The Cd isotope composition of atmospheric aerosols from the Tropical Atlantic Ocean

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Abstract
Stable isotope compositions can potentially be used to trace atmospheric Cd inputs to the surface ocean and anthropogenic Cd emissions to the atmosphere. Both of these applications may provide valuable insights into the effects of anthropogenic activities on the cycling of Cd in the environment. However, a lack of constraints for the Cd isotope compositions of atmospheric aerosols is currently hindering such studies. Here we present stable Cd isotope data for aerosols collected over the Tropical Atlantic Ocean. The samples feature variable proportions of mineral dust-derived and anthropogenic Cd, yet exhibit similar isotope compositions, thus negating the distinction of these Cd sources by using isotopic signatures in this region. Isotopic variability between these two atmospheric Cd sources may be identified in other areas, and thus warrants further investigation. Regardless, these data provide important initial constraints on the isotope composition of atmospheric Cd inputs to the ocean.

1. Introduction
Variations in stable isotope composition have recently been employed to study the environmental cycling of Cd, particularly in the ocean. Cadmium is subject to internal cycling in the ocean, with removal through biological uptake in surface waters and regeneration at depth due to remineralization of organic material [Boyle et al., 1976; Bruland, 1980]. This regenerated Cd is returned to the surface through deepwater convection, diapycnal mixing, and upwelling, constituting the dominant Cd source to ocean surface waters [Bruland, 1980]. These biogeochemical processes produce mass-dependent Cd isotope variations, whereby surface waters evolve to "heavier" isotope compositions with increasing Cd depletion [Ripperger et al., 2007; Abouchami et al., 2011; Xue et al., 2013; Abouchami et al., 2014]. Deviations from the expected relationship between Cd concentrations and isotope compositions due to biological cycling have been used to deconvolve the effects of processes such as water mass mixing and removal through sulfide precipitation on the distribution of Cd in the ocean [Xue et al., 2013; Yang et al., 2014; Janssen et al., 2014; Conway and John, 2015]. External inputs of Cd should also perturb the coupled Cd concentration and isotope composition distributions imparted by biological cycling [Ripperger et al., 2007; Yang et al., 2012, 2014]. Hence, Cd isotopes will be a useful tracer of external inputs to ocean surface waters. To this end, it is necessary to constrain the Cd isotope compositions of external oceanic inputs. Currently, limited data have been published for the composition of riverine fluxes [Lambelet et al., 2013], while only unpublished results are available for atmospheric aerosols from a single locality [Yang et al., 2015].

Tracing external, atmospheric inputs of Cd to the surface ocean is pertinent for understanding the impact of anthropogenic activities on marine Cd inventories. Atmospheric Cd sources are currently dominated by emissions from high-temperature anthropogenic processes, most importantly metal smelting (particularly of Pb-Zn ores), coal combustion, and waste incineration [Nriagu and Pacyna, 1988, Pacyna and Pacyna, 2001, Pacyna et al., 2009; Cheng et al., 2014]. During these high-temperature processes, Cd is vaporized and condenses onto fine (<1 μm) particles in the atmosphere [Roes et al., 2000; Cloquet et al., 2006]. Such particles are capable of undergoing long-range transport before deposition to terrestrial and marine environments [Duce et al., 1991; Gelado-Caballero et al., 2012].

Cadmium has a relatively long residence time in the ocean of ~10^4–10^5 years, reflecting its internal cycling [Simpson, 1981]. Therefore, recent external anthropogenic Cd inputs are unlikely to have significantly

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affected the bulk marine Cd inventory. However, atmospheric inputs are potentially an important Cd source to ocean surface waters of certain regions and this has been highlighted by reconstructions of past surface water Cd concentrations using coral archives [Shen et al., 1987]. Temporal variations in surface water Cd concentrations at the Galapagos Islands are consistent with changes in upwelling water strength. However, the temporal pattern at Bermuda closely resembles that of North American industrial Cd emissions over the past century, suggesting the importance of anthropogenic Cd inputs to surface water of this region [Shen et al., 1987]. Variations in Cd isotope compositions are potentially a useful tool for distinguishing regions where external atmospheric inputs provide important contributions to surface water Cd inventories. Such regions will be particularly prone to perturbation by anthropogenic Cd emissions. Furthermore, it has been suggested that Cd isotope composition variations can be used to distinguish between natural and anthropogenic sources of Cd in the environment [e.g., Cloquet et al., 2006]. Since evaporation/condensation processes are capable of inducing significant mass-dependent Cd isotope fractionations, the emission of Cd by high-temperature industrial processes is expected to be associated with distinct isotopic signatures [Wombacher et al., 2004; Cloquet et al., 2006]. The observed Cd isotope variations between the products (i.e., ash and slag) and starting materials (i.e., ore minerals and coals) of Pb-Zn smelting and coal combustion support this hypothesis [Cloquet et al., 2006; Shiel et al., 2010; Martinková et al., 2016]. Such isotopic variability has been exploited to trace anthropogenic sources of Cd to sediments proximal to Pb-Zn mining and smelting operations [Cloquet et al., 2006; Gao et al., 2008, 2013, Chrastrý et al., 2015, Wen et al., 2015]. Furthermore, Shiel et al. [2012, 2013] interpreted Cd isotope data for marine bivalves in the context of anthropogenic and natural Cd sources to coastal waters.

Despite these important potential applications, the Cd isotope composition of atmospheric aerosols has yet to be thoroughly investigated. Here we present Cd isotope and trace metal abundance data for atmospheric aerosols from the eastern Tropical Atlantic Ocean (Figure 1). While the chosen study area is subject to the transport of large quantities of mineral dust emitted from North Africa, aerosols in this region are commonly also highly enriched in anthropogenic Cd [Gelado-Caballero et al., 2012; Patey et al., 2015]. The sample set is therefore well suited for the investigation of the isotope compositions of these two important atmospheric Cd sources.

2. Samples and Analytical Techniques

Eleven aerosol samples were collected in the eastern Tropical Atlantic during the GEOTRACES GA06 section cruise (D361, February–March 2011; Figure 1), by high volume sampling (1 m$^3$ min$^{-1}$) [Chance et al., 2015; Bridgestock et al., 2016]. In parallel to this, three size-fractionated samples (SF7, SF25, and SF26) were obtained by using a six-stage impactor [Marple and Willeke, 1976]. All aerosols were collected onto precleaned
Whatman 41 cellulose fiber filters (203 mm × 241 mm) that were stored frozen (−20°C) in zip-lock plastic bags prior to sample preparation (Text S1 and Table S1 in the supporting information).

Eight of the aerosol samples were collected north of the Intertropical Convergence Zone (ITCZ), with air mass back trajectory analyses indicating that they originated from North Africa (Table S1). The three remaining aerosols are from within/south of the ITCZ, and air mass back trajectories show that they did not encounter land in the 5 days preceding collection [Bridgestock et al., 2016].

The nonsize-fractionated samples were split into two portions, with 25–50% and 12–50% of the total exposed filter area subjected to total acid digestion (using concentrated HF, HClO₄, and HNO₃) and a leaching procedure (dilute ammonium acetate solution, pH 4.7), respectively, at Imperial College London [Bridgestock et al., 2016]. Aliquots of these subsamples were taken for determination of elemental concentrations at the Natural History Museum, London (Text S2). The Pb and Al contents of these subsamples were previously reported [Bridgestock et al., 2016]. Size-fractionated samples were subjected to the same leaching procedure as the nonsize-fractionated aerosols, at the University of East Anglia [Powell et al., 2015; Chance et al., 2015]. The Cd and Pb contents of the leachates were subsequently determined by inductively coupled plasma–mass spectrometry (ICP-MS) (Text S2). Results for the size-fractionated sample SF7 were reported previously [Jickells et al., 2016].

2.1. Cadmium Isotope Measurements

The low abundance of Cd in the atmosphere (~1–100 pg m⁻³) makes precise determination of Cd isotope compositions for atmospheric aerosols challenging [Guerzoni et al., 1999; Gelado-Caballero et al., 2012]. Hence, only total digestion and leachate subsamples of nonsize-fractionated samples, corresponding to 50% of the total exposed filter area, were analyzed for Cd isotope compositions; other subsamples contained insufficient Cd to yield precise data. For the selected samples, the blank of the sample collection and digestion/leaching procedure amounted to 1.3–3.1% of the total Cd content (Table S2). Aliquots equivalent to between 66 and 85% of the total digestion and leachate solutions, with approximately 5–25 ng of Cd, were taken for Cd isotope analysis. The Cd aliquot of subsample ISO-21_TOTAL, featuring 25 ng of Cd, was further split into two separate aliquots (ISO-21_TOTAL and ISO-21B_TOTAL) with approximately 15 and 10 ng of Cd, to assess the external reproducibility of the analytical procedure (Table S2).

Cadmium isotope compositions were determined at the Mass Spectrometry and Isotope Geochemistry at Imperial College London Laboratories by using established techniques. These employ multiple collector–inductively coupled plasma-mass spectrometry (MC-ICP-MS), in conjunction with a Cd double spike (DS) prepared from enriched ¹¹¹Cd and ¹¹³Cd, for instrumental mass bias correction [Xue et al., 2012]. Appropriate quantities of Cd DS were equilibrated with the sample aliquots prior to chemical separation of Cd from the sample matrix with a three-stage chromatographic procedure, utilizing Biorad AG 1X8 anion exchange and Eichrom TRU-spec resins (Text S3 and Table S3). Liquid-liquid extraction with heptane was subsequently employed to remove residual organics leached from the Eichrom TRU-spec resin [Murphy et al., 2016]. Finally, purified Cd solutions were evaporated to dryness and redissolved in 1 ml of 0.1 M HNO₃ for isotopic analysis. The Cd blank for the chemical separation procedure was consistently <10 pg, which is negligible relative to the quantity of natural Cd processed (5–20 ng).

Cadmium isotope measurements were conducted by using a Nu Plasma MC-ICP-MS instrument (Nu Instruments). Sample solutions were introduced by using an Aridus II desolvation unit (CETAC Technologies) equipped with a Micromist glass nebulizer operated at flow rates of 110 to 115 μl min⁻¹. The sensitivity obtained for Cd was between 200 and 300 V ppm⁻¹. Analyses of samples were bracketed by measurements of mixtures of the standard reference material (SRM) National Institute of Standards and Technology (NIST) 3108 Cd with the Cd DS at comparable spike/sample ratios and dilutions. Measurement protocols followed those previously described [Xue et al., 2012, Murphy et al., 2016] and data are presented as ε¹¹⁴/¹¹⁰Cd values relative to NIST 3108 Cd (equation (1)) [Abouchami et al., 2013].

$$\varepsilon^{114/110}\text{Cd} = \left[\frac{^{114}\text{Cd}^{110}\text{Cd}_{\text{Sample}}}{^{114}\text{Cd}^{110}\text{Cd}_{\text{NIST 3108}}}\right] - 1\right] \times 10^4$$

The raw isotopic ratios were processed off-line to calculate ε¹¹⁴/¹¹⁰Cd values corrected for instrumental mass bias and isobaric interferences [Ripperger and Rehkämper, 2007; Xue et al., 2012; Murphy et al., 2016].
The quoted precision of the Cd isotope data was estimated from the reproducibility of the bracketing analyses of matching NIST 3108 Cd-Cd D5 mixtures, which was ±1 to ±2 ε114/110Cd (2 SD; Table S2). Additional SRMs were analyzed to validate the accuracy and precision of the isotope measurements (Table S4 and Text S4) with results in good agreement with published values [Yi et al., 1998; Wombacher et al., 2003; Abouchami et al., 2013; Wiggenhauser et al., 2016].

3. Results

Total atmospheric concentrations of Cd, Pb, Zn, and Cu range from 3.8 to 40.3 pg m$^{-3}$, 0.12 to 4.11 ng m$^{-3}$, 0.7 to 9.8 ng m$^{-3}$, and 0.26 to 4.16 ng m$^{-3}$, respectively. Atmospheric Al concentrations, a proxy for mineral dust, vary between 68 and 5048 ng m$^{-3}$ [Bridgestock et al., 2016] (Table S2). Crustal enrichment factors (EF$_{crust}$) are used to assess the relative proportions of the trace metals derived from mineral dust and anthropogenic sources in the aerosols and are calculated by normalizing the trace metal/Al ratio of the aerosol samples (X/Al$_{sample}$) to that of the upper continental crust (X/Al$_{ucc}$) (equation (2)). Crustal ratios are taken from Rudnick and Gao [2003].

\[
EF_{crust} = \frac{X/\text{Al}_{sample}}{X/\text{Al}_{ucc}}
\]

The EF$_{crust}$ values range from 4 to 107 (Cd), 2 to 15 (Pb), 1 to 23 (Zn), and 1 to 23 (Cu) (Table S2). Normalization using other elements primarily associated with mineral dust (Ti, Mn, Fe, Sc, and Th) for the calculation of EF$_{crust}$ values yields results that agree within a factor of 2, compared to those calculated with Al (Figure S1 and Table S5 in the supporting information). The EF$_{crust}$ values for Cd and Pb display a strong positive correlation ($r^2 = 0.99$), omitting two anomalous samples. Likewise, the EF$_{crust}$ values for Zn and Cu display a strong positive correlation ($r^2 = 0.99$) but exhibit weaker relationships to EF$_{crust}$ values for Cd ($r^2 = 0.44$ and 0.40, respectively; Figures 2a–2c; Cu not shown). For all trace metals, EF$_{crust}$ values generally decrease with increasing atmospheric Al concentrations (Figures 2d–2f; Cu not shown).

For the size-fractionated aerosol samples SF7, SF25, and SF26, higher proportions of leachable Cd and Pb generally reside in the >1 μm size fractions (Figure 3 and Table S6). Sample SF25, furthermore, exhibits an anomalous enrichment of these metals in the 5 μm fraction.

The Cd isotope compositions of the analyzed aerosol samples are relatively constant at ε114/110Cd = −1.9 to 1.9, except for ISO-16Leach, characterized by ε114/110Cd = −5.4 ± 1.3 (Table S2 and Figure 2g). This latter leachate subsample features 2.8 times more Cd than the corresponding total digest, ISO-16Total. It is conceivable that this anomalously high Cd content may be due to the heterogeneous distribution of Cd on the filter or contamination during handling, storage, and/or leaching of the filter. However, contamination seems unlikely as it would require the addition of at least 18 ng Cd, which is significantly more than the combined blank of the sampling and leaching procedure, consistently assessed to be <1 ng. Nonetheless, the results for this subsample should be regarded with caution.

Results for replicate analyses of ISO-21Total (ISO-21aTotal and ISO-21bTotal) and analyses of total digests and leachates from the same aerosol sample (ISO-21, ISO-12, and ISO-23) are all identical within analytical uncertainty. With the aforementioned exception of ISO-16Leach, between S1 and 86% of the total aerosol Cd contents were released during leaching. These relatively high solubilities reflect the labile nature of Cd associated with both anthropogenic sources and mineral dust [Guerzoni et al., 1999; Hsu et al., 2005]. Thus, it appears that there is no resolvable difference in the isotope composition of soluble and refractory species of Cd in the aerosols, and no resolvable isotopic fractionation was observed for the leaching process (Text S4).

The Cd isotope compositions determined for leachates are therefore assumed to be representative of the total digests, if no separate data were available for the latter.

4. Discussion

4.1. Atmospheric Cd Sources

The range of EF$_{crust}$ values for the aerosols indicates variable contributions of Cd, Pb, Zn, and Cu from mineral dust and anthropogenic emissions. The negative trends between EF$_{crust}$ data and atmospheric Al concentrations (Figures 2d–2f), a proxy for atmospheric mineral dust loadings, are a characteristic of relatively constant “background” concentrations of anthropogenic trace metals that are diluted by sporadic emission and...
transport of mineral dust [Chester et al., 1993; Chester et al., 1996; Guerzoni et al., 1999; Patey et al., 2015; Bridgestock et al., 2016]. Although it is uncertain how closely the chosen Cd/Al_{ucc} reference ratio approximates North African mineral dust, extension of the trend in Figure 2d to the lowest EF_{crust} Cd values of 4 to 5 suggests that, at the very least, results >5 represent enrichments of anthropogenic Cd. Without additional constraints, the importance of anthropogenic Cd to the samples featuring the lowest EF_{crust} Cd values (ISO-5, ISO, 11, and ISO-8), is unclear. Samples ISO-14, ISO-16, and ISO-25, with the lowest atmospheric Al concentrations and the highest EF_{crust} Cd \approx 50–107, are dominated by anthropogenic Cd. The remaining aerosols (ISO-7, ISO-12, ISO-19, ISO-21, and ISO-23) with EF_{crust} Cd \approx 9–17 are likely to contain anthropogenic Cd contributions of at least 50–60%, assuming that a value of \approx 5 represents pure North African mineral dust. Importantly, the use of other mineral dust-derived elements (e.g., Ti, Sc, and Th) for normalization during calculation of EF_{crust} Cd data all support the notion of significant anthropogenic Cd contributions to these samples (Figure S1 and Table S5).
Comparison of EF$_{\text{crust}}$ Cd values to those of Pb, Cu, and Zn may yield insights into the specific processes responsible for the observed anthropogenic Cd enrichments. The strong correlation between EF$_{\text{crust}}$ values for Cd and Pb likely reflects a common anthropogenic source of these metals (Figure 2a). Notably, enrichments of anthropogenic Pb in these samples are supported by independent constraints from Pb isotope variations [Bridgestock et al., 2016]. Furthermore, the anthropogenic Pb of these aerosols features unradiogenic isotope compositions, indicative of derivation from older Pb ores [Sangster et al., 2000; Bridgestock et al., 2016]. Emissions from Pb-Zn smelting operations are therefore the most probable common anthropogenic source of these metals.

Two samples (ISO-7 and ISO-12) were omitted from the regression of the EF$_{\text{crust}}$ values for Cd and Pb, as the anthropogenic Pb in these samples appears to originate from the residual use of leaded petrol in Algeria [Bridgestock et al., 2016]. Indeed, these samples, particularly ISO-7, deviate from the relationship due to excess enrichments of anthropogenic Pb, supporting this interpretation (Figure 2a).

Smelting of Pb-Zn ores is also considered to be a major anthropogenic source of Zn and Cu to the atmosphere [Nriagu and Pacyna, 1988]. The reason for the weaker relationship between the EF$_{\text{crust}}$ values of Zn and Cu with those for Cd (and Pb) is unclear (Figure 2b). It may reflect additional atmospheric sources of anthropogenic Zn and Cu, which do not affect Cd and Pb, or vice versa. Alternatively, the distinct volatilities of Cd, Pb, Zn, and Cu during the different stages of smelting operations may affect the relative abundances at which these metals are emitted [e.g., Diaz-Somoano et al., 2006].

Anthropogenic enrichments of trace metals are generally higher in finer particles of $<1 \mu$m, while natural mineral dust is mainly composed of particles $>1 \mu$m [e.g., Fomba et al., 2012]. The higher proportions of leachable Cd and Pb that reside in the sub-1 $\mu$m fractions of samples SF7 and SF26 thus provide further evidence for anthropogenic enrichments of these metals (Figure 3). In detail, larger proportions of leachable Pb are concentrated in the sub-1 $\mu$m fraction of these size-fractionated samples than are observed for Cd. This is to be expected, since the leaching preferentially extracts anthropogenic over natural Pb, due to the distinct solubility of these components [Bridgestock et al., 2016]. Conversely, it has been shown that the leaching procedure likely releases anthropogenic and mineral dust-derived Cd in similar proportions [Guerzoni et al., 1999; Hsu et al., 2005]. Samples SF25 and SF26 were collected during the same period as ISO-25 (Figure 1 and Table S1), whereby the latter exhibits the highest observed EF$_{\text{crust}}$ values for Cd and Pb, of 107 and 15, respectively. The Cd and Pb contents of these samples are hence likely dominated by anthropogenic emissions. The cause for anomalous enrichment of these metals in the 5 $\mu$m fraction of SF25 is unclear but may be related to the absorption of anthropogenic metals onto coarser mineral dust particles [e.g., Koçak et al., 2005; Erel et al., 2006].
4.2. Isotope Compositions of Anthropogenic and Mineral Dust-Derived Cd

The currently available data for terrestrial rocks indicate limited Cd isotope variability [Wombacher et al., 2003; Schmitt et al., 2009]. Based on results for three loess samples, the Cd isotope composition of the upper continental crust is assumed to be $\varepsilon^{114/110}$Cd $= -0.1 \pm 0.7$ (mean $\pm 2$ SD) [Schmitt et al., 2009; Rehkämper et al., 2012]. North African mineral dust is therefore also likely characterized by $\varepsilon^{114/110}$Cd $= 0$, consistent with the isotope compositions determined for the aerosols (Figure 2g).

The isotope composition of Cd emitted by anthropogenic processes will depend on both the composition of the source materials and any isotope fractionation incurred during processing and emission. As previously argued, Pb-Zn smelting is likely to be the dominant anthropogenic Cd source to the aerosols. This Cd is ultimately derived from Zn ore minerals, most importantly sphalerites, which display a large range of $\varepsilon^{114/110}$Cd values between $-16$ and $8$ [Wombacher et al., 2003; Shiel et al., 2010; Zhu et al., 2013, Chrastý et al., 2015, Wen et al., 2015; Wen et al., 2016; Zhu et al., 2016; Martinková et al., 2016] (Figure 2g). Furthermore, the emission of Cd from Pb-Zn smelting is thought to be associated with a fractionation toward “lighter” isotope compositions, with fume-derived Cd exhibiting $\varepsilon^{114/110}$Cd values 5 to 6 units lower than the precursor ores [Cloquet et al., 2006; Shiel et al., 2010]. However, the magnitude of this fractionation will likely vary, depending on the specific technological processes employed in the smelting operations [Chrastý et al., 2015, Martinková et al., 2016].

Based on this information, the isotope composition of anthropogenic Cd in the atmosphere is likely to vary significantly, with signatures that are potentially distinct from mineral dust (Figure 2g). However, the majority of aerosols analyzed here display reasonably constant $\varepsilon^{114/110}$Cd values of $-1.9$ to $1.9$, with no discernable difference between samples featuring high and low EF$_{crust}$ Cd. As such, isotopic variations are of limited use for distinguishing between these two atmospheric Cd sources, at least in this region. This observation urges caution for studies attempting to use Cd isotope variations to trace anthropogenic Cd sources to the environment. Given the somewhat surprising nature of this result, it is emphasized that the integrity of the data are beyond reasonable doubt, with the Cd isotope methods employed here being carefully validated both as part of the current [Text S4 and Table S4] and a number of previous studies [Xue et al., 2012, Murphy et al., 2016, Wiggenhauser et al., 2016].

The results, however, do not preclude that resolvable differences in the isotope composition of these two atmospheric Cd components are recorded in other regions. Such variations are expected in principle but are difficult to predict. For example, preliminary results for anthropogenic aerosols collected in the South China Sea indicate unusually “heavy” Cd isotope compositions, with $\varepsilon^{114/110}$Cd values of 1 to 18 [Yang et al., 2015]. In contrast, subsample ISO-16Leach, with significant quantities of anthropogenic Cd, exhibits a distinctly low $\varepsilon^{114/110}$Cd value of $-5.4$ (Figure 2g). This is the only aerosol analyzed for Cd isotopes that was collected south of the ITZC, potentially reflecting a distinct composition of anthropogenic Cd transported by south-easterly winds (Figure 1). However, it is also conceivable that the unusual result for this sample reflects contamination during collection or processing; hence, this interpretation should be regarded with caution (see section 3). Clearly, additional studies are required to further investigate and develop possible isotopic tracing of Cd in aerosols. Needed in particular are investigations of isotope fractionation during industrial processing and emission of Cd and further stable isotope data for Cd source materials and anthropogenic Cd in the atmosphere of other regions.

Regardless, the new data set provides important constraints for the isotope composition of atmospheric Cd inputs to ocean surface waters, and this addresses a significant gap in our current understanding of the global biogeochemical Cd cycle. Notably, Cd isotope variations in seawater could be used to study the importance of atmospheric inputs versus deep upwelling as sources of Cd to ocean surface waters [Ripperger et al., 2007; Yang et al., 2012; Yang et al., 2014]. The Cd inventories of regions, for which external atmospheric inputs are important, will thereby be particularly prone to changes in anthropogenic emissions and natural mineral dust inputs.

5. Conclusions

Novel results for the Cd isotope compositions of atmospheric aerosols collected over the Tropical Atlantic Ocean are presented. These aerosols contain variable proportions of Cd derived from North African
mineral dust and anthropogenic emissions. Despite this, they display reasonably constant Cd isotope compositions, with all samples but one featuring $^{114/110}$Cd values of $\sim 1.9$ to 1.9. This demonstrates that natural and anthropogenic sources of Cd to the atmosphere cannot be distinguished in this region based on their isotopic signature. On a global basis, however, the Cd isotope compositions of anthropogenic emissions are expected to vary significantly, due to the observed isotopic variability of relevant source materials and the isotope fractionations that can be incurred during industrial processing and emission of Cd.

The data provide important initial constraints on the isotopic composition of atmospheric Cd inputs to surface ocean waters. Such constraints are required to utilize Cd stable isotope variations in seawater to study the importance of atmospheric inputs versus upwelling as sources of Cd to ocean surface waters. In the future, Cd isotope data may hence help to identify regions of the ocean surface that are particularly prone to being affected by anthropogenic Cd emissions and changes in natural mineral dust inputs.

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