

Trace Element Composition of Suspended Matter in the Changjiang Estuary Mouth

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Abstract

Suspended matter from the mouth of the Changjiang estuary in the East China Sea were analyzed to obtain concentrations of 35 elements. In order to examine the possible input of anthropogenic heavy metals from the river, the X/Al ratios (the concentration of each element X as a fraction of Al concentration) in the suspended matter were derived. The main sources of the elements in the suspended matter were natural particles such as soil particles or plankton in the Changjiang estuary mouth.

Introduction

Most chemical elements transported by rivers to the sea occur in particulate form. In the sea, these particles from rivers are mixed with sediments from the sea bed and organic particles produced by plankton in the surface layers of the sea. Characterization of the origins of suspended matter, and evaluation of their degree of contamination, has been previously done in the Scheldt estuary by analyzing the elemental composition of the suspended matter (Regnier and Wollast 1993).

The Changjiang River is the largest source of freshwater flowing into the East China Sea with a discharge of about 1×10^{12} m³/y, and a solid load of about 5×10^8 t/y (Milliman et al. 1985). Therefore, the river affects not only the estuary but also the marine environment and ecosystem over a wide area of the East China Sea. As part of a

US-China cooperative study on sediment dynamics in the Changjiang estuary, Edmond et al. (1985) reported the results from field surveys in June 1980 and November 1981, corresponding to the flood season and dry season, respectively. Conservative or non-conservative behaviors of dissolved trace elements were observed during estuarine mixing, and the net flux of dissolved trace elements from the river to the sea was calculated. As part of a France-China cooperative study on the biogeochemistry of the Changjiang estuary, Zhang et al. (1990) reported the results from field surveys undertaken in January 1986 and July 1986, which correspond to the dry season and flood season, respectively. The elemental composition of suspended matter, analyzed by instrumental neutron activation analysis, remained almost constant during estuarine mixing. In addition, the “exchangeable” fraction of elements in suspended matter, analyzed according to the method of Tessier (1979), was lower in the Changjiang estuary than in the Rhone or Gironde estuaries. Therefore, pollution from industrialized regions was less in the Changjiang estuary than in European rivers.

The collaborative research project between Japan and China on ‘Environmental loading from river inputs and their effects on the marine ecosystem in specified areas of the East China Sea’ has been running since 1997. As part of our research program, field surveys were conducted offshore from the Changjiang River in October 1997 and May 1998, which corresponded to seasons of plankton blooms. In this study, the distribution and elemental composition of suspended matter were analyzed in order to understand the roles of riverine input and primary production in the mouth of the Changjiang estuary.

Materials and Methods

The investigation was carried out between latitudes 31°00'N and 32°00'N and longitudes 122°30'E and 124°00'E, the area in the East China Sea specified in the agreement of the Japan-China Collaborative Research Project (Fig. 1). Two cruises were conducted from October 19 to 20, 1997 (autumn cruise) and May 14 to 17, 1998 (spring cruise), aboard the research vessel “Haijian 49” of the China State Oceanic Administration. At 15 stations in the specified area (A1 to C5, Fig. 1), vertical profiles of temperature, salinity, pH, dissolved oxygen, and redox potential of water were measured *in situ* (Surveyor II, Hydrolab). At 9 stations (C1, B1, A1, C3, B3, A3, C5, B5, and A5), seawater was collected from the surface layer, and at 5 stations (C1, A1, C3, C5, and A5) in autumn and at C1 in spring, seawater was collected from the surface, middle (according to the water depth), and bottom (a few meters above the sea bed) layers using 20-L Niskin samplers. In addition, daily sampling was done in a mesocosm constructed in the Changjiang estuary (Koshikawa et al. 1999). Immediately after sampling, the samples were filtered on board the research vessel through Nuclepore® filters (0.4-μm pore size) using a closed system of pressure filtration in a clean box (Nakayama 1997). The filters with the suspended matter were kept below -20°C and delivered to the laboratory in Japan.

In the laboratory, the filters with suspended matter were dried at 60°C and weighed. The concentration of suspended matter in each sample was calculated as {[the weight of filter with suspended matter) – (the weight of blank filter)] / (the volume of the seawater filtered)}. For each sample, 2 filters with suspended matter were taken; one was subjected to acid digestion followed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis, the other was subjected to instrumental

neutron activation analysis (INAA). Acid digestion was done at 140°C with HNO₃-HClO₄-HF in Teflon double vessels (Okamoto 1984). The resulting solution was dried and dissolved in dilute HNO₃, and then subjected to ICP-AES analysis to obtain the concentrations of 18 elements (Al, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Ni, P, S, Sc, Sr, Ti, Pb, V, Y, and Zn; Nishikawa 1986). The concentrations of 19 elements (As, Ce, Co, Cs, Eu, Fe, Hf, La, Lu, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, and Yb) were obtained by INAA according to the method of Koyama and Matsushita (1980). The concentrations of Fe and Sc obtained by ICP-AES and INAA agreed well; thus concentrations of 35 elements were obtained altogether.

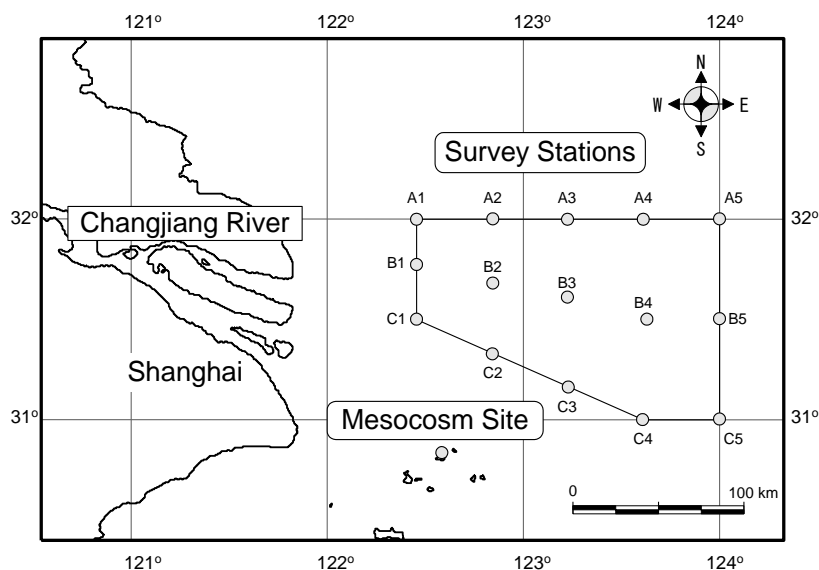


Figure 1. Location of investigation area

Results and Discussion

Elemental compositions of the suspended matter from the 2 cruises were normalized to that of aluminum concentration and X/Al ratios (the concentration of each element X as a fraction of Al concentration) were derived. Particles from different sources were expected to have different X/Al ratios according to season, station, and sampling depth.

P/Al showed large variation, from 0.01 to 0.33. Surface water samples showed higher P/Al ratios than did the middle or bottom water samples (Fig. 2); surface samples at stations A3, B3, and C3 in autumn showed higher P/Al ratios than did other stations in autumn. The variation in P/Al was correlated with the organic carbon content of the suspended matter ($R = 0.875$; Okamura, pers. comm.), and was therefore related to the abundance of plankton. Zn/Al also showed large variation, from 0.001 to 0.012, and was correlated with that of P/Al ($R = 0.885$). The intercept of the regression line $\{(Zn/Al) = 0.02 (P/Al) + 0.001\}$ was close to the ratio for the earth's crust ($Zn/Al = 0.001$; Bowen 1979) and the slope was close to the ratio of Zn/P in plankton ($Zn/P = 0.03$; Morel 1985). P/Al was also correlated with Sr/Al, Ba/Al, S/Al, and Mg/Al. These elements have 2 main sources—crustal particles from the river and plankton from the surface layers of the sea—and the contributions of the 2 sources varied at different stations.

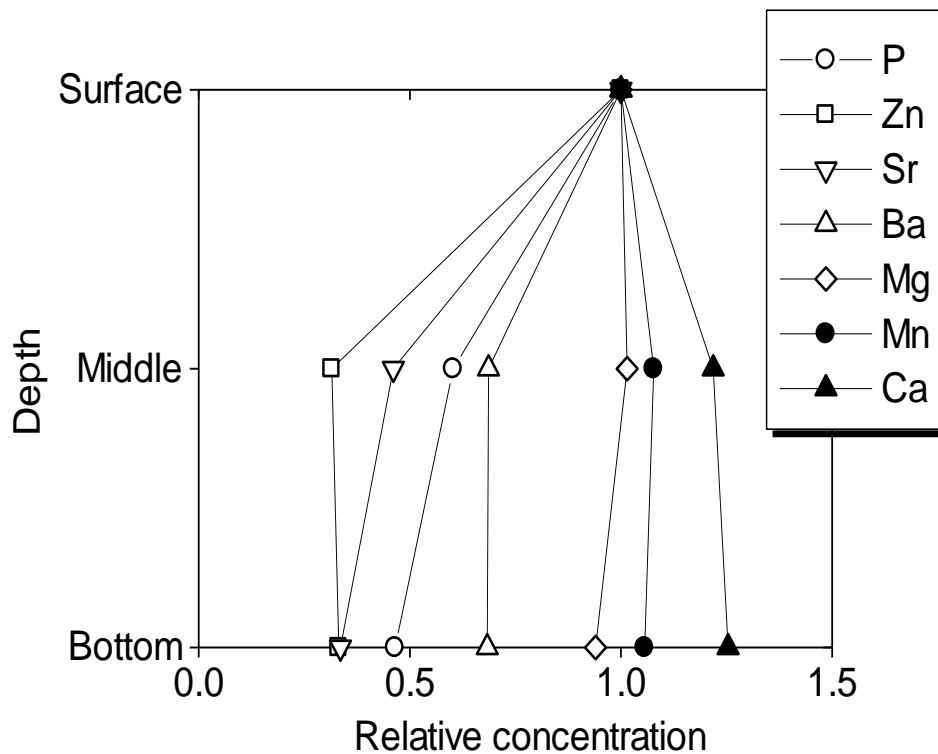


Figure 2. Vertical profile of elemental composition of suspended matter. (autumn, station C5)
Relative concentration = $(X/Al) / (X/Al)_{\text{surface}}$

The Mn/Al ratios were almost constant, but the Mn/Al ratios of bottom waters (0.011 ± 0.001) were higher than those of surface waters (0.008 ± 0.002) (Fig. 2). The Ca/Al ratios of bottom waters (0.35 ± 0.05) were also higher than those of surface waters (0.23 ± 0.12). The higher Mn and Ca concentrations in suspended matter from bottom waters may be due to re-suspension of bottom sediments (Iseki et al. 1999) because the bottom sediments contain more Mn and Ca ($Mn/Al = 0.013 \pm 0.003$, $Ca/Al = 0.36 \pm 0.08$; Noel, pers. comm.) than do particles suspended in surface waters.

The X/Al ratio of As, Ce, Co, Cs, Fe, Hf, La, Ni, Pb, Sc, Sm, Th, Ti, V, Y and Yb remained constant regardless of season, station or depth, which implies that the sources of these 16 elements do not change. Their X/Al ratios were close to either mean crust or median soil contents (Bowen 1979).

The other 10 elements in this study are not discussed here; 6 of them—Cr, Cu, Eu, Lu, Sb, and Ta—were present at concentrations close to the detection limit, and the remaining elements—Nd, Tb, Rb, and U—were detected in a few samples only.

Similar elemental compositions were found in the mesocosm samples. As the plankton population in the mesocosm increased, P/Al, Zn/Al, Sr/Al, Ba/Al, S/Al and Mg/Al all increased, while X/Al of other elements, such as Fe and Mn, remained constant.

From temperature and salinity distributions, it was shown that the Changjiang water plume (below 30‰ salinity) flows in the surface layer (less than 10 m depth) and

reaches as far east as longitude 123°E in autumn and longitude 124°E in spring. Salinity of the water had almost no influence on elemental composition of the suspended matter. During the spring cruise, the elemental composition of the suspended matter remained constant, while salinity at the surface varied from 11‰ at C1 to 32‰ at A5.

Conclusions

The behavior of the elements could be classified into 3 groups. The first group comprised P, Zn, Sr, Ba, S and Mg, which were related to the abundance of plankton; the second group was Mn and Ca, which were affected by re-suspension of bottom sediments; and the third group consisted of the other 16 elements, which showed constant X/Al ratios and were thus related to crustal particles or soils.

In this preliminary observation, no influence of anthropogenic heavy metals could be detected. However, it does not mean there is no input of pollutants from the river—large amounts of natural particles from the river exist in this area and they can dilute and hide the effects of pollutants. In order to focus on anthropogenic pollutants, more advanced methods for selective detection of anthropogenic matter (such as the sequential extraction procedure of Tessier et al. (1979)) need to be applied.

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