

RESEARCH LETTER

10.1002/2017GL072748

Key Points:

- Novel Cd isotope composition data for aerosols are presented addressing an important gap in understanding of the global Cd cycle
- Similar Cd isotope compositions are observed for aerosols dominated by mineral dust-derived and anthropogenic Cd
- These results provide useful constraints for studies concerning the marine biogeochemical Cd cycle

Supporting Information:

- Supporting Information S1
- Text S1

Correspondence to:

L. Bridgestock,
luke.bridgestock@earth.ox.ac.uk

Citation:

Bridgestock, L., M. Rehkämper, T. van de Flierdt, K. Murphy, R. Khondoker, A. R. Baker, R. Chance, S. Strekopytov, E. Humphreys-Williams, and E. P. Achterberg (2017), The Cd isotope composition of atmospheric aerosols from the Tropical Atlantic Ocean, *Geophys. Res. Lett.*, *44*, doi:10.1002/2017GL072748.

Received 24 JAN 2017

Accepted 13 MAR 2017

Accepted article online 20 MAR 2017

©2017. The Authors.

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

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

Luke Bridgestock^{1,2} , Mark Rehkämper¹ , Tina van de Flierdt¹ , Katy Murphy¹ , Roulin Khondoker¹ , Alex R. Baker³ , Rosie Chance^{3,4} , Stanislav Strekopytov⁵ , Emma Humphreys-Williams⁵ , and Eric P. Achterberg⁶ 

¹Department of Earth Science and Engineering, Imperial College London, London, UK, ²Now at Department of Earth Sciences, University of Oxford, Oxford, UK, ³School of Environmental Sciences, University of East Anglia, Norwich, UK, ⁴Now at Wolfson Atmospheric Chemistry Laboratory, Department of Chemistry, University of York, York, UK, ⁵Imaging and Analysis Centre, Natural History Museum, London, UK, ⁶Geomar-Helmholtz Centre for Ocean Research, Kiel, Germany

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 [Raes *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 ~10⁴–10⁵ years, reflecting its internal cycling [Simpson, 1981]. Therefore, recent external anthropogenic Cd inputs are unlikely to have significantly

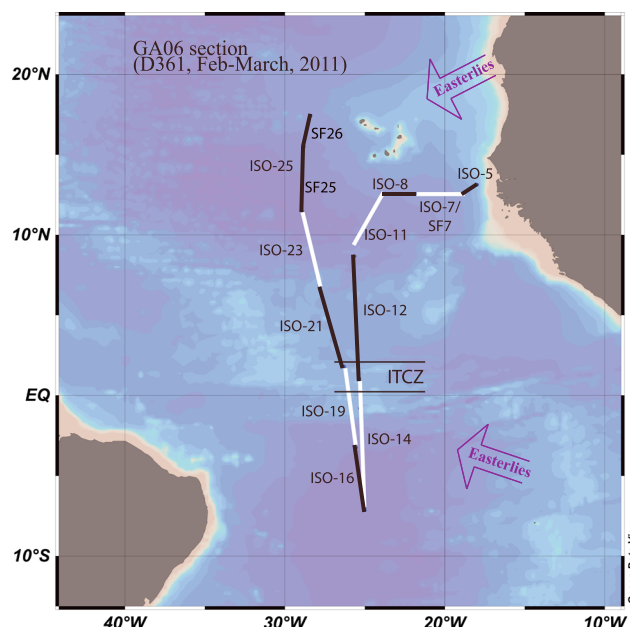


Figure 1. Map of aerosol sampling locations. Samples were collected during the GEOTRACES GA06 section cruise (D361, February–March 2011) on board the RRS Discovery. The white and black stretches indicate the area over which the samples were collected, with “ISO” and “SF” denoting nonsize-fractionated and size-fractionated aerosols, respectively. The purple arrows display the main meteorological regimes, while the thin black lines denote the position of the Intertropical Convergence Zone during the cruise. Figure was produced by using Ocean Data View [Schlitzer, 2015].

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, Chrastný *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 ($1 \text{ m}^3 \text{ min}^{-1}$) [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-21a_{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 ε^{114/110}Cd values relative to NIST 3108 Cd (equation (1)) [Abouchami *et al.*, 2013].

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

The raw isotopic ratios were processed off-line to calculate ε^{114/110}Cd 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 DS mixtures, which was ± 1 to ± 2 $\epsilon^{114/110}\text{Cd}$ (2SD; 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; Wiggenghauser *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 ($X/\text{Al}_{\text{sample}}$) to that of the upper continental crust (X/Al_{ucc}) (equation (2)). Crustal ratios are taken from Rudnick and Gao [2003].

$$\text{EF}_{\text{crust}} = (X/\text{Al}_{\text{sample}})/ (X/\text{Al}_{\text{ucc}}) \quad (2)$$

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 $\epsilon^{114/110}\text{Cd} = -1.9$ to 1.9, except for ISO-16_{Leachr}, characterized by $\epsilon^{114/110}\text{Cd} = -5.4 \pm 1.3$ (Table S2 and Figure 2g). This latter leachate subsample features 2.8 times more Cd than the corresponding total digest, ISO-16_{Total}. 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-21_{Total} (ISO-21a_{Total} and ISO-21b_{Total}) 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-16_{Leachr}, between 51 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

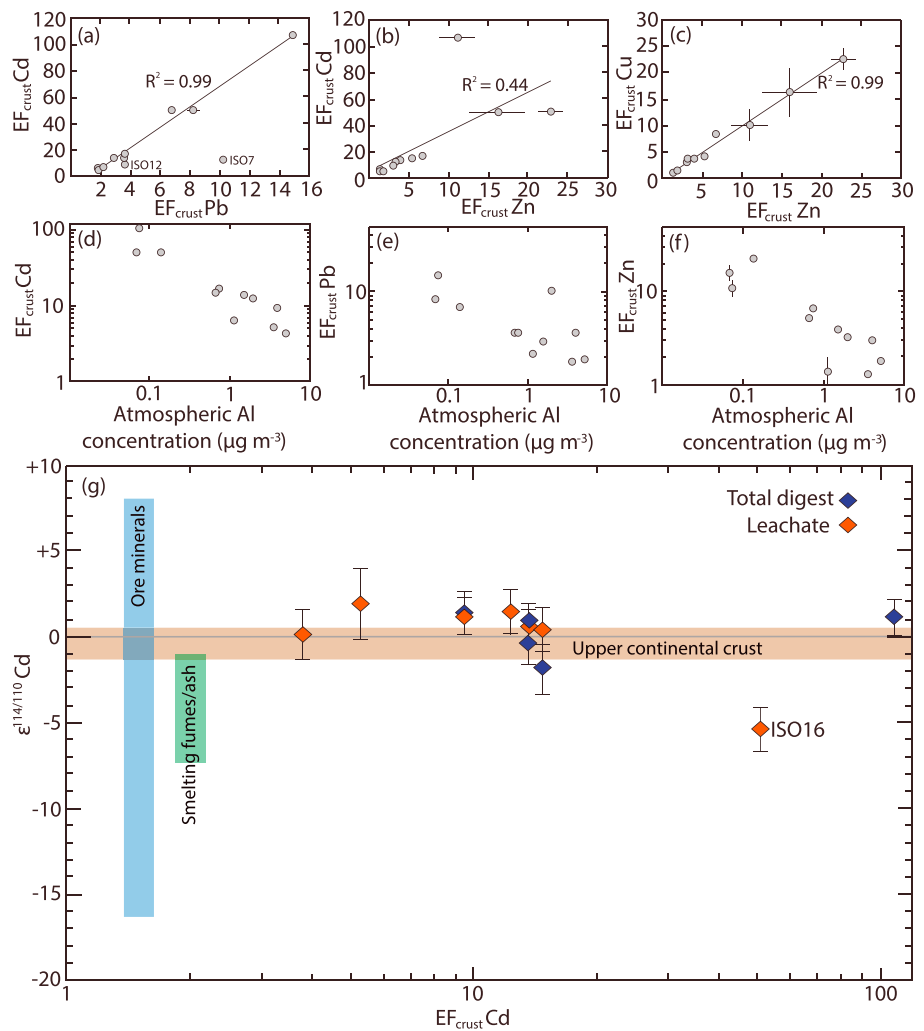


Figure 2. Trace metal enrichment factors and Cd isotope composition of the samples. (a–c) The relationships between the EF_{crust} values for Cd, Pb, Zn, and Cu. Two anomalous samples (ISO-7 and ISO-12), which record anthropogenic Pb sourced from leaded petrol usage, are labeled and omitted from the regression of EF_{crust} values for Cd versus Pb in Figure 2a [Bridgestock et al., 2016]. (d–f) The relationships between trace metal EF_{crust} values and atmospheric Al concentrations, a proxy for atmospheric mineral dust concentrations. (g) Cd isotope compositions for the total aerosol digests and leachate subsamples as a function of Cd enrichment factors. For leachate subsamples, the EF_{crust} values of the corresponding total digests are plotted. The colored bars denote the Cd isotope compositions of the upper continental crust [Schmitt et al., 2009], fumes/ash from metal smelting operations [Cloquet et al., 2006; Shiel et al., 2010; Chrastrý et al., 2015], and ore minerals [Wombacher et al., 2003; Shiel et al., 2010; Zhu et al., 2013; Chrastrý et al., 2015; Wen et al., 2015, 2016; Zhu et al., 2016; Martinková et al., 2016].

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 ≈ 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 ≈ 9–17 are likely to contain anthropogenic Cd contributions of at least 50–60%, assuming that a value of ~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).

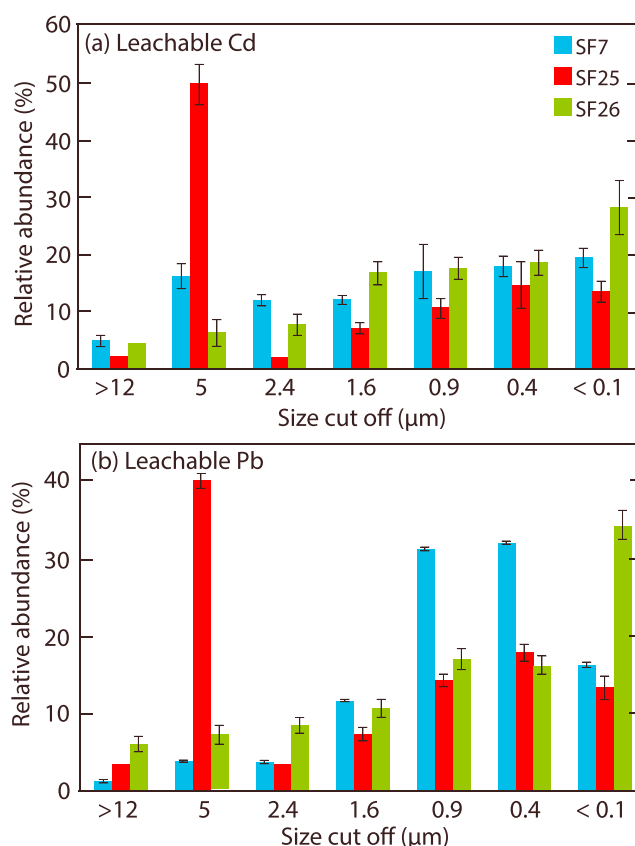


Figure 3. Distributions of leachable Pb and Cd contents for the different size fractions of samples SF7, SF25, and SF26. The calculation of relative trace metals abundances between the size fractions for subsamples where trace metal contents were below the limits of detection, assumed a maximum possible value (i.e., the value of the detection limit). The latter procedure generates uncertainties of $\leq 3\%$ in relative abundances, similar to or smaller than the analytical uncertainty.

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_{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 $<1 \mu\text{m}$, while natural mineral dust is mainly composed of particles $>1 \mu\text{m}$ [e.g., Fomba et al., 2012]. The higher proportions of leachable Cd and Pb that reside in the sub- $1 \mu\text{m}$ 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- $1 \mu\text{m}$ 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_{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 $5 \mu\text{m}$ 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].

Comparison of EF_{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_{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_{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).

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 $\epsilon^{114/110}\text{Cd} = -0.1 \pm 0.7$ (mean \pm 2 SD) [Schmitt *et al.*, 2009; Rehkämper *et al.*, 2012]. North African mineral dust is therefore also likely characterized by $\epsilon^{114/110}\text{Cd} \approx 0$, 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 $\epsilon^{114/110}\text{Cd}$ values between -16 and 8 [Wombacher *et al.*, 2003; Shiel *et al.*, 2010; Zhu *et al.*, 2013; Chrastrý *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 $\epsilon^{114/110}\text{Cd}$ 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 [Chrastrý *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 $\epsilon^{114/110}\text{Cd}$ 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, Wiggerhauser *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 $\epsilon^{114/110}\text{Cd}$ values of 1 to 18 [Yang *et al.*, 2015]. In contrast, subsample ISO-16_{Leach}, with significant quantities of anthropogenic Cd, exhibits a distinctly low $\epsilon^{114/110}\text{Cd}$ value of -5.4 (Figure 2g). This is the only aerosol analyzed for Cd isotopes that was collected south of the ITCZ, 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 $\epsilon^{114/110}\text{Cd}$ values of -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 isotope 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.

Acknowledgments

The captain, crew, and cruise participants of the RSS *Discovery* during the D361 cruise are thanked for their role in this study, along with Katharina Kreissig and Barry Coles for their technical support. All relevant trace metal abundance and Cd isotope data for the aerosol samples are provided in the supporting information. Authors acknowledge funding from the NERC grants NE/J021636/1 and NE/H005390/1 for L. B. M.R., and T. v.d.F.; NE/G016585/1 for R. C. and A.B.; and NE/G015732/1 for E.P.A. There are no competing financial interests.

References

- Abouchami, W., S. J. G. Galer, H. J. W. de Baar, A. C. Alderkamp, R. Middag, P. Laan, and M. O. Andreae (2011), Modulation of the Southern Ocean cadmium isotope signature by ocean circulation and primary productivity, *Earth Planet. Sci. Lett.*, *305*, 83–91.
- Abouchami, W., S. J. G. Galer, T. J. Horner, M. Rehkämper, F. Wombacher, Z. C. Xue, and P. F. Holdship (2013), A common reference material for cadmium isotope studies—NIST SRM 3108, *Geostandards Geoanal. Res.*, *37*, 5–17.
- Abouchami, W., S. J. G. Galer, H. J. W. de Baar, R. Middag, D. Vance, Y. Zhao, and M. O. Andreae (2014), Biogeochemical cycling of cadmium isotopes in the Southern Ocean along the Zero Meridian, *Geochim. Cosmochim. Acta*, *127*, 348–367.
- Boyle, E. A., F. Sclater, and J. M. Edmond (1976), Marine geochemistry of cadmium, *Nature*, *263*, 42–44.
- Bridgestock, L., et al. (2016), Return of naturally sourced Pb to Atlantic surface waters, *Nat. Commun.*, *7*, 12,921, doi:10.1038/NCOMMS12921.
- Bruland, K. W. (1980), Oceanographic distributions of cadmium, zinc, nickel, and copper in the North Pacific, *Earth Planet. Sci. Lett.*, *47*, 176–198.
- Chance, R., T. D. Jickells, and A. R. Baker (2015), Atmospheric trace metal concentrations, solubility and deposition fluxes in remote marine air over the south-east Atlantic, *Mar. Chem.*, *177*, 45–56.
- Cheng, K., H. Z. Tian, D. Zhao, L. Lu, Y. Wang, J. Chen, and Z. Huang (2014), Atmospheric emission inventory of cadmium from anthropogenic sources, *Int. J. Environ. Sci. Tech.*, *11*, 605–616.
- Chester, R., M. Nimmo, M. Alarcon, C. Saydam, K. J. T. Murphy, G. S. Sanders, and P. Corcoran (1993), Defining the chemical character of aerosols from the atmosphere of the Mediterranean Sea and surrounding regions, *Oceanol. Acta*, *16*, 231–246.
- Chester, R., S. Keyse, and M. Nimmo (1996), The influence of Saharan and Middle Eastern desert-derived dust on the trace metal composition of Mediterranean aerosols and rainwaters: An overview, in *The Impact of Desert Dust Across the Mediterranean*, pp. 253–273, Springer, Netherlands.
- Chrastrý, V., E. Cadkova, A. Vanek, L. Teper, J. Cabala, and M. Komarek (2015), Cadmium isotope fractionation within the soil profile complicates source identification in relation to Pb-Zn mining and smelting processes, *Chem. Geol.*, *405*, 1–9.
- Cloquet, C., J. Carignan, G. Libourel, T. Sterckeman, and E. Perdrix (2006), Tracing source pollution in soils using cadmium and lead isotopes, *Environ. Sci. Technol.*, *40*, 2525–2530.
- Conway, T. M., and S. G. John (2015), Biogeochemical cycling of cadmium isotopes along a high-resolution section through the North Atlantic Ocean, *Geochim. Cosmochim. Acta*, *148*, 269–283.
- Diaz-Somoano, M., S. Unterberger, and K. R. G. Hein (2006), Prediction of trace element volatility during co-combustion processes, *Fuel*, *85*, 1087–1093.
- Duce, R. A., et al. (1991), The atmospheric input of trace species to the world ocean, *Global Biogeochem. Cycles*, *5*, 193–259, doi:10.1029/91GB01778.
- Erel, Y., U. Dayan, R. Rabi, Y. Rudich, and M. Stein (2006), Trans boundary transport of pollutants by atmospheric mineral dust, *Environ. Sci. Technol.*, *40*, 2996–3005.
- Fomba, K. A., K. Muller, D. van Pinxteren, and H. Herrmann (2012), Aerosol size-resolved trace metal composition in remote northern tropical Atlantic marine environment: Case study Cape Verde Islands, *Atmos. Chem. Phys. Discuss.*, *12*, 29,535–29,569.
- Gao, B., Y. Liu, K. Sun, X. R. Liang, P. Peng, G. Sheng, and J. Fu (2008), Precise determination of cadmium and lead isotopic compositions in river sediments, *Anal. Chim. Acta*, *612*, 114–120.
- Gao, B., H. D. Zhou, X. R. Liang, and X. L. Tu (2013), Cd isotopes as a potential source tracer of metal pollution in river sediments, *Environ. Pollut.*, *181*, 340–343.
- Gelado-Caballero, M. D., P. Lopez-Garcia, S. Prieto, M. D. Patey, C. Collado, and J. J. Hernandez-Brito (2012), Long-term aerosol measurements in Gran Canaria, Canary Islands: Particle concentration, sources and elemental composition, *J. Geophys. Res.*, *117*, D03304, doi:10.1029/2011JD016646.
- Guerzoni, S., E. Molinaroli, P. Rossini, G. Rampazzo, G. Quarantotto, G. De Falco, and S. Cristini (1999), Role of desert aerosol in metal fluxes in the Mediterranean area, *Chemosphere*, *39*, 229–246.
- Hsu, S. C., F. J. Lin, and W. L. Jeng (2005), Seawater solubility of natural and anthropogenic metals within ambient aerosols collected from Taiwan coastal sites, *Atmos. Environ.*, *39*, 3989–4001.
- Janssen, D. J., T. M. Conway, S. G. John, J. R. Christian, D. I. Kramer, T. F. Pedersen, and J. T. Cullen (2014), Undocumented water column sink for cadmium in open ocean oxygen-deficient zones, *Proc. Natl. Acad. Sci. U.S.A.*, *111*, 6888–6893.
- Jickells, T. D., A. R. Baker, and R. Chance (2016), Atmospheric transport of trace elements and nutrients to the oceans, *Philos. Trans. R. Soc. A*, *374*, 20150286, doi:10.1098/rsta.2015.0286.
- Koçak, M., N. Kubilay, B. Herut, and M. Nimmo (2005), Dry atmospheric fluxes of trace metals (Al, Fe, Mn, Pb, Cd, Zn, Cu) over the Levantine Basin: A refined assessment, *Atmos. Environ.*, *39*, 7330–7341.
- Lambelet, M., M. Rehkämper, T. V. de Flierd, Z. C. Xue, K. Kreissig, B. Coles, and P. Andersson (2013), Isotopic analysis of Cd in the mixing zone of Siberian rivers with the Arctic Ocean—New constraints on marine Cd cycling and the isotope composition of riverine Cd, *Earth Planet. Sci. Lett.*, *361*, 64–73.

- Marple, V. A., and K. Willeke (1976), Impactor design, *Atmos. Environ.*, *10*, 891–896.
- Martinková, E., V. Chrástří, M. Francová, A. Šípková, J. Čuřík, O. Myška, and L. Mižič (2016), Cadmium isotope fractionation of materials derived from various industrial processes, *J. Hazard. Mater.*, *302*, 114–119.
- Murphy, K., M. Rehkämper, K. Kreissig, B. Coles, and T. van de Flierdt (2016), Improvements in Cd stable isotope analysis achieved through use of liquid-liquid extraction to remove organic residues from Cd separates obtained by extraction chromatography, *J. Anal. At. Spectrom.*, *31*, 319–327, doi:10.1039/C5JA00115C.
- Nriagu, J. O., and J. M. Pacyna (1988), Quantitative assessment of worldwide contamination of air, water and soils by trace metals, *Nature*, *333*, 134–139.
- Pacyna, J. M., and E. G. Pacyna (2001), An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide, *Environ. Rev.*, *9*, 296–298.
- Pacyna, J. M., E. G. Pacyna, and W. Aas (2009), Changes of emissions and atmospheric deposition of mercury, lead, and cadmium, *Atmos. Environ.*, *43*, 117–127.
- Patey, M. D., E. P. Achterberg, M. J. Rijkenberg, and R. Pearce (2015), Aerosol time-series measurements over the tropical Northeast Atlantic Ocean: Dust sources, elemental compositions and mineralogy, *Mar. Chem.*, *174*, 103–119, doi:10.1016/j.marchem.2015.06.004.
- Powell, C. F., A. R. Baker, T. D. Jickells, H. W. Bange, R. J. Chance, and C. Yodle (2015), Estimation of the atmospheric flux of nutrients and trace metals to the Eastern Tropical North Atlantic Ocean, *J. Atmos. Sci.*, *72*, 4029–4075.
- Raes, F., R. Van Dingenen, E. Vignati, J. Wilson, J. P. Putaud, J. H. Seinfeld, and P. Adams (2000), Formation and cycling of aerosols in the global troposphere, *Atmos. Environ.*, *34*, 4215–4240.
- Rehkämper, M., F. Wombacher, T. J. Horner, and Z. Xue (2012), Natural and anthropogenic Cd isotope variations, in *Handbook of Environmental Isotope Geochemistry*, pp. 125–154, Springer, Berlin.
- Ripperger, S., and M. Rehkämper (2007), Precise determination of cadmium isotope fractionation in seawater by double spike MC-ICPMS, *Geochim. Cosmochim. Acta*, *71*, 631–642.
- Ripperger, S., M. Rehkämper, D. Porcelli, and A. N. Halliday (2007), Cadmium isotope fractionation in seawater—A signature of biological activity, *Earth Planet. Sci. Lett.*, *261*, 670–684.
- Rudnick, R., and S. Gao (2003), 3.01—Composition of the continental crust, in *Treatise on Geochemistry*, vol. 3, edited by H. D. Holland and K. K. Turekian, pp. 1–64, Pergamon, Oxford.
- Sangster, D. F., P. M. Outridge, and W. J. Davis (2000), Stable lead isotope characteristics of lead ore deposits of environmental significance, *Environ. Rev.*, *8*, 115–147.
- Schlitzer, R. (2015), Ocean Data View. [Available at <http://odv.awi.de>.]
- Schmitt, A. D., S. J. G. Galer, and W. Abouchami (2009), Mass-dependent cadmium isotopic variations in nature with emphasis on the marine environment, *Earth Planet. Sci. Lett.*, *277*, 262–272.
- Shen, G. T., E. A. Boyle, and D. W. Lea (1987), Cadmium in corals as a tracer of historical upwelling and industrial fallout, *Nature*, *328*, 794–796.
- Shiel, A. E., D. Weis, and K. J. Orians (2010), Evaluation of zinc, cadmium and lead isotope fractionation during smelting and refining, *Sci. Total Environ.*, *408*, 2357–2368.
- Shiel, A. E., D. Weis, and K. J. Orians (2012), Tracing cadmium, zinc and lead sources in bivalves from the coasts of western Canada and the USA using isotopes, *Geochim. Cosmochim. Acta*, *76*, 175–190.
- Shiel, A. E., D. Weis, D. Cossa, and K. J. Orians (2013), Determining provenance of marine metal pollution in French bivalves using Cd, Zn and Pb isotopes, *Geochim. Cosmochim. Acta*, *121*, 155–167.
- Simpson, W. R. (1981), A critical review of cadmium in the marine environment, *Prog. Oceanogr.*, *10*, 1–10.
- Wen, H. J., Y. X. Zhang, C. Cloquet, C. W. Zhu, H. F. Fan, and C. G. Luo (2015), Tracing sources of pollution in soils from the Jinding Pb-Zn mining district in China using cadmium and lead isotopes, *Appl. Geochem.*, *52*, 147–154.
- Wen, H., C. Zhu, Y. Zhang, C. Cloquet, H. Fan, and S. Fu (2016), Zn/Cd ratios and cadmium isotope evidence for the classification of lead-zinc deposits, *Sci. Rep.*, doi:10.1038/srep25273.
- Wiggenhauser, M., M. Bigalke, M. Imseng, M. Müller, A. Keller, K. Murphy, K. Kreissig, M. Rehkämper, W. Wilcke, and E. Frossard (2016), Cadmium isotope fractionation in soil-wheat systems, *Environ. Sci. Technol.*, *50*, 9223–9231.
- Wombacher, F., M. Rehkämper, K. Mezger, and C. Munker (2003), Stable isotope compositions of cadmium in geological materials and meteorites determined by multiple-collector ICPMS, *Geochim. Cosmochim. Acta*, *67*, 4639–4654.
- Wombacher, F., M. Rehkämper, and K. Mezger (2004), Determination of the mass-dependence of cadmium isotope fractionation during evaporation, *Geochim. Cosmochim. Acta*, *68*, 2349–2357.
- Xue, Z. C., M. Rehkämper, M. Schonbachler, P. J. Statham, and B. J. Coles (2012), A new methodology for precise cadmium isotope analyses of seawater, *Anal. Bioanal. Chem.*, *402*, 883–893.
- Xue, Z. C., M. Rehkämper, T. J. Horner, W. Abouchami, R. Middag, T. van de Flierdt, and H. J. W. de Baar (2013), Cadmium isotope variations in the Southern Ocean, *Earth Planet. Sci. Lett.*, *382*, 161–172.
- Yang, S. C., D. C. Lee, and T. Y. Ho (2012), The isotopic composition of cadmium in the water column of the South China Sea, *Geochim. Cosmochim. Acta*, *98*, 66–77.
- Yang, S. C., D. C. Lee, and T. Y. Ho (2014), The isotopic composition of dissolved cadmium in the water column of the West Philippine Sea, *Front. Mar. Sci.*, *1*, 61, doi:10.3389/fmars.2014.00061.
- Yang, S. C., D. C. Lee, and T. Y. Ho (2015), Cd isotope composition in the aerosols of the South China Sea, *Goldschmidt Abstr.*, *2015*, 3507.
- Yi, W., A. N. Halliday, D.-C. Lee, and M. Rehkämper (1998), Precise determination of cadmium, indium and tellurium using multiple collector ICP-MS, *Geostand. Newsl.*, *22*, 173–179, doi:10.1111/j.1751-908X.1998.tb00689.x.
- Zhu, C., H. Wen, Y. Zhang, H. Fan, S. Fu, J. Xu, and T. Qin (2013), Characteristics of Cd isotopic compositions and their genetic significance in the lead-zinc deposits of SW China, *Sci. China Earth Sci.*, *56*, 2056–2065.
- Zhu, C., H. Wen, Y. Zhang, and H. Fan (2016), Cadmium and sulfur isotopic compositions of the Tianbaoshan Zn-Pb-Cd deposit, Sichuan Province, China, *Ore Geol. Rev.*, *76*, 152–162.