

## Trace metal cycling in the surface water of the South China Sea: Vertical fluxes, composition, and sources

Tung-Yuan Ho,<sup>a,b,\*</sup> Wen-Chen Chou,<sup>c</sup> Ching-Ling Wei,<sup>d</sup> Fei-Jan Lin,<sup>d</sup> George T. F. Wong,<sup>a,b</sup> and Hui-Ling Lin<sup>e</sup>

<sup>a</sup>Research Center for Environmental Changes, Academia Sinica, Taipei, Taiwan

<sup>b</sup>Institute of Hydrological and Oceanic Sciences, National Central University, Zhongli, Taiwan

<sup>c</sup>Institute of Marine Environmental Chemistry and Ecology, National Taiwan Ocean University, Keelung, Taiwan

<sup>d</sup>Institute of Oceanography, National Taiwan University, Taipei, Taiwan

<sup>e</sup>Institute of Marine Geology and Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan

### *Abstract*

We deployed floating traps in the surface waters of the South China Sea on four occasions at depths of 30 m, 100 m, and 160 m from 2006 to 2007 to quantify vertical metal fluxes in the surface water and examine trace metal composition in the sinking particles to investigate their sources. The elements determined include 13 trace metals and 8 major elements. The fluxes for most of the bioactive elements at 30 m varied markedly during different seasons and strongly co-varied with organic matter production, but the fluxes at 160 m were low and consistent under different seasons, showing that most of the elements were internally recycled in the surface water during productive seasons. Most of the bioactive trace metals in sinking particles were correlated with biogenic P, and their P-normalized quotas were also strongly associated with lithogenic Al. The ratios of metals to Al and P for most of the bioactive trace metals were significantly higher than the ratios in lithogenic particles and than intracellular quotas in plankton, respectively, indicating that the trace metals in the sinking particles were abiogenic, nonlithogenic, and adsorbed on biogenic particles. The comparable fluxes between aeolian deposition and the sinking particles in the mixed layer demonstrate that the highly enriched trace metals in the sinking particles were attributed to input from anthropogenic aerosols. The coupling and transport of anthropogenic trace metals with biogenic particles in oceanic surface waters may be an important mechanism for trace metal cycling in global oceans.

Trace metals serve important roles as regulators of ocean processes, including marine ecosystem dynamics and global carbon cycling (Henderson et al. 2007). Consequently, identifying biogeochemical processes that regulate internal cycling of trace metals and quantifying their rates and fluxes in marine water columns are vital to establishing the roles they play as regulators and recorders of ocean processes (Anderson and Henderson 2005). Biogenic particles generated in oceanic surface water are one of the most important forcings regulating the internal cycling of trace metals in marine water columns (Turekian 1977; Whitfield and Turner 1987; Kuss and Kremling 1999). The particles interact with both dissolved and particulate bioactive trace metals through processes like active biological uptake or passive adsorption. In particular, large biogenic particles, mostly composed of detritus and hard parts of sizable phytoplankton and zooplankton and fecal pellets of zooplankton, serve as the predominant components of sinking particles in oceanic surface waters (Bruland 1983; Fowler and Knauer 1986; Alldredge and Jackson 1995). These particles become dominant agents in transporting major and trace elements from oceanic surface waters to deep waters. In addition, particle fluxes regulate the concentrations and availability of trace metals in oceanic water columns. Thus, the elemental composition of marine plankton and sinking particles, and the fluxes of sinking particles in oceanic surface waters are essential

information for understanding how trace metals are internally cycled in oceanic water columns.

Intracellular trace-metal composition or quotas in phytoplankton assemblages provide us fundamental information to understand how trace metals are transported and associated with biogenic particles. With the efforts carried out by both field and laboratory studies during the past three decades, we now obtain fairly convincing numbers on intracellular trace-metal composition in marine phytoplankton assemblages (Martin and Knauer 1973; Ho et al. 2003; Ho 2006). Based on the intracellular quota information, our recent field study observed that overwhelming amounts of trace metals were adsorbed on phytoplankton cellular surface in the offshore deep-water time-series station in the South China Sea, Southeast-Asian-Time-Series (SEATS). Compared to metal:Al ratios in crustal composition, the highly elevated metal:Al ratios observed in the phytoplankton samples indicated that the adsorbed extracellular metals were abiotic and nonlithogenic. We hypothesized that the most likely source for the highly enriched extracellular metals was anthropogenic aerosols containing markedly soluble trace metals (Ho et al. 2007).

Atmospheric input is a major source of bioactive trace metals in the surface waters of the open ocean. The majority of soluble trace metals originating from both wet and dry deposition would precipitate in seawater, then associate with suspended and/or sinking particles due to their low solubility in seawater and the adsorption properties on particles. The subtropical and tropical

\* Corresponding author: tyho@gate.sinica.edu.tw

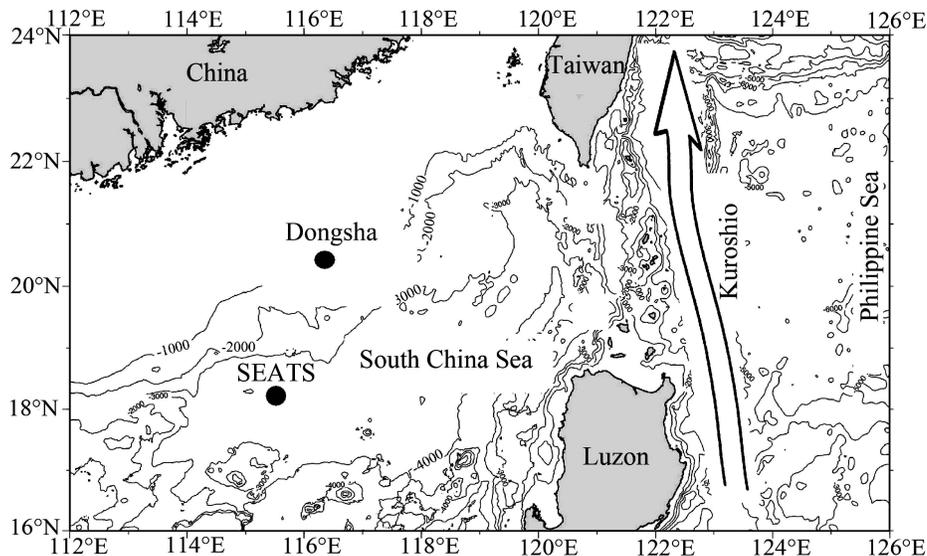


Fig. 1. Location of the sampling site SEATS (115°34'E, 18°15'N) and Dongsha atoll (116°43'E, 20°42'N) in the northern South China Sea.

Western Pacific Ocean is known to receive high aerosol deposit originating from dust storms and anthropogenic and biomass burning (Jickells et al. 2005; Lin et al. 2007). In this study, we have deployed neutrally buoyant particle traps in the surface water of SEATS station for four occasions to collect sinking particles at depths of 30 m, 100 m, and 160 m in the sea to quantitatively investigate vertical fluxes of trace metals in the surface water and to investigate the trace metal sources in the sinking particles. To the best of our knowledge, previous flux studies have deployed their particle traps in deep waters so that our understanding of trace metal fluxes in the surface water of deep oceanic waters remain unclear. The trace metal fluxes and composition reported here provide useful information for us to better understand how trace metals cycle in oceanic surface waters.

## Methods

**Sampling site**—The sampling site, SEATS, was located in the northern South China Sea basin with a bottom depth of 3783 m (Fig. 1). The northern South China Sea experiences northeastern monsoon in winter from October to April and southwestern monsoon in summer from May to September annually. Observed by satellite images, anthropogenic aerosols from fossil-fuel and biomass burning originating from China and Southeast Asia are brought to the region all year long (Lin et al. 2007).

Occasionally, the winter monsoon may also induce dust storms originating from the deserts in central China and input lithogenic particles to the surface water. This semiclosed deep-water basin also lies in a region surrounded with high fluvial input from the shelf, mainly from the Pearl River next to the northern South China Sea and the Mekong River next to the southern South China Sea. Lateral transport of lithogenic particles from the continental shelf and break may be significant in the shelf-sea region. More oceanographic background about the South China Sea can be found in Wong et al. (2007a).

The sinking particles at the SEATS station were collected with a custom-made floating sediment-trap array, which consisted of eight cylindrical Plexiglass tubes (6.4-cm diameter and 9.53 aspect ratio) with honeycomb baffles covering the trap mouths (Wei et al. 1994). The arrays were deployed at the SEATS site at three depths (30 m, 100 m, and 160 m) for ~ 2 d during each cruise (Table 1). The trap solutions were prepared in a polypropylene bottle by adding 800 g of Merck GR grade NaCl to 20 liters of subsurface seawaters taken near the trap deployment location, in which trace metal concentrations were known to be very low (Wen et al. 2006). The total trace-metal masses in the sinking particles collected in the tubes for the metals were at least one order of magnitude higher than the total trace-metal masses originating from the NaCl salts; thus, the possible contamination from the brine water is ignorable. Upon recovery, the sinking particles in the brine water of a tube were filtered

Table 1. The detailed information of the cruise time, sampling location, and period.

ID No.	Cruise No.	Deployed depth (m)	Deployment/recovery time	Deployment/recovery location
SEATS-FT2	ORI-812	30, 100	19:00 h 20 Oct/07:00 h 22 Oct 2006 (36 h)	115°39'; 18°19'/unrecorded
SEATS-FT3	ORI-821	30, 100, 160	18:10 h 15 Jan/13:10 h 17 Jan 2007 (43 h)	115°40'; 18°16'/115°44'; 18°11'
SEATS-FT4	ORIII-1239	30, 100, 160	18:50 h 30 Jul/18:50 h 01 Aug 2007 (48 h)	115°40'; 18°14'/116°01'; 18°02'
SEATS-FT5	ORI-845	30, 100, 160	11:30 h 23 Oct/07:30 h 25 Oct 2007 (44 h)	115°30'; 18°17'/115°21'; 18°48'

through 47-mm precombusted GF/F filters for organic carbon analysis. The sinking particles of the other tube were filtered through 47-mm 0.45- $\mu\text{m}$  polycarbonate filters for trace metal analysis. In a land-based laboratory, the swimmers retained on the filters were manually removed using plastic forceps and the samples were then freeze-dried for further chemical processing and analysis.

**Pretreatment and analysis**—After being freeze-dried, the filters for organic carbon analysis were fumed for 24 h with concentrated HCl to remove extracellular calcium carbonate, then were analyzed using an elemental analyzer (Carlo Erba). The filters for trace metal analysis were soaked in a mixture of 1.8 mL super-pure nitric acid and 0.2 mL super-pure hydrofluoric acid (Seastar) in 10-mL acid-washed microwavable Teflon vials. The sample filters and blank filters were digested in a microwave oven (MARS, CEM) at 180°C for 15 min with a 10-min ramp from room temperature to 180°C. After complete digestion, the samples were evaporated to almost dryness on hot plates at 80°C under a trace-metal clean hood. Super-pure nitric acid was added to the samples, and they were diluted sequentially with Element grade Milli-Q water to obtain samples in 3% nitric acid solution, which were ready for inductively coupled plasma mass spectrometer (ICPMS) analysis. Except organic carbon, the concentrations of all other elements analyzed were determined by using a sector field double-focusing high-resolution ICPMS (Element XR, Thermo Scientific), fitted with a de-solvation system (APEX and Spiro, Elemental Scientific). The sensitivity and stability of the instrument were adjusted to optimal condition before analysis. The analysis was conducted with sensitivity around  $10^6$  counts  $\text{s}^{-1}$  for  $1 \mu\text{g L}^{-1}$  in and the analytical precision was normally between 1% and 2%. External and internal standards were both applied for concentration quantification. The details of the analytical precision, accuracy, and detection limits of the ICPMS method were described in Ho et al. (2003, 2007).

**Aeolian deposition fluxes**—A time-series aerosol collection station has been established since April 2007 on Dongsha Island, a coral reef atoll in the northern South China Sea near the SEATS site (Fig. 1). Trace metal concentrations in aerosols are available for the two occasions of this study, July and October in 2007. Daily aerosol samples were collected using Whatman 41 cellulose filters and a flow-controlled total suspended particle high-volume air sampler (Thermo Electron). After collection, the filters were stored in separate sealed plastic bags prior to analysis in laboratory. Filters were digested and pretreated in a mixture of super-pure hydrofluoric acid and  $\text{HNO}_3$ . Trace metal concentrations in the aerosols were determined by ICPMS. Dry-deposition fluxes of trace metals are estimated by multiplying trace metal concentrations in the atmosphere by their deposition velocities suggested by Duce et al. (1991). We used  $2.0 \text{ cm s}^{-1}$  as the deposition velocity for lithogenic-type metals: Al, Fe, Ti, Mn, Ba, and  $0.5 \text{ cm s}^{-1}$  for other anthropogenic metals. Since January 2009, in addition to dry-deposition collection, total deposition samples (dry and wet deposition) have also

been collected weekly (F.-J. Lin unpubl.). The fractions of dry deposition to total deposition are available, which are 0.35 (P), 0.06 (Ba), 0.61 (Al), 0.61 (Fe), 0.08 (Ti), 0.55 (Mn), 0.30 (V), 0.05 (Co), 0.03 (Ni), 0.13 (Zn), 0.05 (Cd), and 0.35 (Pb). Total aeolian deposition fluxes for trace metals during July and October 2007 are obtained by dividing dry-deposition fluxes by their averaged fractions.

## Results

The raw data of elemental fluxes in sinking particles are presented in Table 2 and Figs. 2, 3. Figure 2 shows the fluxes of organic carbon and their correlation with the fluxes of organic P for all depths and seasons. It should be noted that the sampling, the sample pretreatment, and the analytical methods in determining organic carbon and phosphorus were completely independent for the two elements and their samples were also obtained from different tubes of the floating traps. The vertical fluxes of organic C and P presented in Figs. 2, 3 show that their vertical profiles are almost identical and the C:P ratios were also very close to the Redfield ratio, indicating that the sampling, pretreatment, and analytical procedures are reliable and the data quality is high. The fluxes of organic carbon during the four temporal occasions varied markedly at 30 m (Fig. 2), with the highest value observed in January and lowest value in July, which were  $59 \text{ mmol C m}^{-2} \text{ d}^{-1}$  (or  $0.71 \text{ g C m}^{-2} \text{ d}^{-1}$ ) and  $3.2 \text{ mmol C m}^{-2} \text{ d}^{-1}$  (or  $0.038 \text{ g C m}^{-2} \text{ d}^{-1}$ ), respectively. The fluxes of organic C decreased exponentially with depths and their seasonal differences become less significant at the two deeper depths, which were around or less than two-fold of difference among different seasons at 100 m and 160 m. Strong exponential decay of the organic matter in the surface happened mainly during the productive seasons, but not for the low-production summer season.

As shown in Fig. 3, the elemental fluxes at 30 m were spanned over seven orders of magnitude among the elements determined, from  $10,000 \mu\text{mol m}^{-2} \text{ d}^{-1}$  for Ca to  $0.001 \mu\text{mol m}^{-2} \text{ d}^{-1}$  for Th (Table 2; Fig. 3). In general, the magnitude of elemental fluxes followed the sequence:  $\text{Ca} > \text{S} \cong \text{P} \cong \text{Mg} > \text{Al} \cong \text{Fe} > \text{Sr} > \text{Zn} \cong \text{Ti} > \text{Ni} \cong \text{Cu} \cong \text{Mn} \cong \text{Pb} \gg \text{Co} \cong \text{V} \cong \text{Mo} \cong \text{Cd} \gg \text{U} \cong \text{Th}$ . Except for data obtained at the low-production summer time, the vertical fluxes of biogenic elements like P, S, Mg, Sr, Ca, and many other trace metals (including Cd, U, Co, Ni, Cu, Zn, Ti, Pb, Mo, Fe) all decreased with increasing depth in the surface water from 30 m to 160 m (Fig. 3). This feature indicates that they were associated with biogenic matters to some extent, either incorporated into cellular biomass or adsorbed on biogenic particle surfaces. However, the vertical fluxes of a few lithogenic-type metals (Al, Ba, V, and Th) generally did not vary over a factor of two at different depths for same season, indicating that these elements may be transported vertically through abiogenic agents, particularly in the deeper depths. The elements with weak flux gradients, such as Ni, Cu, Mn, and Fe, may thus be attributed to relatively equivalent transport agents between biogenic and abiogenic particles.

Trace metal composition in sinking particles is presented in Fig. 4. Due to historical reason to express the Redfield

Table 2. The raw data of elemental fluxes at 30 m, 100 m, and 160 m in the South China during the four occasions from October 2006 to October 2007. The residence times ( $\tau$ ) of the elements were estimated and presented at the bottom of the table.

Sampling			Elemental flux ( $\mu\text{mol m}^{-2} \text{d}^{-1}$ )								
Yr	Date	Depth (m)	C	Mg	Al	Si*	P	S	Ca	Ti	V
2006	18–24 Oct	30	39,000	523	100	4163	425	658	1398	2.1	0.140
		100	17,400	454	76	2340	192	415	1606	1.7	0.106
2007	12–19 Jan	30	59,100	893	88	1109	712	1125	15,180	10.0	0.121
		100	12,800	257	65	718	191	385	6179	5.1	0.089
		160	7600	118	93	555	55	113	2133	2.9	0.127
2007	28 Jul–03 Aug	30	8600	153	45	510	64	105	897	1.0	0.059
		100	9800	216	96	528	96	138	880	1.1	0.058
		160	3200	108	59	454	47	80	331	0.80	0.057
2007	21–30 Oct	30	40,000	362	79	456	290	765	10,498	7.3	0.133
		100	13,600	223	74	442	94	201	1898	2.7	0.103
		160	8800	147	98	412	61	149	1796	2.1	0.111
$\text{nmol L}^{-1}$ ( $\mu\text{mol m}^{-3}$ )		0–160	$2 \times 10^6$	$5 \times 10^7$	5.0	$1 \times 10^4$	500	$3 \times 10^7$	$1 \times 10^7$	0.3	30
$\tau$ (yr)		0–160	350	$2 \times 10^5$	0.026	9.2	4.0	$10^5$	3100	0.069	140

\*Si data might be underestimated due to the partial loss in sample digestion with hydrogen fluoric acid. The data can be used for reference only.

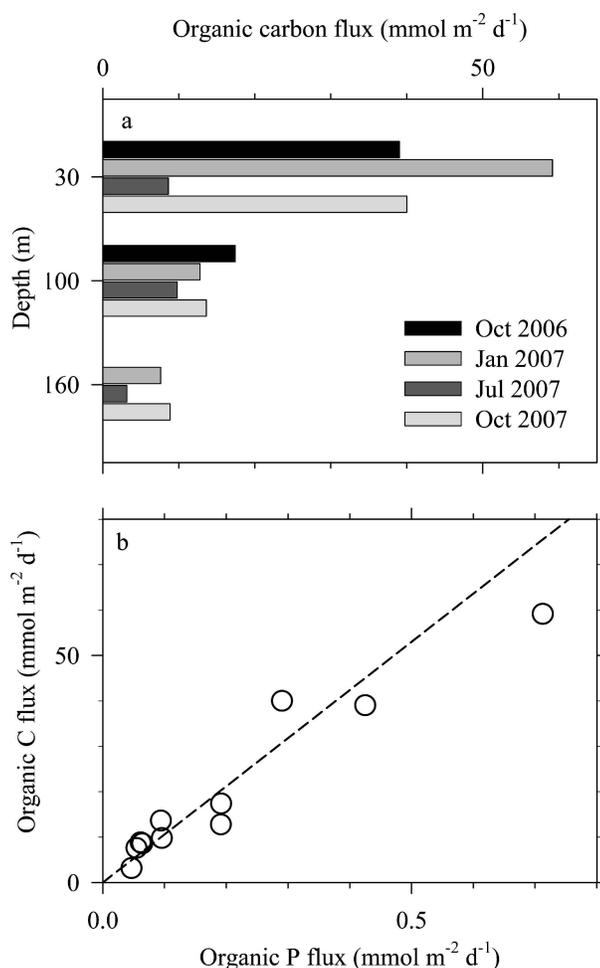


Fig. 2. (a) Comparison of the organic carbon fluxes at the three depths for all cruises in this study. (b) The correlation of the fluxes of organic carbon and phosphorus. The overall average of the C:P ratios in the data set is 109. The dashed reference line stands for the Redfield ratio, 106.

ratio by normalizing C and N to P, previous trace-metal studies have expressed trace metal composition in marine plankton assemblages by normalizing trace metals to P (Collier and Edmond 1984; Kuss and Kremling 1999; Ho et al. 2003). To compare with previous intracellular metal quotas reported, the fluxes or concentrations determined in the sinking particles were also presented by normalizing them to P (Fig. 4). Overall, the ratios of metals to P for most of the bioactive trace metals were significantly higher than the intracellular quotas in plankton, which are presented with the dashed lines in the figures.

## Discussion

*Primary production and vertical fluxes*—The production and transport of organic matter in the euphotic zone is critical in regulating trace metal cycling in marine water columns (Martin and Knauer 1973; Deuser et al. 1983; Bruland et al. 1991). Trace metals can be either incorporated into organic matter or adsorbed on the surface. The packaging of the biogenic and lithogenic particles due to the adsorption of abiotic particles on biogenic particles is known to be an important process in transporting trace metals in oceanic surface waters (Coale and Bruland 1985; Jickells et al. 1990). Early sediment-trap studies have observed strong correlation between biogenic organic matter and lithogenic particles even in the deep water of open oceans (Deuser et al. 1983; Jickells et al. 1984). In our study site, the seasonal variability of primary production has been intensively studied (Chen 2005; Tseng et al. 2005). The seasonal production pattern observed is unique in low-latitude oceanic waters, with highest production during winter with strong northeastern monsoon and lowest production during summer. Elevated production during winter is mainly caused by the coupling effect of surface cooling and wind-induced mixing (Tseng et al. 2005). The mixing layer depth may be deepened from 20 m during summer to 80 m in winter so that the nutrients in the deeper

Table 2. Extended.

Elemental flux ( $\mu\text{mol m}^{-2} \text{d}^{-1}$ )												
Mn	Fe	Co	Ni	Cu	Zn	Sr	Mo	Cd	Ba	Pb	Th	U
1.43	75	0.088	1.43	2.80	4.14	52.9	0.017	0.0279	0.82	3.52	0.00156	0.00218
1.10	46	0.054	1.20	3.28	4.57	12.9	0.039	0.0173	1.66	1.82	0.00119	0.00215
1.79	57	0.110	4.16	2.12	9.92	50.3	0.084	0.0841	0.81	0.85	0.00083	0.00338
1.47	36	0.023	1.79	1.14	4.98	27.4	0.059	0.0165	0.93	1.12	0.00054	0.00159
1.77	42	0.027	1.03	0.51	2.88	11.7	0.036	0.0035	1.55	0.69	0.00065	0.00068
0.39	36	0.023	2.69	1.35	2.20	7.9	0.012	0.0056	0.27	0.27	0.00040	0.00078
0.82	42	0.027	4.03	1.49	3.08	4.2	0.012	0.0060	0.46	0.37	0.00094	0.00128
0.93	33	0.019	1.92	1.64	2.39	1.3	0.013	0.0029	0.67	0.22	0.00071	0.00099
1.88	102	0.045	1.86	1.12	7.68	81.4	0.029	0.0493	1.60	0.93	0.00126	0.00249
1.22	69	0.045	2.99	1.56	3.73	9.7	0.019	0.0090	1.74	0.90	0.00103	0.00098
1.11	46	0.023	1.23	1.18	2.76	5.5	0.014	0.0071	1.19	0.44	0.00115	0.00095
0.4	5.0	0.04	3.0	1.0	1.0	10 <sup>5</sup>	100	0.10	40	0.060	10 <sup>-4</sup>	13
0.14	0.056	0.80	0.99	0.42	0.17	7100	2100	10	15	0.058	0.052	6500

water can be mixed with the surface water to elevate primary production in winter. The seasonal integrated primary production reported by Tseng et al. (2005) ranged from 0.11 g C m<sup>-2</sup> d<sup>-1</sup> in summer to about 0.30 g C m<sup>-2</sup> d<sup>-1</sup> in winter, consistent with the integrated primary production reported by Chen (2005), which ranged from 0.19 g C m<sup>-2</sup> d<sup>-1</sup> to 0.55 g C m<sup>-2</sup> d<sup>-1</sup> for summer and winter, respectively. By using nitrate-based new production, Chen (2005) also reported integrated new production

in the top 100 m. New production was generally low for summer and autumn, ranging from 0.03 g C m<sup>-2</sup> d<sup>-1</sup> to 0.07 g C m<sup>-2</sup> d<sup>-1</sup>, but it was up to 0.26 g C m<sup>-2</sup> d<sup>-1</sup> during winter.

In this study, the fluxes of organic carbon during the four temporal occasions also varied markedly at 30 m (Fig. 2), consistent with the seasonal change of the primary production data reported previously, with the highest value observed in January and lowest value in July, which were

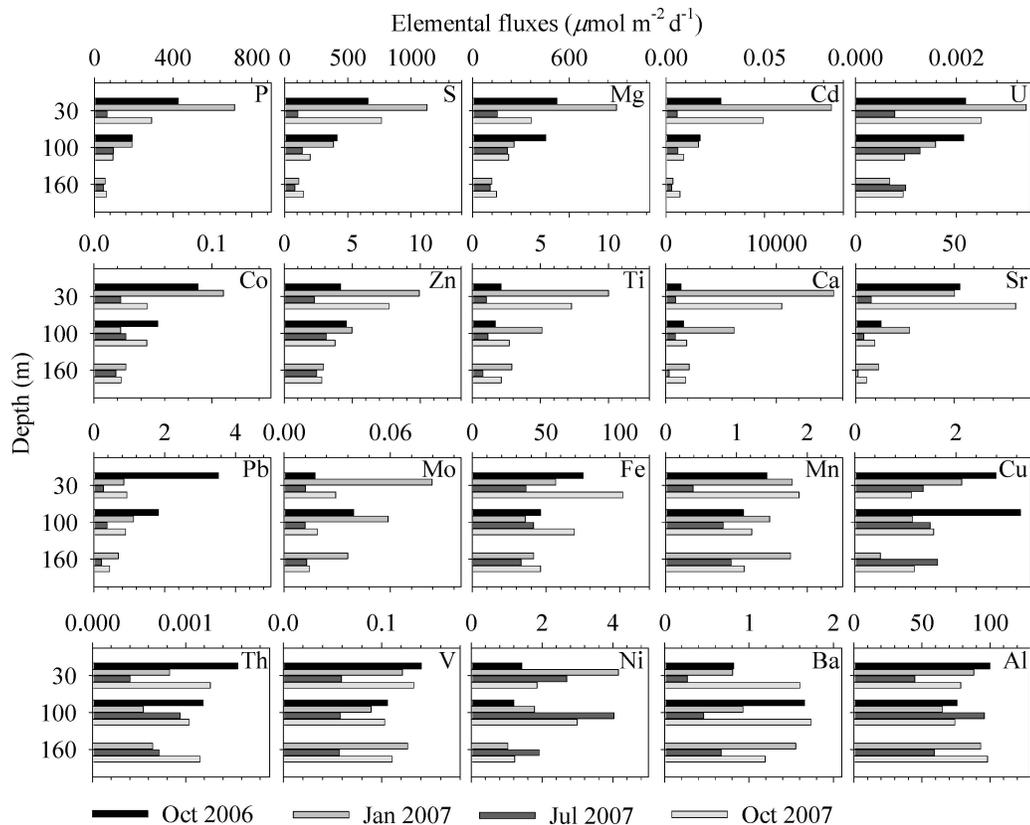


Fig. 3. The elemental fluxes at the depths of 30 m, 100 m, 160 m of the South China Sea for the four occasions, October 2006, January 2006, July 2006, and October 2007.

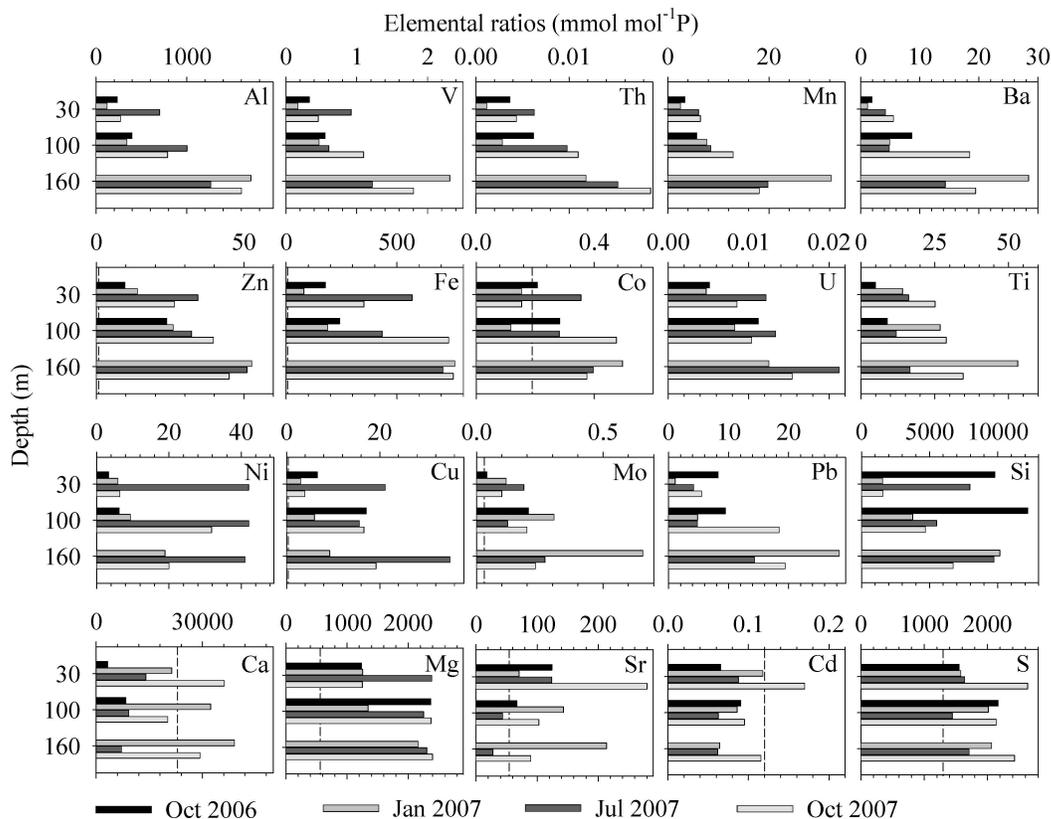


Fig. 4. P-normalized elemental quotas in the sinking particles collected at the depths of 30 m, 100 m, 160 m of the South China Sea during the four sampling occasions, October 2006, January 2006, July 2007, and October 2007. The vertical dashed lines represent the intracellular element-to-P ratios in marine plankton assemblages, shown in the bracket for the elements: Zn (0.8), Fe (7.5), Co (0.19), Cu (0.38), Mo (0.03), Ca (23000), Mg (560), Sr (54), Cd (0.12), and S (1300)  $\text{mmol mol}^{-1} \text{P}$  (Ho et al. 2003; Ho 2006). The individual range of the elemental quotas for Fe, Zn, Mn, Cu, Ni, Co, and Cd in marine plankton are 3.6–7.4, 0.8–3.0, 0.3–1.6, 0.18–0.52, 0.21–1.4, 0.10–0.19, and 0.07–0.54  $\text{mmol mol}^{-1} \text{P}$ , respectively, based on the seven reliable laboratory and field studies for trace metal quotas in marine plankton cited by Ho (2006).

$0.71 \text{ g C m}^{-2} \text{ d}^{-1}$  and  $0.038 \text{ g C m}^{-2} \text{ d}^{-1}$ , respectively. Contrary to temporally varied elemental fluxes at 30 m, the similarity in organic matter fluxes at 160 m in different seasons indicates that most of the increase in new production during the productive seasons was recycled in the top 160 m. The seasonal variability of organic matter fluxes at the deeper depth was less significant than the shallowest depth. This may be partially attributed to the strong seawater density gradient in the surface water which slows down the sinking rate of particles and enhances the respiration of organic matter.

Figure 3 shows that the fluxes of many bioactive trace metals exhibit significantly similar temporal and vertical patterns with organic matter production. Overall, the trace metal fluxes exhibit exponential decrease from 30 m to 160 m with the highest value being during winter and lowest value during summer (Fig. 3). The elements that are most significantly correlated with organic matter fluxes include: Sr, Mo, Cd, U, Mg, S, Ca, Ti, Co, Zn, all with statistical  $p$ -values  $< 0.05$ . Relative to the elements mentioned above, the fluxes of Al, Ba, Th, Fe, V, Ni, Cu, and Pb did not exhibit overall significant correlation with organic matter fluxes (Fig. 3), though many of them still

display the same seasonal trend with organic matter at 30 m during different seasons. The insignificant correlation between these metals and organic matter fluxes is most likely due to the elevated contribution of lithogenic particles at the deeper depths. As shown in Fig. 3, Al fluxes were comparable overall among all seasons and depths and only varied by a factor of two, ranging from  $50 \mu\text{mol m}^{-2} \text{ d}^{-1}$  to  $100 \mu\text{mol m}^{-2} \text{ d}^{-1}$ . Our previous studies also show that the Al concentrations in suspended particles of the surface water from the water surface to 200 m increased with depth, and vertical Al fluxes in the deep water also increased with depth (Ho et al. 2007, 2009), indicating that there has been a strong bottom-up input of lithogenic particles in the euphotic zone. The ratios of Al:P shown in Fig. 4 also exhibit elevated values with depth, again showing that the deeper the water the higher percentages of lithogenic particles are in the sinking particles. The contribution of lithogenic particles to trace metals significantly increases with depth.

With the vertical flux information in the surface water, the residence time of the elements in the top 160-m zonation can be estimated by dividing the total mass of the elements in the zonation by the elemental fluxes

measured by assuming that the vertical export is the major removal pathway in the zonation (Table 2). The averaged elemental fluxes at 160 m were obtained by averaging the elemental fluxes (Table 2). The total elemental inventories in the top 160-m are estimated by multiplying total averaged elemental concentrations by 160 m. The total averaged elemental concentrations were obtained and compiled from several previous studies on trace metals in the South China Sea (Nozaki 2001; Wen et al. 2006; Ho et al. 2007). For the elements Th, U, Pb, Ti, Mn, Ba, V, Ca, Sr, Ba, S, and Mg, the soluble metal concentrations reported by Nozaki (2001) were used. All others are obtained from the studies of Wen et al. (2006) and Ho et al. (2007). As shown in Table 1, the residence time sequences from shortest to longest are: Al (10 d) > Th  $\cong$  Fe  $\cong$  Pb  $\cong$  Ti (20 d) > Mn (50 d) > Zn (60 d) > Cu (150 d) > Co (290 d) > Ni (1 yr) > P (4.0 yr) > Cd (9.7 yr) > Ba (15 yr) > V (140 yr) > C (350 yr) > Mo (2100 yr) > Ca (3100 yr) > U (6500 yr) > Sr (7100 yr) > S (110,000 yr) > Mg (180,000 yr). The residence times of the lithogenic-type metals are particularly short (like Al, Fe, and Ti), possibly due to the high bottom-up fluxes of lithogenic particles rapidly moving in and out of the surface zone. In addition, particle reactive metals (such as Al, Fe, Mn, Th, and Pb) would have relatively short residence time in the surface water where particle fluxes are high. In contrast to the lithogenic metals, the residence times of P and Cd are relatively long. Both are representative bioactive elements that are mainly incorporated into organic matter, again showing strong respiration of organic matter in the top 160 m in the water column. With the strong seasonal variability of aeolian aerosol input in the northern South China Sea, seasonal variability for trace metal concentrations may be observed for some metals in the surface water, particularly for the elements with residence time shorter than a year.

*Lithogenic and anthropogenic sources*—With an understanding of trace metal composition in both biogenic and lithogenic particles, we may quantify the relative contribution of biogenic and lithogenic particles in the sinking particles. Phosphorus and aluminum, with their contrasting known abundance in both biogenic and lithogenic particles, correspondingly, are useful proxies to evaluate the relative contribution of biotic and abiotic sources for trace metals in sinking particles. By assuming constant trace-metal composition in both biogenic and abiogenic particles, their quantitative relationship can be obtained as the following mass balance formula:

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

where [M] is total concentration of metals in particles, [P] is phosphorus concentration in biogenic particles, [Al] is aluminum concentration in abiogenic particles, 'a' is P-normalized metal quotas in biogenic particles, and 'b' is Al-normalized metal quotas in abiogenic (assuming mainly lithogenic) particles.

Although biogenic hard parts, mainly composed of calcite and silica, contribute a major mass portion in

sinking biogenic particles, the concentrations of trace metals and phosphorus in the hard parts are relatively low, such that the contribution of trace metals from the hard parts to overall biogenic particles is ignorable, particularly in the surface waters where organic matters are abundant. Metal:P ratios in biogenic organic particles may reasonably represent overall ratios in biogenic particles. To illustrate the relative contribution of biotic and abiotic particles, the metal quotas of the samples are expressed by plotting the ratios [M]:[P] or [M]:[Al] with the known stoichiometric constants of a and b, which are shown as the vertical dashed lines in the plots for comparison in Figs. 4, 5.

After normalizing to P, the quotas of Mg, Ca, Sr, Cd, and S in the sinking particles over different depths and seasons exhibited comparable value to the known intracellular quotas (Ho et al. 2003; Ho 2006), indicating that these elements were mainly incorporated into biogenic organic matter (Fig. 4). The quotas of most other elements were greatly above the known intracellular metal quotas in biogenic particles and increased with increasing depth. Using Zn and Fe as examples, Zn quotas ranged from 10 mmol mol<sup>-1</sup> P to 50 mmol mol<sup>-1</sup> P; Fe quotas ranged from 100 mmol mol<sup>-1</sup> P to 700 mmol mol<sup>-1</sup> P. Both are one to two orders of magnitude above their known averaged intracellular quotas in marine plankton of 0.8 mmol mol<sup>-1</sup> P and 7.5 mmol mol<sup>-1</sup> P, respectively (Ho et al. 2003; Ho 2006). In addition to Zn and Fe, many other trace metals, including Al, Ti, V, Mn, Co, Ni, Cu, Mo, Ba, Pb, Th, and U, exhibit similar patterns, with increasing and highly enriched quotas with depth. Compared to the known intracellular metal quotas in marine plankton, these highly enriched metal quotas in the sinking particles indicate that most of the metals were abiotic and many of the trace metals were adsorbed on biogenic particle surfaces, particularly at the depth of 30 m (Fig. 3). These results are exactly like what we observed in the suspended marine phytoplankton assemblages reported in our previous study (Ho et al. 2007). The only exception is Cd, which has been observed to be integrated into biogenic organic matter from the surface water to the deep water (Ho et al. 2009).

Because the surface of biogenic particles serve as adsorption agents for transporting trace metals into deeper water, the community structure of phytoplankton could play a role in influencing vertical trace-metal transport through sinking particles in the water column. The composition of the hard parts of different marine phytoplankton may influence the adsorption behaviors of trace metals. It is known that the phytoplankton is dominated by diatoms when the northeastern monsoon starts blowing in October and mixes up major nutrients in deeper water with surface water. With nitrate concentrations going down, coccolithophores follow the diatom bloom and become dominant phytoplankton phylum in the surface water (Chen et al. 2007), which generally lasts from January to March. Indeed, coccolithophores and coccoliths were dominant suspended particulate material in the surface water during January 2007, and were both observed by microscope and also supported by the elevated Ca fluxes

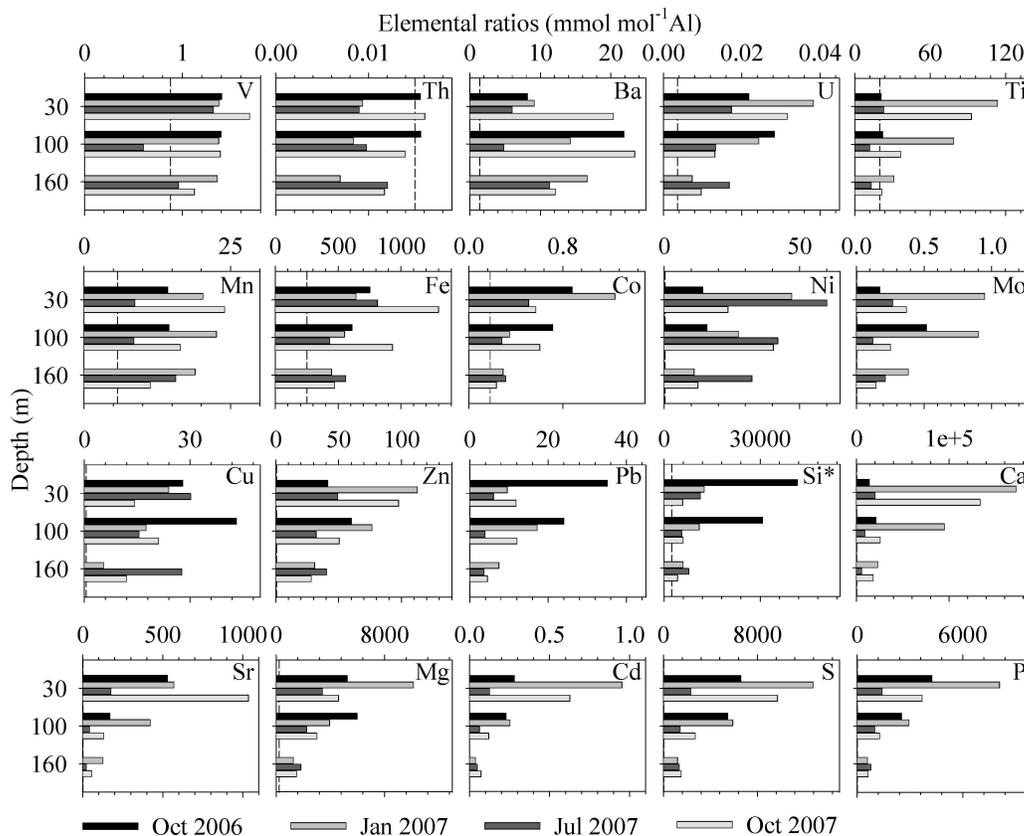


Fig. 5. Al-normalized elemental quotas at the depths of 30 m, 100 m, 160 m of the South China Sea for the four occasions, October 2006, January 2007, July 2007, and October 2007. The vertical dashed lines represent elements-to-Al ratios in the bottom-up lithogenic particles, shown in the brackets for the elements: V (0.88), Th (0.015), Ba (1.4), U (0.0036), Ti (20), Mn (5.7), Fe (252), Co (0.18), Ni (0.32), Mo (0.0034), Cu (0.49), Zn (0.54), Pb (0.043), Si (2417), Ca (225), Sr (0.8), Mg (235), Cd (0.0006), S (31), and P (8.3)  $\text{mmol mol}^{-1}$  Al. Most of the ratios are obtained from the study of Calvert et al. (1993) for the sediment sample number labeled as GGC1, which was located around  $117^{\circ}50'E$ ,  $14^{\circ}00'N$ , relatively close to our SEATS site, except Cd, Th, and U, which are obtained from the study of Taylor (1964). The averaged crustal ratios ( $\text{mmol mol}^{-1}$ : Al) from the study of Taylor (1964) are: V (0.90), Th (0.015), U (0.0036), Ti (39), Mn (5.7), Fe (331), Co (0.14), Ni (0.40), Cu (0.30), Zn (0.40), and Si (3286), which are fairly close to the ratios shown in this figure.

(Figs. 3, 6). We also observed that the elements associated with P are highly associated with Ca. After normalizing P, many trace metal quotas were still strongly associated with the ratios of Ca:P, indicating that adsorption on calcium carbonate surface is important. For example, Ti and Zn exhibit even stronger correlations to Ca than to P (Fig. 7).

Likewise, after normalizing to Al, the ratios of V:Al and Th:Al exhibit comparable value, within a factor of 2, over different depths and different seasons to the ratios of the lithogenic value reported by Calvert et al. (1993), indicating that significant amounts of the elements in sinking particles were from lithogenic particles (Fig. 5). However, most of other elements-to-Al ratios decreased with increasing depth and their metal:Al ratios were far above the known lithogenic composition in the sampling site (Fig. 5). Three possible sources may contribute to these highly enriched trace metals, which include atmospheric aerosol input, bottom-up deep-water input, or riverine lateral transport input. As discussed, the possibility to have a bottom-up input for the highly enriched trace metals in the sinking particles can be first excluded (Ho et al. 2007, 2009). The

concentrations of Al and Fe at 600 m and 3300 m from 2004 to 2005 exhibited a strong linear correlation with a slope of 0.253 mol:mol Al (T. Y. Ho unpubl.), which is analytically the same as the Fe:Al ratio 0.252 mol:mol observed in the composition of the sediments in the South China Sea stations close to our sampling site (Calvert et al. 1993). Moreover, the decreasing M:Al ratios with depth shown in Fig. 5 also indicate that the deeper the depth the higher the percentage of lithogenic particles accounted for in the sinking particles. The Fe:Al ratios in the sinking particles collected in the surface waters were significantly higher than the ratios at 600 m and 3300 m (Fig. 8). The possibility of lateral riverine input for the highly enriched trace metals in the sinking particles can also be excluded. The major riverine water source close to the SEATS sampling site in the northern South China Sea is the Pearl River. We measured the suspended particles in the surface waters at the three stations between the SEATS site and the Pearl River mouth and observed that trace metal composition in the suspended particles collected in the surface waters at the river mouth station (Pearl River, PR) were

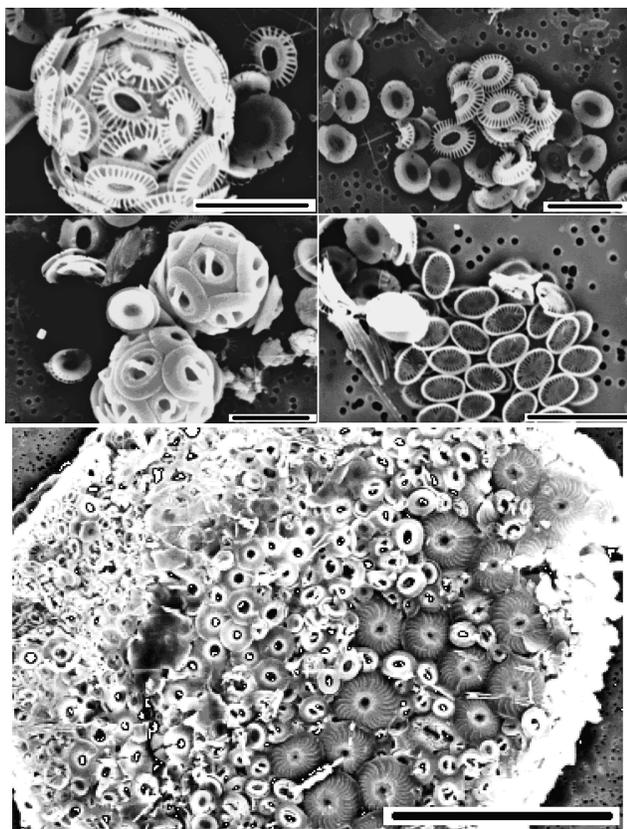


Fig. 6. Scanning electron microscopic images for the suspended particles collected at 30 m in the cruise of January 2007. The bars in the lower right corners of the top four images stand for 5  $\mu\text{m}$ ; the bar in the bottom image stands for 30  $\mu\text{m}$ . This bottom image was a large suspended particle with diameter around 100  $\mu\text{m}$ , which was covered with various coccoliths.

mainly lithogenic, and the signal of lithogenic particles did not reach the surface water at the other coastal stations located on the continental shelf and rise, indicating that horizontal lithogenic particle transport from the Pearl River to the SEATS is negligible (Ho et al. 2007).

Because bottom-up vertical transport and horizontal riverine transport are both featured with lithogenic particles in the region, the only possible source to cause the highly enriched metals in the sinking particles of the surface water is due to atmospheric deposition. Aerosol input is known to be a major allochthonous trace-metal source in oceanic surface water (Jickells et al. 2005). The northern South China Sea is right next to populous southern China, which has been one of most rapidly industrializing regions globally. In particular, coal burning is dominant in Chinese fossil-fuel consumption, which accounts for about one-third of global coal consumption. Results from the moderate resolution imaging spectroradiometer and the Quick scatterometer demonstrate that anthropogenic fine aerosols reach the atmosphere of the South China Sea and the Western Pacific Ocean during the high-pressure northeastern monsoon period (Lin et al. 2007). In addition, huge population centers in surrounding developing countries of the South China Sea region would

also guarantee a steady and increasing input of anthropogenic aerosols from both fossil-fuel and biomass burning in the region all year round. Indeed, studies show that aerosols above the South China Sea feature anthropogenic properties (Lin et al. 2007; Zhang et al. 2007).

*A model for trace metal cycling in the upper ocean*—We propose a schematic model for trace metal cycling in the surface water of the South China Sea (Fig. 9). Sinking particles in the surface water are composed of biogenic, lithogenic, and anthropogenic particles all together and the relative contribution of each kind of particles to trace metal composition in suspended and sinking particles varies greatly with depth. Although biogenic particles serve as major agents for transporting trace metals, the contribution of intracellular trace metals to most of the trace metals in the sinking particles is trivial. The major source for most of the trace metals in the sinking particles of the mixed layer is from aeolian deposition, in which most of the trace metals are anthropogenic. Anthropogenic trace metals originating either from dry or wet deposition through aeolian transport are mostly soluble. Soluble trace metals may be either chelated by soluble organic ligands or precipitated to hydroxide metals or other chemical precipitates. Both nonsoluble aerosol particles and precipitates adsorb on biogenic particles, which serve as agents to vertically transport the trace metals from the mixed layer to the deep waters. The contribution of lithogenic particles to the sinking particles increases with depth as the concentrations of resuspended lithogenic particles increase with depth. These lithogenic particles can be transported by biogenic particles or sink down by themselves as shown in Fig. 9.

To validate this schematic model, we examine trace metal composition in the sinking particles and compare the trace metal fluxes estimated from floating traps with the fluxes of their major sources: trace metal fluxes from aeolian deposition and trace metal fluxes from vertical water exchange below the mixed layer.

The highly enriched M:Al ratios indicate that most of the metals are anthropogenic and most likely to originate from aeolian deposition (Fig. 5). Using Zn as an example, a trace metal known to be of anthropogenic origin in aerosols, Zn:Al quotas ranged from 30  $\text{mmol mol}^{-1}$  to 100  $\text{mmol mol}^{-1}$  Al in the sinking particles—two to three orders of magnitude higher than standard Zn:Al ratios (0.54  $\text{mmol mol}^{-1}$ ) in the lithogenic particle in the sampling site. These highly enriched Zn:Al ratios in the sinking particles are comparable with averaged Zn:Al ratios in the aerosol samples collected on Dongsha atoll, varying from 45  $\text{mmol mol}^{-1}$  to 300  $\text{mmol mol}^{-1}$  Al for July and October 2007 (Table 3). Thus, >99% of Zn in the sinking particles of the euphotic zone originates from anthropogenic aerosols. In addition to Zn, other trace metals, including Ni, Cu, Mo, and Pb, also exhibit highly enriched M:Al ratios in the aerosols and the sinking particles.

To estimate the contribution of bottom-up input of dissolved metals from vertical water exchange to the trace metal fluxes in the mixed layers, the input of dissolved trace metals through water exchange from the water below the mixed layer is estimated by multiplying water exchange

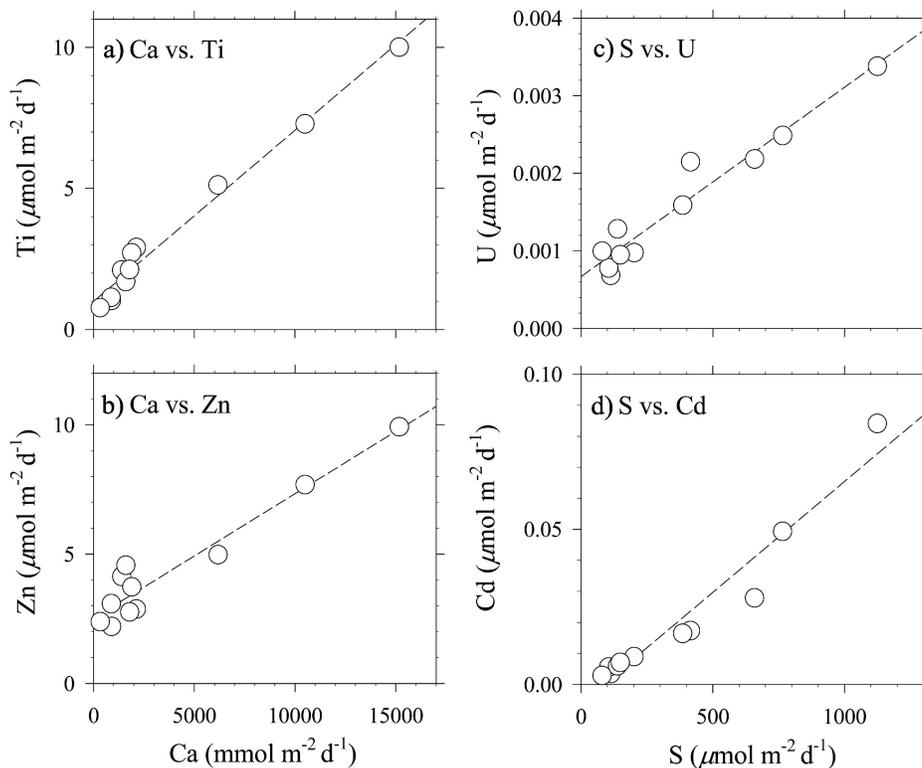


Fig. 7. Flux correlation for the element groups (a) Ca vs. Ti, (b) Ca vs. Zn, (c) S vs. U, and (d) S vs. Cd. Ti and Zn are known to be adsorbed on particle surfaces and S, Cd, and U are known to be incorporated into organic matter.

rates to trace metal concentration transformed to sinking particles in the mixed layer (Table 3). Under steady-state assumption in the mixed layer, the approach may only be meaningful to estimate the input when the elemental concentrations transformed to sinking particles in the mixed layer can be estimated. The elements that may be qualified for the estimate include Cd, Zn, Fe, and P, which are generally considered to be biologically active elements with significant concentration gradients in the euphotic zone due to intensive biological uptake. By multiplying the water exchange rates using  $0.15 \text{ m d}^{-1}$  by the averaged dissolved concentrations of the trace metals at the bottom depth of the mixed layer (Table 3), which are 1 nM, 0.2 nM, and 0.02 nM for Fe, Zn, and Cd, respectively, estimated fluxes for Fe, Zn, and Cd are  $0.15 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ ,  $0.03 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ , and  $0.003 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ , respectively, only accounting for 0.9%, 0.4%, and 1.8% and 2%, 6%, and 13% of the aeolian deposition fluxes in July and October 2007, respectively. Thus, bottom-up input of the dissolved metals through water exchange plays a minor role in supplying the trace metals to the mixed layer. However, it is worth noting that the input of vertical water exchange becomes more significant for Cd and P during low aerosol deposition season (Table 3). If biological regenerated production is a major process for cycling trace metals in the mixed layer, trace metal composition in the sinking particles should also exhibit similar elemental composition to intracellular trace-metal quotas in phytoplankton.

Indeed, Cd : P ratios in the sinking particles are comparable to intracellular Cd quota in plankton (Ho et al. 2009).

In terms of top-down vertical fluxes, we compare trace metal fluxes originating from aeolian transport, including dry and wet deposition, with trace metal fluxes in the mixed layer at 30 m during July and October 2007 (Table 3). Considering the possible uncertainties that may be caused and propagated through various processes during sampling, analysis, and flux calculation between the two independent studies, many of the trace metals exhibit markedly similar fluxes between aeolian deposition and vertical fluxes in the mixed layer, particularly for the elements Mg, Ba, Al, Ti, Mn, V, Co, Cu, Zn, and Pb (Table 3). These comparable data between the two fluxes demonstrate that aeolian deposition is the major source for most of the trace metals in the sinking particles of the mixed layer.

As for the elements Ca, Sr, P, and Fe, the vertical fluxes are much higher than the aeolian deposition. It is expected that biological uptake and regeneration of Ca and Sr are extensive in the surface water so that the sinking fluxes of Ca and Sr would be much higher than the aeolian deposition because coccolithophores are dominant phytoplankton in the region (Fig. 6). For Fe, the input of particulate Fe from the deep water could be an important source in the surface water. With the high Fe fluxes and inputs in the surface water, Fe is unlikely to be a limiting nutrient for phytoplankton in the oceanic region.

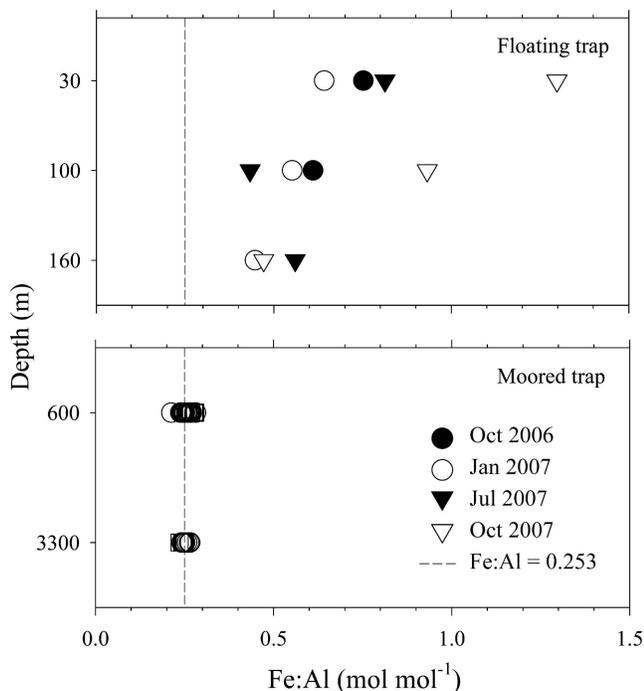


Fig. 8. The comparison of Fe:Al ratios in the sinking particles of the surface water with the ratios in the sinking particles of the deep water collected by moored sediment traps deployed at 600 m and 3300 m at the SEATS station (T.-Y. Ho unpubl.). The data from October 2006, and January, July, and October 2007 are presented by solid circle, open circle, solid reverse triangle, and open reverse triangle, respectively. The averaged ratios of Fe:Al is 0.253 mol: mol in the sinking particles of the deep water, which is analytically the same as the Fe:Al ratio 0.252 mol: mol observed in the sediments collected from the northern South China Sea station (Calvert et al. 1993).

Even for lithogenic-type trace metals Fe, Mn, Ti, Co, and U, their metal:Al ratios in the sinking particles of the mixed layer are generally elevated although most of them are under a factor of 10 to the standard lithogenic ratios (Fig. 5). Using mass balance and the specific composition of the two end members (resuspended lithogenic particles

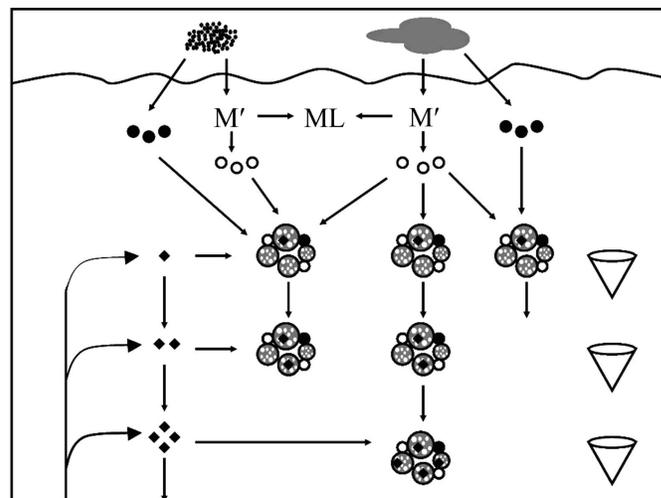


Fig. 9. A schematic model for trace metal cycling in the surface water of the South China Sea. The trace metals originating either from dry or wet deposition can be soluble ( $M'$ ) or nonsoluble (solid circle). The soluble trace metals may be either chelated by soluble organic ligand (ML) or precipitated to hydroxide metals or other chemical precipitates (open circle). Both the nonsoluble aerosol particles (solid circles) and the precipitates (open circles) may adsorb on biogenic particles, represented by the porous large circle symbols. The diamond symbols stand for the lithogenic particles originating from the deep water. Their concentrations increase with depth. These lithogenic particles can be transported by biogenic particles or just sink down by themselves.

from the deep-water and atmospheric aerosols), the relative contribution of the metals from the two different sources at different depths may be approximately estimated. We split abiotic term in the previous mass balance equation into two terms: lithogenic particles from the deep water and sinking particles from aeolian deposition. Because metal:P ratios in the sinking particles are much higher than the known intracellular metal quota in plankton assemblages (Fig. 4), the term for trace metals originating from intracellular biogenic organic matter is ignorable. We assume that the M:Al ratios in the sinking

Table 3. The comparison of elemental fluxes through aeolian deposition on Dongsha atoll with the sinking fluxes estimated by the floating traps in the mixed layer at 30 m (Table 2) and the bottom-up input of the selective dissolved elements to the mixed layer through vertical water exchange. The unit for all numbers is  $\mu\text{mol m}^{-2} \text{d}^{-1}$ .

Date	Source	P	Mg*	Ca*	Sr*	Ba	Al	Fe	Ti	Mn	V	Co	Ni	Cu*	Zn	Cd	Pb
Jul 07	Aeolian	3.9	220	140	0.38	0.75	12	7.6	6.0	0.21	0.074	0.019	0.20	4.2	0.54	0.024	0.08
Jul 07	Sinking	64	150	900	7.9	0.27	45	36	1.0	0.39	0.059	0.023	2.7	1.4	2.2	0.006	0.27
Oct 07	Aeolian	6.8	600	280	0.87	2.6	38	17	10	1.1	0.13	0.037	0.7	2.6	8.2	0.16	0.90
Oct 07	Sinking	290	360	10,500	81	1.6	79	102	7.3	1.9	0.13	0.045	1.9	1.1	7.7	0.05	0.93
	Bottom-up	15†	nd	nd	nd	nd	nd	0.15†	nd	nd	nd	nd	nd	nd	0.03†	0.003†	nd

\* The dry to total aeolian deposition fluxes were not determined (nd) for Mg, Ca, Sr, and Cu. We assume the fractions for Mg, Ca, Sr to be 0.1 (or 10%) by referring to the fraction of Ba and the fraction for Cu to be 0.2 (20%) by referring to the fraction for Zn.

† The water exchange rates are available through three independent studies. Using physical terms including the mixed-layer deepening rate, the vertical velocity of water parcel, and the advection of water parcels, Qu (2001) estimated the overall water entrainment or detrainment rates to vary seasonally, ranging from  $32 \text{ m yr}^{-1}$  to  $95 \text{ m yr}^{-1}$  during June–October in the northern South China Sea. Using the mass balance of water and salinity, Chen et al. (2001) reported the overall upwelling rate to be  $55 \text{ m yr}^{-1}$  in the water column of the South China Sea. Using the mass balance between net primary production and the limiting nutrient supply (nitrate and nitrite), Wong et al. (2007b) estimated the overall vertical water exchange rate in the mixed layer to be  $41 \text{ m yr}^{-1}$  at the SEATS site. These rates are equivalent to  $0.11 \text{ m d}^{-1}$ ,  $0.15 \text{ m d}^{-1}$ , and  $0.09\text{--}0.26 \text{ m d}^{-1}$ . Here, we use  $0.15 \text{ m d}^{-1}$  to be the vertical water exchange rate for the estimate.

Table 4. Trace metal fractions derived from atmospheric fractions in the sinking particles in the surface water.\*

Date (month and yr)	Depth (m)	Anthropogenic %				
		Ti	Mn	Fe	Co	U
Oct 2006	30	9	47	48	66	53
	100	10	48	34	50	71
Jan 2007	30	100	80	37	100	100
	100	66	92	29	16	60
Jul 2007	160	19	72	19	10	11
	30	11	16	54	31	40
	100	0	15	17	10	28
Oct 2007	160	1	54	29	13	38
	30	80	100	100	37	81
	100	24	59	65	40	28
	160	10	31	21	5	17

\* The standard lithogenic ratios (M:Al) are 12, 5.7, 252, 0.18, and 0.0036 mmol mol<sup>-1</sup> for Ti, Mn, Fe, Co, and U, respectively. The ratios are from either Calvert et al. (1993) or Taylor (1964). We use the lowest Ti:Al ratio observed in the sample (12 mmol mol<sup>-1</sup>; Fig. 5), to be the lithogenic ratios because it is lower than the lithogenic ratio (20 mmol mol<sup>-1</sup>; Calvert et al. 1993). The data in Table 3 indicate that the trace metal fluxes of the aeolian deposition and the sinking particles are comparable. We assume the highest M:Al ratios in the sinking particles at 30 m during high deposition season to be the representative ratios for anthropogenic particles. The M:Al ratios from aeolian deposition are 113, 29, 1298, 1.24, and 0.038 mmol mol<sup>-1</sup> for Ti, Mn, Fe, Co, and U, respectively (Table 2).

particles collected at 30 m during high aerosol input season may represent the trace metal composition in aeolian aerosols, supported by their comparable fluxes (Table 3). M:Al ratios in the sediments of the South China Sea (Fig. 5) can generally represent the trace metal composition in lithogenic particles from the deep water. Then, the mass balance can be expressed as

$$[M : Al] = b(1 - f)_{\text{litho}} + c(f)_{\text{atmos}} \quad (2)$$

where 'b' is Al-normalized metal ratio in resuspended lithogenic particles from the sediment, 'c' is Al-normalized metal ratios in sinking particles through atmospheric deposition, 'f' is the fraction of trace metals in the sinking particles derived from atmospheric deposition. '1 - f' is the fraction of trace metals in the sinking particles derived from resuspended lithogenic particles.

Using Fe as an example, the Fe:Al ratio in resuspended lithogenic particles is 252 mmol mol<sup>-1</sup> (b), which would be the end member for lithogenic particles originating from deep water (Fig. 5), and Fe:Al ratio is 1300 mmol mol<sup>-1</sup> (c) at 30 m during high aerosol input season, which is the end member of atmospheric aerosols, the fractions (f) of atmospherically derived Fe at different depths can be calculated by  $[(M : Al) - b] : (c - b)$ , ranging from 17% to 65% at the depths of 100 m and 160 m (Table 4). The relative contribution of aeolian and resuspended particles in the sinking particles at different depths for Ti, Mn, Co, and U are shown in Table 4. Overall, the atmospheric fractions are higher at depths of 30 m and 100 m during high aeolian deposition months but seasonal variability at 160 m is not significant. It may be attributed to the steady

bottom-up fluxes of lithogenic particles at 160 m among different seasons coupled with intensive internal cycling of trace metals above 160 m during high aeolian deposition seasons. In addition, elevated M:Al ratios for these lithogenic-type metals suggest that anthropogenic aerosol through aeolian deposition may play a significant role in the sinking particles for these elements, particularly during high aeolian deposition season.

In terms of seasonal pattern, the seasonal variabilities of the sinking fluxes for many of the elements at 160 m are much less significant than the ones at 30 m (Fig. 3). Aeolian deposition is known to be the major source for the elements Mg, Ti, Co, Zn, Cd, and Pb. With strong seasonal variability of the aeolian deposition in the South China Sea, comparable fluxes among different seasons at 160 m suggest that most of the elevated input through aeolian deposition in the surface water during high deposition season would be recycled between the water below the mixed layer and 160 m. Elemental concentrations in the zone between 30 m and 160 m are expected to have seasonal gradients for the elements with residence times shorter than seasonal time scale. Trace metals in the zonation (at least including Ti, Zn, and Pb) are expected to show elevated concentrations during winter season when aeolian input is high, and relatively low concentrations during summer season from June to August.

Overall, this study shows that the trace metal input from atmospheric deposition exhibits comparable value to the sinking fluxes of many trace metals in the mixed layer, demonstrating that aeolian input of anthropogenic trace metals is a dominant source for most of the studied trace metals in the surface water of the South China Sea. This finding also validates our previous hypothesis that the abiogenic and nonlithogenic trace metals adsorbed on marine phytoplankton assemblages were mainly derived from highly soluble anthropogenic aerosols (Ho et al. 2007). The relative contribution of resuspended lithogenic particles to the trace metal fluxes in the sinking particles increases with depth, especially for lithogenic-type metals like Al, Fe, and Ti. Except Cd (Ho et al. 2009), intracellular and biogenic trace metals account for an insignificant portion of the trace metals in the sinking particles. However, biogenic particles serve as dominant agents to adsorb and transport trace metals from the surface water to the deep water. With the lasting input of anthropogenic aerosols during the past decades and with the relatively short residence times of some anthropogenic trace metals in the surface water, the dissolved concentrations of some anthropogenic-type trace metals may increase with time in the surface water and also have resulted in penetration to the deep water. Due to the increasing input of anthropogenic aeolian deposition over large oceanic regions, the coupling and transport of anthropogenic trace metals with biogenic particles in oceanic surface waters (as shown in Fig. 9) may be a common mechanism for trace metal cycling in global oceans.

#### Acknowledgments

We thank two anonymous reviewers for providing invaluable comments; the personnel of the sediment-trap laboratory of

National Sun Yat-Sen University, in particular Francy Kuo, who has been in charge of deploying the floating traps and collecting the trap samples in the South China Sea; the personnel of the R/V *Ocean Research 1* and R/V *Ocean Research 3* for their assistance in deploying the traps during the cruises; and the research assistants, Bing-Nan Wang and Wen-Chen Hsieh, at the Research Center for Environmental Changes for their help in laboratory analytical work. This research was supported by grant No. National Science Counsel 97-2628-M-001-031 and 98-2611-M-001-004-MY3 by the Taiwan National Science Council, and by the Academia Sinica through a thematic research grant titled "Atmospheric Forcing on Ocean Biogeochemistry (AFOBi)." The RCEC publication No. is RCEC-HO-201001.

## References

- ALLDREDGE, A. L., AND G. A. JACKSON. 1995. Aggregation in marine systems—preface. *Deep-Sea Res. Part II* **42**: 1–7, doi:10.1016/0967-0645(95)90003-9
- ANDERSON, R. F., AND G. M. HENDERSON. 2005. GEOTRACES: A global study of the marine biogeochemical cycles of trace elements and their isotopes. *Oceanography* **18**: 76–79.
- BRULAND, K. W. 1983. Trace elements in sea-water, p. 157–220. In J. P. Riley and R. Chester [eds.], *Chemical oceanography*, v. 8. Academic Press.
- , J. R. DONAT, AND D. A. HUTCHINS. 1991. Interactive influences of bioactive trace-metals on biological production in oceanic waters. *Limnol. Oceanogr.* **36**: 1555–1577, doi:10.4319/lo.1991.36.8.1555
- CALVERT, S. E., T. F. PEDERSEN, AND R. C. THUNELL. 1993. Geochemistry of the surface sediments of the Sulu and South China Seas. *Mar. Geol.* **114**: 207–211, doi:10.1016/0025-3227(93)90029-U
- CHEN, C. T. A., S. L. WANG, B. J. WANG, AND S. C. PAI. 2001. Nitrogen budgets for the South China Sea basin. *Mar. Chem.* **75**: 281–300, doi:10.1016/S0304-4203(01)00041-X
- CHEN, Y. L. L. 2005. Spatial and seasonal variations of nitrate-based new production and primary production in the South China Sea. *Deep-Sea Res. Part I* **52**: 319–340, doi:10.1016/j.dsr.2004.11.001
- , H. Y. CHEN, AND C. W. CHUNG. 2007. Seasonal variability of *coccolithophore* abundance and assemblage in the northern South China Sea. *Deep-Sea Res. Part II* **54**: 1617–1633, doi:10.1016/j.dsr2.2007.05.005
- COALE, K. H., AND K. W. BRULAND. 1985.  $^{234}\text{Th}$ : $^{238}\text{U}$  disequilibria within the California current. *Limnol. Oceanogr.* **30**: 22–33, doi:10.4319/lo.1985.30.1.0022
- COLLIER, R., AND J. EDMOND. 1984. The trace-element geochemistry of marine biogenic particulate matter. *Prog. Oceanogr.* **13**: 113–199, doi:10.1016/0079-6611(84)90008-9
- DEUSER, W. G., P. G. BREWER, T. D. JICKELLS, AND R. F. COMMEAU. 1983. Biological control of the removal of abiogenic particles from the surface ocean. *Science* **219**: 388–391, doi:10.1126/science.219.4583.388
- DUCE, R. A., AND OTHERS. 1991. The atmospheric input of trace species to the world ocean. *Glob. Biogeochem. Cycles* **5**: 193–259, doi:10.1029/91GB01778
- FOWLER, S. W., AND G. A. KNAUER. 1986. Role of large particles in the transport of elements and organic compounds through the oceanic water column. *Prog. Oceanogr.* **16**: 147–194, doi:10.1016/0079-6611(86)90032-7
- HENDERSON, G. M., AND OTHERS. 2007. GEOTRACES—an international study of the global marine biogeochemical cycles of trace elements and their isotopes. *Chem. Erde* **67**: 85–131, doi:10.1016/j.chemer.2007.02.001
- HO, T. Y. 2006. The trace metal composition of marine microalgae in cultures and natural assemblages, p. 271–299. In D. V. Subba Rao [ed.], *Algal cultures: Analogues of blooms and applications*. Science.
- , A. QUIGG, Z. V. FINKEL, A. J. MILLIGAN, K. WYMAN, P. G. FALKOWSKI, AND F. M. M. MOREL. 2003. The elemental composition of some marine phytoplankton. *J. Phycol.* **39**: 1145–1159, doi:10.1111/j.0022-3646.2003.03-090.x
- , L. S. WEN, C. F. YOU, AND D. C. LEE. 2007. The trace-metal composition of size-fractionated plankton in the South China Sea: Biotic versus abiotic sources. *Limnol. Oceanogr.* **52**: 1776–1788.
- , C. F. YOU, W. C. CHOU, S. C. PAI, L. S. WEN, AND D. D. SHEU. 2009. Cadmium and phosphorus cycling in the water column of the South China Sea: The roles of biotic and abiotic particles. *Mar. Chem.* **115**: 125–133, doi:10.1016/j.marchem.2009.07.005
- JICKELLS, T. D., AND OTHERS. 2005. Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science* **308**: 67–71, doi:10.1126/science.1105959
- , W. G. DEUSER, AND R. A. BELASTOCK. 1990. Temporal variations in the concentrations of some particulate elements in the surface waters of the Sargasso Sea and their relationship to deep-sea fluxes. *Mar. Chem.* **29**: 203–219, doi:10.1016/0304-4203(90)90014-4
- , ———, AND A. H. KNAP. 1984. The sedimentation rates of trace elements in the Sargasso Sea measured by sediment trap. *Deep-Sea Res.* **31**: 1169–1178.
- KUSS, J., AND K. KREMLING. 1999. Spatial variability of particle associated trace elements in near-surface waters of the North Atlantic (30°N/60°W to 60°N/2°W), derived by large-volume sampling. *Mar. Chem.* **68**: 71–86, doi:10.1016/S0304-4203(99)00066-3
- LIN, I. I., J. P. CHEN, G. T. F. WONG, C. W. HUANG, AND C. C. LIEN. 2007. Aerosol input to the South China Sea: Results from the MODerate resolution imaging spectro-radiometer, the quick scatterometer, and the measurements of pollution in the troposphere sensor. *Deep-Sea Res. Part II* **54**: 1589–1601, doi:10.1016/j.dsr2.2007.05.013
- MARTIN, J. H., AND G. A. KNAUER. 1973. Elemental composition of plankton. *Geochim. Cosmochim. Acta* **37**: 1639–1653, doi:10.1016/0016-7037(73)90154-3
- NOZAKI, Y. 2001. A fresh look at element distribution in the North Pacific Ocean. *EOS Trans. Am. Geophys. Union* **78**: 221, doi:10.1029/97EO00148
- QU, T. 2001. The role of ocean dynamics in determining the mean seasonal cycle of the South China Sea surface temperature. *J. Geophys. Res.* **106**: 6943–6955, doi:10.1029/2000JC000479
- TAYLOR, S. R. 1964. Abundance of chemical elements in the continental crust: A new table. *Geochim. Cosmochim. Acta* **28**: 1273–1285, doi:10.1016/0016-7037(64)90129-2
- TSENG, C. M., G. T. F. WONG, I. I. LIN, C. R. WU, AND K. K. LIU. 2005. A unique seasonal pattern in phytoplankton biomass in low-latitude waters in the South China Sea. *Geophys. Res. Lett.* **32**: L08608, doi:10.1029/2004GL021111
- TUREKIAN, K. K. 1977. Fate of metals in oceans. *Geochim. Cosmochim. Acta* **41**: 1139–1144, doi:10.1016/0016-7037(77)90109-0
- WEI, C. L., K. L. JEN, AND K. CHU. 1994. Sediment trap experiments in the water column off southwestern Taiwan:  $^{234}\text{Th}$  fluxes. *J. Oceanogr.* **50**: 403–414, doi:10.1007/BF02234963
- WEN, L. S., K. T. JIANN, AND P. H. SANTSCHI. 2006. Physico-chemical speciation of bioactive trace metals (Cd, Cu, Fe, Ni) in the oligotrophic South China Sea. *Mar. Chem.* **101**: 104–129, doi:10.1016/j.marchem.2006.01.005

- WHITFIELD, M., AND D. R. TURNER. 1987. The role of particles in regulating the composition of sea water, p. 457–493. *In* W. Stumm [ed.], *Aquatic surface chemistry: Chemical processes at the particle–water interface*. Wiley.
- WONG, G. T. F., T. L. KU, M. MULHOLLAND, C. M. TSENG, AND D. P. WANG. 2007a. The SouthEast Asian time-series study (SEATS) and the biogeochemistry of the South China Sea—an overview. *Deep-Sea Res. Part II* **54**: 1434–1447, doi:10.1016/j.dsr2.2007.05.012
- , C. M. TSENG, L. S. WEN, AND S. W. CHUNG. 2007b. Nutrient dynamics and nitrate anomaly at the SEATS station. *Deep-Sea Res.* **54**: 1528–1545.
- ZHANG, X., G. ZHUANG, J. GUO, K. YIN, AND P. ZHANG. 2007. Characterization of aerosol over the Northern South China Sea during two cruises in 2003. *Atmos. Environ.* **41**: 7821–7836, doi:10.1016/j.atmosenv.2007.06.031

*Associate editor: Markus H. Huettel*

*Received: 06 October 2009*

*Accepted: 05 April 2010*

*Amended: 12 April 2010*