The biogeochemical behavior of dissolved aluminum in the southern Yellow Sea: Influence of the spring phytoplankton bloom

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Many recent studies have investigated the nutrient-type profiles of dissolved aluminum (Al) in the ocean. Significant scavenging of dissolved Al can occur during phytoplankton blooms, but the mechanism remains unclear. The distribution of dissolved Al in the southern Yellow Sea (SYS) was investigated in winter and spring 2009. Following measurements at grid stations during the spring sampling cruise, two drifting anchor surveys of more than 100 h were conducted to trace the variation of dissolved Al concentration during the spring phytoplankton bloom (SPB). The concentration of dissolved Al in the SYS decreased from 40 nmol/L in February to 30 nmol/L in March and 10–20 nmol/L in April, while the concentration of Chl *a* increased from < 2 µg/L in March to > 4 µg/L in April. The concentration of dissolved Al in the SYS decreased significantly with the development of the phytoplankton bloom, which indicated biological scavenging of dissolved Al from water column. The proportion of dissolved Al scavenged from water column by different phytoplankton species differed at the two drifting stations, with greater removal efficiency demonstrated by diatoms than dinoflagellates. Phytoplankton samples collected from the Chl *a* maximum layer were washed with trace metal clean reagent (oxalate-EDTA-citrate, abbreviate as oxalate solution, Tovar-Sanchez et al., 2003) to enable the surface-scavenged (extracellular) and intracellular Al pools associated with phytoplankton to be differentiated. Thirty-nine to ninety-six percent of the total Al was found to be existed in the interior pools, which indicated that biological absorption was the important way to scavenge dissolved Al during phytoplankton blooms in the SYS.

dissolved aluminum, distribution, spring phytoplankton bloom, southern Yellow Sea

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GEOTRACES is an international program to improve understanding of biogeochemical cycles and the large-scale distribution of trace elements and their isotopes (TEIs) in the marine environment. As one of the TEIs, dissolved aluminum (Al) has been investigated intensively in the Pacific [1–4], Atlantic [5–8], Indian Ocean [9–11], Arctic/Antarctic [12–15], and Mediterranean [16–18]. The concentrations of dissolved Al show a high variability, ranging from 0.1 nmol/L in the surface waters of the Pacific Ocean [2,3] to

174 nmol/L in the Mediterranean [16]. Sources of dissolved Al to the world's oceans mainly include atmospheric inputs [2,3,7,19–22], fluvial inputs [23–25], and dissolution from sediments [26,27]. Fluvial inputs are negligible because of estuarine removal processes, while the atmospheric inputs are the main source of Al to the open ocean. Therefore, dissolved Al in surface water can serve as an ideal tracer for quantifying dust deposition in the open ocean [28–31].

In the surface sea water, Al has a short residence time of only 4 weeks to 4 years [2]. Processes removing Al from sea water include passive scavenging onto particles [1,2,6,7,32]

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and active biological uptake by diatoms [33–37]. By using a global model of Al cycling, Han et al. [31] estimated the relative importance of the aforementioned two processes on the removal of Al from surface sea water. Their results indicated that adsorption of Al on particles dominates the removal of Al (~70%) compared to the biological uptake of dissolved Al to form the siliceous frustule by diatom accounts for ~30%. They suggested that biological uptake will exceed particle scavenging when diatom biomass is high and dust flux is low, especially in coastal areas having frequent phytoplankton blooms. However, the biological mechanisms of removal of Al from seawater are not clear. There are two distinct pools of Al in phytoplankton: that adsorbed extracellularly to the cell surface, and that sequestered internally. Hudson et al. [38] used Ti (III)-EDTA-citrate as a trace metal clean reagent to distinguish between extracellular and intracellular trace metal in marine phytoplankton, and Tovar-Sanchez et al. [39] developed a new reagent (oxalate-EDTA-citrate) to remove surface-bound trace metal, which they successfully applied in a field study of iron.

The southern Yellow Sea (SYS) is a semi-enclosed water body in the western Pacific, bordered by China and the Korean Peninsula. Water circulation in the SYS is characterized by the Yellow Sea Warm Current (YSWC) and currents along the coasts of China and Korea, including the Yellow Sea Coastal Current (YSCC) and the Korea Coastal Current (KCC) [40]. The YSWC transports warm, saline water from the open ocean into the SYS; it is strongest in winter, and disappears or is very weak in summer [41]. The Yellow Sea Cold Water Mass (YSCWM) occurs in the central SYS because of the unique basin and tidal condition [42]. It occurs below 25 m layer, where it forms a strongly stratified layer, that develops in spring, strengthens in summer and disappears in autumn [43]. Although many rivers empty into the SYS from China and Korea, most terrestrial materials and pollutants from the adjacent land masses enter the SYS via the atmosphere in spring [44,45]. Therefore, the spring phytoplankton bloom (SPB) in the SYS usually occurs in April, at that time when Asian dust storms occur frequently [46]. Two mainly phytoplankton types dominate the SPB in the SYS; diatoms and dinoflagellates [47]. As SPBs commonly occur in the SYS without substantial terrestrial input from the adjacent rivers, the SYS is an ideal place to explore the impact of phytoplankton on the biogeochemical behavior of dissolved Al.

Up to now, the biogeochemical behavior of dissolved Al in the SYS is still unclear. Ren et al. [48] made an initial report of dissolved Al concentrations in the SYS, based on measurements at three separate locations. Ren et al. [49] subsequently reported dissolved Al concentrations in spring 2007, following a major Asian dust storm and large scale diatom bloom that occurred 4–5 d after the storm. Their results showed that the phytoplankton bloom affected the concentrations of dissolved Al in the SYS, but the biological removal mechanisms were not investigated. In this study,

we assessed variations in dissolved Al concentrations during the SPB, and investigated the biological mechanisms involved using the oxalate reagent to distinguish between extracellular and intracellular Al associated with phytoplankton collected in the field. The study contributes to understanding of the role of biological removal in the biogeochemistry of Al in the SYS.

1 Materials and methods

1.1 Sample collection and shipboard processing

Two sampling cruises were carried out in the SYS aboard the *R/V Bei Dou*, 12–19 February 2009, and 24 March to 15 April 2009, respectively (Figure 1(a) and (b)). The latter involved a general survey based on gridded stations 24–30 March, and drifting anchor sampling from 30 March to 15 April. The drifting anchor sampling occurred in an area (Figure 1 (b)) predicted to have a phytoplankton bloom, based on historical information. *In situ* chlorophyll *a* (Chl *a*) concentrations were measured using *in vivo* fluorescence to monitor the outbreak of the SPB (Chl *a* > 4 µg/L, [46]). The Chl *a* concentration in the subsurface layer (10–20 m) reached 4 µg/L in Z11 (B20, 35°59.761'N, 123°00.356'E, 72 m depth) and Z4 (B23, 35°30.123'N, 124°00.289'E, 83 m) on 4 and 9 April, respectively, which indicated the presence of a bloom. The research vessel followed buoys launched at 03:30 h on 4 April and at 13:42 h on 9 April, Chl *a* samples were collected every 3 h and dissolved Al samples were collected every 6 h until the bloom disappeared. In total, the buoy tracking at Z11 and Z4 involved 102 h and 126 h of drifting anchor measurement, respectively (Figure 1(c) and (d)).

A CTD profile-rosette assembly with Niskin bottles (Model: Sea-Bird 911^{plus}) was used to obtain depth profiles of temperature, salinity, turbidity and fluorescence in the water column at the grid stations. Discrete water samples were taken for Chl *a*, silicate and Al analyses were collected at depths determined from the CTD readings. Following collection the samples were filtered through pre-cleaned 0.45 µm pore-size cellulose filters (Development Center of Water Treatment Technology, Hangzhou, China; soaked in HCl solution (pH 2) for 24 h and then in Milli-Q water (Millipore, USA) until a neutral pH was reached) in a class 100 clean bench. Suspended particulate matter (SPM) was measured by weighing the dried membrane difference before and after filtration. The filtrates obtained on the first cruise were acidified to pH 2 using HCl, and were stored in LDPE bottles in the dark at room temperature. The filtrates obtained on the second cruise were frozen (–20°C) in LDPE bottles. Blanks were prepared at sea by filtering a known volume of Milli-Q water following the methods used for the seawater samples.

Phytoplankton samples were collected from the Chl *a* maximum layer at the phytoplankton sampling stations

Figure 1 Sampling locations in the southern Yellow Sea. (a) 12–19 February 2009; (b) 24 March–15 April 2009; (c), (d) drifting anchor sampling trajectory conducted at stations Z11 (tracing time 102 h, tracing distance 53.7 km) and Z4 (tracing time 126 h, tracing distance 119.2 km), respectively. The shadow region in Figure 1(b) is the estimated phytoplankton bloom area; ★ drifting anchor stations; ○ phytoplankton sampling stations.

(Figure 1(b)). The samples were filtered through a silk net (200 μm mesh size) to remove zooplankton, then, through a net (20 μm mesh size) to remove fine mineral clay particles. The phytoplankton (four replicates) were removed from the samples onto 0.20 μm Whatman polycarbonate filters by filtration under 2–3 kPa atmospheric pressure to avoid damaging the phytoplankton cells. When the volume in the filter tower was reduced to approximately 50 mL, the vacuum pump was turned off and the cells in each of two filter towers were exposed to 50 mL of oxalate reagent for 5 min, at which time, the vacuum pump was turned back on. The filters were rinsed three times with 5 mL filtered seawater [39], then frozen until digested to measure Al. The amount of extracellular Al was calculated as the difference between the mean of two samples that were washed only with

filtered seawater, and the mean of the double reagent-washed samples.

1.2 Analytical method

In the laboratory, dissolved Al was determined by fluorescence measurements following complexation with lumogallion and extraction into *n*-hexanol [50]. The silicate concentrations were determined in the laboratory using a Skalar SAN^{plus} auto analyzer [51]. The Chl *a* concentration was measured using a Turner Designs 700 fluorometer with the method in the Specifications for Oceanographic Survey (GB/T 12763.4-2007). The membranes supporting filtered phytoplankton cells were digested in $\text{HCl}:\text{HNO}_3$ (3:1) in a closed Teflon system for 30 h at 170°C.

1.3 Quality assurance/quality control

The detection limit for dissolved Al was 0.03 nmol/L (3σ) with a precision of 1% at 40 nmol/L and 6.7% at 1.0 nmol/L [50]. Inter-calibrations of dissolved Al measurements using SArFe and GEOTRACES Atlantic surface and deep water samples showed a difference within 5% (<http://es.ucsc.edu/~kbruland/GeotracesSaFe/kwbGeotracesSaFe.html>). The precision of the silicate detection method was <5% [51]. The precision (4.8%) and recovery (97%–105%) of the digestion method were tested using Chinese reference materials (CRM, GSD-9). The removal efficiency of the oxalate reagent was determined using cultures of the diatom *Thalassi-*

osira weissflogii, which were processed using the same method as that for the field-collected phytoplankton samples. For *T. weissflogii* on washed or not washed membranes, the precision of the total and intra-cellular Al were 3.8% and 19.3% ($n=5$), respectively.

2 Results

2.1 Horizontal distribution of dissolved Al in the SYS

The distributions of temperature and salinity in February and March were similar (Figures 2 and 3), and both parameters increased gradually from north to south. The water

Figure 2 Distributions of temperature ($^{\circ}\text{C}$), salinity, SPM (mg/L) and dissolved Al (nmol/L) in the surface and near bottom layer in the SYS in February 2009.

Figure 3 Distributions of temperature ($^{\circ}\text{C}$), salinity, SPM (mg/L) and dissolved Al (nmol/L) in the surface and near bottom layer in the SYS in March 2009.

column was well-mixed from the surface to the bottom. There was a water mass characterized by higher temperature and salinity in the southeast of the study area, which may have been caused by intrusion of YSWC [41]. The SPM concentration decreased from nearshore to offshore, and was particularly high at the bottom (Figures 2 and 3). In February the highest SPM values occurred in the southernmost area near the Changjiang estuary, which was associated with input of terrestrial material from Changjiang. The range and mean concentrations of dissolved Al found in the SYS during the study are summarized in Table 1, which shows that the mean concentration of Al was higher in February than in March (*t*-test, *P*=0.05). The concentration of dissolved Al decreased gradually from the coastal area to the central SYS, where the lowest concentrations (20–40 nmol/L) were detected. The concentrations of dissolved Al in the southernmost area reached 40–50 nmol/L in February, which is consistent with the relatively high concentrations of SPM.

2.2 Vertical distributions of dissolved Al in the SYS

The LAT36 section, which transects the central SYS, was used to investigate the vertical distribution of dissolved Al (Figure 4). It is evident in the vertical profiles of temperature and salinity that the water column was well mixed during both sampling periods. A water mass characterized by high temperature and salinity was detected, which indicated the involvement of the YSWC. The mean temperature and salinity in March were higher than in February. The concentrations of SPM throughout most of area were 3–5 mg/L, suggesting the entire region was well mixed. Higher concentrations of SPM were observed in the layer near the bottom, particularly in February. The concentrations of dissolved Al were higher in the coastal region, and decreased from nearshore to offshore. In the LAT36 section, the concentrations of dissolved Al in February were higher than in March, particularly in the coastal area. In the central section there existed a water tongue with low dissolved Al concentration of 25–35 nmol/L, consistent with the relatively high temperature and salinity.

2.3 Drifting anchor stations in the SYS

Figure 5 gave the time-series variations of density (Sigma t),

Chl *a* and dissolved Al at Z11 and Z4. As shown in the Figure, during the tracing of drifting anchors with pycnocline of approximately 20 m and 10 m at Z11 and Z4, respectively, the water column was stratified obviously. At station Z11, the concentration of Chl *a* changed over time; the maximum concentration was found at approximately 60 h, and the concentration declined after 80 h. During the SPB the dominant phytoplankton species at Z11 was the diatom *Detonula pumila* (unpublished data, Jun Sun). The concentrations of Chl *a* were high (approximately 3 µg/L) in the upper layer, especially at the layer approximately 10 m, and then decreased to <1 µg/L below 30 m. The concentration of dissolved Al was low in the upper layer, and increased with water depth. The minimum concentration occurred at approximately 60 h, which corresponded to the maximum Chl *a* concentration.

At station Z4 the concentration of Chl *a* was highest in the subsurface layer (approximately 20 m), and decreased to the bottom. The maximum concentration of Chl *a* exceeded 10 µg/L, which was higher than at station Z11, and lasted longer. The dominant phytoplankton species was the dinoflagellate *Heterocapsa sp.* (unpublished data, Sun Jun). The minimum concentration of dissolved Al occurred in the subsurface (10–20 m), which was correlated with the maximum concentration of Chl *a*. At both Z11 and Z4 the correlation between the low concentration of dissolved Al and the high concentration of Chl *a* indicated that significant scavenging of dissolved Al occurred during the SPB.

2.4 Extracellular Al and intracellular Al concentrations in phytoplankton

The phytoplankton samples were washed with oxalate reagent (oxalate-EDTA-citrate) to distinguish extracellular and intracellular Al associated with the phytoplankton (Figure 6). The results showed that the total Al concentration in phytoplankton was higher in the nearshore stations and decreased towards the central SYS, with lower value of 8.6 mg/g appeared at station B6. However, the highest total Al concentration in phytoplankton was discovered at station B26, located in the central of the SYS, which indicated that the Al concentration in phytoplankton was influencing by different phytoplankton species rather than the distance from coast. With increasing Chl *a* concentration the total Al concentration in phytoplankton declined rapidly, especially

Table 1 Temperature, salinity, SPM and concentrations of the dissolved Al in SYS

	February				March			
	Al (nmol/L)	<i>T</i> (°C)	<i>S</i>	SPM (mg/L)	Al (nmol/L)	<i>T</i> (°C)	<i>S</i>	SPM (mg/L)
Surface	26–70	5.3–13.8	31.5–34.2	2.3–46.3	11–102	3.9–10.5	31.4–33.7	2.8–15.9
	45±22	8.6±2.4	32.7±0.7	9.7±11.1	35±18	7.1±1.7	32.6±0.7	4.7±2.8
Bottom	27–128	5.2–13.5	31.5–34.2	3.3–68.7	11–57	3.9–11.0	31.4–33.8	1.5–24.1
	42±12	8.7±2.4	32.8±0.7	14.3±16.4	35±13	8.0±1.8	32.7±0.7	8.9±6.4

Figure 4 Vertical distributions of temperature ($^{\circ}\text{C}$), salinity, SPM (mg/L) and dissolved Al (nmol/L) at section LAT36 in the SYS in February and in March 2009.

at station Z4. Similarly, the intracellular concentrations of Al were low in the central area, but the percent intracellular Al was high (>80%, except at B5). The percent of intracellular Al at most stations exceeded 50%.

3 Discussions

3.1 Influencing factors of the distributions of dissolved Al in the SYS

Dissolved Al in the seawater mainly derives from the

dissolution of weathering products of rocks and soils, with little anthropogenic influence except for the region where is affected by the acid deposition [52]. The concentration of dissolved Al decreased from the coastal area to the central SYS due to the input of coastal currents, including YSCC and KCC, which carried high dissolved Al concentration water masses from the coastal area [49]. In addition, concentration of dissolved Al in the bottom was higher than in the surface, especially in the central SYS, consistent with relatively high concentrations of SPM (Figures 2 and 3), which indicated that sediment resuspension was probably

Figure 5 Variations in density (Sigma t), Chl *a* ($\mu\text{g/L}$) and dissolved Al (nmol/L) at Z11 and Z4 in the SYS during 102 h and 126 h time series sampling.

Figure 6 Percentage of extracellular and intracellular Al associated with phytoplankton at the phytoplankton stations (Z4-1, Z4-2, Z4-3 are three periods during the drifting anchor station Z4, respectively).

the source of dissolved Al close to the bottom [26,27]. There existed a water tongue with lower concentrations

(20–40 nmol/L) of dissolved Al in the central SYS (Figures 2 and 3) and in the central section LAT36 (Figure 4). Incorporation of the distributions of temperature and salinity confirms that the lower concentrations of dissolved Al are due to the incursion of YSWC, a branch of the Kuroshio Water with relatively low levels of dissolved Al [48].

The central SYS is away from direct influence of rivers, and is mainly influenced by both natural and anthropogenic compounds transported by atmospheric depositions [53]. Huge amounts of terrigenous materials were carried into the SYS by the Asian dust storms which occurred frequently. The concentration of dissolved Al in the surface of open ocean was controlled by the fractional dissolution of atmospheric dust deposition [22]. However, the atmospheric depositions are seasonal and sporadic. Based on the statistical results, there were three to four dust storm events per year affected the YS [54]. Based on the field observation which was carried in spring 2007, following an episode of

enhanced Asian dust storm over the SYS at the beginning of observation, the concentrations of dissolved Al in the surface were enhanced up to 197 nmol/L which indicated the influence of dust storm [49]. The estimated atmospheric deposition fluxes of dissolved Al during the dust storm and the non-dust storm days were $114 \mu\text{mol (Al) m}^{-2} \text{d}^{-1}$ and $3.7 \mu\text{mol (Al) m}^{-2} \text{d}^{-1}$, respectively, based on the field observation carried out in spring 2007 [49]. The atmospheric input of dissolved Al is 13-fold higher than the sum of riverine inputs in the SYS, although with the characteristics of seasonal and sporadic. During the sampling periods in this study, there was no obviously increased high value of dissolved Al occurred in the surface layer during the observations in winter and spring 2009, which can indicate the absence of dust storm input. Based on the Micaps meteorology data provided by China Meteorological Administration (CMA), there were four dust events occurred in winter and spring 2009, and only two of them affected the YS, which were occurred during 19–20 February and 14–16 March, respectively. One dust event occurred before the winter cruise, and the other one occurred during the interval between two cruises, which is coincident with no obviously high value of dissolved Al in the surface during the observations. In brief, the distributions of dissolved Al in the SYS in winter and spring 2009 were mainly affected by the mixing of different water masses and resuspension of sediments in the bottom, with litter influence from atmospheric depositions. Biological mediation of the behavior of dissolved Al in the SYS was significant and will be discussed in the next section.

3.2 Biological removal of dissolved Al in the SYS

SPBs occur frequently in the SYS, facilitating study of the removal of dissolved Al by phytoplankton. Xuan et al. [46] divided the development of SPB in the SYS into three successive periods: incubation, occurrence and disappearance. March and April are usually the incubation and occurrence periods, respectively, for the SPB in the SYS. Thus, the concentration of dissolved Al in February can be used as the background value. The concentrations of dissolved Al decreased from 40 nmol/L in February to 30 nmol/L in March and to 10–20 nmol/L in April, while the Chl *a* concentration increased from $<2 \mu\text{g/L}$ in March to $>4 \mu\text{g/L}$ in April. The concentration of dissolved Al in the SYS decreased significantly with development of the phytoplankton bloom, which indicates that biological scavenging of dissolved Al was occurring.

Figure 7 shows the vertical profiles of dissolved Al, Chl *a* and other parameters at stations Z11 and Z4. A thermocline and a halocline developed at 10–20 m, and the maximum concentration of Chl *a* was found below these layers. The concentration of silicate in the upper layer was depleted significantly at station Z11, while this was not the case at station Z4. The different vertical profiles of silicate at the two drift stations during the SPB were probably a result of different dominant phytoplankton species, with *Detonula pumila* at station Z11 and *Heterocapsa sp.* at station Z4. The vertical profiles of dissolved Al showed lower values in the upper layer and higher values in near the bottom layer, which was a similar pattern to that of silicate. The lowest

Figure 7 Vertical profiles of temperature, salinity, dissolved Al and Chl *a* at stations Z11 and Z4 during the drifting anchor sampling.

concentration of dissolved Al coincided with the layer of maximum Chl *a* concentration at both stations, which further indicated biological removal of dissolved Al in the SYS.

However, the removal efficiency of dissolved Al was much lower at station Z4 than at station Z11, although the concentration of Chl *a* was almost three-fold higher at the former (Figure 8); this indicates that the biological scavenging of dissolved Al at station Z11 was more significant. Figure 8 showed the relationship between the concentrations of dissolved Al and Chl *a* in the subsurface layer (Chl *a* maximum layer) at stations Z11 and Z4. The slopes of the lines showing the Al-Chl *a* relationship in the subsurface waters at stations Z11 and Z4 were -4.49 and 0.25 , respectively. The relationship between the dissolved Al and Chl *a* concentrations suggested significant biological removal of Al at Z11 ($P < 0.005$, $n = 15$), but not at station Z4. This may have been because of the different phytoplankton species dominating the SPB at each location. *Detonula pumila* (diatom) and *Heterocapsa* sp. (Dinoflagellates) dominated the SPB at stations Z11 and Z4 respectively, indicating that *Detonula pumila* can scavenge dissolved Al much more effectively. Li et al. [55] also reported that dissolved Al in the coastal area of Zhejiang and Fujian (China) was removed mainly by *Skeletonema costatum* (diatom), rather than by dinoflagellates. Many studies [18,36,37,56] have shown that dissolved Al can be taken up by diatoms, but there have been few studies of this process among dinoflagellates. The relationship between phytoplankton species and dissolved Al removal requires further study.

3.3 Preliminary assessment of the mechanism of biological removal of dissolved Al in the SYS

The trace metal clean reagent provides the means to distinguish between extracellular and intracellular Al in phytoplankton, and to investigate the biological mechanisms of Al removal. As shown in Figure 6, the range of total Al concentrations associated with phytoplankton was $4.4\text{--}48.6$ mg/g, and for the intracellular percentage was $39\%\text{--}96\%$.

Figure 8 Relationship between dissolved Al and Chl *a* in the subsurface layer (Chl *a* maximum layer) at stations Z11 and Z4.

There was a negative correlation between the concentrations of total Al and Chl *a* ($P < 0.05$, $n = 10$). The concentration of total Al in phytoplankton decreased with increasing of Chl *a* concentration, which was caused by the dilution effect of phytoplankton proliferation.

The mean percentage of intracellular Al was $73\% \pm 21\%$, which suggests that most of the scavenged Al was absorbed by phytoplankton during the SPB. Previous studies based on limited observational data [36,49] have indicated that the concentration of dissolved Al is lowest following decline of the SPB. In this study, sampling at the drifting anchor stations occurred over a period of more than 100 h, and showed that the minimum concentration of dissolved Al coincided with the maximum of Chl *a* concentration (Figures 5 and 7). This indicates that the dissolved Al was scavenged by absorption during biological activity, which was reflected in the high intracellular percentage of Al. Thus, biological absorption was the major mechanism associated with scavenging of dissolved Al during this investigation.

However, there were several uncertainties in the use of the oxalate reagent method for differentiating surface adsorption and internal pools of Al in phytoplankton. Firstly, the removal efficiency of the oxalate reagent was not tested because of the lack of an effective isotopic tracer for Al. Secondly, during sample preparation we assumed that all the filtered particles were phytoplankton, but some fine clay particles may have been retained rather than having been removed during the collection of phytoplankton samples by filtrate through $20\text{ }\mu\text{m}$ mesh net. Thus, the intracellular Al percentages may be overestimates, especially those from nearshore stations where the SPM concentrations were relatively high. To assess the reliability of the field data with respect to the percentage intracellular Al in phytoplankton, laboratory incubation experiments were conducted using a range of diatoms (*Nitzschia closterium*, *Skeletonema costatum*, *Thalassiosira weissflogii*) and the dinoflagellate *Proocentrum donghaiense* under various Al enrichment conditions. During the incubation experiments, we used the filtered and sterilized seawater, so in this system there was no interference by clay particles. The results showed that the dissolved Al concentrations decreased significantly during exponential growth of the diatoms, but only decreased slightly during growth of the dinoflagellate. The percentage of intracellular Al was approximately $30\%\text{--}80\%$, and varied with growth phase (unpublished data). The combined results of the field study and incubation experiments, confirm that active absorption of dissolved Al by diatom species occurs. More laboratory incubation experiments and field measurements are needed to clarify the mechanism of biological removal of dissolved Al.

4 Conclusions

This study investigated the dissolved Al concentration in

winter and spring in the SYS. The concentrations in February, March, and April were 42 ± 14 nmol/L, 34 ± 13 nmol/L, and 23 ± 7 nmol/L, respectively. Significant scavenging of dissolved Al occurred during the SPB, which indicates that removal of dissolved Al in the study area was biologically mediated. The results of drifting anchor sampling indicated that the removal of dissolved Al differed between diatoms and dinoflagellate, with the diatoms having much higher removal efficiency. To understand the mechanism of biological removal of Al, washing with the trace metal clean reagent was used to distinguish between the extracellular and intracellular pool associated with the phytoplankton. This showed that the intracellular pool accounted for most of the phytoplankton associated Al, indicating that biological absorption was the predominant mechanism of biological scavenging of dissolved Al during the SPBs investigated.

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