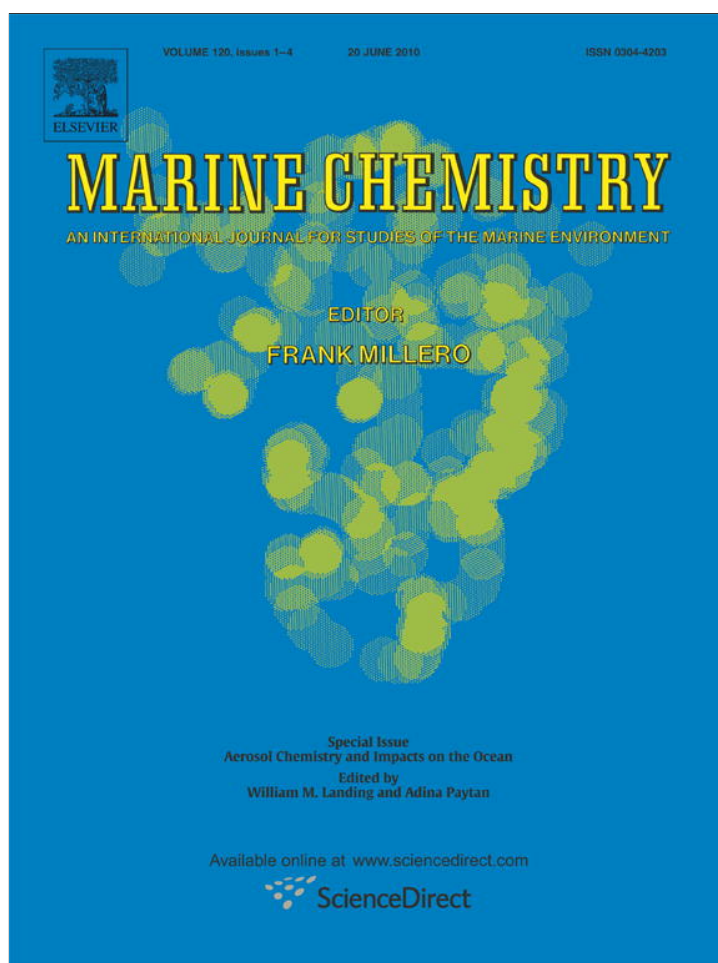


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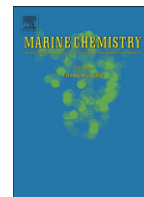
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## Sources, solubility, and dry deposition of aerosol trace elements over the East China Sea

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## ABSTRACT

A total of 47 marine aerosols collected from the East China Sea between the spring of 2005 and the spring of 2007 were analyzed for both the water-soluble and the total concentrations of 25 trace elements and phosphorus and the water-soluble major ions, organic carbon, as well as silicon. During the sampling periods, eight samples were significantly influenced by Asian dust events. The total concentrations of both the chemical species of dust origin and of anthropogenic origin were higher during the Asian dust period, suggesting that the Asian outflow of air pollutants often accompanies the Asian dust advection. Overall, the average solubilities were  $\leq 20\%$  for Al, Fe, Ti, Cr, Y, Sn, Ba, Ni, Ga, and Mo; 20–40% for Co, Cs, Rb, Sb, and Pb; 40–60% for Mn, V, Cu, Ge, and P; and  $\geq 60\%$  for Tl, Sr, As, Zn, Cd, and Se. The solubilities for many elements are lower in the high dust period than during the polluted northeasterly monsoon and the background summer period. A variety of controlling factors of the solubilities of the elements were discussed in this study. The relative importance could be concluded as follows: acid processing > chemical speciation  $\approx$  aerosol source > dust loading. Finally, we estimated the dry depositional fluxes of soluble elements by assuming certain dry deposition velocities for each element. The fluxes were  $39 \pm 50 \mu\text{g}/\text{m}^2/\text{d}$  for soluble Fe and  $41 \pm 74 \mu\text{g}/\text{m}^2/\text{d}$  for the combination of some bioavailable elements (e.g., Zn, Cu, Mn, Ba, Co, V, Ni, and Cd) during the northeasterly monsoon. Atmospheric deposition is an additional source of nutrient elements that may be important not only in the coastal/marginal sea, but also particularly in the remote open ocean because aerosol trace elements are associated mostly with fine mode particles that can be brought farther from the source regions.

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## 1. Introduction

It is widely documented that transition trace metals, such as Fe, Mn, Co, Zn, Cu, and Ni are essential nutrients to marine biota (Butler, 1998; Whitfield, 1998). In the remote oceans, particularly in the high-nitrate low-chlorophyll (HNLC) areas of the open oceans, atmospheric depositions are a vital source of bioavailable Fe and trace elements and bring about biological stimulation (Bishop et al., 2002; Jickells et al., 2005). Recent field measurements have shown that the enhancement in nitrogen fixation and biological blooms in the remote oceans corresponds to the episodic supply by atmospheric deposition (Baker et al., 2003; Yuan and Zhang, 2006).

Asian dust storms annually occur in the late winter and spring in three primary dust regions, namely, the Gobi Desert, the Taklamakan

Desert, and the Loess Plateau. Zhang et al. (1997) estimated China's annual emission of dusts to be 800 Tg, 50% of which is subject to long-range transport to the Pacific Ocean and beyond. In addition to this, large quantities of air pollutants, which include particulate matter, SO<sub>2</sub>, and NO<sub>x</sub>, are spewed out from mainland China, owing to its rapid industrial development and urbanization since the '80s (Carmichael et al., 2002; Wang et al., 2004 and references therein). When the cold high pressure systems, which develop in Siberia and Northern China between late October and early May, move southeastward out of the China continent, the northeasterly monsoon prevails south of 30°N following the passage of the cold front (Lin et al., 2005; Hsu et al., 2008a). Consequently, when Asian dust storms occur in Northern China, Asian dust is lifted and transported southward (Hsu et al., 2004, 2008a). Like Asian dust, air pollutants could also be spread by transport agents out of the main continent particularly when the moving atmospheric systems pass over the urban and industrial cities. Hence, there is a high deposition rate of Asian dust as well as other air pollutants over the East China Sea (ECS) as it is situated right next to

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**Table 1**

A summary of sampling periods, research vessel used (R/V ORI or ORII), cruise number, survey region, and available sample number collected in three seasons, that is, spring, summer, and early winter.

Season	Research vessel_Cruise	Sampling period	Survey region	Sample number
Spring	R/V ORII_1270; 1271; 1273; 1337; 1338; 1340; 1343; 1344; 1421; 1422; 1424; 1428	2005: 3/18–3/22; 3/25–3/29; 4/14–4/18 2006: 3/17–3/20; 3/20–3/24; 3/28–3/30; 4/8–4/9; 4/12–4/13 2007: 3/16–3/17; 3/19–3/24; 3/27–3/31; 4/9–4/14	The southern ECS	33
Summer	R/V OR_756	6/10–6/17/2005	The whole ECS	7
Winter	R/V OR_815	11/6–11/15/2006	The whole ECS	7

the Chinese mainland (Duce et al., 1991; Zhang et al., 1997; Gao et al., 2001). As a result, the atmospheric depositions of both nutrients and toxic species may have a substantial impact on its biogeochemistry, especially with respect to biological bloom and the cycling and budget balance of certain elements. For example, Lin et al. (2000) found that the dissolvable Pb in the surface layer of the southern ECS was the highest reported for the oceans and linearly proportional to the atmospheric deposition flux of eolian Pb. They then suggested that the ECS has been contaminated by airborne anthropogenic substances from Asian outflows, resulting in the disturbance of biogeochemical cycling of Pb in the sea. However, very little is known about the atmospheric depositions of trace metals to the ECS, although it is situated between the open North Pacific Ocean and the region considered as the main source of Asian dust and other air pollutants.

In order to accurately assess the biogeochemical impact of the atmospheric input, atmospheric particulate species of interest must be determined for the bioavailable soluble fraction rather than only for the total concentrations. The percentage of the amount that can be dissolved, referred to as “solubility,” is species-dependent and is controlled by various controlling factors. These factors include the following: (1) the pH of the extracting medium (Statham and Chester, 1988; Lim et al., 1994; Chester et al., 1997, 2000a,b; Desboeufs et al., 1999); (2) the enrichment factor ( $EF_{\text{crust}}$ ) of the element relative to its natural crustal abundance (Chester et al., 1993a; Guerzoni et al., 1999); (3) the particle loading in the solution (Guerzoni et al., 1999); (4) aerosol types and sizes (Davison et al., 1994; Chester et al., 1993a, 1997); (5) photoreduction (Zhuang et al., 1992; Zhu et al., 1993); (6) clouding/aging processing (Mackie et al., 2005); and (7) the presence of organic, acidic, or carbonaceous substances (Zuo, 1995; Desboeufs et al., 2001, 2005). Their relative importance is variable (e.g., Zhuang et al., 1992; Zhu et al., 1993; Hsu et al., 2005a; Chen et al., 2006; Baker et al., 2006) and as such depends on which solutions (such as rainwater, cloud water, fresh water, or seawater) interact with aerosols, which compositions and/or sources dominate aerosols, and which specific metals are of interest. So far, the literature/data on the solubility of marine aerosol-associated metals are limited and mostly concentrate on the Atlantic Ocean and the Mediterranean Sea (Statham and Chester, 1988; Kersten et al., 1991; Chester et al., 1993a; Guieu et al., 1994; Bonnet and Guieu, 2004; Baker et al., 2006), with little data being reported on the Western Pacific Ocean (Zhuang et al., 1992; Hsu et al., 2005a; Buck et al., 2006). Consequently, the likely effects of trace element deposition on marine biogeochemistry are yet to be quantitatively assessed. Aerosol trace metals of anthropogenic origins mostly are associated with fine particles. In contrast, Fe (also Al) is associated mainly with the coarse mineral dust particles. The trace metals in the anthropogenic fine particles can be transported farther away from their sources than those mainly associated with the coarse mineral dust particles, such as Fe. On the other hand, atmospheric depositions of toxic metals, which usually have high mobility, may substantially affect the marine eco-environment (e.g., Lin et al. 2000). Accordingly, we must quantify the contributions of aerosol water soluble trace elements (WSTEs), as well as Fe, to the ocean.

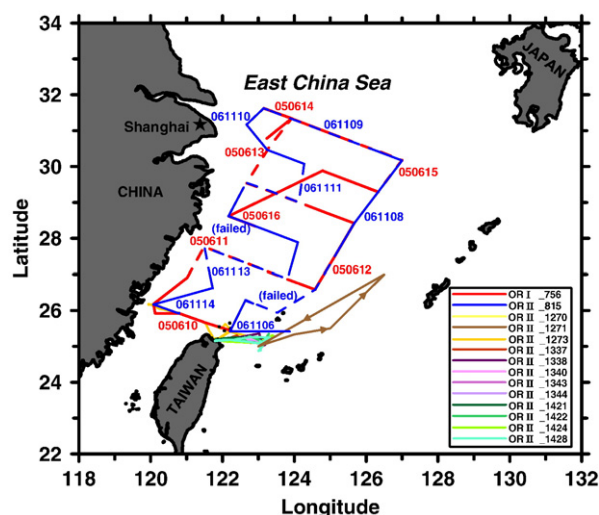
This study is a component of the integrated project called Long-term Observation and Research of the ECS (otherwise known as LORECS) of Taiwan. In this study, the total suspended particulate (TSP) marine aerosol samples were collected on board ship primarily over

the southern ECS during spring (33 samples), summer (seven samples), and early winter (seven samples) cruises between 2005 and 2007 (Table 1 and Fig. 1). The total dissolvable concentrations of a suite of metal elements (Al, Fe, Na, Mg, K, Ca, Mn, Sr, Ba, Ti, Mn, Rb, Co, Ni, Cr, V, Y, Cs, Zn, Cu, Cd, Pb, Sn, Sb, Se, As, Mo, Ge, Ga, and Tl) were analyzed. Hereafter, the total and soluble fractions of a given element are presented as  $X_T$  and  $X_S$ , respectively. In addition, phosphorus, water-soluble silicon ( $Si_S$ ), water-soluble ionic species ( $NH_4^+$ ,  $SO_4^{2-}$ ,  $NO_3^-$ , and  $Cl^-$ ), and water-soluble organic carbon (WSOC) were also determined. Thus, temporal distributions of the chemical species were constructed. The solubilities of selected trace metals were calculated. The dry deposition fluxes of WSTEs during the northeasterly monsoon period were quantified. The controlling factors of aerosol trace metal dissolution and the biogeochemical implications of atmospheric deposition of selected nutrient species were discussed. Data on Fe were published elsewhere (Hsu et al., 2008b) and hence is not discussed here, but its deposition flux is calculated and reported.

## 2. Materials and methods

### 2.1. Sampling

A total of 47 TSP marine aerosol samples were collected on board the R/V Ocean ResearcherII (ORII) and R/V Ocean ResearcherI (ORI) over the



**Fig. 1.** Regional map and ship tracks for 14 investigated cruises over the East China Sea (ECS) between the spring of 2005 and the spring of 2007. A total of 12 springtime cruises were mostly conducted in the southern ECS. The accurate periods for these cruises are given in Table 1. For the two cruises, June 2005 and November 2006, occupied over nearly the whole ECS, with the red and blue lines (solid and dashed lines) indicating the ship tracks, respectively. The sample identifications in bold numbers (yyymmdd) indicate the starting dates of sampling for each sample and are shown aside from the solid/dashed red/blue lines, representing the sampling track for a given sample indicated. During the November 2006 cruise, the sampling for two samples failed, as indicated.

ECS between 2005 and 2007, of which 33 samples were collected from 12 springtime cruises, seven samples from a summer cruise, and seven samples from a winter cruise. The exact date and time of each cruise are shown in Table 1, along with the ship tracks which are shown in Fig. 1. The aerosol sampler used was the TSP high-volume air sampler (Tisch Environmental, Inc.), and it was set up on the upper foredeck (10 m above sealevel for R/VORII and 14 m for R/VORI) and operated at a nearly constant flow-rate of 40 cubic feet per minute (CFM). The sampling time for most samples was around 24 h, but for several other samples the time was shorter or longer than 24 h. The aerosol particles were collected on Whatman® 41 cellulose filters (8" × 10") (Whatman Limited, Maidstone, UK). In this study, November was considered as early winter when the dataset was subdivided into three seasonal groups: spring, winter, and summer, which are usually characterized by high dust, high pollution, and background seasons, respectively, in this study region.

2.2. Chemical analysis

The filter was subdivided into eight equal pieces. For the concentrations of dissolvable material, a piece of the filter was extracted with 25 ml of Milli-Q water (pH ~6.5) on a reciprocating shaker for 0.5 h and at rest for an additional 0.5 h at room temperature (25 °C). Previous

studies showed that the amount of metals leached reaches a constant maximum in 0.5 to 1 h (Kersten et al., 1991; Guerzoni et al., 1999; Hsu et al., 2005a). Thus, a leaching time of ~1 h was adopted here. The extract was filtered through a polycarbonate membrane filter (0.4 μm pore size and 47 mm in diameter from Nuclepore). The filter was rinsed three times with Milli-Q water. The extract together with the rinsings were then diluted to a known final volume (almost around 48 ml) and then used for the determination of the ionic species (5 ml), WSOC (3 ml), and WSTE (40 ml). The solutions for the determinations of WSOC and WSTE were acidified to 0.5% and 1% with H<sub>3</sub>PO<sub>4</sub> and HNO<sub>3</sub> (ultra-pure grade from Merck), respectively. For the concentrations of total metal, another piece of the filter was digested with an acid mixture (4 ml HNO<sub>3</sub> + 2 ml HF; all ultra-pure grades from Merck) using an ultra-high throughput microwave digestion system (MARSXpress, CEM; Corporation, Matthews, NC). Details on the microwave digestion were given elsewhere (Hsu et al., 2008a). The efficiency of the digestion scheme was checked by subjecting a certain amount of a standard reference material (SRM 1648, urban particulate matter, National Institute of Standards and Technology (NIST), USA) to the same treatment.

Major water-soluble ionic species (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>) were analyzed by ion chromatography using a Dionex model ICS-90 (for anion) and a model ICS-1500 (for cation) ion chromatograph equipped

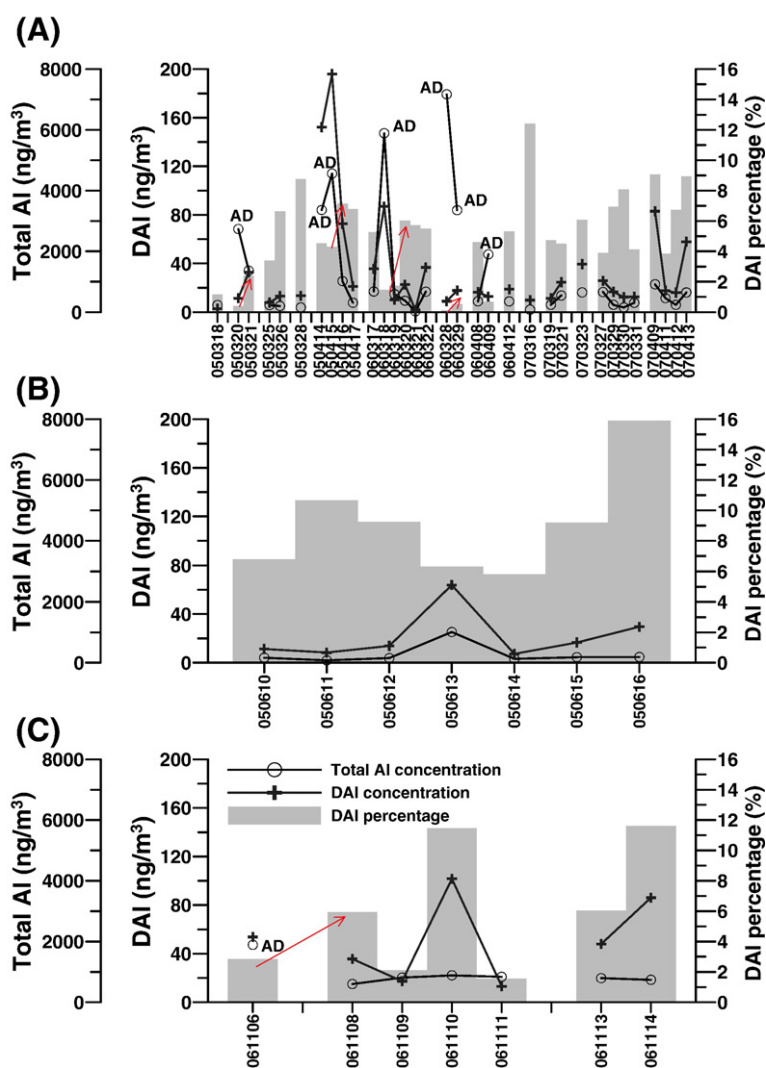


Fig. 2. Time-series of total Al and DAI concentrations and the percentages of DFe accounting for the total Fe for the 12 springtime (A), 1 summertime (B), and 1 wintertime (C) cruises. A total of eight samples indicated by AD were identified to be influenced by AD events, in which the identification was based on the levels of total Al concentration; the details are given in the text. The red arrows indicate the increase in solubility of dust Al after the passages of AD plumes.

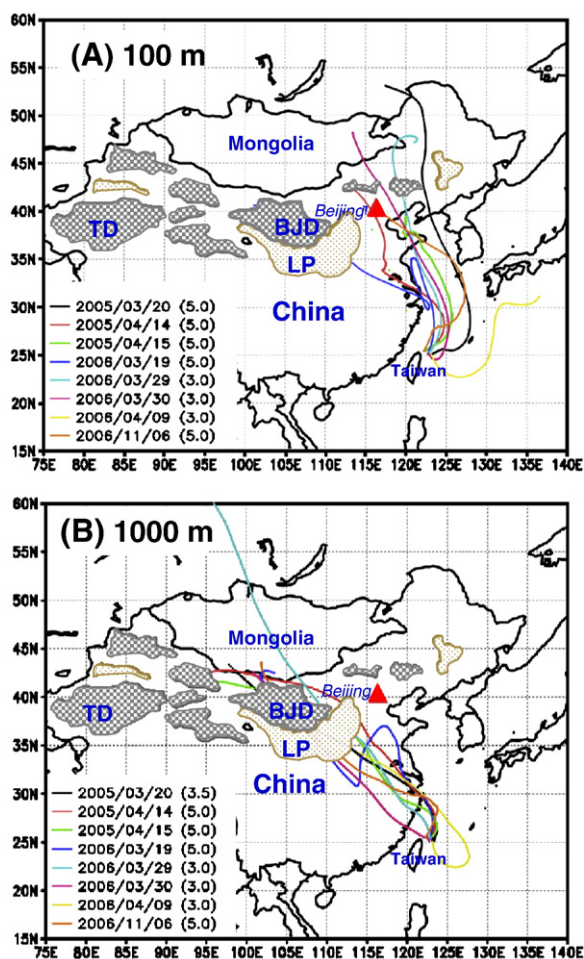


Fig. 3. Results of backward air-mass trajectory analysis at two elevations (100 and 1000 m) for three to five days for the identified eight Asian dust days using the HYSPLIT modeling calculations of NOAA. Numbers in parentheses in the legends of each plot represent the days that the trajectory analyses were calculated. The Badain-Juran Desert (BJD), Loess Plateau (LP), and Taklamakan Desert (TD) are indicated.

with a conductivity detector (ASRS-ULTRA). Soluble major metal ions ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ ) were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) using a Perkin Elmer model Elan 6100 quadrupole-based inductively coupled plasma mass spectrophotometer. The detailed procedures for ion chromatography were presented in Hsu et al. (2007). WSOC was measured by converting organic carbon to carbon dioxide by wet digestion and then analyzing the carbon dioxide formed by using a total organic carbon analyzer (O.I. Analytical Model 1010). The soluble and total concentrations of the trace elements and the concentration of soluble Si were also determined by ICP-MS. The recoveries of a large majority of the elements in the SRM 1648 by the digestion with the  $\text{HNO}_3$ -HF mixture fell within  $\pm 10\%$  ( $n = 5$ ) of the certified values. For the other elements, Se, As, Cs, Sb, and Rb fell within  $\pm 15\%$ , with only noncertified values available for the latter three elements. The digestion solution of the SRM 1648 was also analyzed by ICP-MS at the beginning and at the end of each batch of samples. The total concentrations of the elements were then corrected for any overestimation or underestimation from their average recoveries in the SRM 1648 standard reference material. Reagent and procedural blanks were determined empirically and were then also corrected. Details regarding the ICP-MS analysis were described elsewhere (Hsu et al., 2005b, 2006, 2008a). In the soluble fraction, the detection limits of the elements are at least two orders of magnitude lower than the sample concentration. In the total concentrations, the detection limits are at least one order of magnitude lower than the sample concentrations.

### 2.3. Calculations of solubility and $EF_{\text{crust}}$ value and the PCA analysis

The solubility for a given element was calculated as follows:

$$\text{Solubility (\%)} = C_S / C_T \times 100\%$$

where  $C_S$  and  $C_T$  are the soluble and total concentrations, respectively. The solubility derived from the Milli-Q water extraction may be different from and somewhat higher than those derived from seawater extraction, particularly for dust-derived elements, such as Al and Fe. That is because of the difference in pH of the medium used (Chen et al., 2006). Nevertheless, the estimated solubilities from this study would still be useful in assessing the bioavailability and environmental mobility of certain elements.

The degree to which a given element (X) in an aerosol is enriched or depleted relative to a specific source can be assessed using an enrichment factor (EF). It has been the practice to categorize trace elements in marine aerosols on the basis of their crustal EF, calculated by using the following equation (e.g., Chester et al., 1993a; Hsu et al., 2004, 2005b):

$$EF_{\text{crust}} = (C_X / C_{\text{Al}})_{\text{aerosol}} / (C_X / C_{\text{Al}})_{\text{crust}} \quad (1)$$

where  $(C_X / C_{\text{Al}})_{\text{aerosol}}$  is the concentration ratio of a given element X to Al in aerosols, and  $(C_X / C_{\text{Al}})_{\text{crust}}$  is the concentration ratio of a given element X to Al in the average crustal abundance (Taylor, 1964). However, Kersten et al. (1991) emphasized that EF values should only be treated as significant only in orders of magnitude.

In the current study, the principal component analysis (PCA; Statistical Analysis System, SAS version 8.2, SAS Institute Inc., Cary,

Table 2

Statistical summary (mean  $\pm$  S.D.) of atmospheric concentrations ( $\text{ng}/\text{m}^3$ ) for WSTEs, major ionic species and WSOC for the  $\text{NE}_{\text{NAD}}$  group samples.

	$\text{NE}_{\text{NAD}}$ ( $n = 32$ )	$\text{NE}_{\text{AD}}$ ( $n = 8$ )	Winter ( $n = 7$ )	Spring ( $n = 33$ )	Summer ( $n = 7$ )
Al	21 $\pm$ 25	1.8	2.0	1.0	0.8
Fe	21 $\pm$ 22	1.5	1.9	1.0	0.8
Ti	2.5 $\pm$ 1.5	4.9	1.8	1.3	0.6
Sr	4.8 $\pm$ 3.1	3.6	1.4	1.3	0.6
Ba	1.2 $\pm$ 1.1	4.2	2.2	1.2	1.0
Mn	5.5 $\pm$ 7.1	5.6	2.8	1.2	0.6
V	1.7 $\pm$ 5.1	1.0	1.6	0.9	3.0
Rb	0.62 $\pm$ 1.16	4.0	3.1	1.1	0.8
Ni	0.27 $\pm$ 0.37	1.0	1.3	0.9	1.8
Cr	0.24 $\pm$ 0.21	1.8	1.8	1.0	1.0
Co	0.063 $\pm$ 0.066	3.3	1.9	1.2	0.9
Y	0.015 $\pm$ 0.020	4.5	2.2	1.2	0.6
Cs	0.044 $\pm$ 0.125	3.1	4.0	1.0	0.7
Cu	28 $\pm$ 35	0.8	2.2	0.8	4.6
Zn	38 $\pm$ 89	2.3	3.0	1.0	0.6
Pb	5.6 $\pm$ 15.0	1.2	3.4	0.8	1.2
As	0.74 $\pm$ 1.14	2.8	2.5	1.1	0.6
Se	0.51 $\pm$ 0.81	2.9	2.7	1.1	1.2
Cd	0.36 $\pm$ 0.57	2.9	3.0	1.0	0.5
Sb	0.17 $\pm$ 0.32	2.6	2.5	1.0	0.7
Ga	0.13 $\pm$ 0.27	2.4	3.0	1.0	0.7
Sn	0.060 $\pm$ 0.112	2.1	2.3	1.0	0.9
Tl	0.063 $\pm$ 0.140	3.0	3.7	1.0	0.8
Ge	0.028 $\pm$ 0.058	3.5	3.2	1.1	0.6
Mo	0.040 $\pm$ 0.095	8.0	1.4	1.6	0.8
Si	5.2 $\pm$ 2.9	1.9	1.3	1.1	0.4
P	6.4 $\pm$ 6.1	2.6	2.2	1.1	0.8
$\text{Na}^+$	4238 $\pm$ 3426	1.6	1.3	1.1	0.7
$\text{Mg}^{2+}$	521 $\pm$ 409	1.9	1.3	1.1	0.6
$\text{K}^+$	304 $\pm$ 266	2.8	2.2	1.1	0.8
$\text{Ca}^{2+}$	441 $\pm$ 282	5.6	1.9	1.3	0.5
$\text{NH}_4^+$	1598 $\pm$ 1356	2.0	1.6	1.1	1.1
$\text{Cl}^-$	5241 $\pm$ 6513	1.9	1.3	1.1	0.4
$\text{NO}_3^-$	2355 $\pm$ 2774	2.2	2.0	1.0	1.0
$\text{SO}_4^{2-}$	6061 $\pm$ 4309	2.3	1.6	1.1	1.1
$\text{HSO}_4^-$	4555 $\pm$ 4272	2.0	1.7	1.1	1.7
WSOC	997 $\pm$ 1197	2.4	1.8	1.1	1.3

For other groups, the values represent the concentration ratio relative to the  $\text{NE}_{\text{NAD}}$  group.

NC) was used for assessing the associations among chemical species. The data were standardized beforehand to have zero mean and unit variance. This was performed by utilizing the orthogonal transformation method with Varimax rotation. Only those components with eigenvalue greater than unity were retained, because they can account for a meaningful amount of variance. The retained components have undergone rotation and then used in this study. Factor loadings indicate the correlation of each species with each component and are related to the source emission composition.

### 3. Results and discussion

#### 3.1. Data statistics and temporal distribution

The data sets were subdivided into three groups according to the sampling time: spring, summer, and early winter. Moreover, by adopting a criterion of 1500 ng/m<sup>3</sup> of Al as an indication of the occurrence of a significant Asian dust event (Hsu et al., 2008a), a total of eight events could be identified during the sampling period (Fig. 2). The northeasterly monsoon prevails in both the winter and the spring, while the southeasterly monsoon prevails during summer. According to the prevailing wind and the occurrences of Asian dust events, the samples collected in the spring and the winter were further subdivided into two groups: the NE<sub>AD</sub> (the Asian dust period in the NE monsoon) and NE<sub>NAD</sub> (the non Asian dust period in the NE monsoon) groups. During the Asian dust events, the air mass back trajectories were analyzed by employing the HYSPLIT modeling calculation of NOAA. In agreement with previous studies (Hsu et al., 2008a; Liu et al., 2009), the analyses reveal that the source regions of the Asian dust are located in and around the Gobi Desert and Loess Plateau (Fig. 3). The statistical summary of the soluble and total concentrations of the various elements and ions are given in Tables 2 and 3, respectively. For comparison, we have compiled literature/data on the total concentrations for selected metals from several oceanic regions in Table 4. The values found in this study are quite comparable to those reported in other oceanic regions. In the case of the water-soluble fraction (Table 2), the mean concentrations during the Asian dust periods are much higher than those in the non-Asian dust periods as well as other seasons for all major ionic species and silicon. For the metals, the temporal patterns are more variable. The elements found to have the highest concentrations during the Asian dust period include Ti, Sr, Ba, Mn, Co, Y, and Se. Similar concentrations of Al, Fe, Cr, As, Cd, Sb, Sn, Ge, and P were found during the Asian dust period and in the winter. Maximum concentrations of Zn and Pb were found in the winter and this is consistent with our long-term measurements in northern Taiwan (Hsu et al., 2005b, 2006). In contrast, the maximum concentrations of V, Ni, and Cu were apparent in the summer. However, the total concentrations of all the elements, with the exception of Cu and Zn, were much higher during the Asian dust period.

**Table 3**

As in Table 2, but for the total fraction.

	NE <sub>NAD</sub> (n = 32)	NE <sub>AD</sub> (n = 8)	Winter (n = 7)	Spring (n = 33)	Summer (n = 7)
Al	399 ± 314	8.7	2.2	1.4	0.5
Fe	268 ± 238	8.3	2.7	1.4	0.7
Ti	30 ± 27	7.6	2.6	1.3	0.7
Sr	7.2 ± 4.9	4.5	1.9	1.3	0.6
Ba	5.1 ± 8.0	7.6	3.4	1.3	1.5
Mn	11 ± 12	7.0	3.1	1.3	0.6
V	3.0 ± 8.8	3.0	2.3	1.1	2.4
Rb	1.4 ± 1.9	7.8	3.1	1.3	0.5
Ni	1.1 ± 1.0	5.1	2.2	1.3	1.1
Cr	3.1 ± 4.3	2.7	1.9	1.1	0.5
Co	0.18 ± 0.15	6.1	2.4	1.3	0.7
Y	0.12 ± 0.13	9.5	3.2	1.3	0.3
Cs	0.10 ± 0.16	7.3	3.5	1.2	0.4
Cu	54 ± 78	1.5	2.9	0.9	3.7
Zn	41 ± 94	3.0	3.5	1.0	0.7
Pb	12 ± 21	4.8	3.6	1.1	0.9
As	0.85 ± 1.4	5.0	2.8	1.2	0.7
Se	0.57 ± 0.94	3.7	3.1	1.1	1.5
Cd	0.37 ± 0.60	4.4	3.4	1.1	0.6
Sb	0.47 ± 0.82	3.4	2.8	1.1	0.8
Ga	0.48 ± 0.75	6.9	3.8	1.2	0.9
Sn	0.58 ± 1.1	3.9	3.3	1.1	0.9
Tl	0.086 ± 0.17	4.5	3.7	1.1	0.8
Ge	0.057 ± 0.11	5.0	3.6	1.1	0.6
Mo	0.22 ± 0.37	5.0	3.0	1.2	0.9
P	10 ± 8.4	5.7	2.4	1.3	0.9
Na	4706 ± 3878	1.7	1.2	1.1	0.7
Mg	658 ± 454	3.1	1.2	1.3	0.7
K	436 ± 303	4.4	2.1	1.2	0.8
Ca	538 ± 328	6.3	2.0	1.3	0.6

**Table 4**

Comparison of aerosol metal mean concentrations (ng/m<sup>3</sup>) in the total fraction between the East China Sea (the northeasterly monsoon period) and other oceanic regions.

	East China Sea (this work)	Irish Sea (Liverpool, UK) (Chester et al., 2000b)	Mediterranean Sea (Tel Shikmona, Israel) (Kocak et al., 2004)	Gulf of Aqaba, Red Sea (Chen et al., 2008)
Al	615	317	952	1081
Fe	410	340	724	683
K	588	–	–	633
Mn	16	8.4	16.7	16.7
V	3.8	7.3	–	5.4
Co	0.25	0.42	–	0.3
Ni	1.5	3.0	–	2.8
Cr	3.7	2.1	2.3	3.0
Cu	58	21	5.9	3.4
Zn	51	36	22.4	14.9
Pb	17	43	24.9	7.0
Cd	0.50	–	0.22	0.1

Elevated concentrations were specifically observed in the crust-originated elements Al, Fe, Ca, Ti, Sr, Ba, Mn, Rb, Co, Y, and Cs (Table 3). In general, it was found that the total concentrations for most metals in the spring are comparable with those reported at Cheju Island, South Korea (Chen et al., 1997). This suggests that most of the particulate species analyzed had common sources (source regions) and/or were subject to similar transport processes (Park et al., 2004). High concentration of anthropogenic species sulfate, nitrate, and ammonium, occurred in the downstream marine areas during the Asian dust period. Zhang et al. (2005) emphasized the significance of dust particles as a medium for pollutant conversion and transportation.

Elemental solubilities are summarized in Table 5. Dust-derived elements Al and Fe had comparable values ranging between 5% and 10%, but during the Asian dust period, the values decreased to 1.1 ± 1.8% for Al and 1.4 ± 2.0% for Fe. The solubility for Al and Fe is very consistent with that observed in the northwest Pacific Ocean, although it is slightly higher than that found in seawater extractions (Buck et al., 2006). For most of the anthropogenic metals Zn, Cd, Cu, Pb, As, and Se, the solubilities reached ~30–80%. Surprisingly, the solubility for Sn was only ~10%, although it is a well-documented anthropogenic element. The solubility of P was up to ~50%. During the Asian dust period, it was around 30%. These values are rather comparable to those (~32%) observed in the Atlantic Ocean (Baker et al., 2006). In the case of other dust-dominated elements (i.e., Ti, Sr, Ba, Co, Mn, Rb, Cs, and Y), the solubilities appeared to be variable, ranging from as low as 10% (i.e., Y and Ti) to as high as 50% (i.e., Sr and Mn).

#### 3.2. Source identification

In this study, we applied three approaches to identify the likely sources of trace metals in aerosols: (1) by performing a PCA, (2) by examining any correlations among the species, and (3) by calculating the crustal EF of the elements. The results from the principal component analyses of the soluble and total fractions are given in Tables 6 and 7, respectively. The results of the crustal EF calculation for each element in the total fraction are depicted in Fig. 4. Overall, the PCA results for the water-soluble and the total fractions agree well with each other. They show that the principal sources include continental dust and anthropogenic sources through long-range transport, sea salt, biofuel/coal combustion, heavy fuel combustion, and metalliferous industries. Crustal EF values for crustally derived elements (Fe, Y, Ti, and Co) were all around unity. In contrast, anthropogenically derived elemental EF (Tl, Mo, Sn, As, Zn, Cu, Pb, Sb, Cd, and Se) were >10. For mixed source-dominated elements (Mn, P, Ba, Rb, Cs, K, Ni, V, Cs, Cr, Ge, and Ga), the enrichment factors were between 2 and 10 (Fig. 4 and Table 8). Accordingly, combining the PCA and EF results, the chemical species may be categorized into four distinct groups: dust-dominated elements, sea salt-dominated element, anthropogenic species, and dust/anthropogenic mixed source-dominated elements.

A strong correlation was found between both total and soluble Al and Fe (Fig. 5). This suggests the domination of dust origin for aerosol Fe (Chen and Siefert, 2004). The mean Fe/Al ratio in the total fraction for the northeasterly monsoon samples (n = 40) is 0.61, which is quite consistent with those (~0.60) measured in the northern China desert and loess areas (Zhang et al., 2003). This is also consistent with the results of air mass trajectory analysis, which indicate that the likely sources of the Asian dust were located in and around the Gobi Desert and the Loess Plateau (Fig. 3). The mean Fe/Al ratio in the soluble fraction, 0.76, is slightly higher than that for the total fraction, suggesting that the solubility for Fe (5.5% in the northeasterly monsoon period and 11% in summer) is higher than that (4% in the northeasterly monsoon period and 9% in summer) for Al. In addition, Fe<sub>3</sub> correlated well with nss-sulfate and WSOC (Hsu et al., 2008b), which is also reflected in the PCA results (Table 6). Hsu et al. (2008b) suggested that the dissolution of Fe in the dust was enhanced by acid processing, and/or a minor fraction of Fe<sub>3</sub> might have originated from the same anthropogenic sources as nss-sulfate and WSOC. In addition, most of WSTEs also correlated well with nss-sulfate and WSOC (Table 8). Similarly, the two instead may be responsible for the correlations observed. For instance, the two possibilities appear to be similarly important for the mixed source-contributed element Mn. For anthropogenic source-dominated elements, including Zn, Pb, Sb, As, and Se, the correlations may be a result of the same sources as

**Table 5**

Statistical summary of the solubility (mean  $\pm$  S.D.; in unit %) for selected aerosol elements in the NE<sub>NAD</sub> group samples over the East China Sea.

	NE <sub>NAD</sub> (n = 32)	NE <sub>AD</sub> (n = 8)	Winter (n = 7)	Spring (n = 33)	Summer (n = 7)
Al	5.1 $\pm$ 2.8	0.2	0.9	0.7	1.7
Fe	7.7 $\pm$ 4.5	0.2	0.7	0.7	1.5
Ti	8.4 $\pm$ 5.6	0.6	0.7	1.0	0.8
Sr	67 $\pm$ 14	0.8	0.7	1.0	1.0
Ba	23 $\pm$ 10	0.6	0.6	1.0	0.6
Mn	49 $\pm$ 12	0.8	0.9	1.0	1.1
V	55 $\pm$ 16	0.3	0.7	0.8	1.3
Rb	45 $\pm$ 16	0.5	1.0	0.9	1.5
Ni	26 $\pm$ 17	0.2	0.6	0.7	1.6
Cr	7.8 $\pm$ 5.4	0.7	0.9	0.9	2.2
Co	36 $\pm$ 12	0.5	0.8	0.9	1.3
Y	13 $\pm$ 6.1	0.5	0.7	0.9	1.7
Cs	44 $\pm$ 20	0.4	1.1	0.8	1.7
Cu	51 $\pm$ 12	0.6	0.8	0.9	1.3
Zn	84 $\pm$ 18	0.8	0.7	1.0	1.0
Pb	45 $\pm$ 16	0.2	0.9	0.7	1.3
As	86 $\pm$ 10	0.6	0.9	0.9	0.9
Se	86 $\pm$ 16	0.8	0.9	1.0	0.9
Cd	87 $\pm$ 13	0.7	1.0	0.9	1.0
Sb	36 $\pm$ 7	0.8	0.9	1.0	0.9
Ga	27 $\pm$ 11	0.3	0.8	0.8	0.8
Sn	10.4 $\pm$ 3.7	0.5	0.7	0.9	1.1
Tl	73 $\pm$ 14	0.7	1.0	0.9	1.0
Ge	50 $\pm$ 11	0.7	0.9	0.9	1.1
Mo	17 $\pm$ 9	1.7	0.5	1.4	1.0
P	61 $\pm$ 22	0.5	0.9	0.8	0.9

For other groups, the values indicate the ratio relative to the NE<sub>AD</sub> group.

sulfate, particularly biofuel/coal combustion. Phosphorus is an essential nutrient to marine phytoplankton, and therefore better understanding on its sources and dissolution behaviors is required to assess its impact. Nevertheless, atmospheric contributions of phosphorus may not be a vital source of inorganic phosphorus in the ECS (Chen and Chen, 2008). As shown in Table 8, P<sub>s</sub> correlated well with nss-sulfate, nitrate, nss-K<sup>+</sup>, and Se. In general, Se in the atmosphere primarily originates from coal combustion, and thus, is usually used as a tracer of coal combustion (e.g., Wen and Carignan, 2007). K-rich aerosol particles are frequently detected in China, which is attributed to the substantial contribution of coal combustion, with coal being the most common fuel source in China (Waldman et al., 1991; Wei et al., 1999). It is also suggested that coal combustion essentially account for the pronounced levels of anthropogenic sulfate. Accordingly, the majority of P<sub>s</sub> may originate from anthropogenic activities. Based on the solubility of ~50% and the crustal EF value of around 2, it could be concluded that approximately half of aerosol-associated phosphorus derives from the continental source, whereas another half comes from anthropogenic sources.

### 3.3. Controlling factors of dissolution

#### 3.3.1. Acid processing

Almost all WSTEs correlated well with nss-sulfate, nitrate, and WSOC, as revealed in a correlation matrix table (Table 8). The good correlations suggest that they may originate from the same sources (or source regions) and experience the same transport processes (cold high-pressure system and the northeasterly monsoon wind) and/or that the dissolution of aerosol elements were enhanced by the presence of acidic constituents. Indeed, it was observed that sulfate and nitrate frequently associate within dust particles, likely existing as coatings on the surface of dust mainly through heterogeneous reactions of acidic gases (e.g., sulfuric and nitric acids) and dust during Asian outflows (Zhang et al., 2005; Sullivan et al., 2007). Zhuang et al. (1992) suggested that the close coupling of dust and sulfate could largely enhance the dissolution of dust Fe to increase the supply of bioavailable Fe in the remote oceans. Hence, acid processing would increase the dissolution not only of dust-associated Fe but also of many aerosol elements of both natural and anthropogenic origins. By employing a model simulation, Meskhidze et al. (2005) found that the dissolution of Asian dust Fe could be enhanced once the dust plume associated with high levels of anthropogenic SO<sub>2</sub> emission (i.e. high SO<sub>2</sub> to dust mixing ratio). In addition, acidification of aerosol particles may be enhanced by photochemical reaction and cloud processing, which will be discussed further in Sections 3.3.4 and 3.3.5.

#### 3.3.2. The origins of aerosol elements

As mentioned above (Fig. 4), the crustal EF value was used to identify the predominant origins by which anthropogenic or natural sources dominated for aerosol elements. In order to assess the effect of elemental origins, we thus examined the correlations of the solubility with logarithmic EF value for each metal (Deguillaume et al., 2005). As a result, only a few metals, which include Pb, Ni, and Ge had moderate correlations (not shown), but with the exclusion of several outlier data points. When clustering all elements, as shown in Fig. 6, several features are identified, although the

relationship between the two parameters is not so strong. Elements with crustal EF values of ~1.0 had low solubility of ~10% and these elements include Al, Fe, Ti, and Y. Co is an exceptional case, with a solubility reaching ~30%. Elements with high EF values of  $\geq 100$  had high solubility ( $\geq 70\%$ ), and these elements include Tl, As, Zn, Cd, and Se, while those with moderate solubility (30–50%) include Cu, Pb, and Sb. Elements with EF values of 2–10 had variable solubility ranging from ~10% to ~65%, and these elements include Cr (~10%), Ni, Ba, Ga, Cs, Rb, V, Ge, Mn, P, and Sr (~65%). Similarly, elements with EF values of 10–100 had variable solubility of 10–20% for Mo and Sn and 65% for Tl. This indicates that elements of anthropogenic origins characterized as high crustal EF may have high solubility, and on the contrary, dust-derived elements characterized as low crustal EF usually have low solubility.

Overall, this is deemed most consistent with the review results of Deguillaume et al. (2005). Nevertheless, from the results of our study, it could be concluded that the sources (or initial compositions) for aerosol elements are an important controlling factor for solubilization, but apparently not the key factor. Chester et al. (1993a) emphasized that the ranking of aerosol elemental solubility is not necessarily identical to their EF values. Furthermore, they suggested that the variations in solubility of selected metals are essentially speciation-mediated, which will be discussed further in Section 3.3.5.

#### 3.3.3. Dust loading

Dust concentration and trace element solubility were examined. Dust concentration was converted from total Al concentration multiplying 12.5, assuming that Al abundance in dust particles is similar to the average crust composition, accounting for 8% (Taylor, 1964). Fe, Al, Ni, V, Rb, and P are among the trace metals examined that showed good correlations, as demonstrated in Fig. 7, of which Fe was taken from Hsu et al. (2008b). To some extent, all the six elements are essentially crustally derived (Al, Fe, and Rb) and dust/anthropogenic mixed source-dominated (Ni, V, and P) groups. Note that not one of the anthropogenic origin-dominated metals like As, Zn, Cd, Sn, Sb, and Se had such a correlation. A similar correlation has been observed previously, but mostly for aerosol Fe (Bonnet and Guieu, 2004; Hsu et al., 2005b; Sedwick et al., 2007). Some previous studies argued that such results could be artifacts resulting from the saturation of the leaching

**Table 6**

Orthogonal transformation rotated principal component matrix for the soluble chemical species of the northeasterly monsoon samples.

	Factor 1	Factor 2	Factor 3	Factor 4
Al	0.81*	0.33	–	–
Fe	0.81*	0.27	–	0.30
Ti	0.38	0.85*	0.27	–
Sr	0.27	0.71*	0.62*	–
Ba	0.54*	0.79*	–	–
Mn	0.58*	0.78*	–	–
V	–	–	–	0.93*
Rb	0.84*	0.51*	–	–
Ni	0.34	–	–	0.89*
Cr	0.85*	0.32	–	0.28
Co	0.58*	0.74*	–	–
Y	0.60*	0.74*	–	–
Cs	0.91*	0.35	–	–
Cu	0.33	–	–	0.70*
Zn	0.79*	–	–	–
Pb	0.94*	–	–	–
As	0.85*	0.44*	–	–
Se	0.87*	0.43*	–	–
Cd	0.83*	0.38	–	–
Sb	0.81*	0.45*	–	–
Ga	0.92*	–	–	–
Sn	0.83*	0.25	–	–
Tl	0.90*	0.38	–	–
Ge	0.86*	0.46*	–	–
Mo	0.45*	0.69*	0.36	–
P	0.76*	0.53*	–	–
Si	–	0.70*	–	–
Na <sup>+</sup>	–	–	0.98*	–
Mg <sup>2+</sup>	–	–	0.97*	–
K <sup>+</sup>	0.69*	0.46*	0.50*	–
Ca <sup>2+</sup>	0.33	0.86*	0.30	–
NH <sub>4</sub> <sup>+</sup>	0.74*	0.53*	–	0.26
Cl <sup>–</sup>	–	–	0.97*	–
NO <sub>3</sub> <sup>–</sup>	0.50*	0.65*	–	0.39
SO <sub>4</sub> <sup>2–</sup>	0.57*	0.63*	–	0.31
Nss-SO <sub>4</sub> <sup>2–</sup>	0.60*	0.62*	–	0.30
WSOC	0.80*	0.30	–	–
Likely source	Continental (dust/pollutant mixed)	Dust dominated	Sea salt	Heavy fuel combustion

Factor loadings smaller than  $\pm 0.25$  are not given. Values greater than 0.40 are flagged by an \*.

**Table 7**  
Orthogonal transformation rotated principal component matrix for the total fraction.

	Factor 1	Factor 2	Factor 3
Al	0.94*	0.29	–
Fe	0.93*	0.36	–
Ti	0.92*	0.31	–
Sr	0.86*	0.30	0.40
Ba	0.89*	0.35	–
Mn	0.85*	0.50*	–
V	–	0.53*	–
Rb	0.84*	0.53*	–
Ni	0.86*	0.42*	–
Cr	0.37	0.39	–
Co	0.90*	0.41*	–
Y	0.93*	0.34	–
Cs	0.73*	0.66*	–
Cu	–	0.39	0.71*
Zn	–	0.73*	–
Pb	0.44*	0.88*	–
As	0.54*	0.80*	–
Se	0.31	0.91*	–
Cd	0.36	0.86*	–
Sb	0.33	0.91*	–
Ga	0.76*	0.64*	–
Sn	0.32	0.91*	–
Tl	0.36	0.92*	–
Ge	0.51*	0.84*	–
Mo	0.47*	0.73*	0.34
TP	0.89*	0.41*	–
Na	–	–	0.90*
Mg	0.66*	–	0.70*
K	0.80*	0.51*	0.27
Ca	0.93*	0.28	–
Likely source	Dust	Pollution (Biofuel/coal/heavy fuel combustion and metalliferous industries)	Sea salt

Factor loadings smaller than ±0.25 are not given. Values greater than 0.40 are flagged by an "\*".

solution with respect to the elements of interest at high-dust loadings (Zhuang et al., 1990; Baker et al., 2006). However, the fact that such trend is still being observed in studies that have used leaching/extraction methods designed to avoid saturation of the leaching solution (e.g., Buck et al., 2006; Sedwick et al., 2007; Wu et al., 2007) suggests that (at least partly) real.

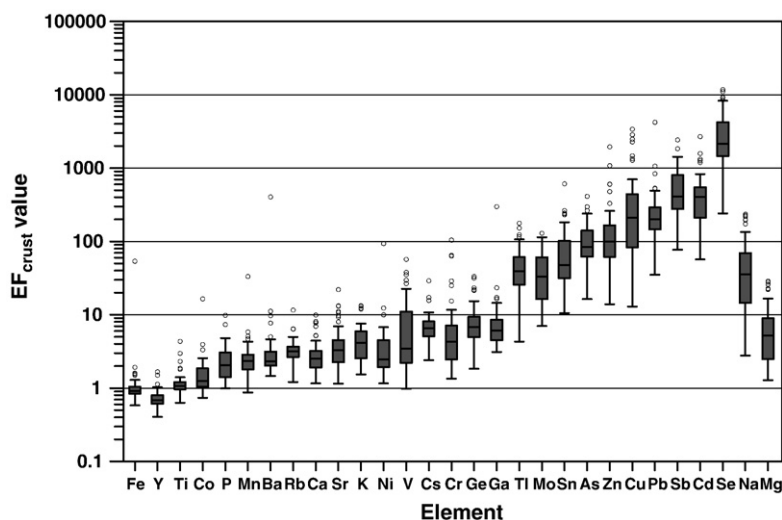
Baker and Jickells (2006) ascribed this dust loading–solubility relationship to the effect of particle size and in turn the surface area to volume ratio of dust particle. As is well known, the concentration of dust particles usually exponentially decrease with travel time/distance during long-range transport (Meskhidze et al., 2005) and their mean size gradually decrease as coarser particles preferentially deposit, which mainly occurs within the first 1000 km far from the sources. Therefore, the decreased size of

dust would have more surface area serving as sink of acid constituents leading to the increase in solubility for dust-derived elements, especially Fe. However, this dust loading effect seems to be insignificant to those anthropogenically derived elements. We inferred that most of the anthropogenic elements initially partition within fine aerosol particles; hence, the size fractionation (also the surface area to volume ratio) and loading effects would not be so important as dust-derived elements. Furthermore, in order to explain the inverse power-law relationship, Sedwick et al. (2007) proposed a mixing model between two distinct air masses characterized by significant differences in total Fe (i.e., dust loading) and Fe solubility. However, during our sampling period, the ECS was mostly under the influence of the prevailing northeasterly monsoon rather than of multiple air masses. This model seems to be inappropriate to our study.

3.3.4. Aging/cloud processing

A number of studies have demonstrated that clouding processes do have involvement in the dissolution of various aerosol species, including trace elements (e.g., Spokes et al., 1994; Deguillaume et al., 2005), with respect to several hydration/evaporation (wetting/drying) cycles for aerosol particles during long-range transport (Desboeufs et al., 2001; Mackie et al., 2005). As illustrated in Fig. 2, during the Asian dust episodes, Al<sub>T</sub> concentration reached a maximum (~2000 ng/m<sup>3</sup> or more) and Al<sub>S</sub> also usually reached a corresponding peak. When the Asian dust plumes passed, Al<sub>T</sub> sharply decreased, while Al<sub>S</sub> moderately decreased and in some cases increased. Therefore, in view of the solubility, the increasing tendency after the Asian dust events is more evident, as indicated by arrows in plots. This phenomenon was also pronounced for Fe, which has been hypothesized to be a consequence of aging/cloud processing (Hsu et al., 2008b). Indeed, during the Asian dust passage, the fronts often occupy around the study area as the high cold continental air mass encounters the hot wet maritime air mass, leading to thick clouds within the marine boundary layer. A major fraction of Asian dust and the associated pollution aerosols preferentially settled down and the remaining aerosols suspended for a longer period of time and perhaps underwent strong cloud processing, which also resulted in acidification of aerosol particles and enhancement in the aerosol dissolution. On the other hand, several studies demonstrated that dissolved transition metal ions are potentially serving as catalyst in the transformation of SO<sub>2</sub>, O<sub>3</sub>, and organic pollutants in clouds (Graedel et al., 1986; Sedlak et al., 1997). Consequently, the pH and acidic substances of cloud droplets would change and in turn affect the dissolution of aerosol metals (e.g., Desboeufs et al., 2001).

For comparison of aerosol element solubility (Fig. 8), we selected two studies from the UK, because such studies from China are not available: one in Birmingham (Birmili et al., 2006) and the other in Edinburgh (PM<sub>10</sub> samples; Heal et al., 2005). Notice that Sn in Birmingham aerosols similarly had a low water-soluble fraction, like ours. Surprisingly, the overall tendencies of selected elemental solubilities are similar to each other, while the magnitudes are somewhat different. When compared to the results of the two UK studies, the NE<sub>AD</sub> samples had lower solubilities, whereas the NE<sub>NAD</sub> samples had higher solubilities. We assumed that the aerosol elements sourced from major cities in China have similar solubilities (or dissolution properties) to those in the two cities of UK. By adopting a similar context as used in Zhuang et al. (1992), Pb, Cd, and As, which are typical elements of anthropogenic origins, had elevated crustal EF values during the Asian dust (112, 197, and 55, respectively) and non-Asian dust (203, 386, and 97, respectively) periods, indicating that they predominantly originated from anthropogenic sources, presumably comprising >98% all the time. However, their solubilities had substantially increased from 11, 63, and 49% in the dust days to 45, 87, and 86% in the common days, respectively. This clearly suggests that the NE<sub>NAD</sub> samples must have been influenced by some kind of atmospheric process that enhances the



**Fig. 4.** Correlations of EF<sub>crust</sub> values and varying elements. In the plot of the upper panel, the ends of the box, the ends of the whiskers, and the line across each box represent the 25th and 75th percentiles, the fifth and 95th percentiles, and the median, respectively; open circles indicate the data outliers.



**Table 8**  
A correlation matrix between WSTEs and  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and WSOC concentrations.

	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	WSOC
Al	<b>0.83</b>	<b>0.60</b>	<b>0.80</b>
Fe	<b>0.82</b>	<b>0.64</b>	<b>0.78</b>
Sr	<b>0.56</b>	<b>0.48</b>	0.37
Ba	<b>0.80</b>	<b>0.75</b>	<b>0.67</b>
Ti	<b>0.71</b>	<b>0.62</b>	<b>0.52</b>
Mn	<b>0.82</b>	<b>0.75</b>	<b>0.65</b>
Co	<b>0.81</b>	<b>0.86</b>	<b>0.71</b>
Ni	<b>0.51</b>	<b>0.58</b>	<b>0.50</b>
Cu	0.25	0.25	0.26
Zn	<b>0.51</b>	<b>0.56</b>	<b>0.66</b>
Cd	<b>0.72</b>	<b>0.73</b>	<b>0.79</b>
Sn	<b>0.69</b>	<b>0.70</b>	<b>0.76</b>
Sb	<b>0.77</b>	<b>0.85</b>	<b>0.78</b>
Tl	<b>0.81</b>	<b>0.77</b>	<b>0.87</b>
Pb	<b>0.64</b>	<b>0.53</b>	<b>0.80</b>
V	<b>0.44</b>	<b>0.51</b>	0.37
Cr	<b>0.77</b>	<b>0.76</b>	<b>0.85</b>
As	<b>0.77</b>	<b>0.79</b>	<b>0.81</b>
Y	<b>0.88</b>	<b>0.74</b>	<b>0.68</b>
Se	<b>0.87</b>	<b>0.75</b>	<b>0.86</b>
Ge	<b>0.82</b>	<b>0.76</b>	<b>0.80</b>
Rb	<b>0.83</b>	<b>0.75</b>	<b>0.81</b>
Cs	<b>0.78</b>	<b>0.71</b>	<b>0.84</b>
Ga	<b>0.73</b>	<b>0.61</b>	<b>0.81</b>
Mo	<b>0.63</b>	<b>0.68</b>	<b>0.53</b>
Si	0.38	<b>0.53</b>	0.31
P	<b>0.82</b>	<b>0.81</b>	<b>0.82</b>

The bold numbers indicate that the correlation coefficients are statistically significant at a confidence level of >95% (i.e.,  $P$  value < 0.05).

dissolution of most aerosol elements; otherwise, these anthropogenic elements should have remained approximately constant solubilities between the two periods. Taken together, the lifetime for the fine pollutant-dominated aerosols during the non-Asian dust period would be longer than that for the coarse dust-dominated aerosols during the Asian dust period. We thus ascribed this increased solubility in the non-Asian dust period to the aging process, which is, in fact, also involved with acid processing. That is because the aerosol particles, including mineral dust, become internally mixed with acidic substances as they age, which have been demonstrated well around the study region. In other words, these aged aerosol particles have been acidified largely, increasing the dissolution of aerosol elements. As a result, each of the three processes (aging, cloud, and acid processing) cannot be easily distinguished from the others.

### 3.3.5. Other likely related factors: photochemical reaction and chemical speciation

Photoreduction has been suggested to be a governing factor for solubilization of dust Fe and some specific aerosol elements, such as Cu and Mn during atmospheric transport (Zhu et al., 1993; Deguillaume et al., 2005). Zhu et al. (1997) observed an evident diel cycle of soluble Fe (II), with high daytime concentration and low nighttime concentration, in which the soluble (II) accounted for, on average, one-fourth of the dissolvable Fe. However, if organic and inorganic anions are both present in the reaction solutions, the dissolution of dust-associated Fe involving photochemical reactions would become more complicated, that is, not necessarily increasing the dissolution. For instance, Zhu et al. (1993) found that oxalate generated from the photochemical reaction of organic matters essentially of combustion origins may produce peroxide, which in turn oxidizes Fe (II), produced from photoreduction, to Fe (III). The solar irradiation stops at night, and notably, the Fe (II) freshly generated in daytime would be mostly oxidized back to Fe (III). Most of the samples in this study were integrated daily, such that the photochemical effect on the dissolution of aerosol elements cannot be exactly evaluated, although some elements were correlated well with WSOC comprising oxalate. In a nutshell, Zhu et al. (1997) concluded that the photochemical process does not have a substantial effect on the dissolution of dust Fe.

Another likely important factor of aerosol element dissolution is that a given element may exist in different chemical forms, that is, either as refractory or labile, in the aerosol particles (Hlavay et al., 1998; Qureshi et al., 2006). Results showing that the solubilities for aerosol elements are not correlated well with their corresponding crustal EF values may indicate that the chemical speciation often appears to be more effective than elemental origins for the dissolution of aerosol elements. For example, Sr and Mn, with respective mean crustal EF values of 2–3 and 3–4, are dominated by the crustal source; in contrast, Sn and Mo, with respective EF values of ~50 and ~30, are dominated by anthropogenic sources. However, the solubility for Sr and Mn reached  $\geq 50\%$  and  $\sim 50\%$ , respectively. For Sn and Mo, on the other hand, it was only  $\leq 10\%$  or  $\sim 20\%$ . Chester et al. (1993a,b) linked the crustal/non-crustal source control on trace metal solubility to the solid state speciation of aerosol metals. Furthermore, they established a clear relationship between the extent to which a trace metal is soluble and the extent to which it is speciated into the exchangeable phase in aerosols. Unfortunately, they considered a limited number of elements (e.g., Al, Fe, Mn, Cu, Zn, and Pb). Both crustally derived Al and Fe essentially existed within the crystalline phase association, and thus, had a

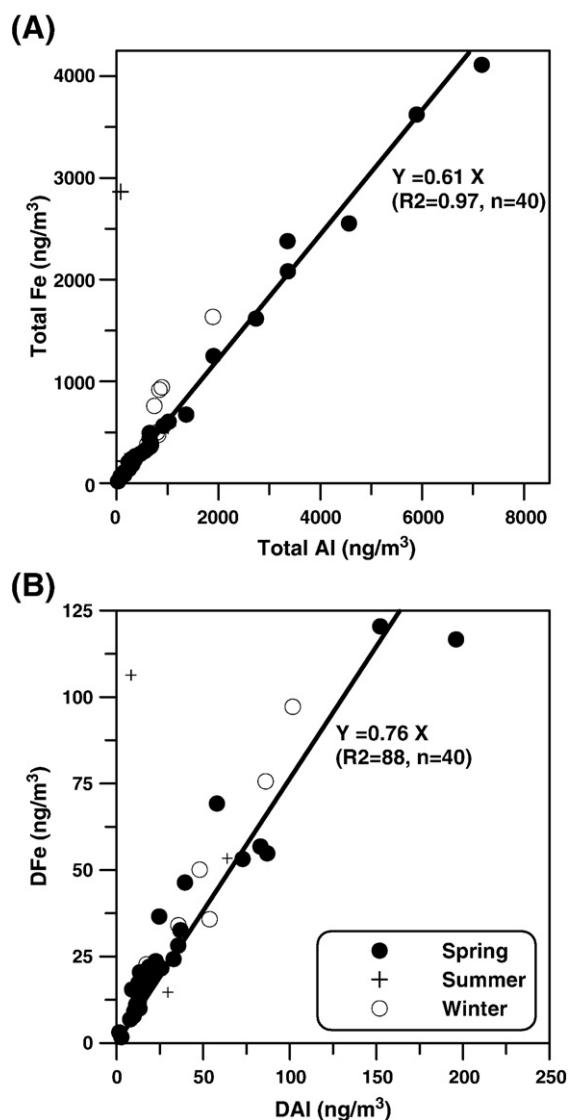
solubility of only  $\sim < 10\%$ . For Mn, its exchangeable association made up 20–40% of the total, consistent with our results showing high solubility ( $\sim 50\%$ ) for Mn. To our understanding, no chemical speciation data for ambient aerosol Sn and Mo are available. However, it is interesting that Sn in sediments (Boughriet et al., 2007; Yuan et al., 2004) and coal ash (Querol et al., 2000) mostly ( $\sim 98\%$ ) partitions within the insoluble crystalline phase. Atmospheric Sn concentrations in Beijing sometimes reached several tens  $\text{ng}/\text{m}^3$ , and it was suggested to be mainly originating from coal combustion and waste incineration (Lei et al., 2004).

### 3.3.6. The dry deposition fluxes of dissolvable TEs, P, Si, and N in the ECS

Because of the limitation of summertime samples available in this study and the prevalence of Asian dust and pollutant outflows particularly in winter and spring, only springtime and winter data were considered as a whole in representing the northeasterly monsoon period. Then, the dry deposition fluxes during this period were roughly estimated as follows:

$$F = V_d \times C_a$$

where  $V_d$  is the dry deposition velocity and  $C_a$  is the atmospheric concentration of aerosol species. For convenience, dry deposition velocities for individual species were assumed to be constant: 2 cm/s for dust derived elements Al, Fe, Si, Ti, Rb, Sr, and Y; 1 cm/s for certain elements of anthropogenic/natural mixed origins, including Mn, Co, Ba, Ni, Cr, V (Chen et al., 2008), and nitrate (considering a major portion of nitrate likely existing as coarse sodium nitrate through acid replacement) (de Leeuw et al., 2003); 0.5 cm/s for other trace elements and P as well; and 0.2 cm/s for ammonium. The dry deposition velocity of 2 cm/s for the typical dust tracer, that is, Al, is assumed to be identical to our estimate based on a long-term measurement of its size distribution in



**Fig. 5.** Correlations of Al and Fe in the total fraction (A) and dissolvable fraction (B), respectively. The linear regression considers both spring and winter samples, but excluding the summer samples.

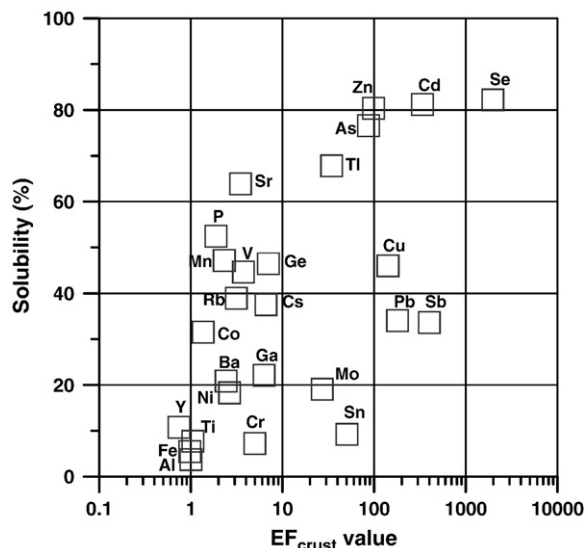


Fig. 6. The scatter plot of solubility and crustal EF value (in logarithmic scale) for all selected elements.

northern Taiwan (Hsu et al., 2008c). Thus, we assumed other dust-dominated elements have the same velocity. Chen et al. (2008) also adopted a velocity of 1 cm/s for the dust/anthropogenic mixed source-dominated elements, as given in Table 9. However, in the case of anthropogenically derived elements, a wide range of velocities from as small as 0.1 cm/s (Chen et al., 2008) to nearly 1 cm/s (Spokes et al., 2001) was assigned. We used an intermediate value of 0.5 cm/s, which is also comparable with a mean value (0.36 cm/s) used in Chen et al. (2008). For nitrate and ammonium, de Leeuw et al. (2003) used 2 and 0.1 cm/s, respectively, while our study used 1 and 0.2 cm/s, respectively. For phosphors, we assigned a velocity of 0.5 cm/s, but Chen and Chen used 2 cm/s and Chen et al. (2008) used 1 cm/s.

As a consequence, the dry deposition fluxes for these selected species were yielded, as given in Table 9. For comparison, we also compiled two literature datasets on the dry deposition fluxes as well as the used dry deposition velocities for selected trace elements in marine aerosols in Table 9. The dry deposition flux of Fe<sub>s</sub> is also calculated to be 39 ± 50 μg/m<sup>2</sup>/d (0.69 ± 0.89 μM/m<sup>2</sup>/d). When compared to that derived for the Chinese marginal seas from the modeling calculation (Gao et al., 2003), they are fairly comparable. For the total inorganic nitrogen (sum of nitrate nitrogen and ammonium nitrogen), the dry deposition fluxes are 0.79 ± 0.95 mg/m<sup>2</sup>/d (56 ± 68 μM/m<sup>2</sup>/d), which are also consistent with the published values (Nakamura et al., 2005). Note that dry deposition of gaseous species, such as nitrogen oxides and nitric acid, also probably contribute a significant fraction of atmospheric deposition of total inorganic nitrogen. Hence, the derived nitrogen flux represents the particulate inorganic nitrogen rather than the total nitrogen. For P, the derived dry deposition in the northeasterly monsoon periods is 3.3 ± 3.2 μg/m<sup>2</sup>/d. Chen and Chen (2008) obtained a yearly dry deposition of total P to be 11.4 mg/m<sup>2</sup>. This corresponds to a deposition flux of 31 μg/m<sup>2</sup>/d regardless of the seasonal variation, in which they used a dry deposition velocity of 2 cm/s, as compared to the 0.5 cm/s we used. Therefore, the inconsistency in the estimate of P dry deposition is caused mainly by the difference in

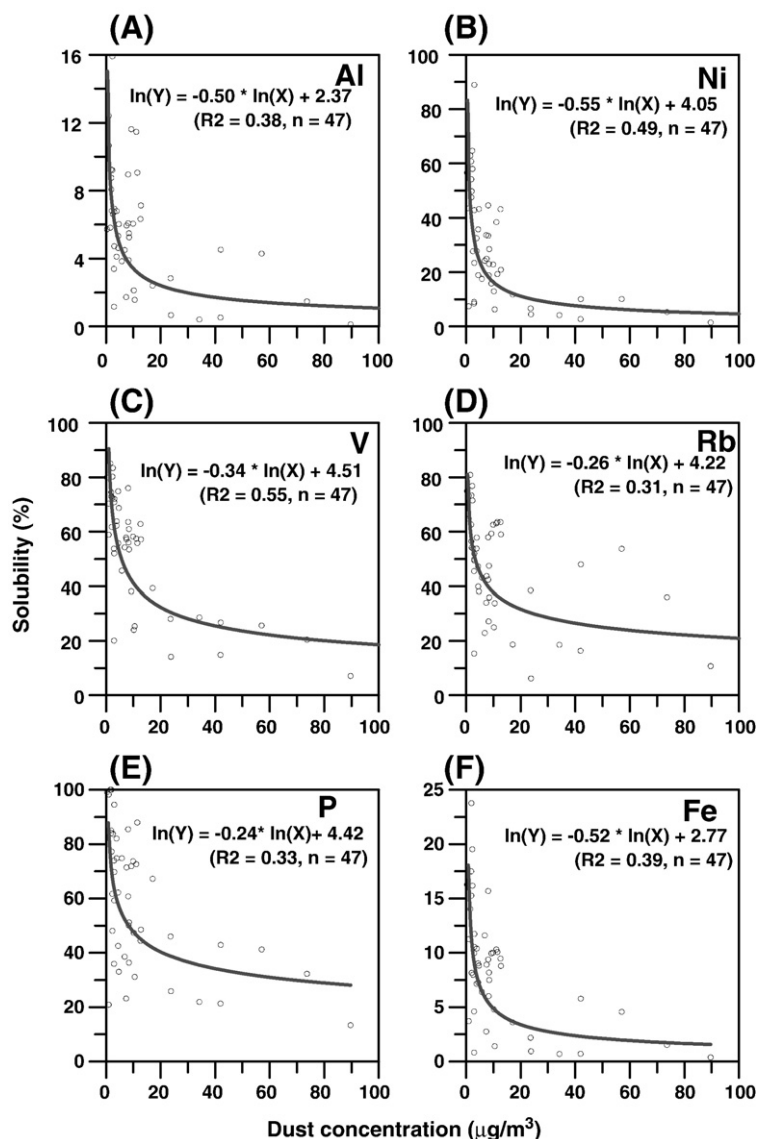


Fig. 7. (A) Correlations of solubility versus dust concentration for Al, V, Ni, V, Rb, P, and Fe, of which for Fe, the plot is taken from Hsu et al. (2008b). They all show an inverse power-law relationship.



the correlations between the solubility and dust concentration displayed an inverse power-law relationship. Consequently, we could conclude that the importance of each controlling factor may follow this sequence: acid processing (atmospheric processing) > chemical speciation  $\approx$  initial composition (elemental sources) > dust loading, of which the relative importance between chemical speciation and initial composition seems to be dependent upon which aerosol element is of interest. The effect of atmospheric processing on the dissolution of aerosol elements is more important to the crustally derived elements than to the anthropogenically derived elements. Nevertheless, we did not find any single process that could fully describe the dissolution of aerosol elements. More complex controlling factors may be involved in the dissolution of aerosol elements, which eventually determine their fate. A better understanding of dissolution processes and the solubility of aerosol-bound elements will facilitate more precise estimations of the impact of trace metal atmospheric depositions.

The yielded dry deposition flux for Fe<sub>s</sub> in the northeasterly monsoon is  $39 \pm 50 \mu\text{g}/\text{m}^2/\text{d}$ . The sum of those potential nutrient elements, including Zn, Cu, Mn, Ba, Co, V, Ni, and Cd, is  $41 \pm 74 \mu\text{g}/\text{m}^2/\text{d}$ , which is highly comparable with that of Fe<sub>s</sub>. This highlights the notion that atmospheric deposition could also be a significant source of these bioavailable trace elements, though most common studies emphasized the importance of eolian Fe. More importantly, WSTEs can be present all year round and not only during Asian dust episodes and are usually associated within fine-sized particles such that they would be transported to a larger extent than coarse dust-associated elements. In addition to nutrient inputs, atmospheric deposition also supply tremendous amounts of toxic chemical species, such as Pb, As, Se, Sn, Sb, and Tl to poison the marine organisms and disturb their biogeochemical cycles in the ECS, which need to be quantitatively evaluated in future.

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