

## Regeneration of Cd, P, and N on the continental shelf of the East China Sea in summer

Kazuo ABE\*

**Abstract** Regeneration of three biolimiting constituents, cadmium (Cd), phosphate ( $\text{PO}_4$ ) and nitrite plus nitrate ( $\text{NO}_2 + \text{NO}_3$ ), was examined on the continental shelf area of the East China Sea in the summer of 1999. Vertical profiles of these constituents showed increase of concentrations toward the sea bottom. The regenerated (molar) ratios to the consumed oxygen ( $\text{O}_2$ ) were estimated to be  $0.00134 \times 10^{-3} : 0.00684 : 0.0998 : 1$  by plotting these constituents against the Apparent Oxygen Utilization (AOU), and these ratios generally agreed with a previous study near the Ryukyu Islands. The apparent increase of Cd,  $\text{PO}_4$ , and  $\text{NO}_2 + \text{NO}_3$  in the bottom layer from winter to summer was around  $0.079 \text{ nM}$ ,  $0.41 \text{ }\mu\text{M}$ , and  $6.1 \text{ }\mu\text{M}$ , respectively, and this was attributable to the active supply caused by the decomposition of the organic matter in the bottom layer in this season.

**Key word:** Regeneration, Cd, P, N, East China Sea

In summer and autumn, the thermocline was well developed in the continental shelf of the East China Sea (Kusakabe et al., 1998) and under this thermocline, the concentrations of nutrients increased due to the decomposition of organic matter (Watanabe et al., 1995). The objective of this study was to examine the regeneration of biolimiting constituents such as cadmium (Cd), phosphate ( $\text{PO}_4$ ), and nitrite plus nitrate ( $\text{NO}_2 + \text{NO}_3$ ) at the shelf edge of the East China Sea in summer.

Water samplings were carried out vertically at five stations across the shelf edge of the East China Sea (DK line) from 0 to 200m using acid-cleaned 10l Niskin bottles aboard the R/V No.3 Kaiyo-Maru of the Nippon Kaiyo Co., LTD., in July 1999 (Fig. 1). The water depths at the stations were 836m, 1,024m, 283m, 127m, and 115m for DK-05, 06, 07, 08, and 09, respectively. The detailed analytical procedure for Cd was described in Abe (2001), and the water samples for Cd at DK08 and DK09 were filtered through a  $0.5 \text{ }\mu\text{m}$  Nuclepore filter. The analysis of  $\text{PO}_4$ ,  $\text{NO}_2 + \text{NO}_3$  was carried out using a Bran+Luebbe

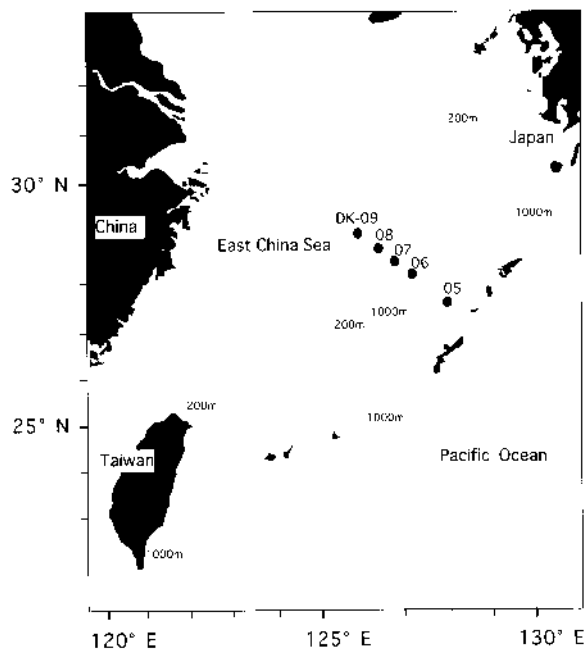


Fig. 1. Sampling sites in this study.

continuous flow analytical system Model Tracs-800, and dissolved oxygen was analyzed on board by Winkler titration.

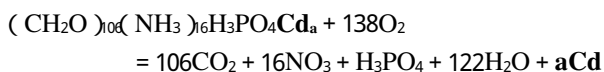
The concentration levels of Cd and nutrients

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\* 西海区水産研究所石垣支所 〒907-0451 沖縄県石垣市字浮海大田148-446 (Ishigaki Tropical Station, Seikai National Fisheries Research Institute, 148-446 Fukai-Ota, Ishigaki Okinawa 907-0451, Japan)

tended to increase toward the inner shelf station, and maxima of approximately 0.2 nM for Cd, 0.8  $\mu\text{M}$  for  $\text{PO}_4$  and 11  $\mu\text{M}$  for  $\text{NO}_2 + \text{NO}_3$  were observed near the bottom at DK08. Cd was inserted into the Redfield-type stoichiometric equation, as were the nutrients as follows (Kudo et al., 1996; Abe, 2001):



**Figure. 2** shows a plot of Cd,  $\text{PO}_4$ , and  $\text{NO}_2 + \text{NO}_3$  against the AOU at stations DK-08, 09, and 07. The regression lines of the data at DK-07 in each panel were calculated as follows:

$$\text{Cd} = 0.0410 + (0.00134 \times 10^{-3}) \times \text{AOU} \quad (r = 0.976) \quad (1)$$

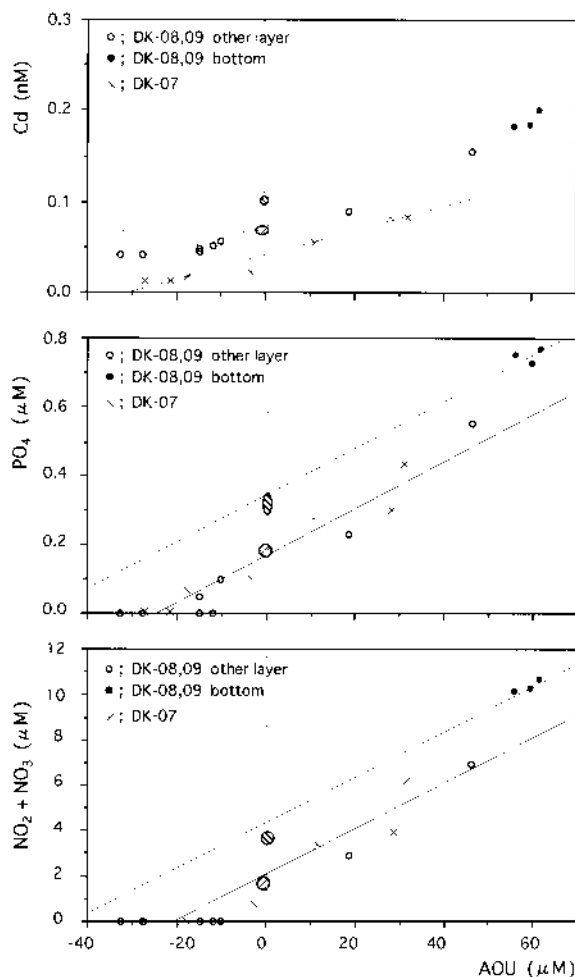
$$\text{PO}_4 = 0.164 + (0.00684) \times \text{AOU} \quad (r = 0.971) \quad (2)$$

$$\text{NO}_2 + \text{NO}_3 = 2.04 + (0.0998) \times \text{AOU} \quad (r = 0.952) \quad (3)$$

Good linearity was obtained at DK-07, and the slopes of these equations denote the regeneration ratios, so the molar ratio of regenerated Cd,  $\text{PO}_4$ , and  $\text{NO}_2 + \text{NO}_3$  to  $\text{O}_2$  was  $0.00134 \times 10^{-3} : 0.00684 : 0.0998 : 1$ . The ratios of the remineralized Cd to P, Cd to N, and N to P were estimated as  $0.196$  ( $\text{nM}_{\text{Cd}} / \mu\text{M}_{\text{phosphate}}$ ),  $0.0134$  ( $\text{nM}_{\text{Cd}} / \mu\text{M}_{\text{nitrite} + \text{nitrate}}$ ), and  $14.6$  ( $\mu\text{M}_{\text{nitrite} + \text{nitrate}} / \mu\text{M}_{\text{phosphate}}$ ), respectively. The Redfield ratio defines the ratio of the regenerated P and N to the consumed  $\text{O}_2$  as  $1 : 16 : 138$  (Redfield et al., 1963), so the ratio noted above was convertible to  $0.185 \times 10^{-3} : 0.944 : 13.8 : 138$ , and, as regards P and N, a slightly slower remineralization was observed. The ratio of remineralization for P was shown to be about  $1 : 150$  in the equatorial surface water (Abe, 2001), which agreed with the result of  $\text{P}(1 : 146)$  in this study. The obtained ratio of Cd to P was very similar to that in a previous report on the remineralization and seawater ratios near the Ryukyu Islands (Abe, 2000; Abe, submitted), and the ratio of N/P was similar to the ratio of  $\text{NO}_3/\text{PO}_4$  in seawater (e.g., Pai and Chen, 1994).

The intercept of the y-axis in **Fig. 2** denotes the preformed fraction, and the preformed Cd,  $\text{PO}_4$ , and  $\text{NO}_2 + \text{NO}_3$  were  $0.041\text{nM}$ ,  $0.164\mu\text{M}$ , and

$2.04\mu\text{M}$  at DK-07, respectively. A preformed fraction itself indicates an initial concentration when the water mass is exposed to excess oxygen in the surface layer. In this study, at DK-08 and 09, the preformed concentration was assumed to indicate the concentration in winter because the water in winter was well mixed and the calculated AOU values were almost  $0\mu\text{M}$  from the surface to the bottom at the station near DK-08 and 09 (Iseki, 1993). The slopes calculated using the data at DK-07 were applied to the DK-08 and 09 plots for the area near the bottom, and the other layers in each panel with the assumption that the remineralization rate at DK-07 was equal to that at the other



**Fig. 2.** Relationship between AOU and Cd,  $\text{PO}_4$ , and  $\text{NO}_2 + \text{NO}_3$ . The solid three lines are regression curves at DK-07. The slope of this line was applied to DK-08 and 09 data for the bottom and the other layers and is shown as a broken line in each panel. The hatched area shows the winter concentration level of the bottom (upper) and the other layer (lower) for each constituents.

stations (Fig. 2). The y-intercept, namely the concentrations in winter at DK-08 and 09 were around 0.11nM and 0.075nM (Cd), 0.34 μM and 0.16 μM (PO<sub>4</sub>), and 4.3 μM and 2.0 μM (NO<sub>2</sub> + NO<sub>3</sub>) for data near the bottom and for the other layers, respectively. These values generally agree with the concentrations (around 0.1nM and 0.07nM of Cd, 0.3 μM and 0.2 μM of PO<sub>4</sub>, and 3.5 μM and 1.8 μM of NO<sub>2</sub> + NO<sub>3</sub> for the deep and surface layer, respectively) at the near station to DK-08 and 09 in the winter (Iseki, 1993; Abe, unpublished data).

The percentage of the regenerated fractions was calculated by dividing the difference between the observed and the preformed values by the observed concentration. Approximately 70~80% of the apparent regenerated fractions for the three constituents were calculated to be near the bottom layer, which suggested that there was an active supply caused by the remineralization in the bottom layer in this season. Near the bottom at DK-08 and 09, high total carbon concentrations over 2.1m mol/l and low pHs below 8.0 were also observed in this study, supporting the idea of the decomposition and remineralization of organic matter in the bottom layer. Tsunogai et al. (1997) showed that the continental shelf zone was a large net source of dissolved inorganic carbon to the ocean, which means that remineralization of biolimiting constituents also occurs actively in the continental shelf zone. The apparent increase in the concentrations in the bottom layer of DK-08 and 09 from winter to summer was around 0.079nM (Cd), 0.41 μM (P), and 6.1 μM (N) (the regeneration ratio was  $0.19 \times 10^{-3} : 1 : 14.9$ ). The enhancement in the bottom layer was considered to be the result of the decomposition of the accumulated biogenic particulate matter.

In conclusion, the concentrations of Cd, PO<sub>4</sub>, and NO<sub>2</sub> + NO<sub>3</sub> in the bottom layer increased at the continental shelf stations in the summer, and these enhancements corresponded to the consumption of dissolved oxygen, which suggested that the apparent increase was attributable to the decomposition and remineralization of biogenic organic matter.

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## References

- Abe K., 2000 : Relationship between Cd and PO<sub>4</sub> off the Ryukyu Islands. *Bull. Seikai Natl. Fish. Res. Inst.*, **78**, 49 - 56 (in Japanese with English abstract)
- Abe K., 2001 : Cd in the western equatorial Pacific. *Mar. Chem.*, **74**, 197 - 211 .
- Iseki K. (ed. in chief), 1993. Preliminary Cruise Report of K92-09, no pages numbering.
- Kudo I., Kokubun H. and Matsunaga K., 1996 : Cadmium in the southwest Pacific Ocean - Two factors significantly affecting the Cd-PO<sub>4</sub> relationship in the ocean - . *Mar. Chem.*, **54**, 55 - 67 .
- Kusakabe M., Honda M., and Nakabayashi S., 1998 : Hydrographic feature of the East China Sea. *Bull. Coastal Oceanogr.*, **36**, 5 - 17 (In Japanese with English abstract)
- Pai S. C. and Chen H. Y., 1994 : Vertical distribution of cadmium in marginal seas of the western Pacific Ocean. *Mar. Chem.*, **47**, 81 - 91 .
- Redfield A.C., Ketchum B. H. and Richard F.A., 1963 : The influence of organisms on the composition of seawater, in "The Sea" (ed. by Hill M. N.) Vol. 2, Wiley-Interscience, New York, New York, pp.26 - 77 .
- Tsunogai S., Watanabe S., Nakamura J., Ono T. and Sato T., 1997 : A preliminary study of carbon system in the East China Sea. *J. Oceanogr.*, **53**, 9 - 17 .
- Watanabe Y., Abe K. and Kusakabe M., 1995 : Characteristics of the nutrients distribution in the East China Sea, in "Global Fluxes of Carbon and Its Related Substances in the Coastal Sea-Ocean-Atmosphere System" (ed. by Tsunogai S., Iseki K., Koike I and Oba T.) M & J International, Yokohama, pp.54 - 60 .

