

## The trace-metal composition of size-fractionated plankton in the South China Sea: Biotic versus abiotic sources

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### *Abstract*

We report the elemental composition (P, Si, Al, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) in the size-fractionated plankton and suspended particulate matter (SPM) in the surface waters of the South China Sea. The size-fractionated plankton were effectively and gently separated by gravity through a novel trace-metal-clean filtration device, equipped with 150-, 60-, and 10- $\mu\text{m}$  aperture nets in sequence to concentrate the plankton. P-normalized metal quotas in the largest fraction, mostly composed of copepods, were close to or slightly lower than the average metal quotas obtained from previous field studies. However, the total metal quotas in the two smaller fractions were 8- to 40-fold higher than the largest one, and they increased with decreasing sizes. The striking correlation between some essential metals and chlorophyll (Chl) in the SPM at the offshore site indicates that the majority of the metals were associated with algae. Nevertheless, the P-normalized metal quotas also showed positive correlations with abiogenic Al and Mn, indicating that most of the metals associated with phytoplankton were from extracellular inorganic particles. Preliminary evidence suggests that the extracellular metals were originally derived from anthropogenic aerosols, which contain abundant dissolvable trace metals. The metal quotas of the zooplankton assemblages have a fairly consistent value as compared to observations from other regions, but algae larger than 10  $\mu\text{m}$  carry overwhelming amounts of extracellular metals even in offshore areas. The stoichiometry concept for trace-metal composition in marine plankton assemblages is unrealistic in the field.

Particles, including both biogenic and abiogenic, play a vital role in controlling trace-metal distribution and cycling in the ocean (Turekian 1977; Whitfield and Turner 1987; Li 1991). In particular, the cycling of many biologically essential trace metals is driven and transformed by biogenic particles generated in the euphotic zones (Collier and Edmond 1984; Bruland et al. 1994). Biogenic particles in oceanic surface waters, mainly composed of

diverse phytoplankton and zooplankton, interact with dissolved and particulate trace metals in ambient seawater through various processes, including active biological uptake, adsorption-desorption, zooplankton grazing and repackaging, particle aggregation, microbial decomposition, and so on. In terms of vertical cycling, large biogenic particles, mostly composed of sizable plankton, such as large diatom, zooplankton, and their hard parts and detritus (Alldredge and Silver 1988), serve as the predominant components of sinking particles and thus are principal agents in transporting both major and trace elements from oceanic surface waters to the deep waters (Bruland 1983; Fowler and Knauer 1986; Alldredge and Jackson 1995). The trace-metal composition in large-sized marine plankton assemblages may thus provide fundamental information for further studies and help models of the cycling processes of trace metals in marine water columns (e.g., Martin and Knauer 1973; Collier and Edmond 1984; Ho et al. 2003).

Given the sampling difficulty of separating abiogenic particles from natural plankton assemblages in seawater and the difficulty of collecting sufficient uncontaminated biomass for trace-metal analysis, there have been only a few reliable field studies reporting the trace-metal composition

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in marine plankton assemblages (e.g., Martin and Knauer 1973; Collier and Edmond 1984; Kuss and Kremling 1999). Most of early trace-metal composition studies on particles were carried out by using 0.4- $\mu\text{m}$  pore-size filters to retain the suspended particulate matter (SPM), which unavoidably collected suspended abiogenic particles as well (Sherrell and Boyle 1992). With the composition contrast between the biogenic and abiogenic particles, the trace-metal composition obtained from the SPM was prone to be strongly weighted by abiogenic particles. Even for the studies where biogenic particles were dominant in the SPM (Martin and Knauer 1973; Martin et al. 1976; Kuss and Kremling 1999), the trace-metal concentrations were still easily and strongly influenced by abiogenic materials.

Bruland et al. (1991) compiled three earlier field studies and proposed an approximation for the metal composition in marine plankton assemblages, represented as  $\text{P}_{1,000}\text{Fe}_5\text{Zn}_2(\text{Cu}, \text{Mn}, \text{Ni}, \text{Cd})_{0.4}$ . Kuss and Kremling (1999), using a large-volume pumping sampling method, also proposed a stoichiometric-type metal composition from nine samples, expressed as  $\text{P}_{1,000}\text{Fe}_5(\text{Zn}, \text{Mn})_2\text{Ni}_1\text{Cd}_{0.5}\text{Cu}_{0.4}\text{Co}_{0.2}$ . Using a synchrotron-based X-ray fluorescence method, Twining et al. (2004) analyzed 268 flagellates and diatoms collected in the Southern Ocean and obtained the elemental ratios:  $\text{P}_{1,000}\text{Fe}_{1.8}\text{Mn}_{0.26}\text{Zn}_{5.4}\text{Ni}_{0.61}$ . In spite of the more divergent quota ranges for some metals, which varied by almost one order of magnitude, the quota average for Fe, Zn, and Cd seemed to be fairly consistent, within factors of three among the data sets (Ho 2006). Since the environmental conditions in these field studies appear to be dissimilar, it seems that some of the essential metal quota averages in plankton assemblages may be considered to be constant, like the Redfield ratios (Redfield et al. 1963).

An alternative for estimating the trace-metal composition in marine plankton is the use of culture studies. Based on limited studies, Morel and Hudson (1985) first proposed that the metal composition in marine algae may have a consistent stoichiometry and suggested the composition would be  $\text{P}_{1,000}(\text{Fe}, \text{Zn}, \text{Mn})_{10}(\text{Cu}, \text{Cd}, \text{Ni})_1$ . In spite of the fact that our understanding of trace metal-phytoplankton interaction has greatly improved during the past two decades (e.g., Sunda and Huntsman 1995, 1997; Morel and Price 2003), there have been no culture studies focusing on obtaining the average metal quotas for algal assemblages until recently. Ho et al. (2003, 2004) chose 15 species representing five major phyla and grew them under an identical culture medium designed to mimic low-metal-concentration conditions in the ocean. Despite the fact that interspecies variability was large, the average quotas obtained were fairly consistent with the average of the field studies; they yielded the metal stoichiometry,  $\text{P}_{1,000}\text{Fe}_{7.5}\text{Mn}_{3.8}\text{Zn}_{0.8}\text{Cu}_{0.4}\text{Co}_{0.2}\text{Cd}_{0.2}$ .

There have been even fewer studies focusing on the metal composition in size-fractionated biogenic particles (Cullen and Sherrell 1999; Twining et al. 2004; Weinstein and Moran 2004). Two of these studies used layered, sandwich filter holders containing various pore-size filters to collect diverse size particles by the use of pumps. For the oligotrophic waters like the South China Sea, where the

highest total SPM is less than 0.5 mg L<sup>-1</sup> in the surface waters, filtering large volumes of seawater is required in order to obtain sufficient large-sized plankton biomass for trace-metal analysis. Using pumps to filter large volumes of seawater through small layered filters to obtain size-fractionated particles might risk breaking the fragile plankton during sampling. A trace-metal-clean filtration device with gentle and large-volume filtration capacity is essential for determining the trace-metal composition in size-fractionated plankton in oligotrophic water.

The importance of biologically essential trace metals for the marine biogeochemical cycle of major elements has been well appreciated over the past two decades and eventually initiated the long-term study of trace elements and isotopes, GEOTRACES. Understanding the internal cycling processes of the trace metals in marine water columns, especially in the surface water, becomes critical to comprehending the overall cycling mechanisms in the ocean (Anderson and Henderson 2005). Compared to our understanding of the elemental composition for major elements, the limited field data sets on plankton metal composition dampen our ability to justify a trace-metal stoichiometry concept for marine plankton (Morel and Hudson 1985).

Here, we used trace-metal-clean sampling techniques and a novel trace-metal-clean filtration apparatus to gently and effectively separate different-sized plankton from nearshore to offshore sites in the surface waters of the oligotrophic South China Sea. We intended to examine the trace-metal composition in the total SPM and the diverse sizes of plankton, especially focusing on the plankton larger than 10  $\mu\text{m}$  because of their dominant role in transporting material to deep waters. We also examined the correlation of the trace-metal concentrations with P and Al to further elucidate the influence of the biotic and abiotic sources on the composition.

## Methods

*Study area*—Located within the Tropic of Cancer, the South China Sea experiences the southwest summer monsoon and the northeast winter monsoon annually. The winter monsoon may induce dust storms, which originate in the Gobi Desert and carry the dust to the ocean, which could become a significant algal nutrient source in the area during the season (Duce and Tindale 1991). The physical force of the winter trade wind is also an essential factor in stirring up the deeper-water nutrients and promoting the primary productivity in the region (Tseng et al. 2005). This semiclosed deep-water basin also lies near regions with high fluvial input, mainly from the Pearl River and the Mekong River.

*Sampling*—The four sampling sites, PR, LEMA, DS, and SEATS, were located in the northern South China Sea and ranged from the Pearl River mouth, the continental shelf, the slope, to 3,500-m-deep water, where the bottom depths of the four stations were 33, 88, 160, and 3783 m, respectively (Fig. 1). All of the samples were collected aboard the *R/V Ocean Research 1* during the winter season

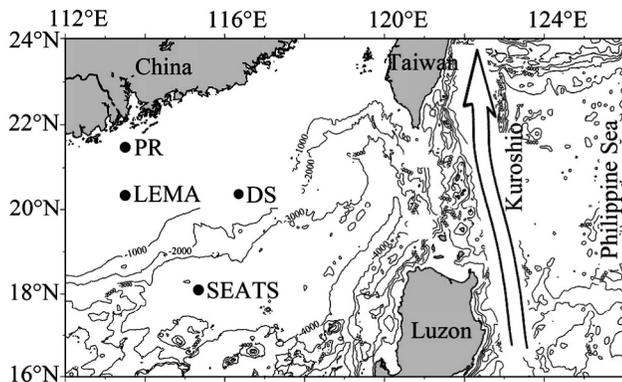


Fig. 1. Location of the sampling sites in the South China Sea. The abbreviated codes, PR (113°50'E, 21°48'N), LEMA (113°54'E, 20°33'N), DS (116°40'E, 20°42'N), and SEATS (115°34'E, 18°15'N) represent the Pearl River mouth site, continental shelf site, Dong Sha Island site, and the South East Asia time-series site, respectively.

from 21 to 30 March 2002. Seawater was collected using 20-liter Teflon-coated Go-Flo bottles (General Oceanics) mounted on a Teflon-coated rosette equipped with a modified epoxy-coated Seabird conductivity-temperature-depth (CTD) and Kevlar wire. Potential temperature, salinity, and density ( $\sigma_\theta$ ) data were obtained from the CTD profiles for the casts from which samples were collected (Fig. 2). Details of the sampling and analysis of major nutrients were described in Wen et al. (2006).

Sampling of the size-fractionated plankton was carried out at the three offshore stations, LEMA, DS, and SEATS, with a particular focus on chlorophyll (Chl) maximum depths. At the time-series station, SEATS, five casts were carried out within 24 h at Chl maximum depths.

We used a patented novel trace-metal-clean filtration device to gently collect the diverse-sized plankton through two filtration steps (Fig. 3). The first step was to concentrate the plankton in the sampling bottles by guiding the seawater into the filtration apparatus. The gravity filtration plankton sampler was made of polycarbonate material, with dimensions of 70 × 30 × 30 cm, and it was equipped with 150-, 60-, and 10- $\mu\text{m}$  aperture changeable Nitex nets in sequence (Fig. 3), which were acid-washed before each use. Before drawing seawater, the water spigots of six 20-liter Teflon-coated Go-Flo bottles on the elevated rosette were first connected to the acid-washed C-flex tubes. The other ends of the C-flex tubes were then connected to the inflow ends of the size-fractionated filtration apparatus (Fig. 3). This close filtration system effectively prevented metal contamination while transferring the samples onboard. The seawater in the bottles flowed through the six directional polytetrafluoroethylene (PTFE) inlets, and the water levels were raised over the top bottle in the device, indicating that the intact size-fractionated biogenic particles were gently separated through the nets and sank into the 100-mL polyethylene bottles fixed at the bottom the of the nets (Fig. 3). The live plankton observed in the sampling bottles indicated the gentleness of the filtration process. With the large surface

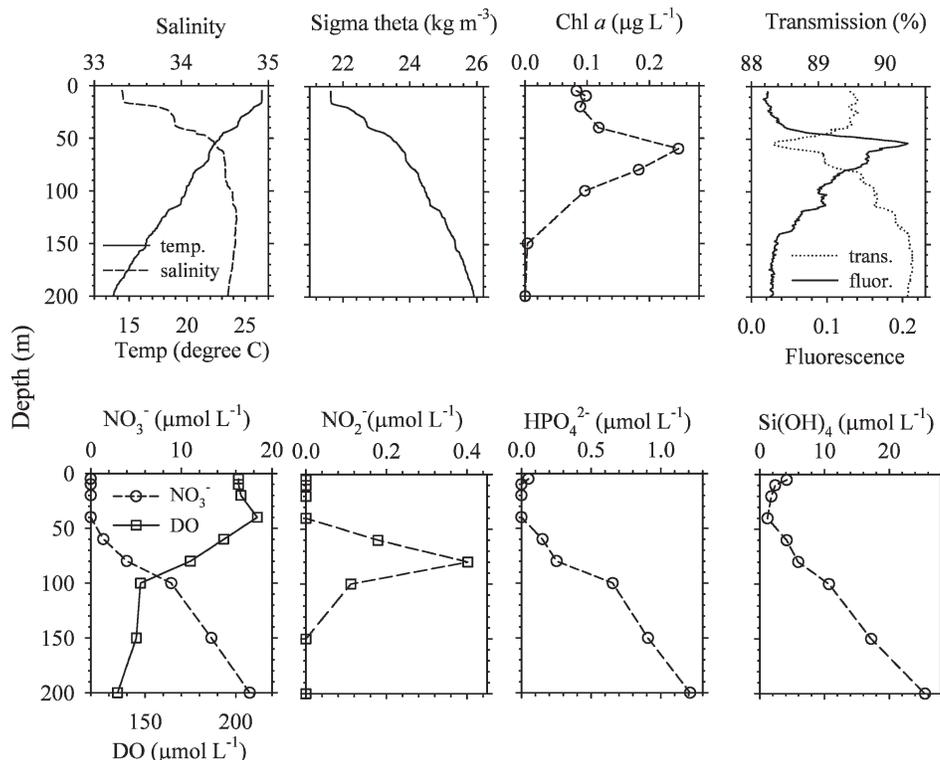


Fig. 2. The vertical profiles of the hydrographic parameters and major nutrients in the surface water of the SEATS station.

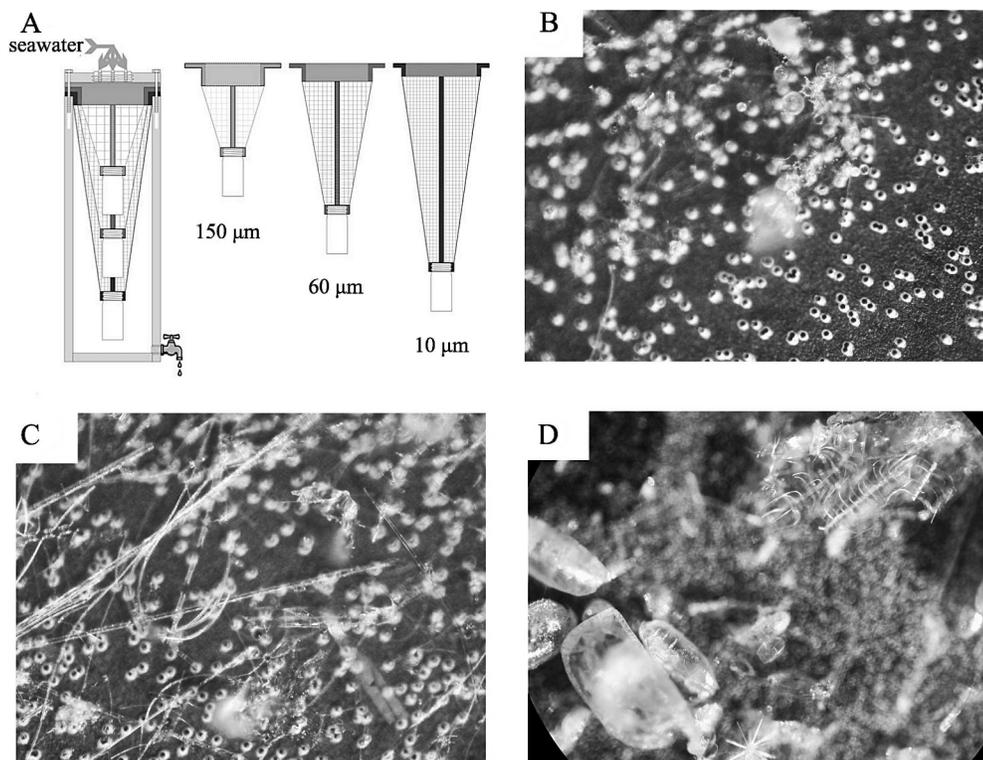


Fig. 3. The size-fractionated plankton-collection device and the magnified images of the freeze-dried size-fractionated plankton on 10- $\mu\text{m}$  filters. The pore sizes of the filters are all 10  $\mu\text{m}$ . (A) The size-fractionated plankton-collection device, patented by Wen et al. in Taiwan (patent number M275880). (B) The plankton size between 10 and 60  $\mu\text{m}$  ( $\times 200$  folds). (C) The particle size between 60 and 150  $\mu\text{m}$  ( $\times 200$  folds); (D) the particle size larger than 150  $\mu\text{m}$  ( $\times 50$  folds).

net area, it took less than 5 min to filter 120 liters of seawater. Before processing the second filtration, the nets were sprayed with trace-metal-clean filtered seawater to rinse out any plankton stuck on the inner surface of the nets.

The concentrated plankton samples collected in the 100-mL polyethylene bottles were then filtered again through an acid-washed filtration apparatus with preweighed acid-washed 47-mm, 10- $\mu\text{m}$  pore-size polycarbonate filters. The samples in the two larger fractions were then passed through the filters in less than a minute by gravity or a very low-vacuum condition. Under a low-vacuum condition ( $< 5$  kPa), the particles in the smallest fraction were filtered through the membrane in a minute. The biogenic particles on the filters were quickly rinsed with Milli-Q water to remove the seawater residue and diminish the influence of the dehydrating salts when determining the plankton dry weight. The rinsing step was kept to a few seconds to avoid causing the breakup of the fragile plankton (Collier and Edmond 1984). The filters with the particles were stored in acid-washed preweighed polyethylene culture dishes and were kept in a freezer onboard and then brought back to a land-based laboratory for further processing. All of the SPM samples were collected in the trace-metal-clean laminar flow bench onboard through 0.4- $\mu\text{m}$  acid-washed polycarbonate filters under 15-kPa vacuum condition using 2 to 4 liters of seawater.

*Analytical methods*—After being freeze-dried and weighed, the filters with the particles were digested with 1 mL of 8-N superpure nitric acids (SeaStar) in 20-mL Teflon vials at 120°C on a hot plate for 24 h (Ho et al. 2003). To reduce the matrix effect caused by silicon (Arslan et al. 2000), hydrofluoric acid was not applied in the digestion step. After diluting the digested solution to 10 mL with Milli-Q water and removing the filter, the solution was centrifuged to remove any particulate residues. All of the elements analyzed in the samples were obtained by using a sector field high-resolution inductively coupled plasma-mass spectrometer (ICP-MS; Element 2, ThermoFinnigan), fitted with a quartz Scott-type double-pass spray chamber and a solvent desolvation system. The analysis was conducted with a sensitivity higher than  $10^6$  counts per second for 10 ppb In under medium resolution. The sensitivity and stability of the machine were adjusted to optimal conditions before sample analysis was undertaken. The detection limits, determined as three times of the standard deviation of a filter blank, were Fe = 2.0, Mn = 0.09, Zn = 1.0, Cu = 1.0, Co = 0.06, Ni = 0.5, and Cd = 0.01 nmol L<sup>-1</sup>, respectively. The accuracy test, using the plankton reference material CRM 414 (BCR, Commission of the European Communities), gave 93% to 102% of the certified value for all of the trace metals that the CRM provided. In addition, the dry weight of Al and Fe made up 6% and 7% of the total SPM collected at the PR site,

respectively, and the M:Al ratios in the total SPM data were also close to the average crustal ratios, suggesting that most of the metals in the abiogenic particles were retrieved by the digestion procedures. More details for testing the precision, accuracy, and detection limit of the method for marine plankton analysis were described by Ho et al. (2003).

## Results

*Trace metals in total SPM*—The raw data of the elemental composition in the total SPM are presented as dry-weight concentrations ( $\mu\text{g g}^{-1}$ ) (Table 1). The P-normalized metal quotas (data not shown in the table) can be calculated from the raw data shown in Table 1. The vertical profiles of the elemental concentrations expressed as nanomoles per liter ( $\text{nmol L}^{-1}$ ) for the nearshore site (PR) and the offshore site (SEATS), are shown in Figs. 4 and 5 for comparison purposes. Significant vertical and spatial variability for the metal concentrations in the SPM were observed. At the PR site, the trace-metal concentrations in the SPM followed the sequence:  $\text{Al} \cong \text{Fe} > \text{Si} > \text{P} > \text{Mn} \cong \text{Ti} > \text{Zn} > \text{V} > \text{Cu} \cong \text{Ni} > \text{Co}$ . At the euphotic zone of the PR site, the concentration profile of Al increased with depth, ranging from 500 to 4,000  $\text{nmol L}^{-1}$  (Fig. 4). Relatively, at the SEATS site, the trace-metal concentrations ( $\text{nmol L}^{-1}$ ) in the SPM followed the sequence:  $\text{P} > \text{Al} > \text{Si} > \text{Fe} > \text{Ti} \cong \text{Zn} \cong \text{Mn} > \text{Cu} > \text{Ni} \cong \text{V} > \text{Co}$  (Table 1). The concentration profiles of Al still increased with depth but only ranging from 1 to 10  $\text{nmol L}^{-1}$  (Fig. 5), almost three orders of magnitude lower than that of the PR. All other elements at the PR site also had a much higher concentration than SEATS. At the PR station, all of the metals exhibited similar vertical profiles to Al (Fig. 4); relatively, in the SEATS station, with the exception of Al, Mn, and Fe, all other elements exhibited similar profiles with P.

*Trace metal in size-fractionated plankton*—The variously sized plankton were well separated during the sampling process (Fig. 3). The elemental concentration and variability in the size-fractionated plankton collected at the DS, LEMA, and SEATS stations are also shown in Table 1. The concentration averages for the diverse size plankton are presented in Fig. 6. Overall, the trace-metal concentrations vary dramatically, spanning over four orders of magnitude, from a highest value around 0.3% for Fe to a lowest value 1 ppm for Co (Fig. 6). Figure 6 shows that the dry-weight-normalized elemental composition varied significantly in the three categorized size-fractionated biogenic particles collected (10–60, 60–150, and  $>150 \mu\text{m}$ ) in the SEATS station, and, generally, the concentrations decreased in correlation to increased size, including Al, Ti, Mn, Fe, Co, Ni, Cu, and Zn.

## Discussion

*Trace-metal composition in SPM*—Aluminum and phosphorus, with their contrasting known abundances in both lithogenic and biogenic particles, respectively (Taylor 1964;

Ho 2006), are good proxies for evaluating the relative biotic and abiotic sources of trace metals (Bruland et al. 1991). The concentration distribution patterns of Al and P in the SPM, together with the distributions of SPM and Chl *a*, were used together to evaluate the relative influence of abiogenic and biogenic particles on the trace-metal contents in the SPM (Figs. 4, 5). By assuming constant trace-metal composition in biogenic and abiogenic particles, the metal concentrations may be simply expressed with the following formula:

$$[\text{M}] = a[\text{P}] + b[\text{Al}] \quad (1)$$

where [M] is the total concentration of the metal in the particulate matter; [P] is the phosphorus concentration in biogenic particles; [Al] is the aluminum concentration in abiogenic particles; *a* is the P-normalized metal quotas in biogenic particles; and *b* is the Al-normalized metal quotas in abiogenic (assuming lithogenic) particles

Once the metal stoichiometry for the biogenic P and the abiogenic Al in the particles are known, the relative contributions of the two particles to the metal content can be estimated. In the PR station, a strong correlation between SPM and Al and other metals was observed (Fig. 4). In addition, the Al-normalized metal molar quotas were also close to their average elemental ratios in crustal material (Table 2; Fig. 4), clearly indicating that most of the metals were derived from lithogenic particles presumably carried out with the Pearl River water. The SPM and Al concentrations in the PR ranged from 0.5 to 3  $\text{mg L}^{-1}$  and from 200 to 4,000  $\text{nmol L}^{-1}$  respectively, resulting at least 10–30% of the total SPM mass as lithogenic particles, assuming 8% Al content in the abiogenic particles and a complete metal dissolution in the digestion process. Relatively, the biogenic metal concentrations estimated from the biogenic P concentrations, which were around 50  $\text{nmol L}^{-1}$  after correcting for the lithogenic source, were trivial compared with the lithogenic portion estimated from the Al concentrations.

At the SEATS station, the Al concentrations in the euphotic zone, which ranged from 2 to 10  $\text{nmol L}^{-1}$ , were two to three orders of magnitude lower than the PR station and apparently decoupled with the vertical distribution pattern of the SPM (Fig. 5). Instead, the vertical distribution of Chl *a*, P concentrations, and the total SPM concentrations all exhibited similar patterns, indicating that the SPM in the euphotic zone were mostly composed of biogenic particles. By assuming 8% Al content in the abiogenic particles, the Al concentrations only results in 0.04–0.2% of the total SPM mass as lithogenic particles. Moreover, the estimated trace metals using the metal:Al (M:Al) ratios in crustal dust could only account for a diminutive portion of the particulate element Ni, Zn, Cu, Co, and P, and a minor but significant portion of the element Mn, Fe, V, and Ti (Fig. 5). In contrast to the vertical distribution patterns at the PR station, the profiles for most of the trace metals were inclined to resemble the P profile pattern, with the exception of the major trace metals in lithogenic particles, Al, Mn, and Fe (Fig. 5). The similarities for the vertical distribution between the metals

Table 1. The elemental composition ( $\mu\text{g g}^{-1}$  to dry weight) in the SPM and the size-fractionated particles.\*

Station	Size ( $\mu\text{m}$ )	Depth (m)	Dry weight (mg)	Sample vol. (L)	Sample no.	Elemental composition ( $\mu\text{g g}^{-1}$ )											
						Al	Si	P	Ti	V	Cr†	Mn	Fe	Co	Ni	Cu	Zn
PR	>0.4	2	0.22	0.58	30	26,214	26,822	4,756	509	40	n.a.	537	22,275	15.0	27	43	303
PR	>0.4	5	0.26	0.58	31	11,727	16,595	4,781	258	24	n.a.	481	25,688	12.7	10	71	307
PR	>0.4	10	0.32	0.58	32	22,237	14,531	3,504	411	35	n.a.	576	37,702	13.0	18	31	152
PR	>0.4	20	0.79	0.58	33	28,291	3,735	2,219	527	42	n.a.	816	30,888	12.6	24	26	162
PR	>0.4	30	1.49	0.58	34	36,405	1,134	1,422	600	50	n.a.	788	33,966	12.5	29	31	140
DS	>0.4	40	0.93	2.0	23	662	2,148	5,463	74	4	n.a.	42	1,936	3.2	64	68	269
SEATS	>0.4	25	0.60	4.2	4	317	1,230	4,233	63	4	n.a.	33	1,852	3.3	9	32	49
SEATS	>0.4	57	0.61	2.1	5	442	2,176	4,006	53	4	n.a.	17	[10,731]	3.8	8	44	78
SEATS	>0.4	57	0.56	1.7	6	364	1,240	4,711	63	5	n.a.	10	224	3.5	3	23	53
SEATS	>0.4	57	0.64	2.3	7	292	2,306	4,936	61	4	n.a.	9	1,112	3.1	7	28	61
SEATS	>0.4	100	0.58	4.3	3	878	1,162	2,887	116	2	n.a.	33	1,623	0.8	12	39	87
SEATS	>0.4	200	0.59	4.2	2	1,757	2,841	1,853	104	4	n.a.	[132]	3,044	1.1	10	31	94
DS	10-60	40	0.99	200	24	896	2,298	4,713	167	6	30	29	2,986	3.1	22	64	105
LEMA	10-60	65	0.73	120	27	1,198	3,518	5,142	114	8	43	33	6,294	3.9	25	96	141
SEATS	10-60	61	0.98	120	8	772	1,521	6,228	141	14	53	29	2,169	3.1	22	91	168
SEATS	10-60	56	1.79	120	11	751	182	5,548	224	11	96	31	1,966	2.6	37	53	165
SEATS	10-60	50	1.26	120	14	1,325	1,487	4,569	128	8	57	27	2,333	3.0	24	95	104
SEATS	10-60	50	1.00	120	17	1,225	1,955	4,657	137	9	39	21	849	3.4	29	77	93
SEATS	10-60	60	1.41	120	20	995	1,397	3,531	111	8	37	15	2,127	2.7	24	58	77
DS	60-150	40	1.45	200	25	308	1,530	7,484	181	5	10	12	1,456	1.7	6	33	54
LEMA	60-150	65	0.80	120	28	585	2,891	6,751	70	7	n.a.	12	3,396	2.5	5	45	81
SEATS	60-150	61	1.29	120	9	527	898	9,737	117	15	45	12	4,158	2.1	15	46	197
SEATS	60-150	56	0.67	120	12	783	3,449	6,715	96	10	60	27	2,562	3.3	21	[342]	159
SEATS	60-150	50	0.92	120	15	438	2,209	7,989	79	10	33	12	1,217	2.5	16	[310]	91
SEATS	60-150	50	0.77	120	18	376	2,854	8,619	68	12	33	12	838	2.9	16	35	100
SEATS	60-150	60	0.85	120	21	505	2,713	7,471	88	9	60	12	4,488	2.6	19	122	[345]
DS	>150	40	2.68	200	26	57	686	7,351	49	6	3	5	201	0.8	4	25	48
LEMA	>150	65	1.02	120	29	250	695	9,729	55	2	6	6	[2,436]	1.8	1	47	85
SEATS	>150	61	10.53	120	10	45	68	25,474	26	5	7	5	236	0.5	5	11	119
SEATS	>150	56	1.22	120	13	186	1,643	9,232	69	5	29	7	[2,010]	1.7	5	21	94
SEATS	>150	50	1.80	120	16	141	797	11,588	27	[34]	8	5	127	1.2	3	10	69
SEATS	>150	50	1.91	120	19	65	714	9,026	35	3	n.a.	5	167	1.1	4	11	66
SEATS	>150	60	3.04	120	22	166	315	11,893	31	[24]	14	6	485	1.0	8	17	84

\* The numbers with the brackets in the table denote that the samples were possibly contaminated during the sampling or analysis processes.

† n.a., data not available.

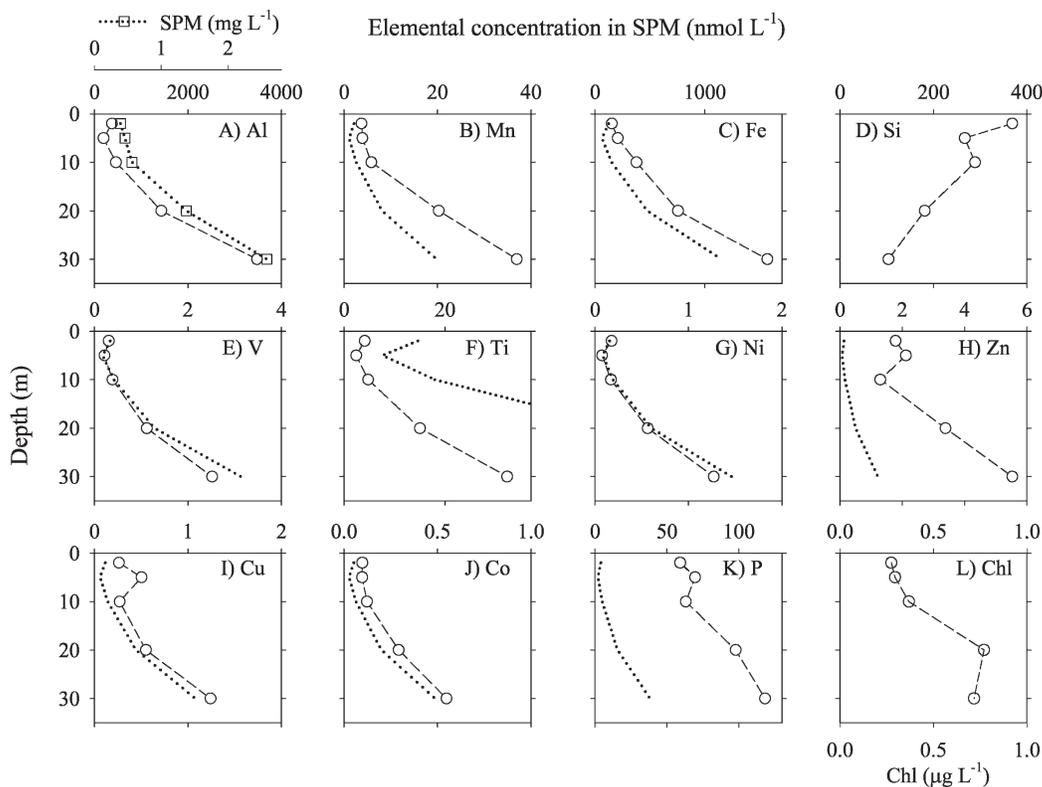


Fig. 4. The vertical concentration profiles of the elements in the SPM, the Chl value, and the total SPM collected in the surface water of the PR site, referenced to the average elemental concentrations obtained from the metal:Al ratios in crustal materials, shown as dotted lines. (A) Al, (B) Mn, (C) Fe, (D) Si, (E) V, (F) Ti, (G) Ni, (H) Zn, (I) Cu, (J) Co, (K) P, (L) Chl.

(V, Ti, Ni, Zn, Cu, and Co) and Chl *a* suggest that these trace metals were mostly associated with phytoplankton.

Spatially, the dry-weight-normalized metal concentrations in the SPM at the stations of DS and SEATS were close to each other, and the metal quotas both were much lower than the PR station (Tables 1, 2), suggesting that the fluvial influence on the trace-metal content at the offshore sites was negligible. At greater depths (100 and 200 m) at the SEATS site, where Al concentrations were higher, the M:Al ratios were lower than at the shallower depths, and they were close to the crustal ratios (Table 2). Nevertheless, the M:Al ratios at Chl maximum depth at the DS and SEATS stations were much higher than the crustal ratios (Table 2). Overall, in spite of the slightly higher biomass and Chl *a* values obtained at PR than SEATS (Fig. 5), the metals in the SPM at the PR station were primarily derived from abiogenic, mainly lithogenic particles. Relatively, the metal contents at SEATS station were mainly associated with biogenic particles, especially for the trace metals with relatively low concentrations in crustal materials.

*Trace-metal composition in size-fractionated plankton*—Despite the fact that most of the trace metals in the SPM collected in the surface water at the SEATS were mainly associated with phytoplankton, the M:P ratios in the SPM were far higher than the metal quota averages in the plankton assemblages obtained in reliable field studies (Table 1). These results suggest that the intracellular

plankton metal quotas alone cannot explain the high metal content found in the biogenic SPM at the SEATS station; this implies that most of the metals were from the abiogenic particles adsorbed on the cellular surface of the phytoplankton. The significance of the extracellular metal portion was further examined according to the size-fractionated plankton metal quotas.

To compare the metal quotas of the size-fractionated plankton with the average plankton metal quotas in previous studies and also with the crustal M:Al ratios, the metal quotas of the samples were expressed by plotting the ratios in a log scale in the following reorganized formats of Eq. 1, as shown in Figs. 7 and 8:

$$[M]/[P] = a + b [Al]/[P] \text{ (or } [M]/[Al] = a[P]/[Al] + b) \quad (2)$$

Based on the definition of Eq. 1, the concentrations of the metals and Al in the P-normalized formula have to be normalized to biogenic P instead of total P. However, with the exception of the SPM samples in PR, the abiogenic P is generally negligible (<1%), estimated using the P:Al ratios in crustal material. Also, a recent study found that the abiogenic extracellular inorganic P pool can be an important P source on marine plankton (Sañudo-Wilhelmy et al. 2004). The extracellular P pool was not significant in this study area, and this is supported by the strong correlation between Chl *a* and P and the inverse correlation between Mn and P.

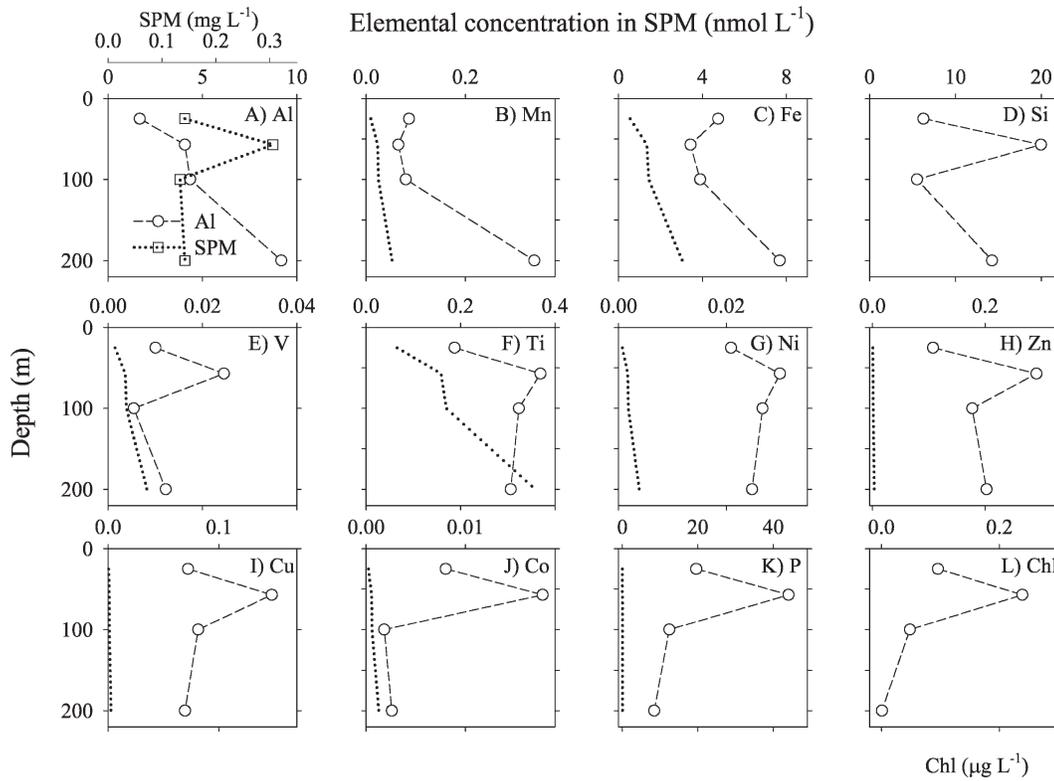


Fig. 5. The vertical concentration profiles of the elements in the SPM, the Chl values, and the total SPM collected in the surface water of the SEAT site, also coupled with the elemental concentration obtained from the average crustal metal: Al ratios, shown as dotted lines. (A) Al, (B) Mn, (C) Fe, (D) Si, (E) V, (F) Ti, (G) Ni, (H) Zn, (I) Cu, (J) Co, (K) P, (L) Chl.

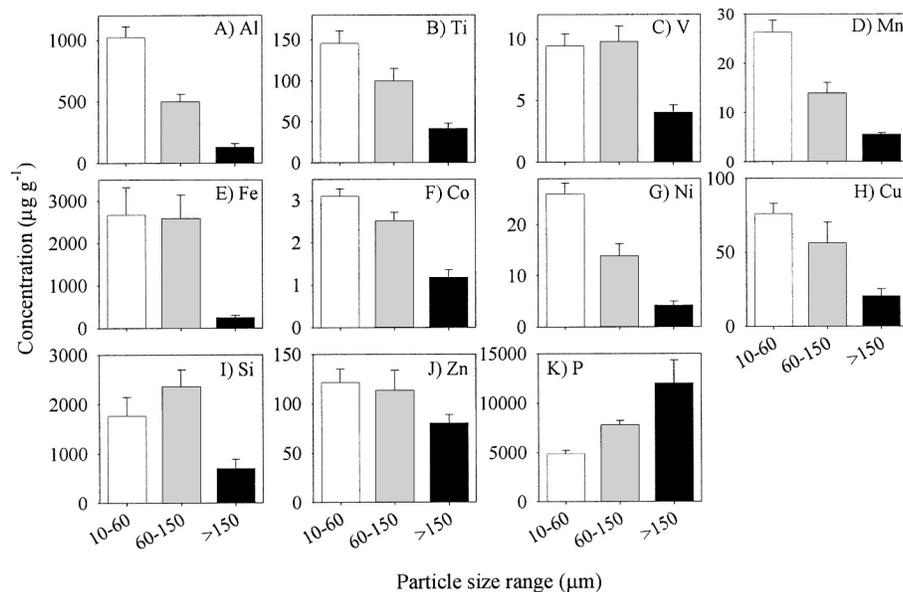


Fig. 6. The comparison of the average metal concentrations in the dried biomass ( $\mu\text{g g}^{-1}$ ) among the three plankton fractions sizes. The error bars represent one standard error. (A) Al, (B) Ti, (C) V, (D) Mn, (E) Fe, (F) Co, (G) Ni, (H) Cu, (I) Si, (J) Zn, (K) P.

Table 2. Comparison of the Al-normalized elemental molar ratios ( $\text{mmol mol}^{-1}$  Al) in crustal dust with the ratios in the SPM.

Station	Depth (m)	Al	Si	P	Ti	V	Mn	Fe	Co	Ni	Cu	Zn
Crustal ratio*		1,000	3,286	11	39	0.9	5.7	331	0.14	0.4	0.3	0.4
PR	2	1,000	983	158	11	0.8	10	411	0.3	0.5	0.7	4.8
	5	1,000	1,360	355	12	1.1	20	1,058	0.5	0.4	2.6	10.8
	10	1,000	628	137	10	0.8	13	819	0.3	0.4	0.6	2.8
	20	1,000	127	68	11	0.8	14	528	0.2	0.4	0.4	2.4
	30	1,000	30	34	9	0.7	11	451	0.2	0.4	0.4	1.6
DS	40	1,000	3,118	7,191	63	2.8	31	1,413	2.2	44.2	43.8	167.5
SEATS	25	1,000	3,732	11,649	111	6.0	51	2,826	4.8	12.4	42.8	63.9
	57	1,000	4,733	7,898	67	4.9	19	Na	4.0	7.9	42.2	73.1
	57	1,000	3,271	11,267	97	6.6	13	298	4.4	4.0	26.5	59.6
	57	1,000	7,584	14,719	118	7.0	15	1,839	4.8	11.5	41.1	86.3
	100	1,000	1,271	2,865	74	1.3	18	893	0.4	6.1	18.7	40.7
	200	1,000	1,553	919	33	1.3	37	837	0.3	2.7	7.6	22.1

\* Taylor (1964).

As shown in Fig. 7, significant positive correlations were observed between M:P and Al:P for all of the metals in the size-fractionated plankton samples. Since most of the metals both in the SPM and the size-fractionated plankton at the SEATS station were mainly associated with

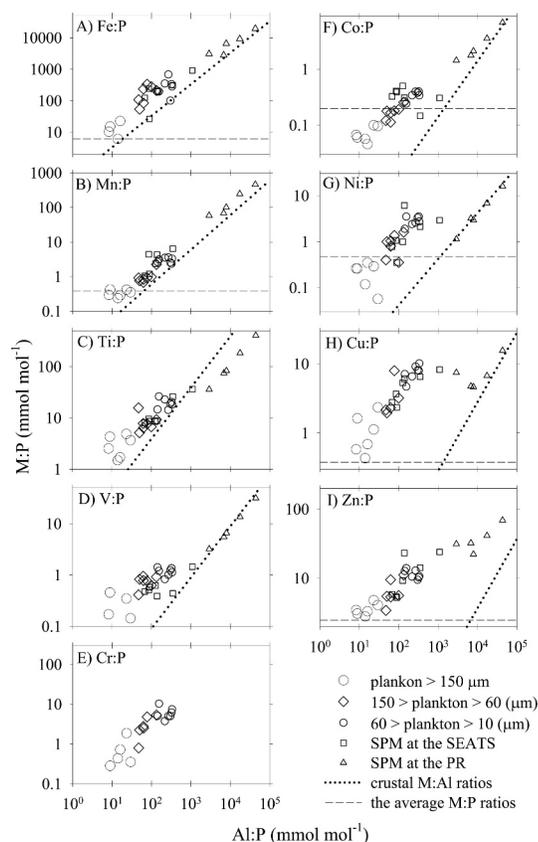


Fig. 7. The comparison of the P-normalized metal quotas with Al:P ratios in all of the particles collected. The x-axis, parallel dashed lines represent the average metal quotas in marine plankton assemblages obtained from previous reliable studies. The dotted lines denote the average metal:Al ratios in crustal material. (A) Fe:P, (B) Mn:P, (C) Ti:P, (D) V:P, (E) Cr:P, (F) Co:P, (G) Ni:P, (H) Cu:P, (I) Zn:P.

plankton, the metals were either located intracellularly or on the cell surface. The high metal quotas and the positive correlation between M:P and Al:P show that the metals in the smaller plankton and the SPM were mostly from abiotic particles, probably in the form of inorganic particles adsorbed on the plankton surface. As the extracellular metals were carried together and transformed together with the plankton themselves, the extracellular metal pool would go with the plankton when they sink or are grazed.

The difference in the metal quotas between the largest and the smallest plankton fractions is about one order of magnitude. Using Mn as an example, the Mn quotas ranged from 0.3 to 4.0  $\text{mmol}:\text{mol P}$  for the largest and the smallest plankton fractions, respectively. Assuming that the metal quota in the largest plankton was mostly intracellular, this result indicates that the metal amount in the extracellular pools was up to 10 times that of the intracellular metal pools. Given the relatively similar biomass dry weight among the three size fractions (Table 1), the much higher surface area:volume ratios in the smaller plankton may also explain the observation of the smaller the plankton, the higher the metal quotas. Since the smaller phytoplankton would be grazed by zooplankton, part of the metals on the phytoplankton would be digested and absorbed and part of them would be repacked into fecal pellets before being transported into deep waters as sinking particles (Wang and Fisher 1998). Determining how the abiotic particles on the phytoplankton are recycled in the deep waters, after being grazed and repackaged to fecal pellets through grazer's gastrointestinal environment, is important for illustrating the whole picture of the internal cycling of the trace metals in oceanic water columns.

The x-axis, parallel dashed lines shown in Fig. 7 denote the average metal quotas in marine plankton assemblages obtained from previous reliable studies (Ho 2006). In the plankton fraction larger than 150  $\mu\text{m}$ , the P-normalized metal quotas for Fe, Mn, Ti, V, Cr, Co, Ni, Cu, and Zn are  $13.5 \pm 7.1$ ,  $0.33 \pm 0.07$ ,  $3.1 \pm 1.4$ ,  $0.28 \pm 0.15$ ,  $0.44 \pm 0.19$ ,  $0.071 \pm 0.022$ ,  $0.22 \pm 0.11$ ,  $1.1 \pm 0.7$ , and  $3.6 \pm 0.7$

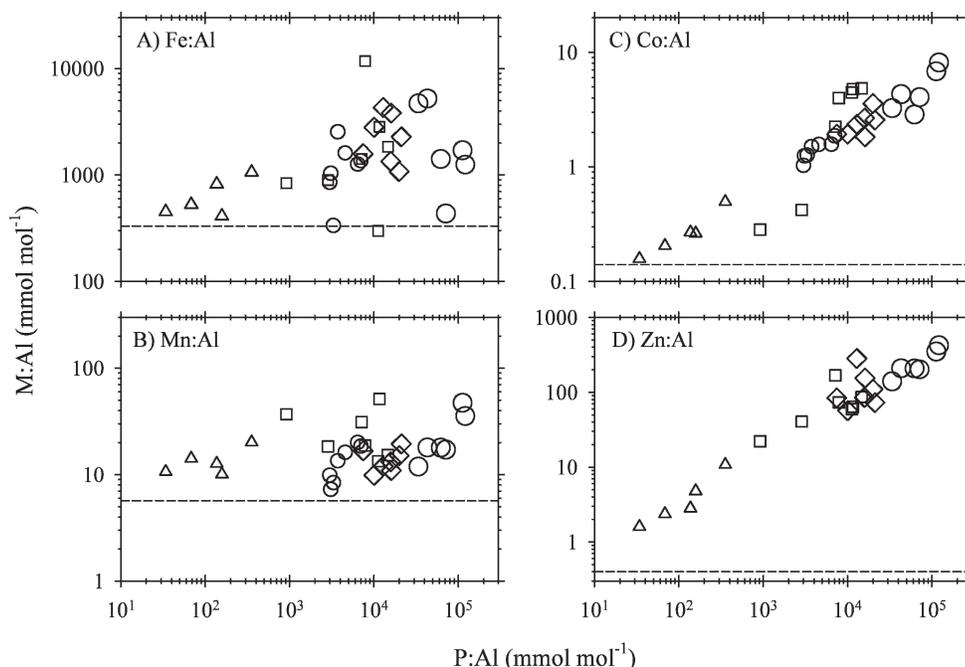


Fig. 8. The comparison of the Al-normalized metal ratios with P:Al ratios in all of the particles collected. The  $x$ -axis, parallel dashed lines represent the metal:Al ratios in crustal material. (A) Fe:Al, (B) Mn:Al, (C) Co:Al, (D) Zn:Al.

(mmol:mol P  $\pm$  one standard deviation), respectively. The lower ends or the averages of the metal quotas for Fe, Mn, Cu, and Zn in the largest plankton fraction are remarkably close to the dashed lines, supporting the argument that the metal composition of marine plankton assemblage may exhibit a rather constant value. However, the metal quotas of Co in the largest plankton assemblages are significantly smaller than the average value. The strong positive linear correlation between Co:P and Al:P in the diverse-sized plankton indicates that the Co quotas in the smaller-plankton fractions were mainly from abiogenic particles. It appears that the truly intracellular Co quotas in the zooplankton assemblage in the South China Sea would be lower than the average reported previously.

The Fe:Al and Mn:Al ratios in the size-fractionated plankton were relatively closer to the crustal ratios as compared to other metals, and the quota differences among different sizes were less significant (Fig. 8), suggesting that the abiotic source was more important for the two metals in the plankton samples. The influence of the abiotic portion can be roughly estimated by using the M:Al ratios in the plankton, assuming all Al are abiogenic. Using Mn as an example, by using the 0.0057 M:Al crustal molar ratio as the average in the abiogenic particles and assuming all of the abiotic Mn from lithogenic particles, the estimated abiogenic Mn quota for the largest plankton fraction is about 0.09 Mn:P (mmol:mol), making up significant but minor quantity in the total Mn quotas ( $0.33 \pm 0.07$  mmol:mol P). Applying the same approach to Fe, the estimated abiogenic Fe in the largest plankton fraction would be 3.3, compared to the average,  $13.5 \pm 7.1$  mmol:mol P. The metal quota averages determined in the largest plankton fraction in this study should be considered as the

upper limit of the intracellular metal quotas in the plankton assemblages. The intracellular Fe or Mn quotas may be even lower if the extracellular metals are composed of non-Al metal oxides such as  $\text{MnO}_2$  or  $\text{Fe}_2\text{O}_3$ . In this case, the trace-metal-clean extracellular metal wash technique is crucial for determining the intracellular metal pools (Tovar-Sanchez et al. 2003). Unfortunately, the technique was still not available when the samples were collected. Moreover, due to the low plankton biomass for each fraction in the oligotrophic waters, which was around 1 mg after filtering 120 liters of seawater in this study (Table 1), it is expected to be highly operationally challenging to accurately determine the extracellular and intracellular metal pools in the size-fractionated plankton.

*Sources of the extracellular metals*—As shown in Table 2, with the exception of Zn, the M:Al ratios in the SPM at the PR station were generally close to crustal M:Al ratios, indicating that the metals were directly from riverine lithogenic particles. In contrast to the nearshore site, the deviations for the M:Al ratios between the SPM and crustal dust were very large at the offshore SEATS site, especially for V, Cr, Co, Ni, Cu, and Zn (Table 2). Similarly, compared to the M:Al ratios in crustal dust, extremely high M:Al ratios were observed in the smaller plankton fractions. For example, the ratios of Zn:Al in the plankton were 100 times higher than the crustal ratios (Fig. 8). The elevated M:Al ratios in the size-fractionated plankton suggest that the extracellular abiogenic metals associated with the plankton were not directly composed of lithogenic particles.

The pulse Mongolian dust storm during March–April has been considered to be the major source of lithogenic

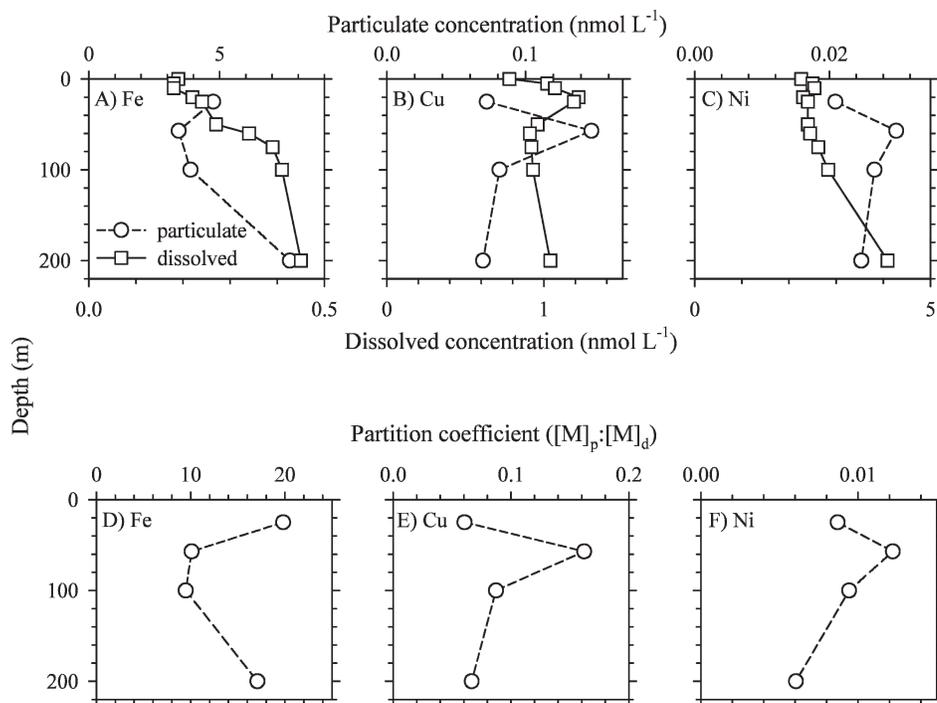


Fig. 9. Comparison of the particulate, dissolved concentrations, and the partition coefficients for Fe, Cu, and Ni in the surface water at the SEATS. The information of the dissolved metals was adopted from the study of Wen et al. (2006). (A) Fe, (B) Cu, (C) Ni, (D) Fe, (E) Cu, (F) Ni.

particles in the western Pacific, including the South China Sea region (Duce and Tindale 1991). However, recent studies have found that the all-year-long anthropogenic aerosols in contact with HCl and HNO<sub>3</sub> are actually a more important aerosol source in the Yellow Sea and East China Sea, indicating that the soluble iron and other metals in the East Asian oceanic region are strongly associated with anthropogenic activity instead of the pulse desert crustal dust input (Meskhidze et al. 2003; Chuang et al. 2005). In the South China Sea area, satellite images also have observed that the steady input of anthropogenic and biomass-burning aerosols in the region is a predominant source of the aerosols in the region (Lin et al. 2007). Moreover, the metal dissolution experiments using the aerosols collected in the South China Sea region also found a very high metal dissolution percentage in the aerosol, especially for the metals like Zn and Fe (Hsu et al. unpubl. data), indicating a strong anthropogenic influence on the aerosol composition and a potentially important trace-metal source in the oceanic region. These observations are consistent with the high extracellular metal composition and high M:Al values that we found in the size-fractionated plankton. Based on these lines of evidence, we propose that the high extracellular metal concentrations on the cell surface mainly come from the metals dissolved in the anthropogenic aerosols containing dissolved trace metals, as found in the Yellow Sea and the East China Sea (Chuang et al. 2005). Under the low pH condition in the aerosols, Fe and other metals in the abiotic particles would be remobilized to eventually become metal salts; once the

aerosols contacted the surface seawater or were brought into the ocean by precipitation, the metal salts in the aerosols would be dissolved, precipitated, and re-adsorbed on particles, presumably the biogenic ones, mainly small phytoplankton. Depending on the solubility of the metals in seawater and the adsorption properties of the algal surface, the metals in dissolved and particulate pools should have a distinct and specific distribution in the seawater. The concentrations of the dissolved metals (Fe, Cu, and Ni) were also collected simultaneously and have already been reported in the study of Wen et al. (2006). The dissolved Fe concentration in the depths of surface water was up to 0.2 nmol L<sup>-1</sup>, but the particulate Fe concentrations were even higher, ranging from 3 to 8 nmol L<sup>-1</sup>, suggesting a strong particulate metal source in the surface water. The metal partition coefficients, the molar ratios of particulate to dissolved concentrations, are shown in Fig. 9. As expected, the partition coefficients of the three metals obey their adsorption property on particulate surface, in the order of Fe ≫ Cu ≫ Ni.

The huge human population number in the developing countries surrounding the South China Sea area would guarantee the steady and probably increasing input of anthropogenic aerosols all year long from the burning of fossil fuel and biomass in the region. This scenario explains why there were such high extracellular metal concentrations on plankton surfaces in the surface waters of the offshore sites in the South China Sea and why the M:Al ratios were highly enriched in the abiogenic metals on the plankton. Further culture addition experiments carried out

by adding the aerosols collected in the region into algal cultures in the laboratory will validate the hypothesis.

In contrast with the areas with low aerosols input, where the abiogenic extracellular metal pool were insignificant (Collier and Edmond 1984; Cullen et al. 2003), the findings of this study reveal that the extracellular metal pool in the fairly large phytoplankton fractions ( $>10\ \mu\text{m}$ ) can have a much higher value than their intracellular pool, even in oceanic offshore sites. Associated with the extensive use of fossil fuel and combusted biomass on Earth, it would be expected that overwhelming extracellular metal adsorption from anthropogenic aerosol metal sources would be common, especially for the oceanic areas close to strong anthropogenic activity. The Redfield stoichiometry concept for the trace-metal composition in marine plankton assemblages would become shaky in these areas in terms of vertical transport. Conceptually, it would still be possible to observe a fairly consistent "intracellular" trace-metal composition in marine plankton assemblages, but the total metal quotas would largely depend on the amount of extracellular pools, and it would likely vary from site to site.

This study reports high-quality trace-metal composition data in diverse-sized plankton collected in the surface water of the oligotrophic South China Sea. The results demonstrate that trace-metal quotas in the three size-fractionated plankton exhibit significant size-dependent variability; in particular, the metal concentrations of the smaller plankton were much higher than the largest fraction, but the significant positive concentration correlations between the metals and Al in the diverse plankton indicate that the majority of the trace metals in the smaller plankton fractions were abiogenic and extracellular. Compared to the M:Al ratios in the terrigenous SPM collected in the coastal waters, the much higher M:Al ratios indicate that the extracellular metals were not directly from the lithogenic SPM but came from the authigenic particles adsorbed on the plankton surface. We propose that the anthropogenic aerosols containing dissolved trace metals are the major source for the extracellular metals. Relatively, the P-normalized trace-metal quotas in plankton larger than  $150\ \mu\text{m}$ , mostly composed of copepods, are as low as the average plankton metal quotas obtained from previous field studies; however, the phytoplankton ranging from 10 to 60 and 60 to  $150\ \mu\text{m}$  carry large amount of trace metals extracellularly. Further studies would be useful to determine whether the extracellular metal adsorption on the relatively smaller phytoplankton is a common phenomenon in oceanic areas with high anthropogenic aerosol input, and how the extracellular metals in the smaller phytoplankton are recycled in oceanic water columns.

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