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# Cd isotopic composition in the suspended and sinking particles of the surface water of the South China Sea: The effects of biotic activities



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### ABSTRACT

We determined the Cd isotopic composition of size-fractionated phytoplankton, zooplankton and sinking particles collected in the top 160 m of a deep water time series station in the South China Sea (SCS) to investigate the fractionation effects of major biotic activities. The isotopic composition ( $\varepsilon^{114/110}$ Cd =  $[(^{114}Cd/^{110}Cd)_{sample}/(^{114}Cd/^{110}Cd)_{NIST 3108} - 1] \times 10^4)$  ranged from -2.5 to +7.0, from -9.3 to +6.7, from -1.2 to +4.5, and from -0.2 to  $+3.2\varepsilon$  in the plankton of size fractions 10–60, 60–150, >150, and >100 µm, respectively. The composition in the two smallest fractions, dominated by phytoplankton, was lower than the ambient seawater value (+8 to  $+9\varepsilon$ ), indicating that the phytoplankton preferentially take up relatively light Cd isotopes. The insignificant difference between the composition of phytoplankton and zooplankton suggests that the fractionation effect through zooplankton grazing may be relatively small. The composition in the sinking particles at 30 m, ranging from +8.1 to +12.8 $\varepsilon$ , was significantly heavier than the composition in the suspended particles and the composition increased with depth, ranging from +11.5 to +20.8 $\varepsilon$  at 100 m, and from +16.0 to +18.0 $\varepsilon$  at 160 m. The increasing isotopic value with depth indicates that the processes of microbial degradation and/or zooplankton repackaging preferentially decomposed relatively light Cd in the sinking particles. The comparable isotopic composition between sinking particles and dissolved Cd indicates that the fractionation effects of major biotic activities. including phytoplankton uptake, microbial degradation and zooplankton repackaging, take place at similar magnitudes and result in insignificant net biological fractionation effects of Cd in the mixed layer.

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# 1. Introduction

Vertically, dissolved Cd is taken up by phytoplankton in the oceanic euphotic zone and is regenerated by heterotrophic organisms in the surface and deep water (Boyle et al., 1976; Bruland, 1980). Horizontally, the low particle reactive property of Cd causes the increase of its concentrations in the deep waters to be associated with deep water age through oceanic thermohaline circulation (de Baar et al., 1994). The concentrations increase by a factor of four from the youngest Northern Atlantic to the oldest Northern Pacific deep waters, ranging from 0.25 to 1.0 nM. Attributed to its complete nutrient-type property and behavior in the ocean, the isotopic composition of Cd in the deep water and environmental recorders, such as Fe–Mn crusts, may have the potential to serve as a proxy to reflect the environmental conditions in oceanic euphotic

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zone (Schmitt et al., 2009). Thus, it is essential to fully understand the major processes regulating Cd isotopic composition in both dissolved and particulate Cd in the ocean.

Several studies have reported the Cd isotopic composition in the water columns of the major open oceans. Ripperger et al. (2007) first revealed that the Cd isotopic composition in oceanic deep waters is relatively consistent among various major oceans, to be around  $+3\varepsilon$ . In addition to the consistent value observed in the deep waters, the Cd isotopic composition in Fe-Mn crusts or nodules collected in global oceans also exhibits relatively consistent Cd isotopic composition, varying from +2 to  $+4\varepsilon$ , over the last 8 million years (Schmitt et al., 2009). It is thus proposed that the isotopic composition in sinking particles are comparable in the deep water of the global oceans and result in similar dissolved isotopic composition in various deep waters (Ripperger et al., 2007; Rehkämper et al., 2012). However, recent studies revealed that water mixing is the dominant process regulating the deep water composition in the water of the Northwestern Pacific Ocean and the Atlantic Ocean (Yang et al., 2014b; Abouchami et al., 2014; Conway and John, 2015).

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Although particles play a vital role in controlling trace-metal distribution and cycling in the ocean, almost all of the Cd isotopic studies in the ocean have focused on its dissolved form. To the best of our knowledge, only a particle related study, mainly focusing on the fractionation effect through sulfide precipitation in the oxygen minimum zone, has been reported (Janssen et al., 2014). Since Cd cycling is driven and transformed by biogenic particles generated in the euphotic zone, biogenic particles in oceanic surface waters. mainly composed of diverse phytoplankton and zooplankton, interact with dissolved and particulate Cd in ambient seawater through biological uptake, microbial degradation and zooplankton repackaging. These processes should play important roles in controlling Cd isotopic distributions in seawater and particles in oceanic surface waters. In terms of vertical cycling, relatively large plankton, such as large diatoms and their hard parts, zooplankton and their fecal pellets and detritus, may serve as major components of sinking particles and thus become the principal agents in transporting both major and trace elements out of the oceanic surface water layer (Sunda, 2012). The isotopic composition of Cd in large marine plankton assemblages and sinking particles may provide fundamental information to establish the controlling processes for Cd isotopic composition in marine water columns.

At the Taiwan time series station in the SCS (SEATS), we have systematically studied the Cd concentration, the major sources and sinks, trace metal cycling mechanisms, and Cd isotopic composition in seawater during the past decade, which provides us with fundamental information to fully investigate the fractionation effects of biotic activities (Wen et al., 2006; Ho et al., 2007, 2009, 2010, 2011a; Yang et al., 2012). Our previous study found that the isotopic composition of the sinking particles in the surface water is almost identical to the composition of dissolved Cd (Yang et al., 2012), suggesting that net biological isotopic fractionation on Cd in the surface water was insignificant. It is also known that atmospheric deposition of anthropogenic aerosols is the major Cd source in the surface water of the SCS, mainly attributed to biomass and fossil fuel burning activities in Southeast and East Asia (Ho et al., 2010, 2011a). Anthropogenic aerosols may thus influence the isotopic composition in the surface water and the biogenic particles (Yang et al., 2012). Building on previous research at the study site, we have further investigated Cd isotopic composition in size-fractionated plankton and sinking particles collected in the euphotic zone of SEATS station to investigate how the biotic processes, including phytoplankton uptake, microbial degradation and zooplankton repackaging, influence Cd isotopic composition in the oceanic surface water.

# 2. Materials and methods

#### 2.1. Sampling

Suspended and sinking particles were collected at the northern SCS deep water time series station known as the South East Asian Time Series (SEATS). The SEATS station is located at 18°N, 116°E with a bottom depth of 3783 m (Fig. 1). The semi-closed SCS is the largest marginal sea in the world. Water exchange between the northern SCS and the Western Philippine Sea primarily occurs through the Luzon Strait (Fig. 1). Detailed information regarding water mass exchange may be found in studies by Qu et al. (2006). Background on the biogeochemical characteristics of the SCS can be found in a study by Wong et al. (2007). Attributed to the large population in the developing countries surrounding the SCS, the input of anthropogenic aerosols in the region is a significant trace metal source in the oceanic region. In the surface water, the aerosol deposition accounts for more than 90% of the total input of many trace metals, such as Zn and Cd (Ho et al., 2010).



Fig. 1. Location of the sampling site, SEATS, in the Northern South China Sea.

Suspended plankton were collected aboard the R/V Ocean Research 1 from October 19 to 20, 2006 (Supplement Section 1). Seawater and size-fractionated plankton were collected using 20 L Teflon-coated Go Flo bottles (General Oceanics) mounted on a Teflon-coated rosette with a modified epoxy coated Seabird CTD and Kevlar wire. The sampling depths of the size-fractionated plankton were mainly collected at chlorophyll maximum depths. A trace metal clean filtration device was used to gently filter 100-200 L of seawater to collect plankton of varying sizes (Ho et al., 2007, 2009). The filtration plankton sampler is made of polycarbonate material and equipped with 150-, 60-, and 10-µm aperture replaceable Nitex nets and three 100 mL polyethylene sampling bottles in sequence, which are acid-washed before each use. The design and the sampling procedures are described in details in the studies of Ho et al. (2007, 2009). Size-fractionated living plankton concentrated from large-volume seawater was collected in the 100 mL polyethylene bottles. The samples were then filtered through an acid-washed filtration apparatus with weighted acidwashed 47 mm polycarbonate filters of 10 µm pore size. They were then quickly rinsed with 18.2  $\Omega$  Milli-O water (Element grade, Millipore, USA) to remove seawater residue.

Zooplankton samples were also collected via plankton tow. The samples were collected in the afternoon of October 21, 2006 at the SEATS station. A net measuring 50 cm in diameter at the opening and a mesh size of 100  $\mu$ m was used, which was towed at  $\sim$ 5 m depth for 10 min as the research vessel traveled at 1 knots. After recovering the net, plankton samples were transferred to a polyethylene bottle and were divided into six sub-samples by filtering the samples with acid-washed 47 mm 10  $\mu$ m pore size polycarbonate filters. They were also rinsed with Milli-Q water to remove seawater residue.

The plankton sub-samples should not simply be considered to be 'replicate' samples because operationally the zooplankton may not be homogeneously distributed on filters in terms of mass and community groups. Although the overall zooplankton mass in the tow bottle was high, many plankton and biotic particles were so sticky that they aggregated together and stayed at the bottom of the bottle. We sub-sampled the plankton simply by shaking the bottles and pouring out roughly similar amounts of seawater by hand into filtration funnels. We filtered and processed 3a, 3b, and 3c sub-samples first because there were only 3 funnels on the filtration apparatus. After sample pretreatment, we then filtered 3d, 3e, and 3f later. The overall Cd mass in the 6 sub-samples ranged

#### Table 1

Cd/Al and Cd/P ratios and Cd isotopic composition in size-fractionated suspended particles collected in the South China Sea.

Sample name	Plankton size (µm)	Depth (m)	[Cd] (pM) <sup>b</sup>	Ratios (mmol mol <sup>-1</sup> )		$\varepsilon^{114/110}$ Cd $\pm 2\sigma^{e}$	$\alpha_{ m phyto-sw}{}^{ m h}$
				Cd/Al <sup>c</sup>	Cd/P <sup>d</sup>		
1a-1	10-60	55	0.64	0.6	0.17	$+3.6\pm1.8$	0.9996
1b-1		55	1.21	0.6	0.15	n.d. <sup>f</sup>	n.a.
2-1		65	0.40	0.4	0.12	$+7.0 \pm 1.9$	0.9999
4-1		58	0.97	1.9	0.25	$-2.5\pm1.4$	0.9990
5–1		58	0.89	0.5	0.17	$+4.9\pm1.9$	0.9997
Ave $\pm 2\sigma_{\text{mean}}^{a}$			$\boldsymbol{0.82 \pm 0.28}$	$\boldsymbol{0.8\pm0.6}$	$\textbf{0.17} \pm \textbf{0.04}$	$+3.3 \pm 4.1$	$0.9995 \pm 0.0004$
1a-2	60-150	55	0.14	3.4	0.16	$+3.7\pm3.3^{g}$	0.9996
1b-2		55	0.14	0.7	0.09	$+6.7 \pm 2.5^{g}$	0.9999
2–2		65	0.18	2.1	0.56	$-9.3\pm0.8$	0.9984
4-2		58	0.37	8.6	0.50	$-6.4\pm0.5$	0.9986
5-2		58	0.18	3.6	0.12	$-2.0\pm1.4$	0.9991
Ave $\pm 2\sigma_{\text{mean}}$			$0.20\pm0.09$	3.7±2.7	$\textbf{0.29} \pm \textbf{0.20}$	$-1.5\pm6.0$	$0.9989 \pm 0.0006$
1a-3	>150	55	0.19	25.4	0.12	$+2.3\pm1.5$	
1b-3		55	0.14	38.9	0.12	$-1.2 \pm 1.4$	
2-3		65	0.11	14.0	0.12	$-0.2\pm1.4$	
4-3		58	0.26	50.5	0.14	$+0.9\pm0.4$	
5–3		58	0.18	19.3	0.09	$+4.5\pm0.6$	
Ave $\pm 2\sigma_{\text{mean}}$			$0.18\pm0.05$	$29.6 \pm 13.4$	$0.11\pm0.02$	$+1.3 \pm 2.0$	
3a	>100 <sup>i</sup>	5	0.09	2.4	0.06	$+2.5\pm1.3$	
3b			0.09	2.5	0.06	$+2.7 \pm 1.7$	
3c			0.07	2.2	0.07	$-0.2\pm1.1$	
3d			0.17	12.2	0.10	$+0.7\pm1.8$	
3e			0.19	6.8	0.11	$+2.4\pm1.8$	
3f			0.22	9.1	0.10	$+3.2 \pm 1.7$	
Ave $\pm 2\sigma_{\text{mean}}$			$0.15\pm0.06$	$5.9\pm3.4$	$\textbf{0.08} \pm \textbf{0.02}$	$+1.9 \pm 1.1$	

<sup>a</sup>  $2\sigma_{\text{mean}} = 2\sigma / (\text{sample number})^{0.5}$ .

<sup>b</sup> Particulate Cd concentrations were obtained using total Cd mass in suspended plankton divided by the total seawater volume filtered.

<sup>c</sup> The Cd/Al ratio, 0.0006 mmol mol<sup>-1</sup>, in lithogenic particles is from the study of Taylor (1964).

<sup>d</sup> The Cd/P ratio, ranging from 0.07 to 0.54 mmol mol<sup>-1</sup>, in phytoplankton is from the study of Ho (2006).

<sup>e</sup> The analytical precision,  $2\sigma$ , were obtained from internal precision of standard and sample measurement. The detailed calculation is shown in Section 3 of Supplementary information. Most of the samples were measured once except the samples 2–2, 4–2, 4–3 and 5–3 which were measured twice or thrice.

<sup>f</sup> n.d.: not determined due to low Cd recovery through column chemistry.

 $^{\rm g}$  The Cd originated from sampling blank accounts for  $\sim$ 8% of the Cd in the samples.

<sup>h</sup> Fractionation factors ( $\alpha_{phyto-sw}$ ) were obtained by using the concentration and isotopic composition of Cd in seawater and suspended plankton by assuming the Cd uptake follows a Rayleigh fractionation. The data of seawater at 60 m, with  $\varepsilon^{114/110}$ Cd to be +8.2 and Cd concentration to be 41 pM, are used for the estimation.

<sup>i</sup> The plankton larger than 100 µm was collected by plankton tow and the sample was divided into six sub-samples, from 3a to 3f.

from 0.07 to 0.22 pM, with the first 3 sub-samples to be much lower than the last 3 sub-samples (Table 1). In addition, the taxonomy and the relative abundance of zooplankton groups on the sub-sampled filters were not homogeneous either. It is common to catch really large but few non-copepod zooplankton (e.g., larval fish), which were unlikely to be homogeneously distributed in the sub-samples either. Significantly different Cd to P elemental ratios in the 6 sub-samples, in which the relative standard deviation  $(2\sigma)$ was up to 54% (data not shown), also indicate the inhomogeneity among the sub-samples. Thus, the isotopic variations  $(2\sigma_{mean})$ among the 6 sub-samples,  $\pm 1.1\varepsilon$ , reflect both the analytical uncertainty and the inhomogeneity of the zooplankton groups and abundance among the sub-samples (Table 1).

Sinking particles were collected with a custom-made floating sediment-trap array, which consisted of eight cylindrical Plexiglass tubes (6.4 cm diameter and 9.53 aspect ratio) with honeycomb baffles covering the trap mouths (Wei et al., 1994). The arrays were deployed at three depths (30 m, 100 m, and 160 m) of the SEATS site for about 2 d during each cruise (Table 2). The trap solutions were prepared in a polypropylene bottle by adding 800 g of Merck GR grade NaCl to 20 L of the seawater taken at the deployment depths. The Cd impurity from Merck GR NaCl would cause the background concentration to increase  $36 \pm 6$  pM in the 75 psu brine water. The natural Cd concentrations were 40, 240, and 240 pM at depths at 30, 100 and 160 m, respectively (Yang et al., 2012), resulting in overall brine water concentrations of 80 pM at 30 m and 280 pM at 100 and 160 m. At first, the Cd/P

ratios in the particles were not associated with the increasing dissolved concentration in the brine solution (Table 2). The ratios not only remained consistent from 30 to 160 m but also within the range of the phytoplankton intracellular Cd quota, indicating that chemical adsorption can be disregarded. Furthermore, because the isotopic composition of natural dissolved Cd in the surface water decreases with depth from +9 to  $+5\varepsilon$  and the relative percentages of the impure Cd in the brine water also decreases with depth, the increasing Cd isotopic composition in the sinking particles cannot originate from impure Cd. Thus, Cd exchange between soluble and particulate Cd in the trap tubes was negligible. Upon recovery, the sinking particles were filtered through 47 mm 0.45 mm pore size polycarbonate filters and rinsed with Milli-Q water to remove seawater residue. After returning to the land based laboratory, the swimmers retained on the filters were manually removed using plastic forceps and the samples were freeze-dried for further chemical processing and analysis.

#### 2.2. Sample digestion and elemental composition analysis

After freeze-drying and weighing, the filters with plankton were digested in 1 mL 8 N super pure nitric acid (Seastar) in 20 mL Teflon vials on a hot plate at 120 °C for 24 h (Ho et al., 2009). The digested solution was then diluted to 10 mL with Milli-Q water. The solution was centrifuged to remove any remaining particulate residues. The sinking particle samples and their blank filters were soaked in a mixture of 1.8 mL super pure nitric acid and 0.2 mL of super pure hydrofluoric acid (Seastar) in 10 mL clean

Elemental fluxes and ratios and Cd isotopic composition in sinking particle samples collected in the South China Sea.

Sampling time	Sample name	Depth (m)	Fluxes $(\mu mol m^{-2} d^{-1})^a$		Ratios (mmol mol <sup>-1</sup> ) <sup>a</sup>		$\varepsilon^{114/110}$ Cd $\pm 2\sigma^{b}$	
			С	Р	Cd*10 <sup>3</sup>	Cd/Al	Cd/P	
19:00 10/20-7:00 10/22, 2006	FT01	30	39000	425	30	0.28	0.07	$+8.5\pm0.9^{\circ}$
	FT02	100	17400	192	21	0.23	0.11	$+11.5\pm1.0$
18:10 1/15-13:10 1/17, 2007	FT03	30	59100	712	109	0.95	0.15	$+8.4\pm0.9$
	FT04	100	12800	191	21	0.25	0.11	$+13.3 \pm 1.2$
	FT05	160	7600	55	4	0.04	0.07	$+18.0\pm1.4$
18:50 7/30-18:50 8/01, 2007	FT06	30	8600	64	7	0.13	0.11	$+12.8\pm1.2$
	FT07	100	9800	96	8	0.06	0.08	$+15.3 \pm 1.1$
	FT08	160	3200	47	3	0.05	0.07	$+16.0\pm1.4$
11:30 10/23-7:30 10/25, 2007	FT09	30	40 000	290	60	0.63	0.21	$+8.1\pm1.2$
	FT10	100	13 600	94	10	0.12	0.11	$+20.8\pm1.1$
	FT11	160	8800	61	8	0.07	0.13	$+17.4\pm1.1$

<sup>a</sup> Data are from Ho et al. (2010).

<sup>b</sup> Each sample was measured once. The calculation of the analytical precision was shown in Supplement Section 3.

<sup>c</sup> The data were published in Yang et al. (2012).

Teflon vials and were subsequently digested in a microwave oven (MARS, CEM) at  $180 \,^{\circ}$ C for 15 min. After complete digestion, the samples were evaporated to dryness on hot plates at  $80 \,^{\circ}$ C under a trace metal clean hood and were re-dissolved with super pure nitric acid (Ho et al., 2010). Following, the sample solution was diluted with Milli-Q water to obtain samples in 3% nitric acid solution, which was then ready for analysis via inductively coupled plasma mass spectrometer (ICP-MS).

The concentrations of trace metals, including Cd, P, Al, Fe, Zn, Ni, Mn, Cu and Co, in the samples were obtained by sector field double-focusing high-resolution ICP-MS (Element XR, Thermo Scientific) fitted with a desolvation system (APEX and Spiro, Elemental Scientific). The sensitivity and stability of the instrument was tuned to optimal conditions before analysis. The analysis was conducted with sensitivity around  $10^6$  counts s<sup>-1</sup> for 1 ng g<sup>-1</sup> In and analytical precision was between 1 to 2%. Precision was 5–10% for the samples collected in July 2007, in which the Cd content was relatively low and the final concentrations of the analytical solution ranged from 0.040 to 0.080 ng g<sup>-1</sup>. External and internal standards were both applied for concentration quantification. The details of the analytical precision, accuracy, and detection limits of the ICP-MS method were described in Ho et al. (2003, 2007).

# 2.3. Cd purification

A portion of digested samples with 2 to 10 ng Cd were taken and added with a suitable mass of Cd double spike (<sup>110</sup>Cd-<sup>111</sup>Cd) to achieve a sample to spike ratio of 1:4. The samples were then purified by applying extraction chromatography in 100 µL shrink-fit polytetrafluoroethylene columns (Ripperger and Rehkämper, 2007; Yang et al., 2012). A three-stage column chemistry that was adapted from the study of Ripperger and Rehkämper (2007) was used. Anion resin AG1X8 (Biorad) was used in the first and the second stages to preconcentrate Cd in the samples and remove major elements, e.g., Na, Mg, and Ca. Another anion resin, TRU (Eichrom), was used in the third stage to further remove Mo and Sn to avoid isobaric interference with Cd. The purified Cd samples were evaporated to dryness, and 0.2 mL, 16 N of super pure nitric acid was added. The samples were evaporated to dryness again and were re-dissolved with 0.5 N of super pure nitric acid to achieve a final sample concentration of approximate 5  $ngg^{-1}$  Cd. The recovery of Cd was overall greater than 90%.

The sampling blank was obtained from blank filters treated with the same procedures as the samples. The blank mass ranged from 110 to 160 pg (139 pg on average, n = 3) for plankton sampling procedures and ranged from 150 to 440 pg (264 pg on average, n = 3) for sinking particle sampling procedures. Compared

to the total Cd content in plankton and sinking particle samples, which ranged from 2 to 232 and from 3 to 43 ng, the sampling blank accounted for 8 to 0.1% and 8 to 0.6%, respectively. Thus, the Cd contamination from the sampling procedures was at least one order of magnitude less than Cd content in the samples and its effects may be disregarded. The column chemistry blank was down to  $1.1 \pm 0.2$  pg  $(1\sigma, n = 4)$  and its effects are also negligible.

#### 2.4. Mass spectrometry analysis

The method for Cd isotopic analysis by mass spectrometry has been reported in detail previously (Yang et al., 2012). Briefly, all of the Cd isotopic measurements were performed using a multicollector ICP-MS (Nu Instruments) with a desolvator nebulizer for the sample introduction system (CETAC Aridus I). Four Cd isotopes, <sup>110</sup>Cd, <sup>111</sup>Cd, <sup>112</sup>Cd, and <sup>114</sup>Cd, were simultaneously measured in each analysis. Potential isobaric interferences from <sup>112</sup>Sn and <sup>114</sup>Sn were corrected within-run by simultaneously monitoring <sup>118</sup>Sn. All of the Cd isotopic compositions in this study are reported as  $\varepsilon$ -notation, which is given by the following equation:

$$\varepsilon^{114}$$
Cd = [(<sup>114</sup>Cd/<sup>110</sup>Cd)<sub>sample</sub>/(<sup>114</sup>Cd/<sup>110</sup>Cd)<sub>standard</sub> - 1] × 10<sup>4</sup>

We have used NIST SRM 3108 as the reference standard. The within-day external reproducibility and internal precision for particle measurement ranged from  $\pm 0.7$  to  $\pm 0.8\varepsilon$  ( $2\sigma$ , n = 5-6) and from  $\pm 0.9$  to  $\pm 1.3\varepsilon$  ( $2\sigma$ , 60 runs per measurement), respectively. The precision were obtained by repeatedly analyzing the Cd standard JMC Cd Münster (ICP standard, lot 502552A). The analytical precision for reported isotopic composition of each sample was obtained from the internal precision of both sample and standard measurements (Supplement Section 3; Conway et al., 2013). The accuracy of the analysis was verified by routinely determining the isotopic composition of the two international Cd standards NIST SRM 3108 and JMC Cd Münster on the same day. We have obtained the isotopic composition of  $-0.8 \pm 1.1\varepsilon$  ( $2\sigma$ , n = 23) for JMC Cd Münster, which is consistent with the validated value of  $-0.81 \pm 0.42\varepsilon$  reported by Abouchami et al. (2012).

#### 3. Results

#### 3.1. Suspended particles

The size-fractionated plankton collected consisted of both large phytoplankton and zooplankton. We observed that the microalgae in most of the size fractions of  $10-60 \mu m$  were dominated by large unicellular diatoms and filamentous phytoplankton, most likely



**Fig. 2.** Comparison of Cd isotopic composition (a), Cd/P ratios (b), and Cd/Al ratios (c) among different size-fractionated plankton collected in the SCS. Comparison between Cd isotope composition and Cd/P ratios (d). The gray bar in plot a stands for the range of the dissolved Cd isotopic composition in the mixed layer (Yang et al., 2012). The gray circle dots shown in plots a, b, and c stand for data obtained from individual plankton assemblage samples. The open circles stand for the averaged value for all samples in different size fractions and the error bars of the symbols stand for  $2\sigma_{mean} = 2\sigma/n^{0.5}$ , *n*: sample number). Plot d exhibits the data for the two plankton sizes, 10–60 and 60–150 µm.

Skeletonema costatum. For sizes ranging from 60 to 150 µm, the plankton were still mainly composed of relatively large filamentous diatoms and unidentified debris. Some zooplankton, including foraminifera, copepods, and biogenic debris were also observed in the size range, but only a minor percentage. In the fraction larger than 100 and 150 µm, copepods were the dominant organisms (Supplement Section 2). It should also be noted that diel vertical migration may cause significant variations of phytoplankton and zooplankton groups and abundance in oceanic euphotic zone. The size-fractionated samples shown in Table 1 were collected from 7 am to 10 pm within two days. Many of the samples collected at different time and depths were highly likely composed of different zooplankton and phytoplankton groups and abundances.

The mass information of the three size-fractionated particles are shown in Table 1, ranging from 0.09 to 1.2 pM. The masses are about 2 orders of magnitude lower than the dissolved pool. It should be noted that the biomass of the size fraction larger than 10  $\mu$ m accounts for a minor mass fraction among suspended particles. The results of our previous studies (Ho et al., 2009; Yang et al., 2012) show that the averaged masses of dissolved and particulate Cd greater than 0.4  $\mu$ m in the top 100 m were approximately 70 and 7 pM, respectively. This indicates that total particulate mass only accounted for about 10% of the total dissolved and particulate Cd. The dissolved Cd represents the majority of total Cd budget in the top 100 m.

The Cd isotopic composition and Cd/P and Cd/Al ratios in the suspended plankton are listed in Table 1 and shown in Fig. 2. The isotopic composition ranges from  $-2.5 \pm 1.4$  to  $+7.0 \pm 1.9$ , from  $-9.3 \pm 0.8$  to  $+6.7 \pm 2.5$ , from  $-1.2 \pm 1.4$  to  $+4.5 \pm 0.6$ , and from  $-0.2 \pm 1.1$  to  $+3.2 \pm 1.7\varepsilon$  in the plankton with sizes 10–60, 60–150, >150, and >100  $\mu$ m, respectively (Fig. 2a). The differences between the isotopic composition among the different fractions are statistically insignificant. The Cd/P ratios in suspended plankton range from 0.06 to 0.56  $\text{mmol}\,\text{mol}^{-1}$  (Fig. 2b), which are comparable to the intracellular Cd quota reported previously in both laboratory and field studies, ranging from 0.07 to 0.54 mmol mol<sup>-1</sup> P (Ho, 2006). In addition, the Cd/Al ratios in suspended plankton vary by two orders of magnitude, ranging from 0.4 to 50.5 mmol mol<sup>-1</sup> (Fig. 2c). All of the ratios are distinctly higher than the Cd/Al ratio of lithogenic particles, which is at  $0.0006 \text{ mmol mol}^{-1}$  (Taylor, 1964), indicating that most Cd in the plankton did not originate from lithogenic sources.



**Fig. 3.** Vertical variations of Cd isotopic composition (a) and Cd fluxes (b) in the sinking particles collected in different seasons at SEATS station. The gray area in plot a and the gray line in plot b stand for the isotopic composition and concentrations in the seawater at SEATS, respectively (Yang et al., 2012).

#### 3.2. Sinking particles

The Cd fluxes and isotopic composition data obtained from sinking particles are presented in Table 2 and Fig. 3. Overall, the Cd isotopic composition varied by about  $13\varepsilon$ , ranging from +8.1 to  $+20.8\varepsilon$ . In terms of vertical variation. Cd isotopic composition generally exhibits comparable patterns with the data obtained from Oct. 2006 and Jan. and Oct. 2007. The isotopic composition of Cd increased from +8.1 to +8.5 $\varepsilon$  at 30 m, from +11.5 to +13.3 $\varepsilon$  at 100 m, and from +17.4 to  $+18.0\varepsilon$  at 160 m, except for an elevated value of  $+20.8\varepsilon$  at 100 m observed in Oct. 2007 (Fig. 3a). Relative to Cd isotopic variation, Cd fluxes decreased with depths exponentially, from values ranging from 30 to 109 nmol  $m^{-2} d^{-1}$  at 30 m to 10 to 21 nmol  $m^{-2} d^{-1}$  at 100 m, and to 4 to 8 nmol  $m^{-2} d^{-1}$ at 160 m (Fig. 3b). The vertical variations of Cd isotopic composition and fluxes in July 2007 were relatively small. The isotopic composition slightly increased by  $3\varepsilon$ , from  $+12.8\varepsilon$  at 30 m to  $+16.0\varepsilon$  at 160 m, and the fluxes decreased by a factor of 2 from 7-8 nmol m<sup>-2</sup> d<sup>-1</sup> at the top 100 m down to 3 nmol m<sup>-2</sup> d<sup>-1</sup> at 160 m (Fig. 3a and 3b). In terms of temporal variation at 30 m, the isotopic composition was relatively light, with values between +8and  $+9\varepsilon$  in Oct. 2006 and Jan. and Oct. 2007. The isotopic composition in July 2007 was elevated to around  $+13\varepsilon$  at 30 m (Fig. 3a).

# 4. Discussions

#### 4.1. Phytoplankton uptake and zooplankton grazing

Based on a laboratory culture experiment using a freshwater green algae species, Lacan et al. (2006) first proposed that phytoplankton may take up relatively light dissolved Cd in the euphotic zone of the ocean. Another recent study also argued that marine phytoplankton would take up relatively light Cd isotopes by carrying out laboratory culture experiment using marine flagellate chlorophyte (John and Conway, 2014). However, no field study has been carried out yet. At the study site of the SCS, we have directly measured Cd isotopic composition in both seawater and phytoplankton collected simultaneously in the same oceanic region to examine the argument. We collected seawater samples at SEATS during the same time as this study and the Cd isotopic composition in the seawater ranged from +8.2 to  $+9.1\varepsilon$  in the top 60 m (Yang et al., 2012). This study observed that the isotopic compositions in the two phytoplankton assemblage fractions were  $+3.3\pm4.1$  and  $-1.5\pm6.0arepsilon$  ( $2\sigma_{
m mean}$ ), which were significantly lighter than seawater. These results demonstrate that phytoplankton do take up relatively light Cd isotopes through ambient seawater in the SCS (Fig. 2a). The isotopic fractionation factors ( $\alpha_{phyto-sw}$ ) through phytoplankton uptake can be obtained from the isotopic difference between phytoplankton and surface seawater (Table 1). The  $\alpha_{\text{phyto-sw}}$  values are 0.9995±4 and 0.9989±6 ( $2\sigma_{\text{mean}}$ ) for the

10–60 and 60–150  $\mu$ m phytoplankton, respectively, which are comparable with the values observed by the culture study, 0.9991  $\pm$  0 (John and Conway, 2014).

Among all of the SCS data, we have observed two extremely light  $\varepsilon^{11\breve{4}/110}$ Cd in the samples of the 60–150 µm fraction, with values of -9.3 and  $-6.4\varepsilon$ . The two samples also possess elevated Cd/P concentration ratios, 0.56 and 0.50 mmol mol<sup>-1</sup> (Table 1 and Fig. 2), suggesting that the two samples may have other extra Cd sources, such as contamination. However, the metal to P ratios from all other trace metals in the two samples, which exhibit comparable values to other samples (Supplement Section 1), do not suggest the potential for contamination. The other possible cause for the elevated ratios and light isotopic composition may be associated with plankton community structure. The sampling time for the two samples with lowest isotopic composition was at 12 pm and 9 pm at the chlorophyll a maximum depth (Supplement Section 1). Due to vertical migration behavior of plankton, different diel sampling time at the chlorophyll a maximum depth might result in the shift of the dominant plankton groups. We also found a negative correlation between  $\varepsilon^{114/110}$ Cd values and Cd/P ratios in the 10–60 and 60–150 µm fraction samples (Fig. 2d), suggesting that the more Cd is assimilated by plankton the lighter the isotopic composition in the plankton, Abouchami et al. (2011) observed different phytoplankton groups at the different sampling sites in the Southern Ocean, and they proposed that the variations of the Cd fractionation effects may have resulted in the uptake of different groups. The series of studies by Sunda and Huntsman (e.g., Sunda and Huntsman, 1998, 2000) demonstrates that diatoms and coccolithophores possess different transporter systems for Cd uptake under various growth conditions. We have already carried out a systematic study for some marine diatoms and coccolithophores and observed different fractionation patterns among different phytoplankton groups (Ho et al., 2011b).

Comparing with the isotopic composition in the surface water, the plankton with size fractions larger than 100 and 150 µm also possessed relatively light isotopic composition, averaging  $+1.9 \pm$ 1.1 and  $+1.3\pm2.0\varepsilon$  ( $2\sigma_{mean}$ ; Fig. 2a), respectively. The two largest fractions were mainly composed of copepods (Supplement Section 2), which primarily assimilate Cd by grazing on phytoplankton (Xu et al., 2001; Wang and Fisher, 1998). Generally, microzooplankton with sizes smaller than 200 µm graze on phytoplankton with sizes ranging from 5 to 20 µm and mesozooplankton larger than 200 µm graze on phytoplankton with sizes ranging from 20 to 200 µm (Wilson, 1973; Riegman et al., 1993; Berggreen et al., 1988). The two size fractions of phytoplankton ingested by microzooplankton or mesozooplankton or copepods were comparable to the 10-60 and 60-150 µm fractions collected. Based on microscopic examination, the 60-150 µm fraction in the water was mainly composed of filamentous phytoplankton, although the possibility a minor contribution by microzooplankton in the samples should not be excluded. We found that there is no statistical Cd isotopic difference between the zooplankton fractions and the two phytoplankton fractions (Fig. 2a), suggesting that the Cd isotopic fractionation through the trophic transfer from the phytoplankton to copepods is insignificant.

#### 4.2. A heterotrophic control on the composition in sinking particles

Several lines of evidence show that Cd in the sinking particles collected in the surface water were biogenic and intracellular. Our previous study observed consistent Cd/P and C/P ratios in sinking particles collected in three different depths of the top 160 m. We found that the ratios were all comparable to intracellular quotas in plankton (Ho et al., 2010), indicating that the majority of particulate Cd were still biogenic Cd. Indeed, except Cd, the study found that many trace metals were adsorbed extracellularly on

plankton. For example, the Zn/P and Fe/P ratios in the sinking particles collected in the mixed layer ranged from 10 to 35 and from 50 to 550 mmol mol $^{-1}$ , respectively. This is at least one order of magnitude greater than the known intracellular Zn and Fe quota in phytoplankton, ranging from 0.8 to 3.0 and from 3.6 to 7.4 mmol mol<sup>-1</sup>, respectively (Ho et al., 2010). The elevated Zn/P and Fe/P ratios indicate that the majority of Zn and Fe in the particles were abiotic and extracellularly adsorbed. In contrast, the Cd/P ratios, ranging from 0.07 to 0.21 mmol mol $^{-1}$ , were comparable to known intracellular Cd quota in phytoplankton, which are 0.07 to 0.54 mmol mol<sup>-1</sup>. Similarly, for the particles collected at 100 and 160 m, the Zn/P and Fe/P ratios increased with depth due to the decomposition of organic matter with depth. However, with the significant decrease of organic matter fluxes with depth, the Cd/P ratios at 100 and 160 m still remain within its known intracellular quota range (Fig. 4 in Ho et al., 2010), indicating that the Cd in the particles were biogenic and intracellular.

Ho et al. (2010) shows that the decreasing patterns of the Cd fluxes with depth exhibit strong linear correlation with the fluxes of organic carbon and phosphorus, with correlation coefficients to be 0.89 and 0.87, respectively. Fig. 3a exhibits that Cd fluxes significantly decreased with depth. The decreasing fluxes from 30 to 160 m accounted for 32, 96, 54 and 87% for Oct. 2006 and Jan., July, and Oct. 2007 of the fluxes observed at 30 m. The strong flux correlation demonstrates that the decreasing Cd in sinking particles with depth was decomposed by heterotrophic processes, mainly microbial degradation or zooplankton repackaging. Overall, Cd isotopic composition in the sinking particles increased with depth for all four cruises, with isotopic fractionation ranging from +3to  $+13\varepsilon$  (Fig. 3a). The increasing isotopic value in sinking particles with depth indicates that the processes of microbial degradation or zooplankton repackaging result in the release of relatively light Cd isotopes from sinking particles to dissolved Cd into seawater. Although sinking particles may be disaggregated to suspended particles again, in terms of mass balance, the suspended particles formed from the disaggregation process would eventually be degraded to soluble Cd. It is known that Cd mainly bonds with thiol functional groups in phytochelatin and metallothionein in biogenic organics (Ahner and Morel, 1995; Ahner et al., 2002; Amiard et al., 2006). Theoretically, the Cd isotopic fractionation mechanism in the compounds is associated with the vibration frequencies of Cd-S bond in the thiol functional groups and the rate constants of microbial enzymatic dissociation reaction of the Cd-S bond (Paneth, 2003). Further experiments are needed to obtain the essential parameters to explain the fractionation effect.

Similar to the isotopic fractionation effects of heterotrophic reactions on essential major elements observed previously (Lehmann et al., 2002; Sigman et al., 2009), the effects of microbial degradation and zooplankton repackaging on Cd isotopic fractionation in the sinking particles should be unidirectional. Thus, the isotopic fractionation pattern of the sinking particles with depth should follow Rayleigh fractionation. Since the organic carbon fluxes exponentially decreased from 30 m to 160 m (Ho et al., 2010), we assume that the sinking particles collected at 30 m can be the original sources of the sinking particles collected at 100 and 160 m. The range of the fractionation factors may be estimated by the following equation with the measured value in the sinking particles.

$$\varepsilon^{114/110}$$
Cd<sub>sp</sub> =  $\varepsilon^{114/110}$ Cd<sub>30 m</sub> - ( $\alpha_{sp-sw}$  - 1) × 10<sup>4</sup> × ln F<sub>p</sub>

 $\varepsilon^{114/110} \rm Cd_{sp}$  denotes Cd isotopic values in sinking particles at depths of 100 or 160 m and  $\varepsilon^{114/110} \rm Cd_{30\,m}$  denotes the values at 30 m.  $\alpha_{\rm sp-sw}$  represents the isotopic fractionation factor between sinking particles and seawater.  $F_p$  denotes the remaining fraction of the Cd at 100 or 160 m to the Cd at 30 m, calculated by the corresponding fluxes.



**Fig. 4.** Comparison of Cd isotopic composition with remained Cd flux fractions in sinking particles. The remained fractions,  $F_p$ , are calculated by the ratios of Cd fluxes at 100 or 160 m to the fluxes at 30 m. The data of sinking particles collected in winter and summer are also shown in plot a and plot b, respectively. The fitting curves in the figures are obtained by using Rayleigh fractionation model with fractionation factors ( $\alpha_{sp-sw}$ ) ranging from 1.0003 to 1.0007. The black curves stand for isotopic composition in sinking particles, and the gray curves stand for isotopic topic topic composition of overall Cd remineralized from sinking particles.



Fig. 5. Comparison of Cd isotopic composition in seawater (SW), suspended particles (Susp.) and sinking particles (Sink.) collected in the top 80 m.

Fig. 4 shows that the fractionation factors between sinking particles and seawater ( $\alpha_{sp-sw}$ ) range from 1.0003 to 1.0007. In comparison with the fractionation factors of phytoplankton uptake obtained from this study or the other laboratory culture study (John and Conway, 2014), the fractionation factors of microbial degradation or zooplankton repackaging are similar in magnitude to phytoplankton uptake. These results suggest that microbial degradation or zooplankton repackaging can be equally as important as phytoplankton uptake in regulating Cd isotopic composition in the surface water.

Our previous argument that net biological isotopic fractionation of Cd in the surface water is insignificant is also supported by this observation. The Cd isotopic composition of the dissolved Cd and biogenic sinking particles were both found to be around +8 to  $+9\varepsilon$  (Yang et al., 2012). By applying the box model and assuming light isotopic composition in the aerosols, Murphy et al. (2014) commented in response to our previous study, proposing that the Cd composition in the sinking particles should be 3 to  $5\varepsilon$  lighter than the dissolved Cd. In our reply (Yang et al., 2014a), we have already shown that their assumption for the aerosol composition is incorrect. They also indicated that the composition in the sinking particles shown in the paper of Yang et al. (2012) may not be representative in the surface water because there was only one sampling data point shown in our previous paper. As what we have shown in this study, the isotopic value in the mixed layer were all comparable, ranging from +8 to  $+9\varepsilon$  in the samples collected during the three cruises observed in winter monsoon season. Moreover, our study shows that microbial degradation and zooplankton repackaging significantly influences the Cd isotopic composition in the sinking particles collected in the northern SCS, which was not taken into consideration by Murphy et al. (2014).

#### 4.3. From suspended to sinking particles

The transformation from suspended particles to sinking particles is regulated by many complicated processes, including primary production, particle sizes, direct physical coagulation, the presence of transparent exopolymer particles, mineral ballast effect, zooplankton grazing and repackaging, microbial degradation, and so on (Boyd and Trull, 2007). The relative importance of each individual process to the transformation is highly location specific (e.g., Boyd and Trull, 2007). The intensive studies carried out previously at SEATS provide us useful information to understand the seasonal patterns of primary production, POM fluxes, and phytoplankton community structure in the oceanic region. Large biogenic suspended particles, including sizable phytoplankton, zooplankton and their detritus, may be an important precursor to sinking particles in the marine water column. Due to the elevated nutrient supply in the euphotic zone because of water mixing, both primary production and POC fluxes are elevated in winter time (Chen, 2005; Ho et al., 2009, 2010). It is known that the percentage of relatively large phytoplankton significantly increase with elevated nutrient supply in the open oceans (e.g., Bidigare and Ondrusek, 1996). Chen (2005) also observed that the percentage of relatively large phytoplankton ( $>3 \mu m$ ) was elevated in winter. A related pigment study observed that the percentage of fucoxanthin, the marker pigment of diatoms, was distinctly elevated in winter time in the SCS (Ho et al., 2015). Further study using the model approach suggests that the elevated downward flux in winter is mainly attributed to the increase of large phytoplankton with sizes larger than 10 µm in the SCS (Liu and Chai, 2009). If large plankton particles are the major source of sinking particles in the water, the Cd isotopic composition in large plankton samples should be associated with the value in the sinking particles. In this study, we found that the Cd isotopic composition in all of the plankton samples collected was distinctly lighter than the sinking particles collected in the same zone (Fig. 5). The elevated isotopic value in sinking particles indicates that heterotrophic transformation processes from relatively large suspended biogenic particles to sinking particles result in the decomposition of relatively light Cd isotopes.

The major transformation processes from suspended particles to sinking particles in the oceanic surface water should thus be associated with microbial degradation and zooplankton repackaging, Altabet (1988) found that the isotopic composition of nitrogen in suspended particles was 3 to 5% lighter than sinking particles in the euphotic zone of the Sargasso Sea, which may be related to the processes of microbial degradation and zooplankton repacking. Heterotrophic bacteria prefer to degrade relatively light N in biogenic particles to form ammonium and yield residual organic matter possessing relatively heavy N isotopes (Lehmann et al., 2002). Since Cd mainly exists in cysteine related compounds intracellularly, including phytochelatin and metallothionein (Ahner and Morel, 1995; Ahner et al., 2002; Amiard et al., 2006), Cd in biogenic particles might undergo similar isotopic fractionation effects as nitrogen in suspended particles. In addition to microbial decomposition, zooplankton repackaging is another possible important process that alters the isotopic composition of biologically essential elements from suspended to sinking particles (Altabet, 1988). In the case of nitrogen, zooplankton ingestion would excrete ammonium with lower  $\delta^{15}N$  than the organic nitrogen taken up, which results in the relatively heavy isotopic composition in fecal pellets (Checkley and Entzeroth, 1985; Altabet, 1988; Sigman et al., 2009). Since fecal pellets are a major component of sinking particles, the repackaging process would cause the essential elements to become relatively heavy in sinking particles. Cd might go through a similar isotopic fractionation effect in the repackaging process, resulting in the isotopic composition in sinking particles to be higher than in suspended plankton.



Fig. 6. A schematic model for Cd isotopic fractionation in the surface water of the SCS through the major biotic processes, phytoplankton uptake, microbial degradation, and zooplankton repackaging. The terms DCd, PCd<sub>phyto</sub>, PCd<sub>zoo</sub>, and PCd<sub>sink</sub> denote the four major Cd pools in the seawater, including dissolved form, phytoplankton, zooplankton, and sinking particles, respectively. The Cd isotopic composition in the aerosols collected above the SCS should vary from +8 to  $+9\varepsilon$ . The aerosols are known to be the dominant source of dissolved Cd in the surface water (DCd). In the euphotic zone, dissolved Cd is transformed to particulate Cd (PCd<sub>phyto</sub>) through phytoplankton uptake. Since phytoplankton prefers to take up relatively light Cd isotopes, the isotopic composition in PCd<sub>phyto</sub> is lighter than DCd ( $\alpha$  < 1). Zooplankton graze phytoplankton and transfer the relatively light Cd into zooplankton biomass (PCd<sub>zoo</sub>) without significant isotopic fractionation ( $\alpha \approx 1$ ). When suspended particles, mainly composed of phytoplankton and zooplankton, are transformed to sinking particles, the processes of microbial degradation or zooplankton repackaging would decompose relatively light Cd isotopes in the organic material and results in elevated isotopic composition in sinking particles ( $\alpha > 1$ ). We propose that the fractionation effects by phytoplankton uptake (green arrow), microbial degradation and zooplankton repackaging (blue arrow) would counteract with each other in the mixed layer and result in insignificant net biological fractionation effects of Cd in the layer. When particles sink with depth, the processes of heterotrophic processes continuously decompose relatively light Cd isotopes in sinking particles and the isotopic composition in  $\text{PCd}_{\text{sink}}$  would be elevated with depth. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

#### 4.4. The implication of biotic fractionation effects on Cd cycling

Integrating all of the biotic fractionation effects observed in this study, we have constructed a schematic model to illustrate the isotopic fractionation processes for Cd internal cycling in the oceanic surface water (Fig. 6). First, relatively light Cd isotopes are taken up by phytoplankton through ambient seawater. Then, the relatively light Cd isotopes in phytoplankton are transferred to zooplankton through grazing without significant Cd isotopic fractionation. The suspended particles, mainly composed of sizeable phytoplankton and zooplankton, are transformed into sinking particles. The processes of microbial degradation or zooplankton repackaging may preferentially release relatively light Cd isotopes and results in heavier isotopic composition in sinking particles than suspended particles. The fractionation effects between phytoplankton uptake and heterotrophic activities may largely cancel each other out and result in a relatively small net Cd isotopic fractionation effect in the mixed layer of the northern SCS. It should be noted that the net effect mainly refers to the whole mixed layer, not a specific depth. It is highly likely that the fractionation effects of the two biotic processes would have different degrees of fractionation effects at different depths in the mixed layer, with relatively high phytoplankton uptake rates in the upper layer of the surface water and relatively high microbial degradation in the lower layer of the surface water.

Our study indicates that both phytoplankton uptake and biological degradation are important processes in controlling Cd isotopic fractionation in the surface water. The fractionation effects of these two processes roughly counteract each other in the mixed layer of the SCS, which ranges from the top 30 to top 80 m from summer

to winter. Thus, the isotopic composition of the sinking particles in the mixed layer would reflect the isotopic composition of the major Cd source in the surface water, the deposition of anthropogenic aerosols. Based on the box model results shown in Fig. 5a of our previous study (Yang et al., 2012), dissolved Cd in the zone below 100 m predominately originates from the vertical advection of the deeper water but not the vertical input of sinking particles. We thus argue that the decrease of the isotopic composition from the bottom of the mixed layer to 160 m is mainly controlled by physical mixing but not the remineralization of sinking particles. Thus, even though the sinking particles possess relatively heavy Cd, their contribution may be insignificant to the dissolved Cd in the layer. Although the two biological processes may be dominant in the mixed layer, the influence of their fractionation effect is insignificant below the mixed layer due to the dominant role of physical mixing with depth.

In the open ocean, the major Cd source of the surface water is believed to originate from the subsurface water. Per what we have shown in our recent paper (Yang et al., 2014b), the depth of 200 m is the end member point of the other water mass in the Western Philippine Sea (WPS), suggesting that the major Cd source in the subsurface water may be from horizontal advection. We have observed elevated Cd isotopic composition at 200 m in the WPS,  $+8\varepsilon$ , which is heavier than the value observed right above 200 m. Similar phenomenon has been observed in several sampling stations shown in the dataset of Conway and John (2015), such as the depths around 200 m at station 1 of USGT-10 section and station 2 of USGT-11 section. In brief, the isotopic composition of the subsurface water layer can vary and be highly dynamic. In addition to the effect of traditional vertical upwelling or advection, the effects of horizontal mixing and biotic processes should be considered in future studies. We think that phytoplankton uptake plays a dominant role in elevating dissolved Cd isotopic value in the very surface water of the open ocean. With the decreasing effects of phytoplankton uptake and heterotrophic processes with depth, either vertical or horizontal mixing processes may become dominant. Further efforts are needed to answer the following questions: whether or not the biological fractionation effects observed in the SCS occur in other oceanic regions, whether or not heterotrophic processes also cause a comparable and reverse fractionation effect on phytoplankton uptake in the surface water of the open oceans, and whether or not the major Cd source of the subsurface water of the open ocean originates from horizontal advection or vertical mixing.

# 5. Conclusions

We determined the isotopic composition of Cd in the sizefractionated plankton and sinking particles collected in the surface water of the SCS to investigate the fractionation effects of major biotic activities. We found that there is no statistical Cd isotopic difference between the zooplankton fractions and the two phytoplankton fractions, indicating that the Cd isotopic fractionation through the trophic transfer from the phytoplankton to copepods may be insignificant. Our study also shows that the fractionation effects of these processes, phytoplankton uptake, microbial degradation and zooplankton repackaging, are all significant and occur at similar magnitudes. Phytoplankton assimilate relatively light Cd isotopes, and, in contrast, the processes of microbial decomposition and zooplankton repackaging release relatively light isotopes. The two counteracted biotic processes possess opposing Cd isotopic fractionation effects with similar magnitudes and thus result in insignificant net biological fractionation effects of Cd in the mixed layer. The importance of physical mixing process in regulating dissolved Cd isotopic composition in oceanic surface water deserves further studies to investigate whether the major Cd source in subsurface water layer mostly originates from horizontal advection or vertical mixing. Future studies with high vertical sampling resolution for dissolved and particulate Cd isotopic composition coupled with water mass identification in the surface water may shed light on their relative importance.

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#### Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2015.07.025.

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