Comment

Comment on "The isotopic composition of cadmium in the water column of the South China Sea"

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Abstract

Yang et al. (2012) found that marine biogenic particles and corresponding surface seawater from the South China Sea were characterized by essentially identical Cd isotope compositions, and inferred that biological Cd isotope fractionation is insignificant at this location. Based on results obtained for a box model that represents Cd cycling in the surface layer, and using published data to constrain the Cd source and sink fluxes, we show that this conclusion is likely to be incorrect. The modeling results indicate that the heavy Cd isotope signature of $\varepsilon^{114/110}Cd \approx +9$ observed by Yang et al. (2012) for the surface South China Sea is most likely a consequence of substantial isotope fractionation (of about 4–6 ε) during uptake of dissolved seawater Cd by phytoplankton.

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1. INTRODUCTION

In their paper, Yang et al. (2012) reported Cd concentrations and isotope compositions for a seawater depth profile from the South China Sea (SCS) in conjunction with the first Cd isotope data for a single sample of biogenic marine particulates. The Cd isotopic compositions of the particles from 30 m water depth were found to be identical, within uncertainty, to the surface water sample ($\varepsilon^{114/110}Cd = +8.7 \pm 0.9$ and $+9.3 \pm 2.7$, respectively). From this and mixing calculations, Yang et al. (2012) inferred that biological isotope fractionation of Cd is insignificant in the surface water of the SCS. In contrast, here we argue that a plausible isotopic mass balance can only be obtained for the surface layer of the SCS if isotopic fractionation is invoked for the incorporation of Cd into marine biomass.

2. BOX MODEL

We represent Cd cycling in the surface layer of the SCS using a box model that features two Cd input fluxes and two output fluxes (Table 1). These inputs are from external

sources (F_{in-A}, primarily atmospheric deposition) and upwelling water masses (F_{in-D}), whilst the outputs are provided by sinking particles (F_{out-P}) and water mass movements F_{out-D} (downwelling and lateral advection).

2.1. Model parameters

2.1.1. Output fluxes of Cd

Based on the data of Yang et al. (2012), we assign the dissolved seawater Cd within the surface layer a (rounded) isotope composition of $\varepsilon^{114/110}Cd = +9$. Yang et al. (2012) postulate that isotope fractionation of Cd does not occur during biological uptake, so the biogenic particles collected at a depth of 30 m are also assigned a (rounded) $\varepsilon^{114/110}Cd$ value of $+9$. These considerations define the Cd isotope compositions of the two Cd sink fluxes, F_{out-D} and F_{out-P}. As the latter is thought to be dominant (Yang et al., 2012), the modeling focuses on scenarios where the proportion of the Cd output flux to particles $f_{out-P} = F_{out-P}/F_{out}$ is greater than 50% (Table 1). Using data from other sources, we suggest that a reasonable estimate can be made for f_{out-P}. The flux of Cd in sinking particles at 30 m in October 2006 (i.e., the time of sample collection) was 28 nmol m^{-2} d^{-1} (Ho et al., 2010). Assuming that the water flux entering the surface layer (with an average upwelling velocity of

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Table 1
Constraints available and applied for the isotope compositions and relative magnitude of the Cd fluxes of the surface layer box model. Also shown are (i) whether a scenario enables a 'realistic' solution for the surface layer (in accord with constraints) and (ii) at which (revised) conditions a realistic solution can be achieved, assuming $\varepsilon^{114/110}Cd_{in-A} \approx -4$ to $+4$ is a rigid boundary condition.

Case	Flux in, F_{in}			Flux out, F_{out}			Realistic solution possible?[a]	(Revised) conditions that enable a realistic solution[b]
	Dissolved	External (atmospheric)		Dissolved	Particles			
	$\varepsilon^{114/110}Cd_{in-D}$	$\varepsilon^{114/110}Cd_{in-A}$	f_{in-A}	$\varepsilon^{114/110}Cd_{out-D}$	$\varepsilon^{114/110}Cd_{out-P}$	f_{out-P}		
A: No biological isotope fractionation (Yang et al., 2012)								
A1: 30 m surface layer	+9	−4 to +4	⩾25%	+9	+9	0–100%	No	None
A2: 90 m surface layer	+4.5	−4 to +4	⩾25%	+9	+9	0–100%	No	None
B: Limited biological isotope fractionation								
B1: 30 m surface layer	+9	−4 to +4	⩾25%	+9	+8	80%	Unlikely	($f_{in-A} \leqslant 16\%$)
B2: 30 m surface layer	+9	−4 to +4	⩾25%	+9	+8	55%	Unlikely	($f_{in-A} \leqslant 11\%$)
B3: 90 m surface layer	+4.5	−4 to +4	⩾25%	+9	+8	80%	No	None
C: Significant biological isotope fractionation								
C1: 30 m surface layer	+9	−4 to +4	⩾25%	+9	+5	80%	Yes	$25\% \leqslant f_{in-A} \leqslant 64\%$
C2: 30 m surface layer	+9	−4 to +4	⩾25%	+9	+3	80%	Yes	$37\% \leqslant f_{in-A} \leqslant 96\%$
C3: 90 m surface layer	+4.5	−4 to +4	⩾25%	+9	+3	80%	Yes	$25\% \leqslant f_{in-A} \leqslant 66\%$

[a] Solutions that cannot achieve $\varepsilon^{114/110}Cd_{in-A}$ of between −4 and +4 are deemed to be unrealistic. Unlikely solutions are in accord with $\varepsilon^{114/110}Cd_{in-A}$, but only at $f_{in-A} < 25\%$.

[b] The values in parentheses of 'unlikely' solutions indicate at which values of f_{in-A} a solution can achieve $\varepsilon^{114/110}Cd_{in-A} \leqslant +4$.

55 m yr^{-1}; Chen et al., 2001) is identical to the water outflow, which is assigned a Cd concentration of 0.048 nM based on SCS data obtained at 20 m depth by Yang et al. (2012), the flux of dissolved Cd leaving the box is 7 nmol m^{-2} d^{-1}. This gives a representative value for f_{out-P} of 80%.

2.1.2. Input fluxes of Cd

The relative proportions and isotope compositions of the two Cd source fluxes are less well constrained. The Cd concentration and isotope composition of the water changes with depth, making the dissolved input flux F_{in-D} dependent on the upwelling depth. Our box model considers two reasonable endmember scenarios. A minimum value of 30 m is supplied by the depth at which the biogenic particles analyzed by Yang et al. (2012) were collected. In this case, F_{in-D} is assigned the properties of the immediately underlying water from 40 m (Yang et al., 2012), which is characterized by [Cd] = 0.037 nM and an $\varepsilon^{114/110}Cd$ value identical to the surface layer (here +9; Table 1). Yang et al. (2012) apply an upwelling rate of 55 m yr^{-1} (Chen et al., 2001), which generates a dissolved flux F_{in-D} of 6 nmol m^{-2} d^{-1}. We also consider that the 'surface' box may be as deep as 90 m, so we assign the upwelling water [Cd] = 0.24 nM and $\varepsilon^{114/110}Cd$ = +4.5, following the results of Yang et al. (2012) for 100 m water depth. As the Cd concentration is significantly higher at this depth there is an increased input flux F_{in-D} of 36 nmol m^{-2} d^{-1}. We also note that dissolved Cd displays decreasing $\varepsilon^{114/110}Cd$ values with depth (Yang et al., 2012), so we only consider cases where incoming water has a lighter $\varepsilon^{114/110}Cd$ than outgoing water.

Atmospheric deposition is likely to be the predominant external source of Cd to the SCS (Yang et al., 2012). Given the high population density of the adjoining coastal areas, it may be largely of anthropogenic origin (Hsu et al., 2007).

Based on published data of Ho et al. (2010), Yang et al. (2012) report an estimated flux F_{in-A} of 92 nmol m^{-2} d^{-1}. When combined with the dissolved input fluxes described above, the proportion of Cd provided by external (primarily atmospheric) sources f_{in-A} ($= F_{in-A}/F_{in}$), can be calculated as 94% and 72% for surface layer depths of 30 and 90 m respectively. However, given the uncertainties in the magnitude of F_{in-D} and F_{in-A}, we consider any scenario that features f_{in-A} values of more than 25% as realistic.

Cadmium isotope data are currently not available for aerosol samples from proximal regions. A likely range of $\varepsilon^{114/110}Cd_{in-A} = -4$ to $+4$ for aerosols can be inferred, however, from reported natural ($\varepsilon^{114/110}Cd = -2$ to $+2$; Rehkämper et al., 2011) and anthropogenic ($\varepsilon^{114/110}Cd = -7.2$ to $+3.3$; Cloquet et al., 2006; Shiel et al., 2010) sources and their mixing in the atmosphere.

2.2. Modeling procedure

Given the dynamic nature of Cd cycling in the upper ocean it is reasonable to assume that the surface layer is at or close to steady state. Therefore, the modeling sets four parameters as constant (f_{out-P}, $\varepsilon^{114/110}Cd_{out-P}$, $\varepsilon^{114/110}Cd_{out-D}$, $\varepsilon^{114/110}Cd_{in-D}$), whilst the proportion of the input flux provided by external sources f_{in-A} is varied to calculate $\varepsilon^{114/110}Cd_{in-A}$. This forward modeling procedure allows us to distinguish between realistic and unlikely combinations of modeling parameters according to the constraints discussed above.

3. MODEL RESULTS

3.1. Scenario A – No biological isotopic fractionation

Following the study of Yang et al. (2012), this scenario assumes that there is no biological isotope fractionation, based on the observation that surface waters and biogenic