

Response

Reply to the “Comment by [Murphy et al. \(2014\)](#) on ‘the isotopic composition of Cadmium in the water column of the South China Sea’”

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Abstract

Our previous study has shown that the Cd isotopic composition in the surface water and the sinking particles in the South China Sea (SCS) are identical at  $\epsilon^{114/110}\text{Cd} \sim +9$ . Therefore, net biological isotopic fractionation of Cd in the surface water was insignificant (Yang et al., 2012). Using a box-model calculation, Murphy et al. (2014) suggested that the particles should have relatively light  $\epsilon\text{Cd}$ , +3 to +5, if the aerosol inputs were characterized with  $\epsilon\text{Cd}$  from  $-4$  to  $+4$ . Consequently, the observed  $+9$   $\epsilon\text{Cd}$  is not representative to the overall SCS phytoplankton exports, and the heavy  $\epsilon\text{Cd}$  observed in the surface water of the SCS must be the results of preferential uptake of light Cd by phytoplankton. Here we argue that their assumption about the aerosol  $\epsilon\text{Cd}$  is most likely incorrect as in the case of SCS. In addition, it is questionable for the heavy  $\epsilon\text{Cd}$  in the surface water reflecting solely by the preferential uptake of phytoplankton. Besides phytoplankton uptake,  $\epsilon\text{Cd}$  in the surface water may also be influenced by microbial degradation and zooplankton grazing. Consequently, an integrated study focusing on the fractionation effects of the processes is necessary to fully understand the major controlling mechanisms on Cd isotopic fractionations in the oceans.

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1. INTRODUCTION

Studies have shown that while  $\epsilon\text{Cd}$  are fairly consistent in the deep oceans,  $\epsilon\text{Cd}$  are relatively heavy in most surface seawaters (e.g., [Rehkämper et al., 2012](#)). This vertical  $\epsilon\text{Cd}$  variation is mainly attributed to the preferential uptake of light Cd isotopes by phytoplankton ([Rehkämper et al., 2012](#)), and the  $\epsilon\text{Cd}$  variations are considered to follow a closed-system Rayleigh fractionation process ([Rehkämper et al., 2012](#)). Our previous study analyzed the  $\epsilon\text{Cd}$  of seawater, as well as the biogenic sinking particles in the sur-

face water of the SCS to examine the fractionation process ([Yang et al., 2012](#)). In contrast to phytoplankton uptake, the dissolved Cd and sinking particles exhibit comparable  $\epsilon\text{Cd}$  of  $+9.3 \pm 2.7$  and  $+8.7 \pm 0.9$ , respectively ([Yang et al., 2012](#)). This suggests that heavy  $\epsilon\text{Cd}$  in the surface water is not necessarily the results of phytoplankton exports ([Yang et al., 2012](#)). Furthermore, the supply of Cd in the surface water of the SCS is mainly from aerosol deposition ([Ho et al., 2010](#)). Consequently, we argued that the  $\epsilon\text{Cd}$  of the aerosols could significantly influence the  $\epsilon\text{Cd}$  in the surface water of the SCS.

Based on mass balance calculations, [Murphy et al. \(2014\)](#) proposed a simple box model to examine our argument. In their model, the input fluxes are simplified as two components, the aerosol deposition ( $F_{\text{in-A}}$ ) and the upwelling of the subsurface water ( $F_{\text{in-D}}$ ), as  $\epsilon^{114/110}\text{Cd}_{\text{in-A}}$

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and  $\epsilon^{114/110}\text{Cd}_{\text{in-D}}$ , respectively. The output fluxes are also simplified as two components, sinking particles ( $F_{\text{out-P}}$ ) and downward plus lateral advection of the surface water ( $F_{\text{out-D}}$ ), as  $\epsilon^{114/110}\text{Cd}_{\text{out-P}}$  and  $\epsilon^{114/110}\text{Cd}_{\text{out-D}}$ , respectively. Assuming a steady-state and mass-balance, their calculations show that if the  $\epsilon^{114/110}\text{Cd}_{\text{out-P}}$  was heavier than +8, the  $\epsilon^{114/110}\text{Cd}_{\text{in-A}}$  would also be heavier than +8. Given the limited studies on isotopic composition of the Cd from anthropogenic aerosols, Murphy et al. (2014) argued that the  $\epsilon\text{Cd}$  of aerosols should fall into the range of  $-4$  to  $+4$ , and the estimated  $\sim+8$  for  $\epsilon^{114/110}\text{Cd}_{\text{in-A}}$  is, therefore, unlikely. Only if the  $\epsilon^{114/110}\text{Cd}_{\text{out-P}}$  lies between  $+3$  to  $+5$ , the model would generate satisfactory  $\epsilon^{114/110}\text{Cd}_{\text{in-A}}$  ranging from  $-4$  to  $+4$ . Consequently, Murphy et al. (2014) claimed that the  $\epsilon\text{Cd}$  in biogenic particles of the surface box would be significantly lighter than that of the seawater, indicating that phytoplankton uptake still prefers light Cd isotopes. As for the observed  $\epsilon\text{Cd} \sim +9$  in the sinking particles (Yang et al., 2012), Murphy et al. (2014) considered it an integrated  $\epsilon\text{Cd}$  signal, which was acquired at different localities and over different timescales, due to difference in residence times between Cd in particles and seawater.

Murphy et al. (2014) raised two important points about the studies of Cd in seawater: (A)  $\epsilon\text{Cd}$  of the aerosols; and (B) net  $\epsilon\text{Cd}$  effects of biological fractionations. With the exception of Yang et al. (2012), all the Cd samples were exclusively done on seawaters. The uptake of light  $\epsilon\text{Cd}$  by phytoplankton was necessary to explain the heavy  $\epsilon\text{Cd}$  observed in the surface water, while the effects of aerosols were often neglected or assumed to have light  $\epsilon\text{Cd}$ . It is shown by Murphy et al. (2014) that if only the  $\epsilon\text{Cd}$  of

seawater is known, it is necessary to assume the effects of biological fractionation to calculate the  $\epsilon\text{Cd}$  of the aerosols, or vice versa. However, if the  $\epsilon\text{Cd}$  of the phytoplankton exports are known (Yang et al., 2012),  $\epsilon\text{Cd}$  of the aerosols is also constrained. Evidently, the questions become: (A) if the inferred  $\epsilon\text{Cd} \sim +9$  for the aerosols are reasonable; and (B) if phytoplankton always prefer light Cd isotopes. In the following paragraphs, we will address these two points.

## 2. DISCUSSION

### 2.1. Cadmium isotopic composition in aerosols

As aerosols are the dominant source of Cd in the surface water of the SCS, given the  $\epsilon\text{Cd}$  in the biogenic sinking particles  $\sim+9$ ,  $\epsilon\text{Cd}$  of the aerosols should be  $\geq+8$ , predicted by the box model of Murphy et al. (2014). This is considered too heavy compared to the range of  $-4$  to  $+4$   $\epsilon\text{Cd}$ , proposed by Murphy et al. (2014), which was based on two studies on aerosols collected from refinery plants in France and Canada. Given the limited aerosol data and light Cd should be preferentially liberated during incineration process, it is reasonable Murphy et al. (2014) selected the range of  $-4$  to  $+4$   $\epsilon\text{Cd}$ . However, the real question should be addressed is whether aerosols collected from refinery plants are representative to that of SCS, originated mainly from the burning of fossil fuels, the most important anthropogenic source of Cd to the environment (Rehkämper et al., 2012). China consumes nearly half of the coal in the world, and flying ashes generated from coal burning are one of the primary sources of aerosols in

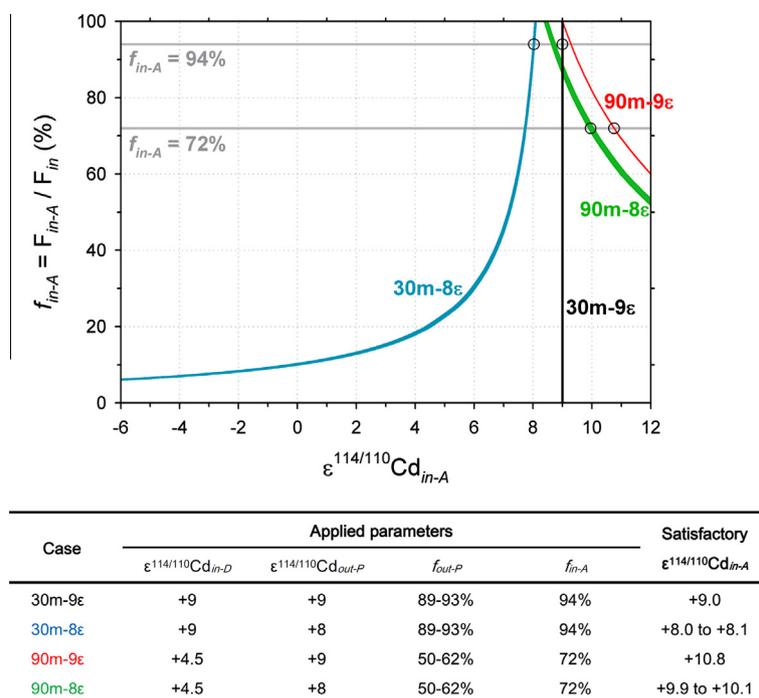


Fig. 1. Parameters applied to the SCS surface water box and the model results. Satisfactory conditions are found if the  $\epsilon^{114/110}\text{Cd}_{\text{in-A}}$  values are  $+9.0$ ,  $+8.0$  to  $+8.1$ ,  $+10.8$ , and  $+9.9$  to  $+10.1$  in the cases of 30m-9 $\epsilon$ , 30m-8 $\epsilon$ , 90m-9 $\epsilon$ , and 90m-8 $\epsilon$ , respectively (the circles), indicating that the  $\epsilon\text{Cd}$  in the aerosols would be heavier than that observed in the refinery plants, ranging from  $-4$  to  $+4$ .

South-East Asia. It is thus questionable that aerosols collected from the two refinery plants are representative to that of the SCS.

There is yet any  $\epsilon\text{Cd}$  reported for the aerosols produced from the burning of fossil fuels. However, the study of Borrok et al. (2010) can help evaluating if lighter  $\epsilon\text{Cd}$  aerosols are preferentially produced by the processes. In contrast to the conventional wisdom, Borrok et al. (2010) observed  $\sim 0.5\%$  heavier  $\delta^{66/64}\text{Zn}$  in flying ashes relative to that in the coal, and which was attributed to the results from a series of complicated mechanisms. Similarly, without any constraint about the sources and the mechanisms generated these flying ashes, it is difficult to assume their  $\epsilon\text{Cd}$  from a simple evaporation scenario.

Using the box model of Murphy et al. (2014), we applied the same calculations with a set of essential parameters listed in Fig. 1 to obtain the  $\epsilon^{114/110}\text{Cd}_{\text{in-A}}$  in aerosols. Our results showed that the  $\epsilon\text{Cd}$  for aerosols would fall from +8.0 to +10.8 (Fig. 1), consistent with the preliminary results of the aerosols collected from the SCS (Lee et al., 2011).

## 2.2. Cadmium isotopic fractionation in marine phytoplankton

Murphy et al. (2014) found that the  $\epsilon\text{Cd}$  of biogenic particles fall within +3 to +5 when using the  $-4$  to  $+4$   $\epsilon\text{Cd}$  for aerosols in their box model results. Therefore, with  $\epsilon\text{Cd}$  of +9 for the surface water of SCS (Yang et al., 2012), they proposed that phytoplankton would preferentially take up light Cd with fractionation factors  $\alpha_{\text{bio-sw}}$  ranging from 0.9994 to 0.9996, comparable to that of Xue et al. (2013). However, as all the previous studies for seawater  $\epsilon\text{Cd}$ , the  $\alpha_{\text{bio-sw}}$  of Xue et al. (2013) was obtained solely from the data of seawater.

The studies of freshwater green algae (Lacan et al., 2006) and *Escherichia coli* culture experiment (Horner et al., 2013) suggested that marine phytoplankton may prefer light Cd. However, the  $\epsilon\text{Cd}$  of the sinking particles reported by Yang et al. (2012) indicated that the fractionation by phytoplankton uptake is more complicated than that shown by these two studies. In addition, the uptake of Cd in phytoplankton may vary under different availabilities of other metal nutrients in seawater (Ho et al., 2011). Lastly, no  $\epsilon\text{Cd}$  fractionation in the surface seawater was observed near the Southern Ocean in the summer (Gault-Ringold et al., 2012). Besides phytoplankton uptake and aerosol input, many other processes may influence the  $\epsilon\text{Cd}$  in seawater, including zooplankton grazing and microbial degradation. Consequently, the  $\epsilon\text{Cd}$  in seawater should be an integrated effect of these processes, rather than phytoplankton uptake alone.

## 3. CONCLUSION

We appreciated the comments of Murphy et al. (2014) to provide us an opportunity to highlight many integrated parts of our study about the cycling of Cd in SCS that were not made clear in Yang et al. (2012). We believe that an integrated study as in the case of SCS is necessary, in order to better constrain the cycling of Cd, or any other element, in the oceans.

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