

Seawater solubility of natural and anthropogenic metals within ambient aerosols collected from Taiwan coastal sites

Shih-Chieh Hsu^{a,*}, Fei-Jan Lin^b, Woei-Lih Jeng^b

^aResearch Center for Environmental Changes, Academia Sinica, Taipei, Taiwan, ROC

^bInstitute of Oceanography, National Taiwan University, Taipei, Taiwan, ROC

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Abstract

To evaluate the bioavailability and environmental mobility of aerosol metals to the seas, ambient aerosol samples collected from two coastal sites, i.e., Hsiyu located at the southwestern tip of the Penghu Islands in Taiwan Strait and Santiaolun on the west coast of Taiwan were determined for the seawater solubility of Al, Fe, Mn, Zn, Ni, Cu, Pb and Cd. The experiment of dissolution kinetics suggested that almost all soluble fractions of studied aerosol metals could be released within 1 h. Thereafter, dissolved particle-reactive metals like Al, Fe and Pb exhibited a slight decrease, suggestive of re-adsorption to residual particles. Seawater solubility of selected metals from Hsiyu aerosols showed the following order: Al (1.3%) = Fe (1.1%) < Pb (20%) ≤ Cu (27%) < Mn (43%) ≤ Zn (45%) ≤ Ni (50%) < Cd (69%). However, solubility data from Santiaolun were larger than those from Hsiyu for all aerosol metals analyzed, attributable to different degrees of anthropogenic contributions to the two sites. Moreover, Pb and Ni showed a positive correlation between solubility and log crustal enrichment factor (EF_{crust}), indicating that the dissolvable percentage is, to some extent, dependent on the anthropogenic contribution for specific aerosol metals and likely due to the presence of considerable contaminants such as organic, acidic and carbonaceous substances for anthropogenic aerosols. In addition, for Al, Fe, Zn and Pb, inverse power-law (log–log) correlations between solubilities and dust loadings have been observed, suggesting that particle scavenging may follow dissolution for certain metals in the marine environment. In conclusion, the dissolution of aerosol metals in seawater is predominantly controlled by which origins dominate their contributions (such as crustal or anthropogenic derivatives) and the behavior of a specific metal in seawater (such as dissolution/adsorption). Aerosol metals have substantial impacts on diverse eco-environments and accurate assessments of environmental impacts of eolian metal depositions must be based on such informative data. Thus more simulation experiments relevant to dissolution of aerosol metals in various natural waters are merited.

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1. Introduction

The dissolution of certain elements bound within aerosol particles in varying solution mediums including seawater and rainwater is crucial for biogeochemical issues with respect to public health (Voutsas and Samara, 2002), environmental mobility (Chester et al., 1994),

*Corresponding author. Tel.: 886 2 26539885x252; fax: 886 2 27833584.

E-mail address: schsu815@rcec.sinica.edu.tw (S.-C. Hsu).

aquatic contamination (Davison et al., 1994), bioavailability (Avila and Rodrigo, 2004; Kersten et al., 1991), marine biogeochemistry (Duce et al., 1991; Guerzoni et al., 1999a; Jickells, 1999) and cloud processes as well (Spokes et al., 1994; Wise et al., 2003). Indeed, a number of the first-row transition metals are suggested as being essential for marine organisms (Bruland et al., 1991; Coale, 1991; Butler, 1998; Sunda and Huntsman, 1998). More importantly, recent studies have demonstrated that eolian dissolvable Fe as well as Zn contributed from long-range transport can stimulate marine production that is closely related to atmospheric CO₂ concentrations and thus also to climate change (Martin and Fitzwater, 1988; Coale et al., 1996; Cooper et al., 1996; Schulz et al., 2004). This relationship has also been confirmed by studies of the paleoclimate from sediment and ice cores and by a series of in situ Fe-fertilizing experiments (Martin et al., 1994; Kumar et al., 1995; Petit et al., 1999; Boyd et al., 2000; Bopp et al., 2003). Further evidence confirms not all eolian Fe but dissolved fractions or specific speciation are available for phytoplankton growth (Hutchins et al., 1999; Barbeau and Moffett, 2000). In contrast to naturally derived compositions, extra contributions from numerous anthropogenic, toxic metals through dissolution of deposited aerosol particles may disturb the original cycles and budget balance in the seas and are thus detrimental to marine organisms (de Vries et al., 1998; Van den Hout et al., 1999). For example, the southern East China Sea off northern Taiwan was found to have the largest surface dissolved Pb concentration ever documented in marginal seas and open oceans over the world, attributable to long-range transported atmospheric Pb deposition from the Chinese mainland (Lin et al., 2000).

The problem of which amounts of natural and anthropogenic metals bound within aerosol particles are deposited in diverse environments is of concern, while the question of which proportion is labile to really interact with the ecosystems and which is refractory (inert, and thus likely to be stable in environments) must be clarified (Duce et al., 1991). Therefore, a better understanding of dissolution behaviors and dissolvable proportions of aerosol metals will facilitate the precise estimation and risk assessment for atmospheric depositions of selected metals with a nutrient (or nutrient-like) nature and toxicity to organisms and plants and has now become urgent. The solubility of aerosol metals in various aqueous media like seawater, rainwater, cloud-water, and fresh water can be affected by a number of controlling factors such as solution pH (Statham and Chester, 1988; Lim et al., 1994; Chester et al., 1997, 2000; Desboeufs et al., 1999), crustal enrichment factor (EF_{crust}) value of certain metals (Chester et al., 1993; Guerzoni et al., 1999b), particle loading in solution (Guerzoni et al., 1999b), aerosol type and size (Davison et al., 1994; Chester et al., 1993, 1994, 1997), photo-

reduction (Zhuang et al., 1992; Zhu et al., 1993) and the presence of organic, acidic or carbonaceous substances (Zuo, 1995; Desboeufs et al., 2001, 2005). Their relative importance is variable, depending on which solutions interact with aerosols, which compositions dominate aerosols, and which specific metals are of interest. So far the literature data on seawater solubility of aerosol metals are limited, and almost all such data are for the Atlantic Ocean and Mediterranean Sea (Statham and Chester, 1988; Kersten et al., 1991; Chester et al., 1993; Guieu et al., 1994; Bonnet and Guieu, 2004); in contrast, little data have been reported for the Pacific Ocean (Zhuang et al., 1992), and particularly for East Asia, which is becoming a sensitive area regarding air pollution and dust outflow. More importantly, some inconsistencies or reference to wide ranges of seawater solubilities for specific aerosol metals exist in previous studies, especially for Fe (Hand et al., 2004; and references therein), and this makes the comparison and utilization of such datasets more difficult.

Marine aerosol samples collected from two sites, an offshore island site (Hsiyu) of the Penghu Islands in the Taiwan Strait (characterized by less anthropogenic impact) and a coastal site (Santiaolun) in western Taiwan near an industrial area, were processed by a series of dissolution experiments and analyzed for a suite of natural and anthropogenic metals including Al, Fe, Mn, Ni, Cu, Zn, Pb and Cd. The purposes of this study were to establish the dissolution kinetics of specific aerosol metals in seawater, to quantify seawater solubilities of specific aerosol metals, and to examine the controlling factors of dissolution of selected aerosol metals. In addition, the limited amount of seawater solubility data for aerosol metals is, to some extent, owing to the analytical difficulties such as interference by the sea salt matrix of seawater and low levels of leached metal concentrations in seawater. In the study, we successfully employed an alternative method to determine the seawater solubility indirectly.

2. Materials and method

2.1. Sampling

Marine aerosol samples were collected from a small volcanic island, Hsiyu of the Penghu Islands in the Taiwan Strait (Fig. 1), over the period February 1991–January 1992. For comparison, aerosol samples were also collected from a coastal site, Santiaolun in western Taiwan neighboring the Taiwan Strait (Fig. 1), in early 1992. The prevailing northeast monsoon winds carry massive quantities of Asian dust and pollutants from mainland China to Taiwan in winter and spring (November–May), and frequent rain, that causes effective removal processes for atmospheric particles, and

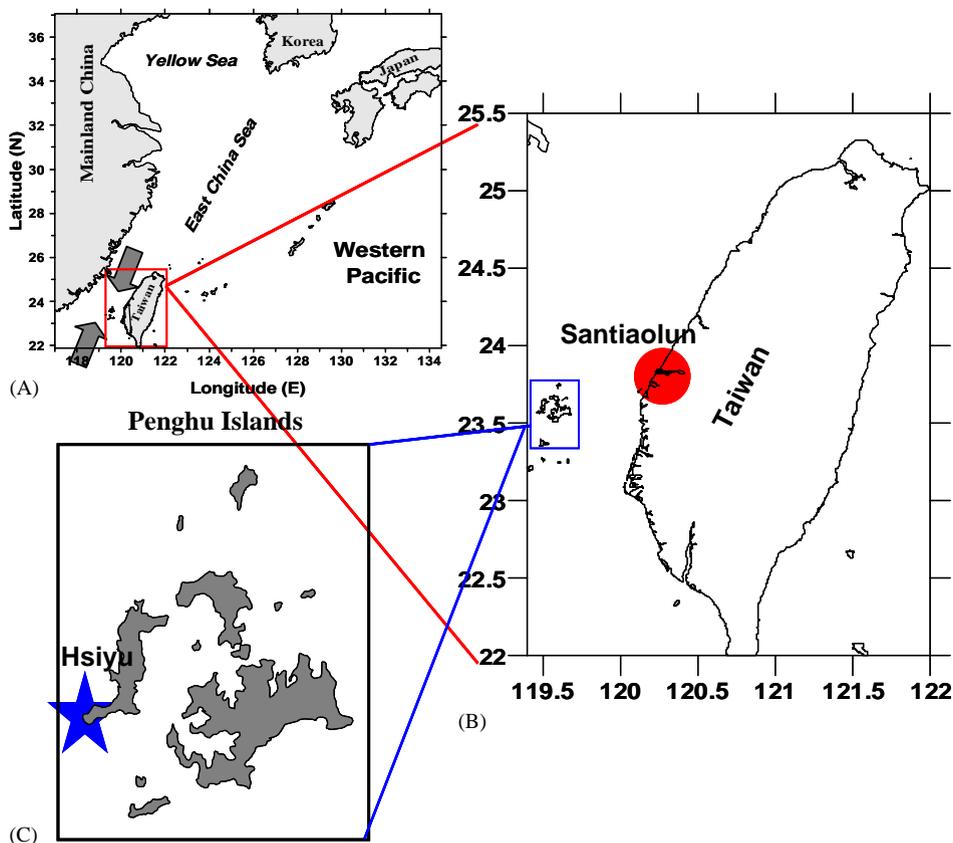


Fig. 1. Sampling location map, including (A) regional map, (B) Taiwan and (C) Penghu Islands in the Taiwan Strait for two sites, Santiaolun (filled circle) in western Taiwan and Hsiyu (filled star) of the Penghu Islands. Arrows in plot (A) indicate the prevailing winds in winter (arrow pointing south) and summer (arrow pointing north).

cessation of intercontinental transport in summer (the rest of the year) usually result in a typical seasonality for numerous dust-derived and anthropogenic metals (e.g. Pb and Cd) in northern Taiwan, thus displaying high winter/spring and low summer concentrations (Hsu et al., 2004, 2005). Air pollutants over the Penghu Islands originate dominantly from long-range transport. The air here is relatively free from local pollution since heavy industries are scarce (Yuan et al., 2004). The same situation as that in northern Taiwan may be encountered at the Hsiyu site. In contrast, the Santiaolun site suffers from local pollution since there are fossil-fuel related industries. The island site is 200m, and the coastal site 500m away from the sea. High volume aerosol samplers (motor model GBM2000H; Andersen Instruments, USA) were set up on the rooftop of residential buildings approximately 10m above ground level for collecting ambient total suspended particles (TSP). The view from sampling sites to the sea was unimpeded. Continuous sampling was conducted regardless of weather conditions. Collection time periods for each aerosol sample varied from 2 to 3 days for the Hsiyu station and were 2

days for the Santiaolun station. Flow rates were recorded with a continuous flow recorder. Whatman[®] 41 cellulose filters (8" × 10") (Whatman Limited, Maidstone, UK), acid-cleaned and conditioned in a desiccator, were employed for filtration. Samplers were operated at a rate of $\sim 60 \text{ m}^3 \text{ h}^{-1}$. Air volumes filtered for each sample were integrated for the whole sampling period. Each sheet of post-collected paper filter was equally folded and placed into an individual PE bag followed by storage at temperatures of $\sim 22^\circ \text{C}$ and relative humidity of $\sim 35\%$ in a desiccator until later analysis.

2.2. Dissolution experiment and chemical analysis

A total of 36 samples (28 from Hsiyu and 8 from Santiaolun) were collected for the dissolution study; two of these (#H0221 and #S0104, see Tables 1 and 2) were chosen for studying dissolution kinetics first. These TSP-laden filters were cut into quarters using ceramic scissors on a class-100 laminar flow bench, with the exception of the two samples chosen for the kinetic experiment which were cut into eight equal pieces. One-quarter of each

Table 1
Results of accuracy and precision ($n = 10$) of analyzing standard reference materials (SRM 1648, urban atmospheric particulate)

Element	Certified value	This work	Accuracy (%)	Precision (%)
Al	$3.42 \pm 0.11\%$	$3.39 \pm 0.07\%$	99	1.9
Fe	$3.91 \pm 0.1\%$	$3.88 \pm 0.03\%$	99	0.9
Zn	$0.476 \pm 0.014\%$	$0.467 \pm 0.007\%$	98	1.4
Pb	$0.655 \pm 0.008\%$	$0.635 \pm 0.006\%$	97	1.0
Mn	860 mg kg^{-1a}	$776 \pm 9 \text{ mg kg}^{-1}$	90	1.1
Cu	$609 \pm 27 \text{ mg kg}^{-1}$	$569 \pm 24 \text{ mg kg}^{-1}$	93	4.2
Ni	$82 \pm 3 \text{ mg kg}^{-1}$	$86 \pm 6 \text{ mg kg}^{-1}$	104	7.1
Cd	$75 \pm 7 \text{ mg kg}^{-1}$	$77 \pm 2 \text{ mg kg}^{-1}$	103	2.9

^aNon-certified value.

filter cut into quarters was used for the dissolution experiment and another for bulk sample analysis by total digestion. In addition, seawater used for the dissolution experiment was taken from the Taiwan Strait on cruise OR310 (February 1992) and immediately subjected to in situ filtration. Back in the land-based laboratory, seawater was irradiated by ultraviolet light (power 1000 W) to break down dissolved organics and then purified through ion-exchange resin columns (Chelex-100) to minimize the content of dissolved metal impurities (approx. $1 \mu\text{g l}^{-1}$ for Al, Mn, Ni, Cu, Zn and Pb, $0.1 \mu\text{g l}^{-1}$ for Fe, and $0.01 \mu\text{g l}^{-1}$ for Cd) at least more than one to two orders of magnitude lower than those in the extracted solutions. For the details for seawater sampling and treatments, refer to Hsu et al. (2003a, b).

In the case of the kinetic experiment, a total of six-eighths of the sample-containing filters were individually placed into 100 ml wide-mouth polypropylene bottles (Nalgene) with 50 ml pretreated seawater (pH = 8.3) and then reciprocally shaken for several time periods (0.5, 1, 3, 6, 12 and 24 h). When each dissolution time was completed, seawater extracts together with aerosol-containing filters were individually filtered through an acid-precleaned polycarbonate membrane filter (47 mm in size with pore size $0.4 \mu\text{m}$, Nuclepore). To eliminate the likely interference of sea salt in chemical analysis, 100 ml distilled deionized water (DDW) was passed through the filter to remove residual seawater after filtration. We believe that the occurrence of additional metal release during the filtration is insignificant based on two facts: (1) prior to the procedure most extractable fractions of metals of interest have been released in the dissolution experiment, as shown below, and (2) undetectable trace metals were found in the rinsing DDW. The residual filters (including cellulose and polycarbonate) were subsequently subjected to acid digestion for analysis of the insoluble fraction rather than directly analyzing the dissolved fraction in seawater in order to avoid interference in

metal measurements. Another eighth of the filter of each of the two selected samples was independently processed by total digestion, for which the general procedures are given below. Accordingly, the seawater solubility of a given metal can be calculated by the following equation:

Solubility

$$= \frac{\text{total concentration} - \text{insoluble concentration}}{\text{total concentration}} \times 100\%.$$

The optimal leaching time was determined to be 1 h based on the dissolution kinetics of metals of interest (Fig. 2), as described in Section 3, and was hence adopted in the subsequent dissolution experiments for other samples. For all other selected sample filters, a quarter was processed by the above-mentioned procedures for seawater dissolution, while another quarter was used for total digestion.

For acid digestion, particulate-laden filters were dissolved in an acid mixture of 10 ml 69% HNO_3 , 5 ml 60% HF and 0.5 ml 70% HClO_4 (Suprapur grade from Merck) in PTFE beakers and heated on a hot plate at $\sim 200^\circ\text{C}$ until complete dissolution. The digestion solution was dried, and the residue was then redissolved in 2 ml 69% HNO_3 and ultimately diluted with DDW to 20 ml (in 2% HNO_3). The digestion method is similar to that of Hsu et al. (2004). Digested solutions were stored in a refrigerator at 4°C for later analysis. All containers used were acid-cleaned prior to use. Metal analysis was made with a Hitachi Z-8100 flameless atomic absorption spectrophotometer (graphite furnace) equipped with a Zeeman correction system. Metal concentrations were quantified by calibrations against working standards prepared from Merck stock standard. A total of six blanks were prepared in the same manner as the samples to ensure experimental quality. Quality assurance and quality control (QA/QC) of data and methods were validated by the measurement of standard reference material NIST-SRM1648 (urban particulate) under total digestion treatment. Accuracy and precision

Table 2

Overall data ($n = 28$) on seawater solubility (%) of various aerosol metals from all Hsiyu samples. Also included is dust loading on each filter (mg per filter), which can be converted to dust concentration in mg l^{-1} by multiplying by 2.5 (see text). Samples were simply separated into two groups, namely a high loading group with dust loading higher than 50 mg per filter and a low loading group with dust loading lower than 50 mg per filter

Sample ID	Al	Fe	Mn	Zn	Ni	Cu	Pb	Cd	Dust loading (mg per filter)
H910224	0.02±0.3 (1 ^a)	0.1±0.6 (1.0)	35±1 (1.6)	33±1 (8)	32±2 (6)	24±2 (5)	6±1 (8)	77±1 (3)	189
H910227	1.5±1.6 (1)	2.0±1.3 (1.0)	61±1 (1.5)	74±1 (75)	61±2 (16)	23±3 (61)	35±1 (94)	86±0 (120)	52
H910305	3.2±3.1 (1)	1.0±2.7 (1.1)	58±1 (1.2)	68±1 (185)	72±1 (28)	27±4 (113)	31±2 (128)	20±3 (226)	26
H910317	1.2±1.2 (1)	0.4±0.9 (1.1)	51±1 (1.4)	59±1 (23)	51±3 (10)	32±2 (22)	22±1 (57)	80±0 (101)	70
H910323	0.8±2.3 (1)	0.6±1.8 (1.1)	50±1 (1.2)	77±1 (76)	69±1 (19)	25±3 (63)	35±2 (117)	81±1 (98)	43
H910408	2.5±2.8 (1)	1.4±3.3 (1.1)	66±1 (2.3)	71±1 (75)	72±2 (45)	40±4 (110)	35±2 (229)	83±1 (341)	27
H910423	1.5±3.0 (1)	1.8±2.7 (1.0)	58±1 (1.3)	75±1 (45)	43±3 (9)	27±3 (52)	39±1 (123)	88±0 (124)	53
H910601	0.1±0.6 (1)	0.1±0.2 (1.7)	9±1 (1.9)	11±1 (35)	3±5 (3)	15±3 (18)	1±1 (46)	58±0 (27)	76
H910610	0.1±0.5 (1)	0.04±0.8 (1.6)	9±2 (1.9)	5±1 (25)	1±3 (4)	17±2 (14)	3±1 (70)	39±1 (76)	79
H910616	0.3±1.5 (1)	0.1±0.9 (1.4)	10±2 (1.6)	18±2 (59)	21±4 (2)	10±4 (28)	6±1 (125)	51±1 (71)	36
H910625	1.2±3.7 (1)	1.4±3.2 (1.1)	49±2 (1.6)	60±2 (69)	60±2 (22)	16±4 (96)	17±3 (103)	81±1 (123)	24
H910704	0.4±1.5 (1)	0.3±1.5 (2.1)	4±2 (2.3)	1±2 (25)	4±5 (3)	11±4 (44)	6±2 (69)	40±1 (48)	49
H910710	1.0±3.0 (1)	0.2±1.4 (1.2)	16±2 (1.5)	14±3 (19)	1±4 (3)	9±4 (55)	1±3 (58)	44±2 (26)	35
H910723	0.3±1.5 (1)	0.6±1.2 (0.9)	9±1 (1.4)	5±2 (22)	68±2 (4)	39±3 (43)	2±1 (37)	69±1 (38)	87
H910801	0.8±2.9 (1)	0.7±2.3 (1.2)	20±2 (1.7)	21±2 (24)	41±3 (4)	22±3 (59)	22±2 (111)	44±2 (51)	28
H910807	0.1±0.6 (1)	0.2±0.4 (0.6)	10±1 (0.8)	5±1 (8)	21±4 (2)	16±3 (18)	2±1 (20)	50±0 (5)	114
H910814	0.7±2.5 (1)	0.3±1.4 (1.2)	30±2 (1.5)	28±2 (25)	34±3 (6)	30±3 (51)	9±3 (58)	79±1 (57)	53
H910823	0.1±0.5 (1)	0.2±0.1 (1.1)	28±0 (1.3)	35±0 (23)	33±3 (4)	18±3 (28)	11±0 (76)	87±0 (88)	93
H910902	1.0±2.3 (1)	1.4±2.0 (1.3)	53±1 (1.9)	61±1 (51)	48±2 (8)	21±3 (47)	23±2 (126)	84±0 (871)	49
H911018	0.5±0.8 (1)	0.2±0.1 (1.4)	28±1 (1.4)	24±0 (10)	8±4 (6)	16±3 (8)	3±2 (30)	72±1 (14)	98
H911022	2.2±1.5 (1)	0.9±1.2 (1.1)	60±1 (1.4)	60±1 (23)	78±1 (27)	45±2 (19)	24±1 (76)	86±0 (68)	35
H911114	0.6±2.0 (1)	0.5±1.4 (2.0)	68±1 (2.7)	65±1 (32)	79±1 (86)	28±4 (19)	33±1 (101)	87±0 (143)	20
H911225	0.7±1.8 (1)	1.7±1.7 (1.5)	64±1 (1.8)	61±1 (43)	82±1 (64)	40±2 (23)	24±2 (88)	77±1 (81)	27
H911228	0.7±1.9 (1)	3.8±1.3 (1.5)	74±1 (3.3)	66±1 (50)	85±1 (113)	37±2 (22)	29±1 (173)	44±1 (111)	23
H911230	6.9±4.4 (1)	2.8±3.8 (2.4)	74±1 (5.4)	72±2 (172)	85±1 (203)	40±4 (98)	31±3 (668)	67±2 (639)	6
H920106	4.7±3.8 (1)	2.6±3.7 (1.9)	72±1 (3.5)	66±1 (63)	83±1 (124)	32±4 (28)	29±3 (239)	91±0 (413)	13
H920116	0.4±1.3 (1)	1.0±2.0 (1.4)	61±1 (2.0)	59±1 (36)	78±1 (37)	34±1 (9)	32±1 (134)	85±0 (94)	61
H920123	2.9±1.6 (1)	5.6±1.3 (1.4)	70±1 (3.0)	69±1 (74)	86±1 (83)	48±2 (17)	45±1 (331)	89±0 (253)	36
<i>Average</i>									
Total	1.3±1.2	1.1±1.2	43±1	45±1	50±1	27±1	20±1	69±1	43
H-loading	0.5±1.3	0.6±1.3	32±1	34±1	36±1	24±1	14±1	73±1	
L-loading	1.9±1.3	1.6±1.3	51±1	53±1	60±1	28±1	24±1	67±1	
L/H ratio ^b	3.4	2.7	1.6	1.5	1.7	1.2	1.8	0.9	

^aNumbers in parentheses are crustal enrichment factors.

^bThe L/H is the ratio of average solubility of certain metals for the low loading group to that for the high loading group.

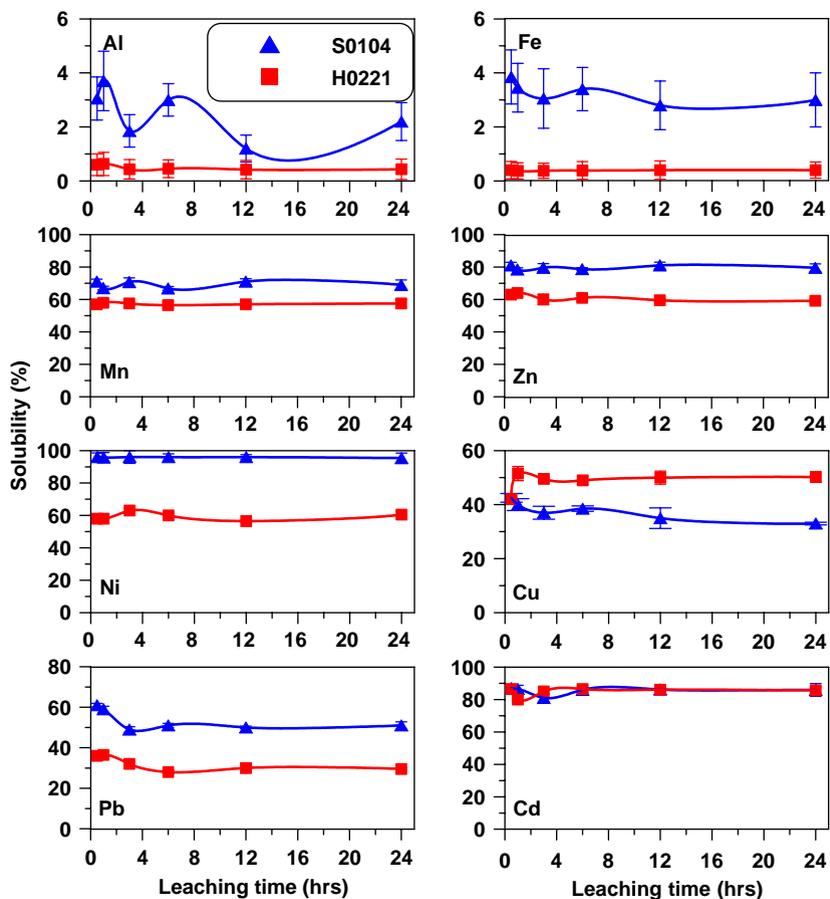


Fig. 2. Dissolution kinetics for selected metals (Al, Fe, Mn, Zn, Ni, Cu, Pb and Cd) in two aerosol samples, one from Hsiyu (sample ID #H0221) and the other from Santiaolun (sample ID #S0104). Error bars indicate the uncertainty of sample handling, analysis as well as the inhomogeneity of six-eighths of each aerosol-laden filter.

($n = 10$) for all selected metals were within a few percent of certified (or non-certified for Mn) values (Table 1), satisfying the QA/QC requirement. Details of chemical analysis have been published elsewhere (Lin et al., 2000; Hsu et al., 2003a, b). Moreover, a uniformity test was carried out by measuring metal concentrations of the four quarters of an aerosol-embedded filter; the mean variability of less than 3% was obtained (1.1% for Al, 0.3% for Fe, 1.1% for Mn, 3% for Cd, 2.7% for Cu, 0.7% for Pb, 2.1% for Zn, and 1.9% for Ni), meeting the experimental demands.

2.3. Methods

To evaluate the anomaly of specific chemical species of ambient aerosols relative to representative compositions of a reference material (e.g., average crust and sea water), an enrichment factor (EF) is defined and the following equation is used for calculation (e.g. Chester

et al., 1993; Hsu et al., 2004, 2005):

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

where $(M/Al)_{\text{aerosol}}$ is the concentration ratio of a given metal M to Al in aerosols, and $(M/Al)_{\text{crust}}$ is the concentration ratio of a given metal M to Al in crust (Taylor, 1964). EF_{crust} values were used to examine the correlation with the seawater solubility for each studied metal, but they should only be treated as order of magnitude indicators (Kersten et al., 1991), as discussed below. In addition, dust loading, another parameter considered for governing the solubility of aerosol metals in seawater, can be calculated by the following equation:

$$\text{Dust loading} = C_{\text{Al}} \times V_{\text{air}} / 8\% / 0.05, \quad (2)$$

where C_{Al} is Al atmospheric concentration, V_{air} the filtered air volume for each sample, 8% the Al abundance in average crust, and 0.051 the leaching seawater volume.

3. Results and discussion

3.1. Dissolution kinetics of aerosol metals in seawater

The dissolution kinetics of selected aerosol metals in seawater is displayed by plotting solubility against leaching time spanning from half an hour to 24 h, as shown in Fig. 2. The error bars plotted in Fig. 2 are comprehensive uncertainties that arose from sample handling, analysis and inhomogeneity, and propagation of errors through calculations. Aluminum reached a maximal solubility at 1 h (nearly 4% for sample S0104 and about 1% for sample H0221), thereafter declined slightly, and maintained at pseudo-equilibrium with a quasi-constant solubility (less than 3% and 1%, respectively). The solubility of Fe is quite similar to that of Al, but its solubility reached a maximum at 0.5 h. Solubility for Pb reached a maximum at 0.5 and 1 h for the two samples, respectively (60% for S0104 and 35% for H0221), thereafter tended to decrease, and after 6 h maintained at rather quasi-constant percentages (50% and 30%); its kinetic pattern is like those of Al and Fe. In the cases of Mn, Zn, Ni and Cd, a common kinetic pattern was shared, i.e. rapidly reaching a maximum before 1 h and thereafter maintaining at their individual quasi-constant solubilities. Note that the quasi-constant solubilities are not identical among elements and between the two samples. For Cu, kinetics are somewhat different between the two samples, showing that one (S0104) is similar to Pb with a low decreasing tendency after reaching a maximum at half an hour, and the other (H0221) is like Mn, Zn, Ni and Cd, revealing a quasi-constant dissolution after reaching a maximum within 1 h. Nonetheless, Desboeufs et al. (2005) addressed the issue, explaining that the dissolution kinetics of aerosol metals is not constant but a function of time. Moreover, according to earlier studies (Zhuang et al., 1992; Bonnet and Guieu, 2004; Desboeufs et al., 2005), the time for reaching the maximal or quasi-constant solubility for aerosol metals was a few minutes only (shorter than ours), but a shorter time may lead to a loss of some information on the dissolution behavior of specific aerosol metals. Desboeufs et al. (2005) calculated the dissolution rates and found that they are very rapid in the first 20 min of leaching and tend to be stable at lower values as compared to initial rates.

In summary, the dissolution behavior of specific metals may essentially depend on the nature of elements in seawater as well as the characteristic of their origins (e.g. anthropogenic versus natural). For those particle-reactive metals such as Al, Fe and Pb, labile fractions appear to be rapidly released from aerosol particles while dissolving in seawater, but a minor fraction of dissolved metals may immediately be subjected to re-adsorption to residual particles (Kersten et al., 1991; Davison et al., 1994), reaching a pseudo-equilibrium

between dissolved and residual particulate metals. With essentially anthropogenic origins, Zn, Cd, Cu, and Ni, elucidated by high EF_{crust} values (Table 2) can easily maintain at quasi-constant maximal solubility and usually have higher solubility compared to the particle-reactive elements (Al, Fe and Pb) and/or crust-derived elements (Al and Fe). It is noted that there are different kinetic patterns between Mn and Fe although their EF_{crust} values are close ($EF_{\text{Fe}} = 0.8$ and $EF_{\text{Mn}} = 1.3$ for sample H0211, and $EF_{\text{Fe}} = 1.0$ and $EF_{\text{Mn}} = 3.8$ for sample S0104), similar to those of Spokes et al. (1994). Apart from their different sources (the mixed crust and anthropogenic sources for Mn and the exclusively crustal source for Fe), they suggested that the chemical associations are essentially responsible for the difference in dissolution patterns of Mn and Fe, dominated by the loose bound, oxide and carbonate phases for Mn and by the refractory, crystalline aluminosilicate phase for Fe. In addition to the above-mentioned factors, chemical interactions between a fraction of dissolved metals with dissolved organic ligands in seawater that likely come from incomplete breakdown of originally existing organic ligands prior to dissolution experiment and/or from freshly organic ligands leached from aerosol particles (Kersten et al., 1991), can affect the solubility. For example, complexation has also been observed for Cu (Maring and Duce, 1989), Fe (Zhuang et al., 1992) as well as some other metals (Maring and Duce, 1990) in seawater, that may alter the dissolution rate, equilibrium concentration, and then seawater solubility of aerosol metals. In summary, the solubility of all interested metals can reach maximal values within 1 h, consistent with earlier studies (e.g. Kersten et al., 1991; Davison et al., 1994). Therefore 1-h exposure was selected for the leaching experiments on other samples in the following section.

3.2. Comparing the seawater solubility of selected aerosol metals between two sites

All data on seawater solubilities for aerosol metals from the two studied sites are given in Tables 2 (Hsiyu) and 3 (Santiaolun). The standard deviations listed in the two tables are comprehensive uncertainties that arose from sample handling, analysis and inhomogeneity, and propagation of errors through calculations. Results reveal that Al and Fe solubilities for the Hsiyu aerosols have low percentages falling within a narrow range from <1% to near 7% (Al) and 6% (Fe) with averages of 1.3% (Al) and 1.1% (Fe). For Santiaolun, Al has a solubility range comparable with that of the Hsiyu aerosols, while Fe has a somewhat higher percentage as compared to Hsiyu, ranging from 1% to 10%. With regard to trace metals, the seawater solubilities of Mn, Zn, Cu and Ni for the Hsiyu aerosols vary greatly by a factor of five or more: range 4–74% (average 43%) for

Mn, 1–77% (45%) for Zn, 9–48% (26%) for Cu, and 1–86% (50%) for Ni. In contrast, relatively constant but higher percentages were found throughout in the Santiaolun aerosols: range 57–79% (average 66%) for Mn, 70–85% (81%) for Zn, 29–54% (42%) for Cu, and 74–91% (83%) for Ni. Aerosols from Hsiyu and Santiaolun have contrasting Cd ranges of 20–91% and 88–91% with averages of 69% and 89%, respectively.

Overall, both dust-derived elements Al and Fe have very low soluble proportions for the two sites (Table 4), attributable to their inert nature in that mineral dust particles predominantly bind within the stable form of crystalline aluminosilicate (Spokes et al., 1994; Bonnet and Guieu, 2004). Comparing the solubility patterns of Mn, Zn, Cu, Ni, Pb and Cd between the two sites, the seawater solubility of the Hsiyu aerosols is quite variable, but (slightly) low relative to that of the Santiaolun aerosols. The former were collected over a long period covering the less-polluted summer and polluted winter, whereas the latter was collected for a short period only in the relatively polluted winter. Fig. 3 illustrates the seasonal patterns of EF_{crust} and solubility of Ni and Pb, sharing a common trend of low summertime but high wintertime values. Accordingly, this fact can explain why most Hsiyu samples with low solubilities are mainly summertime samples, usually characterized by less pollution, which can be elucidated by low EF_{crust} values (Table 2). On the other hand, relatively constant but large solubilities of the Santiaolun samples were observed for anthropogenic metals (Mn, Zn, Cu, Ni, Pb and Cd). For instance, metals in the Santiaolun samples were higher than those in the Hsiyu samples by a factor of 1.3 for Cd to 3.5 for Fe (Table 3). When considering the Hsiyu samples collected in winter alone, it shows higher solubility in the Santiaolun samples but lower solubility in the Hsiyu samples for all studied metals, although the differences become smaller as indicated by small S/H_{winter} ratios in Table 3. Similarly, a number of studies have compared the leachability of aerosol metals of anthropogenic and natural origins principally from urban and rural areas and suggested that chemical speciation is essentially responsible for the different dissolution patterns (Chester et al., 1993; Voutsas and Samara, 2002; Desboeufs et al., 2005). The phase associations may, however, transform into others during transport and the leachability thus changes. For instance, a portion of Pb in vehicle exhaust (also known as the dominant source of Pb in urban air), originally present in the form of halides which are more soluble, can react in the atmosphere to form oxides, which are very sparingly soluble (Maring and Duce, 1990). For further comparison, some literature data on solubilities of specific aerosol metals in a variety of solution mediums are compiled together with ours in Table 4. Overall, our results are generally in agreement with others (Kersten

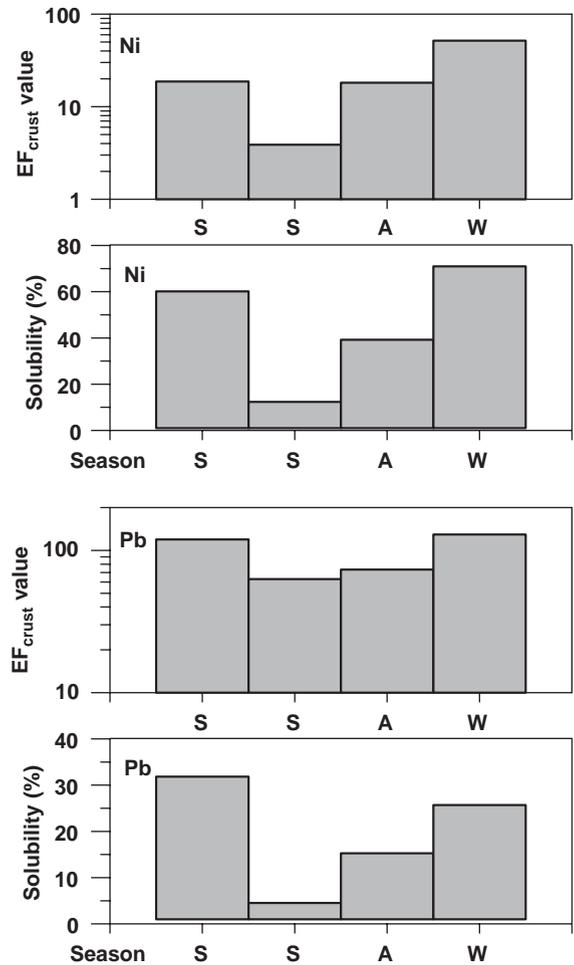


Fig. 3. Seasonality of EF_{crust} value and solubility for Ni (upper panel) and Pb (lower panel), revealing a typical pattern of low in summer and high in winter.

et al., 1991; Spokes et al., 1994; Lim et al., 1994; Guieu et al., 1994; Chester et al., 1997; Guerzoni et al., 1999b; Bonnet and Guieu, 2004). On the other hand, no systematic orders using similar/different leaching agents can be found among these studies, likely revealing that the solution matrix is not the first controlling factor of solubility rather than other factors such as solution pH, speciation of specific metals in aerosol particles and the presence of organic, carbonaceous and acidic constituents (Chester et al., 1993; Voutsas and Samara, 2002; Desboeufs et al., 2005). The relative importance for these factors is inferred to be site-dependent.

3.3. Controlling factors— EF_{crust} value and dust particle loading

The magnitude of dissolvable fractions of specific aerosol metals can be related to several factors such as

Table 3
Overall data ($n = 8$) on seawater solubility of various aerosol metals for all Santiaolun samples

Sample ID	Al	Fe	Mn	Zn	Ni	Cu	Pb	Cd
S911231	1.0±2.0 (1 ^a)	2.0±2.1 (0.9)	57±1 (3.4)	85±0 (558)	80±2 (37)	33±4 (104)	39±1 (599)	89±0 (1823)
S920106	2.0±4.5 (1)	2.9±3.9 (0.9)	69±1 (3.1)	80±1 (295)	86±2 (91)	29±5 (74)	43±2 (490)	90±1 (1213)
S920108	3.6±4.0 (1)	2.4±2.3 (1.1)	71±1 (2.9)	84±0 (196)	87±1 (77)	39±3 (32)	39±1 (302)	91±0 (673)
S920114	0.4±1.1 (1)	1.3±0.2 (0.6)	60±0 (1.0)	70±0 (21)	74±2 (6)	50±2 (4)	33±0 (65)	89±0 (85)
S920118	0.4±1.5 (1)	1.4±1.2 (0.7)	57±1 (1.4)	75±0 (50)	81±2 (13)	54±2 (10)	29±1 (133)	89±1 (326)
S920120	3.2±6.2 (1)	7.9±3.5 (1.2)	79±1 (3.4)	85±1 (340)	91±1 (112)	42±4 (98)	43±2 (563)	91±1 (1164)
S920127	5.7±2.2 (1)	10.0±1.3 (0.8)	71±0 (2.3)	84±0 (137)	86±1 (17)	48±3 (64)	65±0 (549)	88±0 (894)
S920129	4.0±2.0 (1)	5.3±1.3 (0.8)	66±0 (3.1)	83±0 (250)	82±2 (29)	39±3 (83)	49±1 (697)	89±1 (1330)
<i>Average</i>								
	2.5±1.8	4.2±1.6	66±1	81±1	83±1	42±2	43±1	90±1
S/H _{all} ^b	2.0	3.6	1.5	1.8	1.7	1.6	2.1	1.3
S/H _{winter} ^c	1.1	1.7	1.04	1.3	1.1	1.2	1.5	1.2

^aNumbers in parentheses are crustal enrichment factors.

^bS/H_{all} is the ratio of average solubility of a metal in the Santiaolun aerosols to that in all Hsiyu aerosols.

^cS/H_{winter} is the ratio of average solubility of a metal in the Santiaolun aerosols to that in Hsiyu's wintertime aerosols.

EF value, particle loading, pH value of solution medium, and aerosol type (which components dominate the aerosol composition) (Maring and Duce, 1989, 1990; Chester et al., 1993, 1997, 2000; Giusti et al., 1993; Spokes and Jickells, 1996; Guerzoni et al., 1999b). For the Hsiyu aerosols, we examined the correlation between seawater solubility and EF_{crust}. A significantly positive relationship was observed between solubility and log EF_{crust} value for Ni and Pb, as illustrated in Fig. 4, while weak or no correlations were observed for other anthropogenic metals studied (not shown). To some extent, this can be interpreted to mean that aerosol samples with more anthropogenic contributions, as elucidated by high EF_{crust} values, are more soluble than those with more natural contributions, as elucidated by low EF_{crust} values, at least for Ni and Pb. Nonetheless, it seems not to exhibit a simple relationship between solubility and EF_{crust} value for specific metals, otherwise all studied metals would show this correlation. Alternatively, this may indicate that the EF_{crust} value is not the most critical controlling factor of leachability for most aerosol metals. Desboeufs et al. (2005) suggested that the released concentrations are not related to the total metal composition or the particle origin, but are directly associated with the type of liaisons whereby the metals are bound in the solid matrix. They further concluded that in polluted regions the dissolved concentrations of aerosol metals in atmospheric waters are mainly governed by the elemental carbon content. Chester et al. (1993) suggested that the variations in solubilities of Cu, Pb, Zn, Cd and Mn are not directly related to the EF_{crust} value but speciation-mediated. For instance, Mn and Fe have close EF_{crust} values but their solubilities are different with Mn unambiguously higher

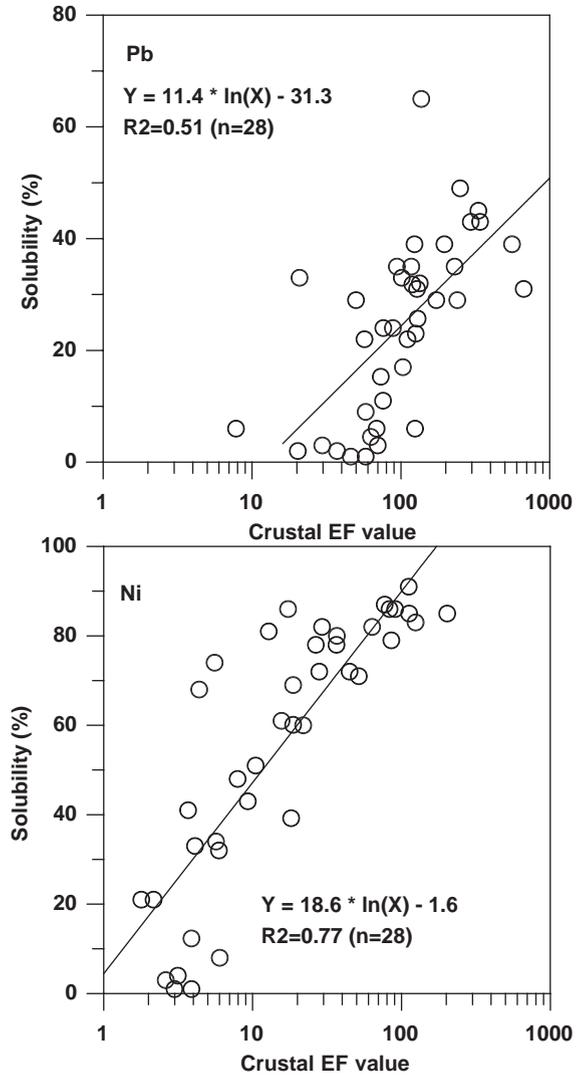
than Fe. Spokes et al. (1994) ascribed this to different phase associations between the two metals. Nevertheless, there still seems to be other complicated factors like dust loading resulting in obscuring the solubility versus EF_{crust} value relationship. Moreover, this does not mean that the ranking of seawater solubility is identical to that of EF_{crust} values for these selected metals (Chester et al., 1993).

Along with EF_{crust} values, significantly inverse power-law (i.e. log–log) relationships were found between solubility and dust loading with a range of 15–473 mg l⁻¹ for Al, Fe, Zn and Pb at a confidence level of 95% (p value < 0.05) (Fig. 5), revealing that the solubility decreases with increasing dust loading. It should be noted that dust particle loading alone was taken into account while other components such as sea salt, carbonaceous, sulfate and nitrate particles were not considered. Guerzoni et al. (1999b) observed exponentially negative relationships between Al, Fe and Pb with total aerosol particle loadings rather than a specific component loading. Our results are very similar to theirs. This likely demonstrates the presence of adsorption and/or re-precipitation processes (Chester et al., 1993; Guerzoni et al., 1999b) that can also be interpreted as the dissolution kinetics of particle-reactive elements like Al, Fe and Pb as described above. Recently, Bonnet and Guieu (2004) found that the percentage of Fe seawater solubility decreases with introduced aerosol particle loading, following a power law, more consistent with our results. They further suggested that such a result facilitates model simulation with respect to the dissolution process. Moreover, the Hsiyu samples were simply separated into two groups, namely a high loading group with dust loading higher than 50 mg per filter and

Table 4

Comparison of average solubility (%) of certain metals for our results and other literature data. Numbers in parentheses are ranges

Location	Aqueous media	Al	Fe	Mn	Zn	Ni	Cu	Pb	Cd	Data source
Hsiyu in the Taiwan Strait	Seawater	1.3 (0.02–6.9)	1.1 (0.04–5.6)	43 (4–74)	45 (1–77)	50 (1–86)	26 (9–48)	20 (1–45)	69 (20–91)	This work
Santiaolun in western Taiwan	Seawater	2.5 (0.3–5.7)	4.2 (1.3–10)	66 (57–79)	81 (70–85)	83 (74–91)	42 (29–54)	42 (29–65)	89 (88–91)	This work
Helgoland in German Bight	Seawater	—	—	—	58	—	41	40	81	Kersten et al. (1991)
Western Mediterranean	Seawater	—	(0.05–2.2)	—	—	—	—	—	—	Bonnet and Guieu (2004)
Western Mediterranean	Rainwater	17	—	—	—	53	76	65	—	Chester et al. (1997)
Iceland	Rainwater	20 (4–54)	—	—	96 (92–99)	—	—	89 (90–98)	—	Lim et al. (1994)
Sardinia	Milli-Q water	6	10	—	—	—	—	20	88	Guarizoni et al. (1999b)
North Africa coast	Simulated cloud water	0.6	0.3	5	—	—	—	—	—	Spokes et al. (1994)

Fig. 4. Correlations of solubility versus log crustal EF value (EF_{Al}) for Pb (upper panel), and Ni (lower panel) for the Hsiyu aerosols. Regression equations are also given.

a low loading group with dust loading lower than 50 mg per filter. This 50 mg per filter is a purely arbitrary value although it is close to the mean loading (43 mg per filter). As a result, the solubilities of selected metals for low loading samples are approximately 20% (for Cu) to over two fold (for Al) higher than those for high loading samples (Table 2), again suggesting that during the dissolution the residual aerosol particles, especially those for dust, may change from a donor in the initial stage to a receptor/scavenger in a later stage for those dissolved metals (Chester et al., 1993; Bonnet and Guieu, 2004). Two physicochemical processes simultaneously occur when aerosol particles enter the seawater, namely the dissolution of Fe from aerosol particles and

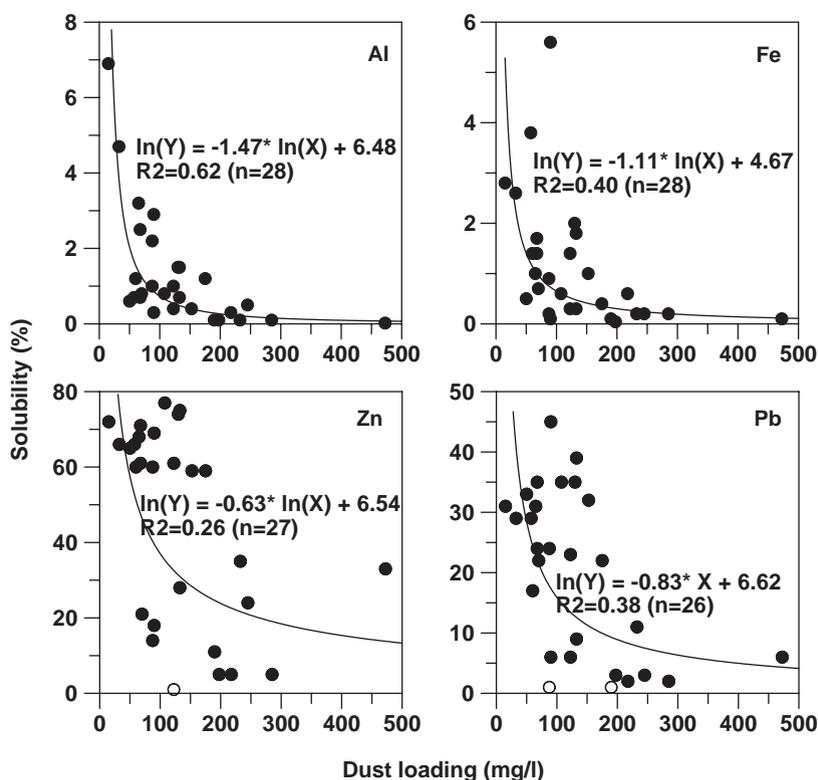


Fig. 5. Power-law correlations (i.e. log–log) of solubility versus dust loading for Al (upper left panel), Fe (upper right panel), Zn (lower left panel), and Pb (lower right panel) for the Hsiyu aerosols. Regression equations are also given. One (for Zn) and two (for Pb) outliers indicated by open circles were not included for regression.

adsorption of dissolved Fe onto the particle surface. This may imply that even pulse-like airborne dust depositions are rather important in stimulating marine productivity because of high dissolved Fe inputs while adsorption processes by abundant dust particles and/or background suspended particulates likely reduce the bioavailable amount of dissolved Fe.

4. Conclusions

The dissolution kinetics of aerosol metals Al, Fe Mn, Zn, Cu, Ni, Pb and Cd revealed that most soluble fractions could be released within 1 h, while slight readsorption occurred for those particle-reactive metals such as Al, Fe and Pb. For the Hsiyu aerosols, the solubilities of selected metals were in the order: Al (1.3%) = Fe (1.1%) < Pb (20%) ≤ Cu (27%) < Mn (43%) ≤ Zn (45%) ≤ Ni (50%) < Cd (69%). This order is not identical with that of EF_{crust} values. The controlling factors of seawater solubility include EF_{crust} value, particle loading and aerosol characteristics. Log solubilities of Pb and Ni correlates with their individual EF_{crust} values, suggesting that more polluted aerosol

particles can generally release more soluble constituents. Additionally, inverse power-law correlations observed between solubilities and dust loadings for Al, Fe, Pb and Zn imply that more abundant lithogenic particles in seawater lead to lower leachable fractions of aerosol metals as these dust-rich aerosol particles appear to switch roles from contributor to scavenger. In summary, this study will facilitate to precisely quantify the input amounts of dissolvable aerosol metals into the sea through dry deposition and then to accurately assess the potential impacts on marine biogeochemistry.

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