

D-1.2.3 Effects of Microbial Activity on the Geochemical Cycling of Land-Derived Toxic Trace Metals in Coastal Waters

Contact Person Kazufumi Takayanagi
Environmental Management Division
National Research Institute of Aquaculture
422-1 Nakatsuhamaura
Nanasei, Mie 516-0193
Tel: 81-5996-6-1820, Fax: 81-5996-6-1962
E-mail: kazufumi@nria.affrc.go.jp

Total Budget for FY1996-FY1998 19,988,000 Yen (FY1998: 6,299,000 Yen)

Abstract

Seawater samples were taken from two coastal stations in the East China Sea near the mouth of the Changjian River in May 1998. Filtered samples were analyzed for Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn, As and Sb. The concentration ranged from 0.1 to 0.4 nM, from 1 to 13 nM, from 9.1 to 17.3 nM, from 21 to 2631 nM, from 18 to 93 nM, from 3 to 8 nM, 1.5 to 11.8 nM, from 0 to 0.5 nM, from 11 to 19 nM from 38 to 90 nM, from 22.0 to 25.9 nM and from 1.19 to 2.07 nM for the above 12 trace elements, respectively. With the exception of Zn and Pb, these concentration levels are similar to other coastal waters, implying no significant effect of the Changjian River could be detected at this sampling time.

Surface seawater samples were also taken from mesocosms installed near the mouth of the Changjian River. Filtered samples were analyzed for the same 12 trace elements. The concentrations of Cd, Cu, Ni, and most prominently As decreased with time in the phosphate-enriched mesocosm. The most likely cause of trace element variations is biological processes including phytoplankton bloom. The speciation study suggests that phytoplankton can actively take up As (V) together with phosphate and concomitantly release As (III). On the other hand, in the phosphate-enriched mesocosm, the concentrations of Mn and Sb increased with time. The concentrations of Mo, V, and Co showed no significant changes.

Key Words Trace Metals, Geochemical Cycling, Biological Activity, Coastal Ecosystem

1. Introduction

Chemical and biological processes occurring in coastal waters can modify the riverine input of elements to the ocean. It is essential to understand these processes in order to construct a precise geochemical mass-balance model and also to accurately predict the fate of discharged wastes into coastal water bodies (Boyle et al., 1974; Aston, 1978).

The concentrations of trace metals are known to fluctuate widely in coastal waters. One of the main causes is biological activity. Organisms can take up trace metals, breakdown organically associated metals, convert dissolved metals into the particulate form or vice versa, and alter the oxidation state of metalloid elements such as As and Sb. Knowing how each process affects metal concentrations can help us understand the geochemical cycling of trace metals in coastal waters. A mesocosm, a closed experimental ecosystem, provides a useful environment for studying these processes. In this study, we installed two mesocosms near the mouth of the Changjian River (Fig. 1). In one mesocosm we elevated the phosphate concentration to investigate how trace metals such as As, Sb, Cd, Cu, Co, Ni, Fe, Mo, V, Mn and Pb respond to enhanced biological activity.

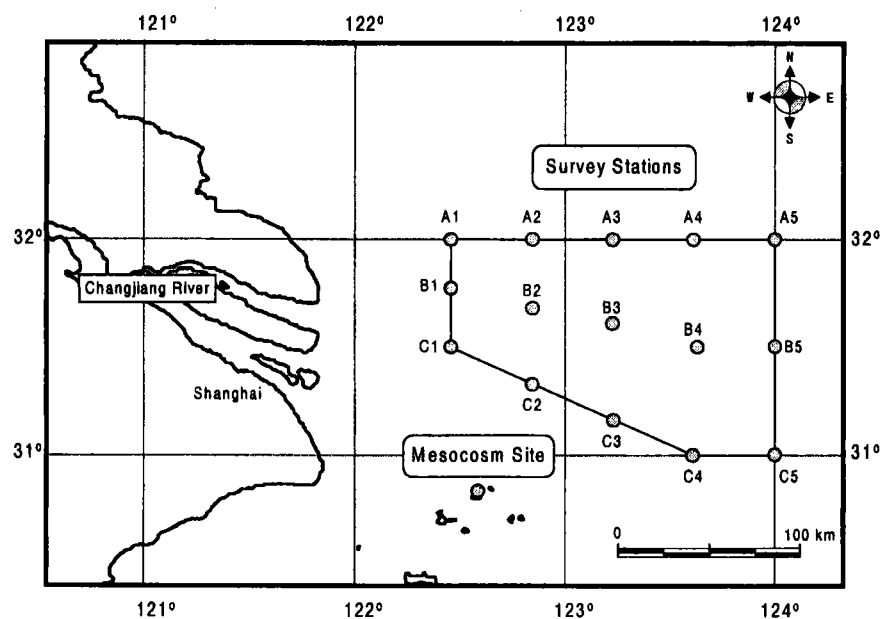


Figure 1. A map of coastal stations and the mesocosm site

2. Materials and Methods

During the mesocosm study, surface seawater samples for trace metals were taken daily. The samples were filtered on board through an acid-washed membrane filter (0.4- μm pore size) immediately after sampling and acidified with HCl to a pH of about 1.5 for storage. In our land-based laboratory, the samples were analyzed for As and Sb by hydride-generation AAS methods (Andrea *et al.*, 1981; Takayanagi & Michel, 1996), and for Cd, Cu, Co, Ni, Fe, Mo, V, Mn and Pb by AAS or ICP-AES after preconcentration onto a Kelex-100 XAD-4 column (Isshiki *et al.*, 1987). Speciation analysis was also done for As, requiring further analysis for both As (III) and As (V).

For comparison, seawater samples were obtained from two other coastal stations (A1 and C1; see Fig. 1). These samples were processed as described above and analyzed for the same 12 trace elements.

3. Results and Discussion

(1) Mesocosm experiment

Of the 12 trace element analyzed, possible contamination was encountered for Fe and Zn, which was indicated by wide fluctuations in concentration from 20 to 130 nM for Fe and 82 to 312 nM for Zn. For Co, Mo and V, no significant trends were observed, ranging from 1 to 2 nM, from 3 to 6 nM, from 16 to 20 nM, respectively. Therefore, this report focuses only on As, Sb, Cd, Cu, Ni, Mn and Pb. Concentration variations in these metals are plotted in Fig. 2 together with nutrient data.

In the control (Fig. 2A), phosphate (PO_4) was depleted, indicating a PO_4 -starved condition. The concentration of silicate (Si) was almost constant at about 26 μM ; that of nitrate (NO_3) decreased from 14.5 to 9.9 μM . In the PO_4 -enriched mesocosm (Fig. 2B), the addition of PO_4 accelerated the decrease of NO_3 and caused depletion of the latter on day 6 of the experiment. It also triggered a slight decline in Si concentration. These results indicate that the addition of PO_4 to the mesocosm stimulated phytoplankton growth. The major

species of the phytoplankton bloom was *Prorocentrum cordatum* (H. Koshikawa, personal communication).

Profiles of the As species (Fig. 2 C & D) showed that there was a decrease in the concentration of As (III+V) and a concomitant increase in the concentration of As (III) both in the control and PO₄-enriched mesocosms. In the control, under PO₄-starved conditions, the concentration of As (III+V) gradually decreased from 24 to 15.4 nM over 5 days. However, in the PO₄-enriched mesocosm, only a slight decrease in As (III+V) concentration occurred in the first 4 days. On day 5, when PO₄ became depleted, the As (III+V) concentration began to decrease sharply to its minimum value of 14.9 nM. This behavior suggests that As may be actively taken up by phytoplankton under PO₄-starved conditions, but that its uptake under PO₄-rich conditions is minor. The similarity in chemical structure of P and As, both of which belong to the VA group in the periodic table, can cause a co-uptake of these elements and utilization of both by phytoplankton. However, such co-uptake seems to be prevented in PO₄-rich conditions. The progressive As (III+V) decrease corresponded well with an increase of As (III), a minor arsenic species in normal seawater. The concomitant As (III) increase was especially significant in the PO₄-enriched mesocosm during the phytoplankton bloom, implying that it may have been produced by phytoplankton.

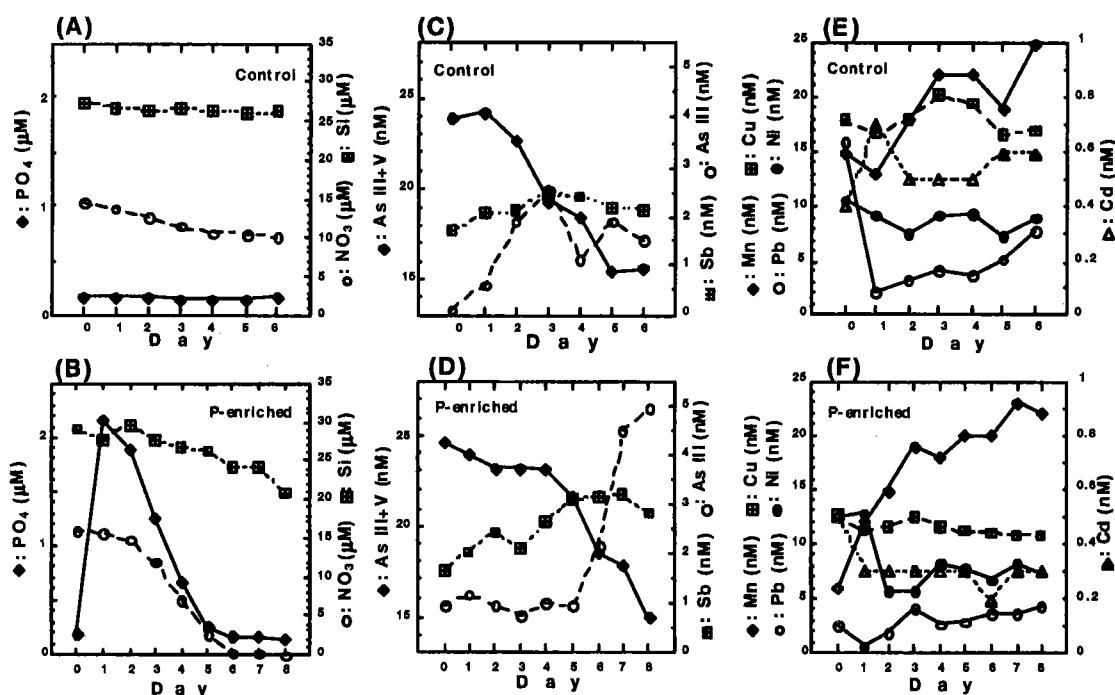


Figure 2. Variations of the metal concentrations in the phosphate enriched mesocosm (D & F) and in the control (C & E). Nutrient Data (A & B) were provided by H. Koshikawa (personal communication).

According to Apte *et al.* (1986), changes in the concentration of PO₄ and As follow the relationship: $\Delta[P] / [P] = D \cdot \Delta [As] / [As]$, where D is the discrimination factor, $\Delta [As]$ is the predicted change in As concentration, $\Delta [P]$ is the observed change in PO₄ concentration, $[As]$ is the observed As concentration, and $[P]$ is the observed PO₄ concentration. In plants, the discrimination factor, D, is known to be between 2 and 10 (Benson *et al.*, 1981). Using our PO₄ and As data, D was calculated to be about 10 in PO₄-rich conditions, implying that the phytoplankton were capable of discriminating between the

two elements. However, under PO_4 -starved conditions, D was about 3, implying that the discrimination became less efficient and that phytoplankton cells may have actively incorporated As. In contrast with the results of our May 1998, tests performed in October 1997 showed that a discrimination factor of 10 was obtained during the entire period of the PO_4 -enriched mesocosm experiment (Fig. 3). We suspect that this difference could be attributed to the presence of a different species of predominant phytoplankton in the mesocosms. In October 1997, the dominant species was *Skeletonema costatum*, while in May 1998, it was *P. cordatum*. Our calculations of D suggest that *S. costatum* can discriminate between PO_4 and As but that *P. cordatum* cannot, especially under PO_4 -starved conditions

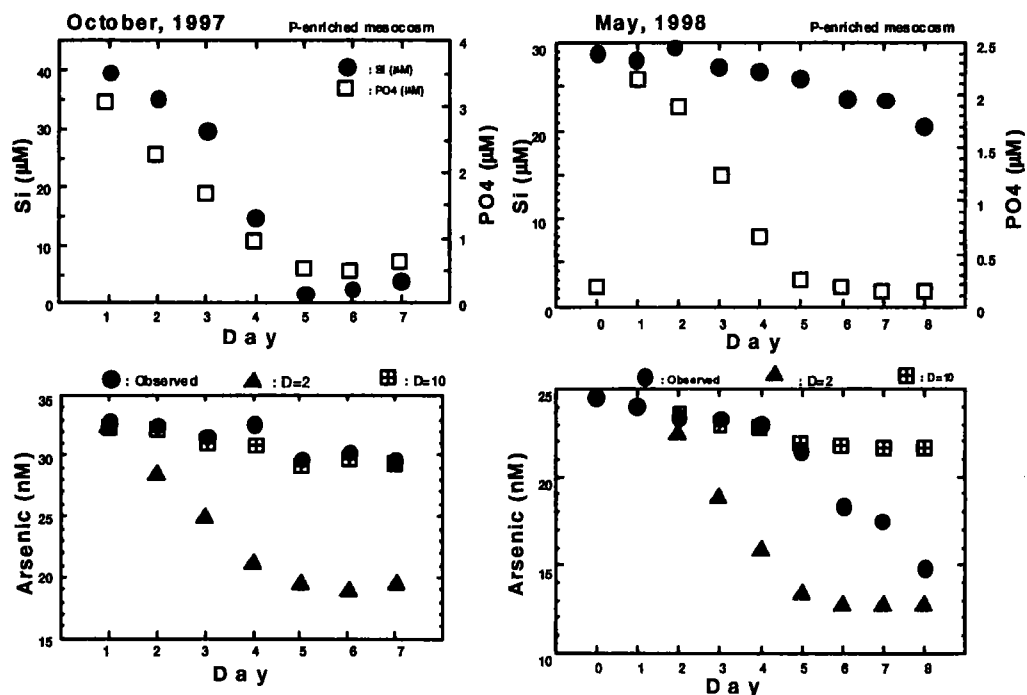


Figure 3. Predicted concentration changes of arsenic in the PO_4 -enriched mesocosm according to the equation of Apte *et al.* (1986).

The concentration of Sb was almost constant in the control at around 2 nM, but it gradually increased from 1.6 to 3.1 nM in the PO_4 -enriched mesocosm (Fig. 2 C & D). The increase could be related to the bloom, although there is no known biochemical function of Sb in phytoplankton. The concentration of Mn also increased during the experiment, particularly in the PO_4 -enriched mesocosm (Fig. 2 E & F). The reason for the Sb and Mn increase is not clear. Further research is necessary to clarify the effects of biological processes on the behavior of Sb and Mn in seawater. Both Cd and Ni tended to decrease during the initial stages of the bloom in the PO_4 -enriched mesocosm, while their concentration remained almost constant in the control at 0.5 and 17 nM, respectively (Fig. 2 E & F). The phytoplankton bloom was again responsible for the decrease. This behavior is consistent with the biogeochemical cycle of Cd, which is similar to that of PO_4 , and also with the biogeochemical cycle of Ni, which is similar to that of Si in the oceanic environment. There was a little variation in concentration of Cu either in the control or in the PO_4 -enriched mesocosm, although Cu is considered to be an essential nutrient for marine organisms (Fig. 2 E & F). Pb showed some increase in concentration in the latter stage of the bloom (Fig. 2 D

& F).

(2) Field survey

Excluding As and Sb, trace element concentrations at coastal stations are listed in Table 1. The nM concentration ranged from 0.1 to 0.4, from 1 to 13, from 9.1 to 17.3, from 21 to 2631, from 18 to 93, from 3 to 8, 1.5 to 11.8, from 0 to 0.5, from 11 to 19, from 38 to 90, from 22.0 to 25.9 and from 1.19 to 2.07 for Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn, respectively. These concentration levels are similar to those found in other coastal waters (Kremling, 1985; Mart and Nurnberg, 1986; Nozaki, 1992). However, a large concentration difference was observed between these two stations. The concentrations at St. A1 were much higher than those observed at St. C1, especially for Co, Fe and Mn. Further research is necessary to clarify the reason for these large concentration fluctuations at relatively close sites.

Table 1 Metal Results from Stations A1 and C1

Station	Depth (m)	Cd (nM)	Co (nM)	Cu (nM)	Fe (nM)	Mn (nM)	Mo (nM)	Ni (nM)	Pb (nM)	V (nM)	Zn (nM)
A1-S	0	0.3	13	16.9	2617	86	8	11.8	1.4	18	77
A1-M	12	0.3	12	15.5	2329	80	8	9.1	0.0	19	69
A1-B	24	0.2	14	15.6	2631	93	8	3.3	0.0	19	90
C1-S	0	0.4	1	17.3	163	18	3	7.6	0.0	11	54
C1-M	13	0.2	2	9.4	358	22	3	1.5	0.5	12	54
C1-B	25	0.1	2	9.1	353	21	3	8.2	0.2	13	38

Vertical profiles of As and Sb are shown in Fig. 4. A distinctive trend was observed for Sb. At St. A1, the concentration at the surface was 1.70 nM and increased with depth to 2.07 nM at the bottom. The opposite trend was observed at St. C1. Our observations clearly demonstrate the dynamic activity of this study area. Clearly, on-going surveys are required to further deepen our understanding of biogeochemical processes taking place in this study area.

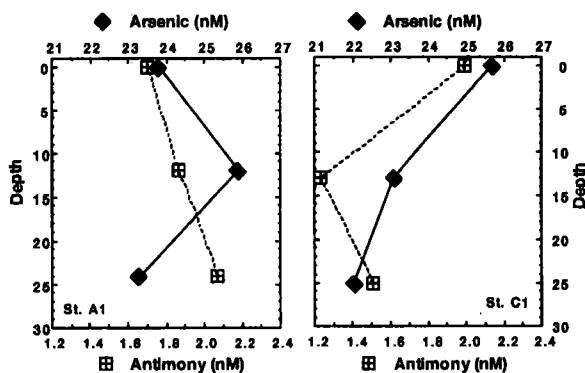


Figure 4. Vertical profiles of As and Sb at Sts A1 and C1.

4. Conclusions

Several trace metals were found to respond to PO₄ enrichment. The response was greatest for As: a decrease in As (III+V) with concomitant increase in As (III). The speciation study suggests that As (V) is taken up by phytoplankton together with phosphate and As (III) is released from phytoplankton cells. The concentrations of Cd, Cu and Ni also decreased with time in the phosphate enriched mesocosm. On the other hand, the concentrations of Mn and Sb increased with time in the phosphate enriched mesocosm. Biological processes including phytoplankton bloom are suggested as a main cause of the variations of these trace elements. However, no response to the phosphate enrichment was observed for the concentrations of Mo, V, and Co.

References

- Andreae, M.O., Asmond, J.-F., Foster, P. and Van't Dack, L., 1981. Determination of antimony (III), antimony (V), and methylantimony species in natural waters by atomic absorption spectrometry with hydride generation. *Anal. Chem.*, 53: 1766-1771.
- Apte, S.C., Howard, A.G., Morris, R.J. and McCartney, M.J., 1986. Arsenic, Antimony and Selenium Speciation During a Spring Phytoplankton Bloom in a Closed Experimental Ecosystem. *Mar. Chem.*, 20: 119-130.
- Aston, S.R., 1978. Estuarine chemistry, In *Chemical Oceanography*, vol. 1, 2nd ed. (Riley, J.P. and Chester, R. eds.), Academic Press, London, pp. 361-440.
- Benson, A.A., Cooney, R.V. and Herrera-Lasso, J.M., 1981. Arsenic metabolism in algae and higher plants. *J. Plant Nut.*, 3: 285-292.
- Boyle, E., Collier, R., Dangler, A.T., Edmond, J.M., Ng, A.C. and Stallard, R.F., 1974. On the chemical balance in estuaries. *Geochim. Cosmochim. Acta*, 38: 1719-1728.
- Kremling, K., 1985. The distributions of cadmium, copper, nickel, manganese, and aluminum in surface waters of the open Atlantic and European shelf area. *Deep-Sea Res.*, 32: 531-555.
- Isshiki, K., Tsuji, F. and Nakayama, E., 1987. Preconcentration of trace metals from seawater with 7-dodeceny-8-quinolinol impregnated macroporous resin. *Anal. Chem.*, 59: 2491-2495.
- Mart, L. and Nurnberg, H.W., 1986. Cd, Pb, Cu, Ni, and Co distribution in the German Bight. *Mar. Chem.*, 18: 197-213.
- Nozaki, Y., 1992. Trace elements in sea water: Their mean concentrations and North Pacific profiles. *Chikyukagaku*, 26: 25-39 (in Japanese).
- Takayanagi, K. and Michel, P., 1996. Semi-automated determination of dissolved antimony in seawater and sediment pore water. *Bunseki Kagaku*, 45: 1115-1120. (in Japanese).