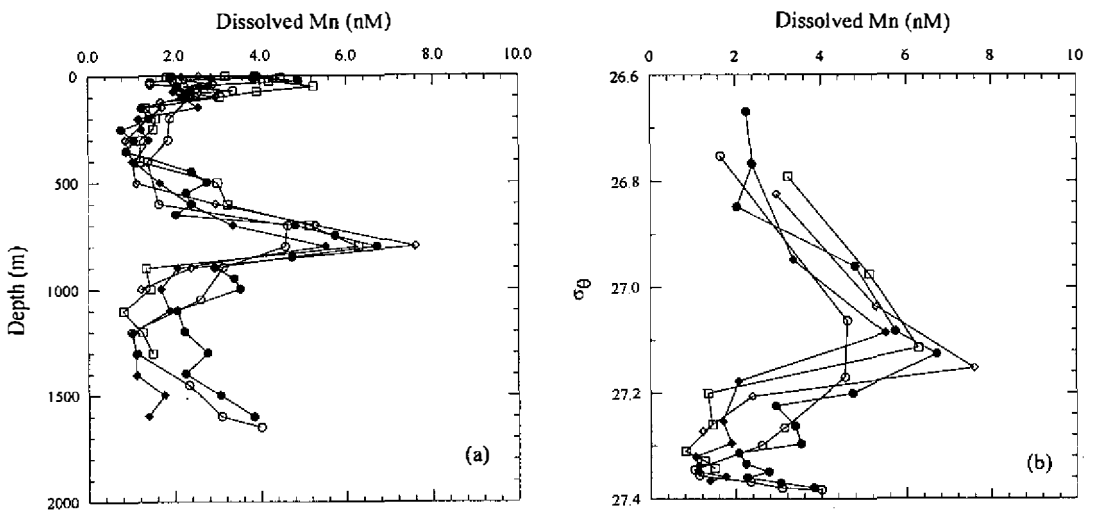

Fig. 1. (a) Vertical profiles of dissolved Mn (DMn), (b) sigma-theta (σ_θ) vs. DMn relationship, in March (◇), May (◆), July (□), September (○) 1995, and January 1996 (●).

with depth to 1-2 nM at about 300 m, and then increases sharply to form a mid-depth maximum of 5-8 nM in the mid-depth water at 400-900 m. The mid-depth maximum was observed for all five cruises. Below the mid-depth maximum, the DMn concentration dropped to less than 2 nM, and then increased steadily towards the sea floor. The repeated observations reveal the persistency and also subtle changes of this feature of the mid-depth DMn maximum. Figure 1(b) shows the plot of DMn concentration vs. σ_θ. The persistent DMn maximum occurs at a narrow density level between σ_θ values 27.1 and 27.2 on all five cruises.

Figure 2 shows the hydrographic parameters observed on the five cruises. The surface temperature varied from 24°C to 30°C, the salinity from 34.35 to 34.65 psu, and σ_θ from 21.5 to 23.0. Such variability occurred throughout the upper water column from the surface down to 500 m, whereas salinity variation occurred down to as deep as 750 m. The T-S diagram shows that the hydrographic properties of the upper water column were mostly within the T-S characteristics of the Kuroshio Water (Gong *et al.*, 1995), indicating the hydrographic variability attributable to the Kuroshio variation. It is probably not coincident that the mid-depth DMn maximum occurred right below the upper water column of more variable hydrographic conditions. The persistency of the DMn maximum at about a depth of 800 m was probably related to the water column stability at this depth. Above this depth, it might be difficult to maintain an enriched DMn perhaps due to the Kuroshio influence.

A single survey of the mid-depth Mn maximum in the Okinawa Trough observed by Wei and Sun (1991) was about 10 nM. The Mn concentration reported by Wei and Sun is in terms of total dissolved Mn (TDMn) because analytical processes used unfiltered sample (Jones and Murray, 1985). In the present study, all samples were filtered through a 0.4 μm Nuclepore filter, therefore the results represent the truly dissolved form. The maximum concentrations of DMn observed in this study were in the range of 5-8 nM, less than the TDMn observed by Wei and Sun, and were reasonable in consideration of the Mn forms present. Further study of the Mn forms has been accomplished by comparing the analytical results for filtered and unfiltered water samples. The values of TDMn was close to twice the values of the DMn (Liu, 1997). Consequently, the DMn is one of the major forms in the Mn enriched waters observed by Wei and Sun. The Mn profile in the Okinawa Trough reported by Wei and Sun showed a rather wide maximum in the depth range of 600-1000 m. In contrast, the DMn profiles observed in this study were rather sharp, suggesting the DMn was confined to a narrow density level. It is conceivable that the wide maximum shape of TDMn reported by Wei and Sun is attributable to a wider distribution of other forms of Mn.

Similar Mn distribution pattern have been observed in the eastern Pacific Ocean off California (Martin and Knauer, 1985; Martin *et al.*, 1985; Sagger *et al.*, 1989). They suggested that the mid-depth Mn maximum primarily resulted from lateral transportation from the continental margin. As suggested by Martin *et al.* (1985), the DMn is potentially a useful tracer for the study of seaward dispersion of water parcels from the continental margins in the western Pacific. Thus, isopycnal transportation could also be responsible for the DMn distribution in the study area. With regard to the lateral transport, the potential mechanisms are the reduction of Mn(IV) oxides in continental margin sediment, and the release of soluble Mn(II), i.e., the organic matter is consumed by minimization processes (Klinkhammer and Bender, 1980). However, since the particulate Mn also exists at the mid-depth Mn maximum, another pos-

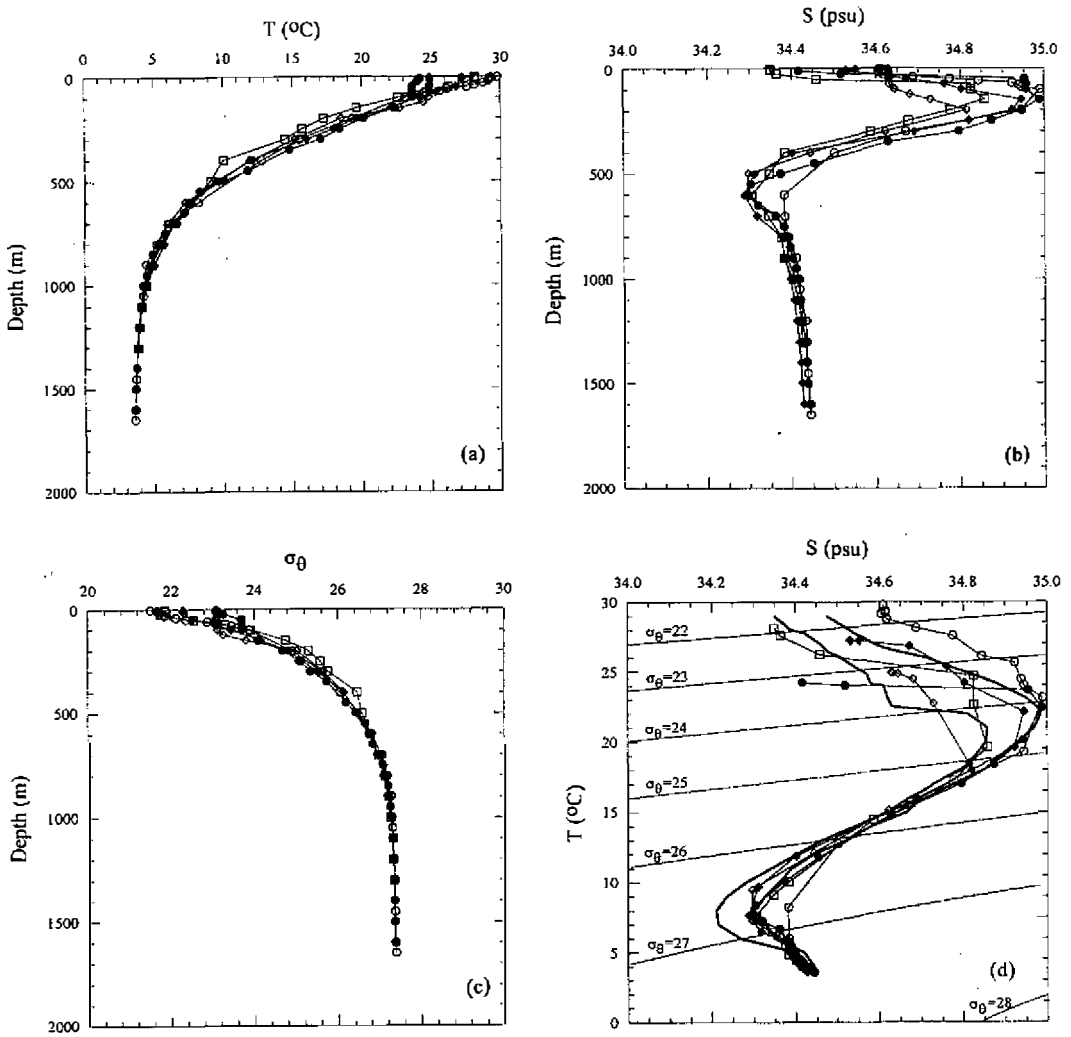

Fig. 2. Vertical profiles of (a) temperature (T), (b) salinity (S), (c) sigma-theta (σ_θ), and (d) T-S diagram, in March (◇), May (◆), July (□), September (○) 1995, and January 1996 (●); T-S characteristics of Kuroshio water mass (within dark lines, Gong et al., 1995).

sible explanation of the mid-depth DMn maximum is the processes of Mn(II) release from particulate organic matter (POM) in the water column (Landing and Bruland, 1980; Johnson *et al.*, 1996). Further study of the biogeochemical processes and the continental-margin transportation is necessary to elucidate the cause of the mid-depth Mn maximum in the southern Okinawa Trough.

In addition, an elevated TDMn concentration of as high as 26 nM near the seafloor was reported by Wei and Sun (1991). They suspected that such high concentration could have

resulted from resuspension of sediments and/or from hydrothermal effluent in the study region. Enrichment of DMn near the bottom was also observed on two cruises of this study. Evidence for manganese sources from the resuspension of sediments or from the influence of a hydrothermal vent plume is inconclusive. However, the maximum value of the DMn was only 4 nM, indicating that particulate Mn was probably the dominant form in the bottom layer.

4. CONCLUSIONS

In conclusion, this study provides repeated observations of the DMn vertical distribution in the southern Okinawa Trough, which reconfirms the previous report of a mid-depth TDMn maximum at around 800 m. The mid-depth water with enriched DMn occurred within a narrow range of σ_θ of 27.1-27.2, which was in a rather stable water column with little hydrographic variability. The mid-depth maximum Mn consisted of both particulate and dissolved forms, with about half the total Mn in this Mn-enriched layer being in the dissolved form. In order to use the DMn as an indicator of seaward dispersion of water parcels in the southern Okinawa Trough, further study of the biogeochemical processes and continental-margin transportation is necessary.

Acknowledgments The authors thank Prof. K.K. Liu, C.T.A. Chen, and two anonymous reviewers for providing valuable suggestions and comments. The study was supported by the National Science Council of the R.O.C. under Grant No. NSC85-2611-M-019-017Y (TMH) and NSC85-2611-M-019-018-K2 (GCG).

REFERENCES

Bender, M. L., G. P. Klinkhammer, and D. W. Spencer, 1977: Manganese in seawater and the marine manganese balance, *Deep-Sea Res.*, **24**, 799-812.

Gong, G. -C., K. -K. Liu, and S. -C. Pai, 1995: Prediction of nitrate concentration from two end member mixing in the southern East China Sea, *Cont. Shelf Res.*, **15**, 827-842.

Glasby, G. P., 1984: Manganese in the marine environmental, Oceangr. Mar. Bilo. *Annual Rev.*, **22**, 169-194.

Jones, C. J., and J. W. Murray, 1985: The geochemistry of manganese in the northeast Pacific Ocean off Washington, *Limnol. Oceanogr.*, **30**, 81-92.

Johnson, K. S., K. H. Coale, W. M. Berelson, and R. M. Gordon, 1996: On the formation of the manganese maximum in the oxygen minimum, *Geochim. Cosmochim. Acta*, 1291-1299.

Klinkhammer, G. P., and M. L. Bender, 1980: The distribution of manganese in the Pacific Ocean, *Earth Planet. Sci. Lett.*, **46**, 361-384.

Landing, W. M., and K. W. Bruland, 1980: Manganese in the North Pacific, *Earth Planet. Sci. Lett.*, **49**, 45-56.

Liu, Y. -J., 1997: Study on the manganese plume in the southern Okimnawa Trough, Master Thesis, National Taiwan Ocean University.

Martin, J. H., and G. A. Knauer, 1980: Manganese cycling in Northeast Pacific waters, *Earth*

Planet. Sci. Lett., **51**, 266-274.

Martin, J. H., and G. A. Knauer, 1984: VERTEX: Manganese transport through oxygen minima, *Earth Planet. Sci. Lett.*, **67**, 35-47.

Martin, J. H., and G. A. Knauer, 1985: VERTEX: Lateral transport of Mn in the north-east Pacific Gyre oxygen minimum, *Nature*, **314**, 524-626.

Martin, J. H., G. A. Knauer, and W. W. Broenkow, 1985: VERTEX: the lateral transport of Mn in the northeast Pacific, *Deep-Sea Res.*, **32**, 1405-1427.

Pai, S. C., T. H. Fang, C. T. A. Chen, and K. L. Jeng, 1990: A low contamination Chelex-100 technique for shipboard preconcentration of heavy metals in seawater, *Mar. Chem.*, **29**, 295-306.

Saager, P. M., H. J. W. De Baar, and P. H. Burkill, 1989: Manganese and iron in Indian Ocean waters, *Geochim. Cosmochim. Acta*, **53**, 2259-2267.

Sunda, W. G., R. T. Barber, and S. A. Huntsman, 1981: Phytoplankton growth in nutrient rich seawater: importance of copper-manganese cellular interactions, *J. Mar. Res.*, **39**, 567-586.

Wei, C. L., S. J. Sun, and C. S. Huang, 1991: Manganese distribution in the water column off northeast Taiwan-a preliminary investigation, *Acta Oceanogr. Taiwanica*, **26**, 85-93.

Wei, C. L., 1995: Particle dynamics and transport processes in the East China Sea, Workshop for Integrated Oceanographic Research Programs (WIORP), K51.

Yeats, P. A., and P. M. Strain, 1990: The oxidation of manganese in seawater: rate constants based on field data, *Estuar. Coast. Shelf Sci.*, **31**, 11-24.