Isotope Tracing of Long-Term Cadmium Fluxes in an Agricultural Soil

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S Supporting Information

ABSTRACT: Globally widespread phosphate fertilizer applications have resulted in long-term increases in the concentration of cadmium (Cd) in soils. The accumulation of this biotoxic, and bioaccumulative metal presents problems for the management of soil-plant-animal systems, because the magnitude and direction of removal fluxes (e.g., crop uptake, leaching) have been difficult to estimate. Here, Cd isotopic compositions ($\delta^{114/110}$Cd) of archived fertilizer and soil samples from a 66 year-long agricultural field trial in Winchmore, New Zealand, were used to constrain the Cd soil mass balance between 1959 and 2015 AD, informing future soil Cd accumulation trajectories. The isotopic partitioning of soil Cd sources in this system was aided by a change in phosphate source rocks in 1998 AD, and a corresponding shift in fertilizer isotope composition. The dominant influence of mixing between isotopically distinct Cd end-members was confirmed by a Bayesian modeling approach. Furthermore, isotope mass balance modeling revealed that Cd removal processes most likely increased in magnitude substantially between 2000 and 2015 AD, implying an increase in Cd bioaccumulation and/or leaching over that interval. Natural-abundance stable isotopes are introduced here as a powerful tool for tracing the fate of Cd in agricultural soils, and potentially the wider environment.
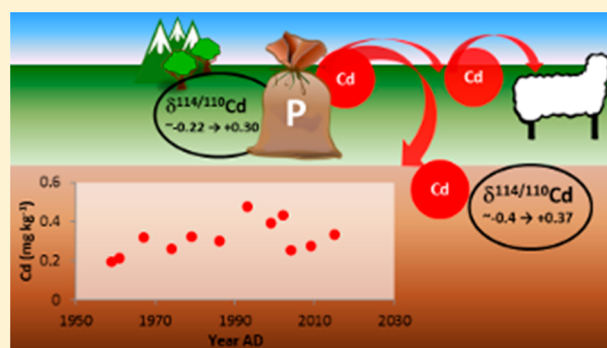
INTRODUCTION

Cadmium (Cd) is a harmful metal that has accumulated in agricultural soils, mainly as a result of phosphate fertilizer applications.[1−5] Cadmium is a natural contaminant in phosphate source rocks[6] which persists in fertilizers and can accumulate in soils, plants and higher organisms. In 1997 AD, responding to concerns over Cd accumulation in agricultural soils, the New Zealand (NZ) fertilizer industry changed the main source of phosphate fertilizers from Nauru (guano-derived) phosphorite (about 450 mg Cd kg⁻¹ P) to a mixture of new sources including Moroccan source rocks, with the effect of lowering Cd concentrations in fertilizers. Since 1997 AD, fertilizers produced in NZ have had no more than 280 mg Cd kg⁻¹ P.[7,8]

Research on long-term Cd accumulation trends in soils benefits from field trials run over several decades with continuity of land-management practice. A recent study addressing Cd concentration in soils from the long-term Winchmore field trial in New Zealand showed that the rate of Cd accumulation started to reach a plateau in the period since ∼2000 AD.[9] This indicated that post 2000 AD, Cd inputs in fertilizers were lower than outputs from the soil zone (leaching, plant uptake). However, the extent to which the soil Cd burden (after 2000 AD) was from historical or recent fertilizer applications remained in question.

Stable isotope ratio analysis is a powerful tool for the source identification of environmental contaminants, assuming that end-members are isotopically distinct and isotope fractionations are small and/or well constrained. This approach is increasingly being applied to the study of the origin, and environmental history of heavy metals and other anthropogenic contaminants,[10,11] including in atmospheric aerosols,[12,13] water,[14−16] sediment[17−20] and soil[14,21−26] and even materials as diverse as meteorites and lunar soil.[27,28] Cadmium stable isotopes are being more routinely applied to the study of cadmium's environmental mobility and fate,[29] and can also inform the biogeochemistry of the soil−plant system including plant-uptake of Cd,[11] which has been shown to fractionate Cd between soil and wheat, with preferential accumulation of lighter isotopes over heavier isotopes in roots relative to grain.

Difficulties in the management of Cd accumulation in agricultural soils are currently compounded by uncertainty over

the sources of Cd, since routine Cd monitoring is a comparatively recent phenomenon. It is also difficult to evaluate the effect that management strategies have on the accumulation of Cd and delineate whether changes in the total Cd pool reflect historical, or more recent Cd additions. Therefore, the objective of this research was to evaluate the utility of Cd stable isotope ratios as a tracer of Cd sources in soil samples from the long-term Winchmore field trial, where annual superphosphate (a manufactured P fertilizer) applications began in ca. 1949 and have continued to the present day. Based on the Cd isotopic composition of the control site subsoil (approximating native soil−Cd), topsoil samples from the Winchmore archive, as well as historical and recent fertilizers, we calculated the changing proportion of Cd in Winchmore topsoil through time using a Bayesian mixing model. This approach was extended using an isotope-enabled Cd mass balance to evaluate the influence of fertilizer inputs and removal mechanisms on Cd accumulation through time.

■ MATERIALS AND METHODS

Study site. Soil samples were taken from the Winchmore research farm on the Canterbury Plains of the South Island, New Zealand (43° 47 S, 171° 48 E, 167 m above sea level, annual rainfall 740 mm/yr[9]). The soil at Winchmore is Lismore Stony Silt loam (Orthic Brown [New Zealand], Udic Ustochrept [USDA]) which is developed from moderately weathered greywacke loess.[9] The selected physical and chemical characteristics of the soil including pH, organic carbon, nitrogen and soil texture were reported by Condron and Goh.[30] The soil is developed on outwash plains formed by the weathering of the Southern Alps, which are dominantly composed of greywacke sandstone gravels, stratigraphically defined as Paleosols.[31] Two different trials were conducted at Winchmore: long-term fertilizer and long-term irrigation trials that were established in 1952 and 1949, respectively. For the irrigation trial, 250 kg ha^{-1} of superphosphate was applied annually, but irrigation was applied at different soil moisture trigger values (dryland treatment with no irrigation, 10% moisture and 20% moisture). Soil samples were selected from the top 7.5 cm of the irrigation trial (dryland treatment; plot 15) from 1959, 1961, 1967, 1974, 1979, 1993, 1999, 2002 (Waikato University Archive), 2004, and 2009 (courtesy of Richard McDowell, AgResearch), and an additional sample was collected in 2015. One control plot soil sample from unfertilized (native) soil was taken from the subsurface layer (25−30 cm depth) of an adjacent paddock which has the same geology and was expected to have a similar chemical composition to the topsoils (before fertilization). Phosphate rock and fertilizer samples were obtained from Ballance Agri-Nutrients Ltd. (Tauranga, New Zealand), including samples from Nauru and Christmas Island (main sources of phosphorite for phosphate fertilizer manufacture prior to 1997 AD[8]), fertilizer from the mid-1980s, and archived fertilizers from 1998, 2000, 2001, 2005, 2007, 2009, 2011, 2013, and 2015 (all used in the Winchmore trials) were also analyzed. Isotopic analyses were performed on two independently chemically processed aliquots of each sample of soil, phosphorite or fertilizer, with the exception of fertilizers from 1998, 2001, 2005, 2011, and 2013, for which just one sample was analyzed for isotopic composition.

Cadmium Concentration and Isotopic Composition Analysis of Soils and Fertilizers. All samples were dried and sieved (<2 mm) and then digested using a method described in

Salmanzadeh et al.[32] with some minor modifications: The reagents were pipetted out of the polypropylene tube without any filtration and transferred to clean polypropylene tubes for ICP-MS analysis at the University of Waikato. The samples were not filtered in order to avoid any introduction of Cd from filter papers.[33,34] To avoid any contamination, sample preparation was carried out in a class-100 laminar flow hood. Also, all sample tubes and vials were thoroughly acid-washed in clean reagent grade HCl at room temperature, then in 50% quartz distilled HCl (overnight). Finally all lab-ware was rinsed thoroughly (5 times with Milli-Q deionized water). All acids were purified in a Savillex DST-1000 acid purification system to parts-per-trillion (ppt)-grade (Cd blank <100 ppt). Cadmium concentration was determined by using a quadrupole ICP-MS (PerkinElmer Elan, Waltham, MA) at University of Waikato, New Zealand following calibration using NIST-traceable standards (Inorganic Ventures, Christiansburg, VA, USA).

After measuring the concentration of Cd, aliquots of each sample digest, corresponding to approximately 50 ng of Cd, were transferred to University of Otago, New Zealand for isotopic analysis following a double-spike method (full methods provided in Supporting Information (SI) Methods 1, Table S1).

Cadmium isotopic composition is generally expressed as the deviation of $^{114}Cd/^{110}Cd$ ratio of a sample with respect to the $^{114}Cd/^{110}Cd$ composition of a standard in parts per-thousand ($\delta^{114/110}Cd$) (eq 1). In this study, Cd isotopic composition was measured by multiple-collector ICP-MS (MC-ICPMS) using a Nu Plasma-HR instrument (Nu Instruments Ltd., U.K.) and methods modified from previous protocols.[35,36] A DSN 100 desolvating nebulizer fitted with a ∼100 μL/min perfluoroalkoxy (PFA) nebulizer was used as the sample introduction system. The NIST 3108 Cd isotope standard sourced from the National Institute of Science and Technology (NIST), U.S., was used as the "zero delta" normalizing standard.[37] Repeat measurements of the NIST 3108 standard give rise to an external reproducibility of 0.04 δ that is comparable to the 2 SE internal precision associated with individual measurements (SI Figure S1). Using these protocols, standard reference materials give values that are identical, within error, to certified values.[35−38]

$$\delta^{114/110}Cd = \left[\frac{(^{114}Cd/^{110}Cd)_{sample}}{(^{114}Cd/^{110}Cd)_{NIST3108}} - 1 \right] \cdot 1000 \tag{1}$$

All Cd concentrations reported in this study were determined by isotope dilution using eq 2:

$$[Cd]_{sample} = \frac{\left(\frac{^{114}Cd}{^{111}Cd}\right)_{mixture} - \left(\frac{^{114}Cd}{^{111}Cd}\right)_{spike}}{\left(\frac{^{114}Cd}{^{111}Cd}\right)_{sample} - \left(\frac{^{114}Cd}{^{111}Cd}\right)_{mixture} \cdot \frac{mass\ of\ spike}{mass\ of\ sample} \cdot \frac{[^{111}Cd]_{spike}}{fraction\ of\ ^{111}Cd\ in\ the\ sample}} \tag{2}$$

where $^{114}Cd/^{111}Cd_{mixture}$, $^{114}Cd/^{111}Cd_{sample}$, and $^{114}Cd/^{111}Cd_{spike}$ are the $^{114}Cd/^{111}Cd$ ratios of the spike-sample mixture, sample and double spike, respectively, after correction for the instrumental mass bias, while $[^{111}Cd]_{spike}$ is the concentration of ^{111}Cd in the double spike and $[Cd]_{sample}$ is the Cd concentration of the sample.

Sequential Extraction Method. In an attempt to constrain the Cd speciation in the Winchmore soil system, the topsoil collected in 2015 (two replicates) was sequentially

extracted following the method of Sun et al.[39] (full method provided in SI Methods 2, Table S2).

Bayesian Mixing Model. Stable isotope data combined with a Bayesian modeling approach have been used before to estimate the contribution of multiple sources of elements in environmental samples.[15,40,41] However, this is the first time this approach has been used for the Cd stable isotope system. We used an open source linear isotopic mixing Bayesian modeling strategy devised by Arendt, Aciego and Hetland[14] to estimate the fractional contribution of different sources of Cd through time. Matlab 2013 was used with code introduced by Arendt, Aciego and Hetland[14] with some modifications: Arendt, Aciego and Hetland[14] defined the code based on the isotope ratios of two different elements (for example $\delta^{18}O$ and δD), but we instead defined the model based on the isotope ratio of a single element ($\delta^{114/110}Cd$). The original Matlab code was configured for three different sources, but we defined only two sources for pre-2000 soils and three sources for post-2000 soils.

pH Adsorption Edge Experiment. pH is the most important variable controlling the adsorption of metals to soil surfaces.[42] Therefore, a pH adsorption edge experiment was carried out to determine the pH-dependency of Cd adsorption on Winchmore topsoil. This experiment followed the method by Lee et al.[43] (full method provided in SI Methods 3, Figure S3). Ideally, this can inform the potential of Cd to adsorb to soil under varying solution pH.

Cadmium Balance (CadBal) Model. A cadmium mass balance model (CadBal) has been available since 2005 in New Zealand, to estimate the potential accumulation of Cd in NZ soils.[7,9] This model estimates the accumulation of Cd based on input data including the initial Cd concentration, farm and soil type, soil dry bulk density, fertilizer application rate, leaching, erosion, and atmospheric accession. We used this model to estimate the future concentration (up to 2030 AD) of Cd in topsoil and to compare our results with those of McDowell[9] who studied the same site and reported a trend toward stabilizing Cd concentrations in the period after 2000 AD. CadBal was used to estimate the concentration of Cd through time based on four scenarios and using two sets of input data (Table 1, SI Table S4).

Isotope Mass Balance Using CadBal Output. An isotope mass balance approach was taken to constrain the importance

Table 1. Mean Concentrations and Isotopic Compositions of Cd in Topsoil (0-7.5 cm), Fertilizer and Phosphorite Samples, And the Control Subsurface Soil (25-30 cm)

sample	Cd (mg kg^{-1})[a]	$\delta^{114/110}Cd \pm 2$ SE
native (unfertilized) subsoil	0.02	−0.33 ± 0.04
topsoil 1959	0.16	0.27 ± 0.04
topsoil 1961	0.22	0.10 ± 0.04
topsoil 1967	0.24	0.20 ± 0.04
topsoil 1974	0.23	0.20 ± 0.04
topsoil 1979	0.25	0.23 ± 0.05
topsoil 1986	0.29	0.14 ± 0.03
topsoil 1993	0.40	0.12 ± 0.04
topsoil 1999	0.35	0.15 ± 0.04
topsoil 2002	0.35	0.16 ± 0.05
topsoil 2004	0.29	0.09 ± 0.05
topsoil 2009	0.29	0.08 ± 0.03
topsoil 2015	0.30	0.15 ± 0.03
fertilizer 1980s	31.8	0.25 ± 0.04
fertilizer 1998	26.4	0.10 ± 0.05
fertilizer 2000	27.0	0.18 ± 0.04
fertilizer 2001	14.6	0.01 ± 0.05
fertilizer 2005	21.0	−0.11 ± 0.05
fertilizer 2007	23.3	−0.11 ± 0.04
fertilizer 2011	15.4	−0.11 ± 0.06
fertilizer 2013	20.6	−0.12 ± 0.05
fertilizer 2015	8.27	−0.17 ± 0.03
nauru phosphorite	96.4	0.22 ± 0.04
Christmas Island phosphorite	38.0	0.12 ± 0.04

[a]Instrumental uncertainties are ±0.9% (2 SE).

of fertilizer inputs to topsoils relative to losses via cropping (i.e., grass growth and grazing) and leaching to groundwater. The input and output terms in this mass balance were constrained using CadBal (see previous section and I Methods 4) which generates loss terms for these vectors. CadBal is able to generate loss terms for erosion and input terms for atmospheric deposition, but these were neglected because of their very low magnitude (see SI Table S4). The resulting mass balance equation is given below (eq 3).

$$[Cd]_{n+1_{soil}} \times \delta_{n+1_{soil}} = ([Cd]_n + \delta_n)_{soil} + ([Cd]_{n_{fert}} + \delta_{n_{fert}})_{inputs} - ([Cd]_{n_{corp}} \times \delta_{n_{crop}} + [Cd]_{n_{teach}} \times \delta_{n_{teach}})_{outputs} \quad (3)$$

δ_n is the isotope ratio of the compartment in per mil, and $[Cd]_n$ is Cd concentration and derived as follows (eq 4):

$$[Cd]_{n+1} = [Cd]_n + (Cd_{input}ha^{-1} - Cd_{output}ha^{-1})_n /$$
$$(bulk\ density \times depth\ ha^{-1}) \quad (4)$$

Isotope fractionation in each input and output term is calculated by multiplying the δ value (e.g., $\delta_{n\ leach}$) by an appropriate α value (e.g., $\alpha_{soil\text{-}leachate}$), where α defines the equilibrium partitioning of Cd isotopes between the reactant and product (eq 5).

$$\delta_a + 1000 = (\delta_b + 1000) \times \alpha_{a-b} \quad (5)$$

This modeling utilized α values taken from Wiggenhauser et al.[11] which were selected on the basis of relevance (i.e., similarity to soil properties). However, the available literature on Cd isotope fractionation factors do not currently cover soil-

grass and soil-water partitioning. Because of this deficiency we have approximated these terms using data from soil-wheat systems and extractable soil solutions $(Ca(NO_3)_2)$,[11] respectively.

RESULTS AND DISCUSSION

Cd Composition of Soils, Fertilizers and Source Rocks. The Cd concentration and Cd isotopic composition of soils, fertilizers and phosphate rocks are presented in Table 1. Where data are available for two independently processed aliquots of the same sample (i.e., true replicate measurements of the soil), both Cd concentration and Cd isotopic composition are reported as the mean of the two replicate analyses with the two standard error of the mean values, calculated using the method of Conway et al.[44] Corresponding data for each individual analysis is given in the SI (see Table S3). Otherwise, data is

reported as the mean value and 2 SE uncertainty for a single analysis, as per standard analytical protocols.

The concentrations of Cd in Nauru and Christmas Island rocks (Table 1) were in the range of previously reported concentrations (86−100 mg kg^{-1} for Nauru and 31−56 mg kg^{-1} for Christmas Island phosphorite[3,8,45−47]). Cadmium concentrations in Winchmore plot-15 topsoils increased across the period 1959−2000 AD from ca. 0.16 to 0.35 mg kg^{-1} (Figure 1a), replicating the change in concentration reported
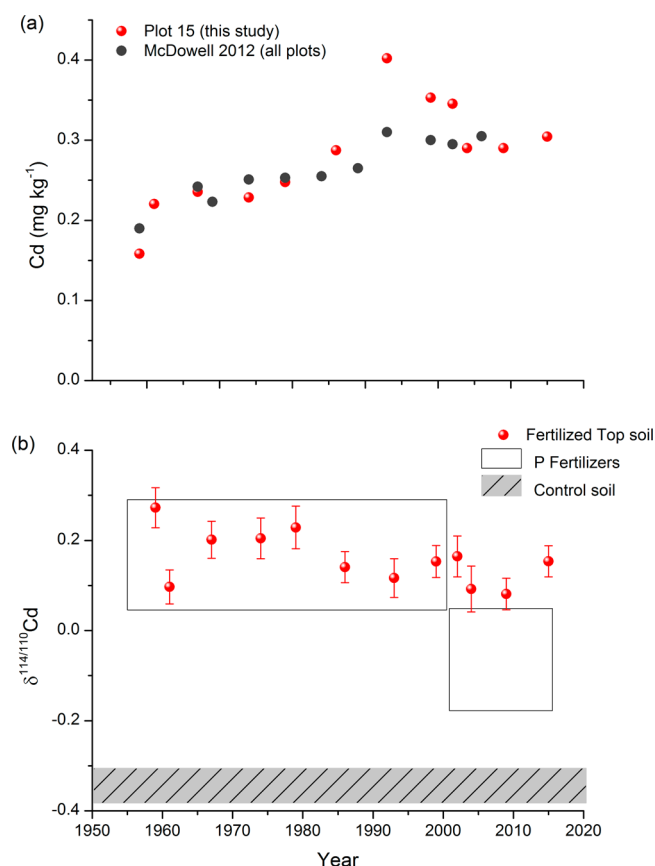

Figure 1. Time series of Cd in topsoil samples from Winchmore (a) data from plot 15 (dryland treatment-this study; error bars are 2 SE range) and data from McDowell[9] representing the mean concentration of Cd in topsoil in all irrigation trial plots (b) the Cd isotope ratios of fertilized soils over the period 1959−2015 (error bars show the 2 SE range of analytical uncertainty in $\delta^{114/110}$Cd values), blank rectangles represent the 2 SE range of isotope ratios from P fertilizer sources before and after 2000 AD, and the hatched rectangle shows the 2 SE range of isotope ratios of the control soil.

across the whole site by McDowell.[9] The Cd isotope ratios of fertilized soil samples were enriched relative to the control site subsoil throughout this interval, and were in the range of $\delta^{114/110}$Cd in pre-2000 (including 2000 AD) fertilizers and phosphorite samples (Table 1, Figure 1); which also fall within the typical range of sedimentary rocks excluding polluted and industrial samples (ranging from −0.4 to +0.4 $\delta^{114/110}$Cd)[48] and loess deposits (ranging from −0.45 to 0.34).[49] Cadmium isotope ratios in the fertilizer and phosphorite samples studied here were all well within these ranges (Table 1).

The ranges of $\delta^{114/110}$Cd in Winchmore topsoils from these time series are comparable to the $\delta^{114/110}$Cd ratios characteristic of pre-2000 AD fertilizer samples. Topsoils were enriched in ^{114}Cd relative to the lower $\delta^{114/110}$Cd of the control site subsoil,

the latter being most consistent with $\delta^{114/110}$Cd observed in some wind-blown (loess) deposits.[48] It was necessary to use the subsoil from the control site at Winchmore to approximate the native soil Cd composition, because Cd in the topsoil of the control site was likely to have been impacted by windblown cross-contamination from adjacent fertilized paddocks and by translocation of fertilizer-derived Cd by grazing ruminants.

The Cd isotope results from Winchmore topsoils indicate that fertilizer applications from ∼1950 AD onward substantially affected the $\delta^{114/110}$Cd of topsoils, such that by 1959 (first data point in our time series) the topsoil Cd concentration and Cd isotope ratio had been substantially modified from the natural situation (approximated by our control (Table 1)). Depleted $\delta^{114/110}$Cd values, presumably characteristic of the original (unfertilized) topsoil, were not observed in the earliest samples from our time series (1959 AD) which were taken a full nine years after the onset of fertilizer application, by which time we argue Cd concentrations and isotope ratios had been shifted substantially. Overall, the Cd isotope ratios of all fertilized soil samples were closest to the Cd isotopic compositions of pre-2000 AD fertilizers (Figure 1), suggesting that pre-2000 AD fertilizers strongly dominated the Cd budget in the Winchmore soils even after 2000 AD. However, this assessment does not account for potential fractionation effects in either fertilizers or soil samples, and this needs to be evaluated before sources can be attributed based on Cd isotope data.

Cadmium Isotope Fractionation in Soil and Fertilizer Samples. To produce a single superphosphate fertilizer (as used at Winchmore throughout the entire trial), finely ground phosphate rocks, largely consisting of fluorapatite ($Ca_5(PO_4)_3F$), are reacted with sulfuric acid and during this process all of the Cd originally present in the phosphate rock is retained within the fertilizer.[50−52] Due to the high volatility and low boiling point (765 °C) of Cd,[29,48,53] large (∼0.6% level) isotope fractionations of Cd can occur during high-temperature industrial processes such as smelting and combustion.[54−56] However, Cd isotopic fractionation characteristics of the aforementioned high-temperature industrial processes, do not appear to occur during phosphate fertilizer manufacture which is carried out under low thermal conditions. This is borne out by a comparison between the $\delta^{114/110}$Cd of pre-2000 AD fertilizers and their Nauru and Christmas Island source rocks (Table 1; Figure 1). The data assembled here indicates that phosphate fertilizers retain an $\delta^{114/110}$Cd composition consistent with the guano-derived phosphorites of Nauru and Christmas Island.[57] This indicates that either no Cd isotopic fractionation occurs during industrial processing, or that all Cd is quantitatively transferred from the phosphate source rock to the superphosphate fertilizer so that no net isotopic fractionation of Cd is observed.

A large degree of Cd isotopic fractionation in soil samples can occur due to biogeochemical processes in soils,[11] therefore the potential for in situ fractionation processes must be considered before mixing models can be used for source identification. Processes within agricultural soils that could cause Cd isotope fractionation include 1. Redox processes: elements usually occurring with one oxidation state (such as Cd) in natural systems tend to exhibit smaller isotopic variations in comparison to other metals with multiple oxidation states.[10] However, Cd has a strong affinity for sulfides, forming in the presence of free H_2S under euxinic (anoxic and sulphidic, rather than anoxic, suboxic or oxic) conditions, so Cd is strongly redox-sensitive in this sense and

potentially fractionates during CdS formation. This is unlikely to be an issue in the free-draining soils of Canterbury, where sulfate reduction is inhibited by atmospheric gas exchange. 2. Adsorption processes: reactions with organic matter and soil mineral surfaces have potential to induce Cd isotopic fractionation.[10] Simulations of Cd isotopic fractionation in hydrothermal fluids between Cd species (cadmium hydroxide, cadmium nitrates, cadmium hydrates, cadmium chloride, and cadmium hydrosulfides) do not support a strong role for Cd speciation,[54,58] although adsorption of Cd to synthetic birnessite (Mn oxyhydroxide) has been shown to cause a small fractionation effect at low ionic strength.[59,60] 3. Biological cycling: plant uptake has been shown to cause Cd isotope fractionation[11] with diffusion and adsorption being largely responsible for Cd fractionation at the root-solution inter-face.[10,61] In addition, permil-level Cd isotopic fractionation (by adsorption of lighter isotopes) has been observed during Cd uptake by phytoplankton (unicellular plants in the sunlit surface ocean).[36,44,62,63] 4. Natural weathering processes can also lead to Cd isotopic fractionation.[64]

The enriched Cd isotopic composition of fertilized soils compared to the native soil show that there was some potential that the Cd isotope ratios in fertilized soils could have been fractionated due to biogeochemical or weathering processes in the soil zone.[11,65,66] The fractionation of Cd isotopes within the fertilized soil samples during biological assimilation (i.e., by in situ bacterial communities, uptake by plant roots, or trans-location in infiltrating soil water) is assessed in the section on Cd mass balance modeling (Mass Balance Modeling of Cd).

Source Identification of Cd. The following analysis takes a simple mixing approach and neglects potential fractionation effects, which are expected to be damped by the significant input signal of fertilizer-derived Cd. This latter point is addressed by mass balance modeling in a later section Mass Balance Modeling of Cd). Large changes in the $\delta^{114/110}$Cd of superphosphate are expected to have imparted changes in residual soil isotope values of a magnitude proportional to the fractional accumulation of Cd (based on the analysis of fertilizers (Table 1)).

Cadmium isotopic differences between end-members can be readily delineated using a $\delta^{114/110}$Cd versus 1/Cd mixing diagram (Figure 2a).[26,29,49] Soils did not align along a single line (Figure 2a) which indicates that Cd in fertilized soil samples originated from at least three different sources (i.e., native soil, pre-2000 AD fertilizer and post-2000 AD fertilizer), and also may have been affected by in situ processes.[29] The $\delta^{114/110}$Cd of control soil did not follow a trendline with the fertilized soil samples, and was well isolated from the soils in terms of both Cd concentration and Cd isotope ratio (Figure 2a).

Bayesian Attribution of Soil Cd Sources. Based on the clear difference between the Cd isotopic end-members identified in this study, a binary mixing model was applied for pre-2000 AD soil samples, and a three-source mixing model was applied for post-2000 AD soil samples (Table 2). Different strategies were considered in selecting the end-members to calculate the fractional contribution of different sources through time (Table 2). Given the relatively small sample size in our set ($N = 26$) we acknowledge that our approach is constrained and would be enhanced by additional replicate measurements. However, the Bayesian approach followed provides the best means of estimating the accompanying errors.
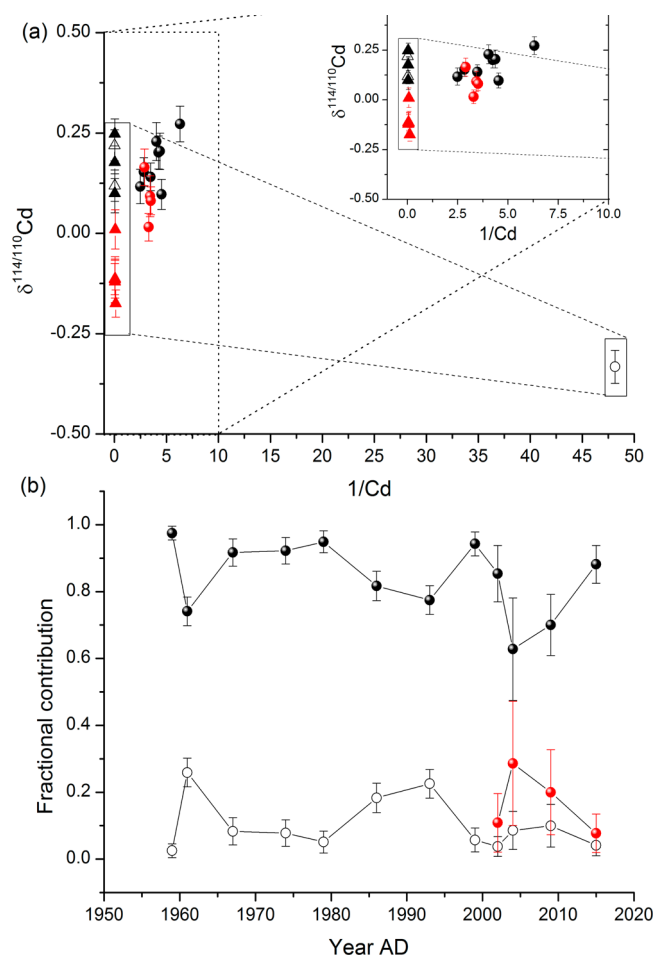

Figure 2. Source partitioning of Cd in Winchmore plot 15 soil samples (a) Cd isotopic composition versus inverse Cd concentration (mg kg^{-1}) of pre-2000 AD (black circle) and post-2000 AD (red circle) soil samples defined by control soil (open circle), phosphate rocks (open triangle), pre-2000 AD fertilizers (black triangle), and post-2000 AD fertilizers (red triangle) (error bars are ±2 SE from the mean); (b) Fractional contribution of different sources of Cd in Winchmore soil samples based on a Bayesian Cd isotope mixing model for pre-2000 AD fertilizers (black circle), post-2000 AD fertilizers (red circle), and control soil (open circle).

The fractional contribution of different sources (Figure 2b) was calculated using a Bayesian mixing model (Arendt, Aciego, and Hetland[14]) which uses the variances of end-member compositions to compute the uncertainty inherent in the fractional contribution of sources. The model assumed that the uncertainties associated with the Cd isotopic compositions of end-members are uncorrelated, normally distributed, and represented by the two standard errors of the measurements. It was also assumed that there are only three possible contributing sources in any one modeled mixture. For pre-2000 AD soil samples, two possible contribution sources were considered, since phosphate fertilizers were mainly sourced from a single Pacific island (Nauru) during this time. For post-2000 AD soils, three different sources were identified (Table 2). The detailed assumptions and limitations inherent in the modeling approach can be found in Arendt, Aciego, and Hetland.[14] These authors showed that the estimations of the fractional contribution of different sources are more precise if the end-member isotopic compositions are distinct from one another, which is the case in the pre-2000 AD Cd isotopic data

Table 2. Different End-Members Considered for Calculation of the Fractional Contribution of Cd Sources through Time in Topsoil Samples

soil	endmember-1	endmember-2 (pre-2000 fertilizer)	endmember-3 (post-2000 fertilizer)
1959−1993	native soil	fertilizer 1980s	
1999	native soil	average of fertilizer 1980s and fertilizer 1998	
2002 and 2004	native soil	average of fertilizers 1980s, 1998 and 2000	fertilizer 2001
2009	native soil	average of fertilizers 1980s, 1998 and 2000	average of fertilizers 2001, 2005 and 2007
2015	native soil	average of fertilizers 1980s, 1998 and 2000	average of fertilizers 2001, 2005, 2007, 2011, 2013, 2015

(Figure 2a). However, because the pre- and post-2000 AD fertilizers were closer in composition than the native soil, this contributed to greater uncertainty in the model. Despite this source of uncertainty, the Bayesin mixing model demonstrates that Cd in the topsoil samples predominantly corresponds to inputs from Nauru-derived (pre-2000 AD) fertilizers. This is particularly clear in the 2015 AD analysis. We can conclude that Cd derived from Nauru continues to predominate in the soil up to the present day.

The mixing model outputs (Figure 2b) show from 2000 AD toward the present, fertilizer $\delta^{114/110}$Cd became increasingly isotopically distinct from the Nauru-derived fertilizers, thus increasing the confidence of the estimation of source contributions in the mixing model (Figure 2b). The estimate from 2015 AD shows that residual Cd in the Winchmore soil to the present day is dominated by historical fertilizer inputs. Hence, variability in the estimated fractional contribution between 2000 and 2015 AD can be rationalized as a possible statistical artifact arising from the close similarity of end-member $\delta^{114/110}$Cd values through this period. According to the mixing model the time-averaged fractional contribution of each source was about 10% for native soil, about 80% for pre-2000 AD fertilizers and about 17% for post-2000 AD fertilizers (Figure 2b). The results are therefore consistent with Cd in Winchmore soil samples being primarily derived from Nauru fertilizers, which is consistent with previous studies that have shown the typically long residence times of Cd in soil (e.g., up to 3000 years).[67,68]

What Caused the Recent Plateau in Winchmore soil Cd? McDowell[9] documented the recent decline in soil Cd accumulation at Winchmore. This study has extended McDowell's analysis and has confirmed that Cd concentration in the topsoil has indeed plateaued. Furthermore, Cd isotopic analysis identifies pre-2000 AD fertilizers as the predominant source of Cd in the system. One possible conclusion based on this observation is that recent applications of Cd are not tending to accumulate. It is possible that this newer Cd is unable to effectively compete for adsorption sites in the soil matrix, thereby displacing the older Nauru-derived Cd. An alternative hypothesis is that in situ fractionation of Cd isotopes by pasture growth and/or leaching are modifying the observed isotope compositions (Figure 1b).

The analysis of sequential topsoil extracts confirmed that only a relatively small proportion (37%) of the total Cd was readily exchangeable (displacement by Mg^{2+} at pH 7) (SI Figure S2). Therefore, excluding hydrological changes associated with climate over the period, we identify two probable drivers of the concentration plateau:

> Reduced Cd inputs associated with the industry Cd management strategy
> Increases in the loss of Cd from the soil zone

As McDowell[9] has documented, pH in the soil from the fertilizer trial at Winchmore changed throughout the series, with shifts between pH ∼ 6.0 and ∼5.6 over the period of soil Cd stabilization (1990−2015 AD). In order to evaluate the possible impact of soil pH changes, a Cd pH adsorption edge experiment was completed. This showed that the pH dependency of Cd adsorption is likely to be most strongly modulated between pH values of 3.5 and 5.3 (SI Figure S3). The pH of the control site subsoil in 2015 AD was determined at pH 5.4 and plot 15 topsoil from the same year had a pH of 5.2. The Cd adsorption efficiency of soil through time was estimated based on linear regression ($R^2 = 0.96$) between %Cd adsorbed and pH in the adsorption edge experiment between pH values of 5.3 and 8 (SI Figure S3). The estimated Cd adsorption efficiency change corresponded to a shift of slightly greater than 2% (between pH 5.4 and 6.0). Over the same interval (1990−2015 AD), the Cd concentrations in plot 15 topsoil (this study) declined by ∼25%. This is therefore inconsistent with a pH control on Cd adsorption capacity. In order to better understand the mechanisms of Cd accumulation and loss at Winchmore, a mass balance modeling approach was taken.

Mass Balance Modeling of Cd. McDowell[9] showed that reduced loading of Cd from fertilizer is sufficient to explain the observed Cd accumulation trends at Winchmore *assuming* lower total Cd in superphosphate fertilizer applications. Our analysis of fertilizer samples from the period 1998−2015 (Table 1) demonstrates that fertilizer Cd was actually higher (204.0 ± 66.8 mg Cd kg^{-1} P; $n = 8$) during this period than that assumed by McDowell previously[9] (140 ± 60.62 mg Cd kg^{-1} P; $n = 3$). This difference in total concentration resulted in a large overprediction of soil Cd accumulation during the period post-2000 AD based on our better-constrained input data (Figure 3a).

The results of Cd mass balance modeling completed in this study and in McDowell[9] demonstrate that the fertilizer Cd concentration data of McDowell best represented the period of early Cd accumulation between 1949 and 1998, whereas the detailed determinations of fertilizer Cd between 1998 and 2015 AD in this study provide improved constraint on Cd accumulation trends post-2000 AD (Figure 3a; see SI Table S4 for details of modeling scenarios). The second scenario (blue curve (Figure 3a)) overestimated Cd accumulation over the entire record because only two fertilizer samples for the period pre-2000 AD were considered (just one fertilizer sample for period of 1949−1998), whereas McDowell[9] used five pre-2000 AD fertilizers. The third scenario (red curve (Figure 3a)) combined McDowell's pre-1998 AD fertilizer concentration data (isotope ratio from our pre-1998 AD samples) and the post-1998 AD fertilizers characterized in this study. This third modeling scenario provides an improved fit to topsoil concentrations and isotope ratios through the period 1959−2000 AD (Figure 3a,b). However, important discrepancies were observed between the modeled and measured data after 2000 AD. Most importantly, the third scenario model output
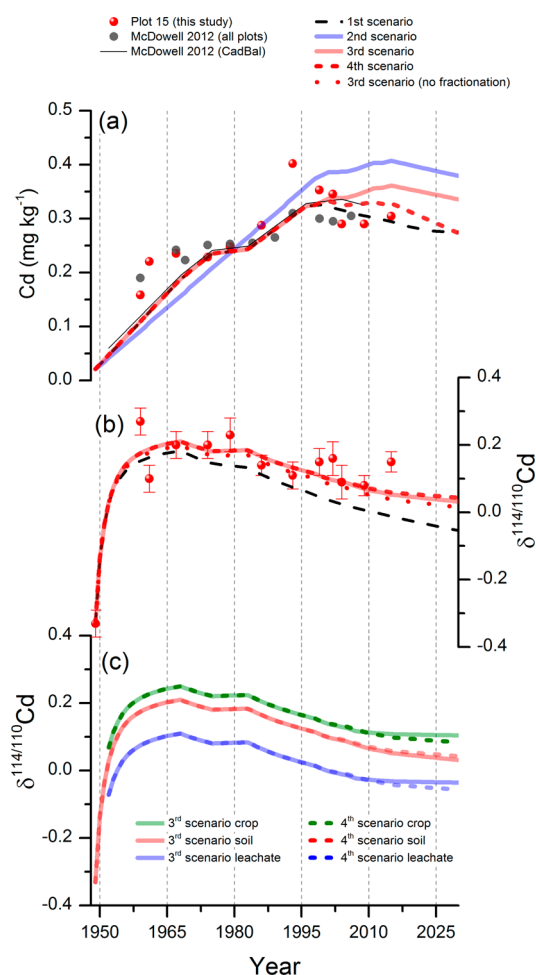
Figure 3. Results of Cd mass balance modeling in CadBal for the period of topsoil fertilization at Winchmore including a prediction up to the year 2030 AD. (a) Cd concentration in Winchmore topsoils (symbols) and the dryland optimized CadBal model outputs (lines); (red symbols = this study-plot 15; gray symbols = McDowell[9] study-average of all plots; solid black line = McDowell[9] all irrigation plots; black dashed line = Plot 15, first scenario; blue line = Plot 15, second scenario; red line = Plot 15, third scenario; red dashed line = Plot 15, fourth scenario); (b) Measured and modeled Cd isotope ratios based on CadBal outputs, isotope ratios measured in fertilizers and the fractionation factors of Wiggenhauser et al.;[11] lines designate modeling scenarios as in (a), red dots are the third scenario with no fractionation (α factor not applied); (c) modeled scenario 3 (solid) and scenario 4 (dashed) isotope ratios in topsoil (red lines), leachate (blue lines) and pasture (green lines).

overpredicted the concentration of Cd in topsoil in the most recent period (Figure 3a). This overestimation was tested in a fourth scenario, in which the leaching rate was doubled for the post-2000 AD period. The results of scenario four (SI Table S4) showed a closer correspondence to the measured Plot 15 Cd concentrations, post-2000 AD (red dashed line (Figure 3a)). The doubling of Cd removal by leaching did not substantially alter the modeled soil isotope ratio between the third (red line (Figure 3b)) and fourth scenarios (red dashed line (Figure 3b)).

The mass balance modeling results confirm that recent applications of P fertilizer have not resulted in an accumulation of Cd consistent with the model boundary conditions (for crop uptake/leaching (SI Table S4)) which gave good agreement for the period prior to 2000 AD (Figure 3a). This implies that

removal of Cd by either leaching or crop uptake has increased during this most recent period. The modeled Cd isotope data appear to be consistent with this interpretation (Figure 3b). Slightly more enriched values of Cd isotopes in plot 15 soil (than predicted by scenario 4) may therefore indicate that

(1) in situ processes acting on Cd may have fractionated the residual Cd pool toward heavier values than predicted by the Cd fractionation factors used here (Wiggenhauser et al.[11]); or

(2) Cd from recent fertilizer applications contributed less to the total soil Cd isotope composition than predicted by the model (which assumes perfect mixing).

The modeled isotope ratios given in Figure 3b-c extend to 2030 AD and provide the means to systematically test the process of Cd accumulation and loss at this site. It would be beneficial to extend the analysis of Cd isotopes in the future to include Cd accumulated by pasture and Cd leached to groundwater. The predicted trend in exchangeable Cd over time is shown in Figure 3c.

Environmental Significance. This study has shown that Cd isotope ratios in fertilized soils were distinguishable from the control soils and were comparable to the source rocks used in fertilizer manufacture. Cadmium isotopic analysis is therefore a promising tool to trace the fate of fertilizer-derived Cd in the environment beyond the soil zone, provided the influence of possible additional biogeochemical processes that can potentially modify the Cd isotope signals of the soils are well constrained, and that the Cd isotopic composition and Cd concentration of the native soil are well-known. If the declining trend observed at Winchmore is emblematic of Cd behavior in soil systems elsewhere, it follows that the Cd is migrating from the soil zone, either through uptake by plants and animals, or by translocation down the soil profile and via erosive losses. Cadmium isotopes may therefore offer the potential to trace this Cd and monitor its environmental impact, at least in areas where substantial Cd contamination from other activities is scarce.

◼ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b00858.

Table S1−S4, Figure S1−S3, Supplementary Methods 1−4, Matlab code (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. M.S. completed all laboratory work (column chemistry, extractions etc.) and the Bayesian and isotope mass balance modeling. MC-ICP-MS analyses were conducted by E.G. and C.S. A.H. secured funding, sampled soils from Winchmore, cowrote the final text with M.S., and produced the final versions of the figures for publication. L.S. provided archived Winchmore soil samples. C.J. assisted with Matlab coding. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Santonen, T.; Aitio, A.; Fowler, B. A.; Nordberg, M., Chapter 8 - Biological Monitoring and Biomarkers. In *Handbook on the Toxicology of Metals*; 4th ed; Academic Press: San Diego, 2015; pp 155−171.

(2) Gray, C. W.; McLaren, R. G.; Roberts, A. H. C.; Condron, L. M. Solubility, sorption and desorption of native and added cadmium in relation to properties of soils in New Zealand. *Eur. J. Soil Sci.* **1999**, *50* (1), 127−137.

(3) Loganathan, P.; Hedley, M. J.; Grace, N. D.; Lee, J.; Cronin, S. J.; Bolan, N. S.; Zanders, J. M. Fertiliser contaminants in New Zealand grazed pasture with special reference to cadmium and fluorine — a review. *Aust. J. Soil Res.* **2003**, *41* (3), 501−532.

(4) De Boo, W. Cadmium in agriculture. *Toxicol. Environ. Chem.* **1990**, *27* (1−3), 55−63.

(5) Mann, S. S.; Rate, A. W.; Gilkes, R. J. Cadmium Accumulation in Agricultural Soils in Western Australia. *Water, Air, Soil Pollut.* **2002**, *141* (1), 281−297.

(6) Mar, S. S.; Okazaki, M. Investigation of Cd contents in several phosphate rocks used for the production of fertilizer. *Microchem. J.* **2012**, *104*, 17−21.

(7) Roberts, A. H. C.; Longhurst, R. D. *A cadmium balance model for New Zealand pastoral systems*; Report prepared for the New Zealand Fertiliser Manufacturer's Research Association: AgResearch, Hamilton, New Zealand, 2005.

(8) Cadmium Working Group Report One: Cadmium in New Zeland Agriculture. https://www.mpi.govt.nz/document-vault/10079 (13 June 2017).

(9) McDowell, R. W. The rate of accumulation of cadmium and uranium in a long-term grazed pasture: implications for soil quality. *N. Z. J. Agric. Res.* **2012**, *55* (2), 133−146.

(10) Wiederhold, J. G. Metal stable isotope signatures as tracers in environmental geochemistry. *Environ. Sci. Technol.* **2015**, *49* (5), 2606.

(11) Wiggenhauser, M.; Bigalke, M.; Imseng, M.; Müller, M.; Keller, A.; Murphy, K.; Kreissig, K.; Rehkämper, M.; Wilcke, W.; Frossard, E. Cadmium Isotope Fractionation in Soil−Wheat Systems. *Environ. Sci. Technol.* **2016**, *50* (17), 9223−9231.

(12) Félix, O. I.; Csavina, J.; Field, J.; Rine, K. P.; Sáez, A. E.; Betterton, E. A. Use of lead isotopes to identify sources of metal and metalloid contaminants in atmospheric aerosol from mining operations. *Chemosphere* **2015**, *122*, 219−226.

(13) Lee, P. K.; Yu, S. Lead isotopes combined with a sequential extraction procedure for source apportionment in the dry deposition of Asian dust and non-Asian dust. *Environ. Pollut.* **2015**, *210*, 65−75.

(14) Arendt, C. A.; Aciego, S. M.; Hetland, E. A. An open source Bayesian Monte Carlo isotope mixing model with applications in Earth surface processes. *Geochem., Geophys., Geosyst.* **2015**, *16* (5), 1274−1292.

(15) Cable, J.; Ogle, K.; Williams, D. Contribution of glacier meltwater to streamflow in the Wind River Range, Wyoming, inferred via a Bayesian mixing model applied to isotopic measurements. *Hydrol. Process.* **2011**, *25* (14), 2228−2236.

(16) Song, S.; Mathur, R.; Ruiz, J.; Chen, D.; Allin, N.; Guo, K.; Kang, W. Fingerprinting two metal contaminants in streams with Cu isotopes near the Dexing Mine, China. *Sci. Total Environ.* **2016**, *544*, 677−85.

(17) Chae, J. S.; Choi, M. S.; Song, Y. H.; Um, I. K.; Kim, J. G. Source identification of heavy metal contamination using metal association and Pb isotopes in Ulsan Bay sediments, East Sea, Korea. *Mar. Pollut. Bull.* **2014**, *88* (1−2), 373−82.

(18) Gao, B.; Zhou, H.; Liang, X.; Tu, X. Cd isotopes as a potential source tracer of metal pollution in river sediments. *Environ. Pollut.* **2013**, *181*, 340−343.

(19) Lepak, R. F.; Yin, R.; Krabbenhoft, D. P.; Ogorek, J. M.; DeWild, J. F.; Holsen, T. M.; Hurley, J. P. Use of Stable Isotope Signatures to Determine Mercury Sources in the Great Lakes. *Environ. Sci. Technol. Lett.* **2015**, *2* (12), 335−341.

(20) Feng, X.; Foucher, D.; Hintelmann, H.; Yan, H.; He, T.; Qiu, G. Tracing Mercury Contamination Sources in Sediments Using Mercury Isotope Compositions. *Environ. Sci. Technol.* **2010**, *44* (9), 3363−3368.

(21) Watmough, S. A.; Hughes, R. J.; Hutchinson, T. C. 206Pb/207Pb Ratios in Tree Rings as Monitors of Environmental Change. *Environ. Sci. Technol.* **1999**, *33* (5), 670−673.

(22) Phillips, D. L.; Koch, P. L. Incorporating Concentration Dependence in Stable Isotope Mixing Models. *Oecologia* **2002**, *130* (1), 114−125.

(23) Wong, S. C.; Li, X. D.; Zhang, G.; Qi, S. H.; Min, Y. S. Heavy metals in agricultural soils of the Pearl River Delta, South China. *Environ. Pollut.* **2002**, *119* (1), 33−44.

(24) Kersten, M.; Xiao, T.; Kreissig, K.; Brett, A.; Coles, B. J.; Rehkämper, M. Tracing Anthropogenic Thallium in Soil Using Stable Isotope Compositions. *Environ. Sci. Technol.* **2014**, *48* (16), 9030−9036.

(25) Chrastný, V.; Čadková, E.; Vaněk, A.; Teper, L.; Cabala, J.; Komárek, M. Cadmium isotope fractionation within the soil profile complicates source identification in relation to Pb−Zn mining and smelting processes. *Chem. Geol.* **2015**, *405*, 1−9.

(26) Wen, H.; Zhang, Y.; Cloquet, C.; Zhu, C.; Fan, H.; Luo, C. Tracing sources of pollution in soils from the Jinding Pb−Zn mining district in China using cadmium and lead isotopes. *Appl. Geochem.* **2015**, *52*, 147−154.

(27) Wombacher, F.; Rehkämper, M.; Mezger, K.; Bischoff, A.; Münker, C. Cadmium stable isotope cosmochemistry. *Geochim. Cosmochim. Acta* **2008**, *72* (2), 646−667.

(28) Schediwy, S.; Rosman, K. J. R.; de Laeter, J. R. Isotope fractionation of cadmium in lunar material. *Earth Planet. Sci. Lett.* **2006**, *243* (3−4), 326−335.

(29) Cloquet, C.; Carignan, J.; Libourel, G.; Sterckeman, T.; Perdrix, E. Tracing source pollution in soils using cadmium and lead isotopes. *Environ. Sci. Technol.* **2006**, *40* (8), 2525.

(30) Condron, L. M.; Goh, K. M. Effects of long-term phosphatic fertilizer applications on amounts and forms of phosphorus in soils under irrigated pasture in New Zealand. *J. Soil Sci.* **1989**, *40* (2), 383−395.

(31) Leamy, M. L.; Milne, J. D. G.; Pullar, W. A.; Bruce, J. G. Paleopedology and soil stratigraphy in the New Zealand Quaternary succession. *N. Z. J. Geol. Geophys.* **1973**, *16* (3), 723−744.

(32) Salmanzadeh, M.; Balks, M. R.; Hartland, A.; Schipper, L. A. Cadmium accumulation in three contrasting New Zealand soils with the same phosphate fertilizer history. *Geoderma Regional* **2016**, *7* (3), 271−278.

(33) John, M. K.; VanLaerhoven, C. J. Error in cadmium determinations due to adsorption by filter papers. *Bull. Environ. Contam. Toxicol.* **1976**, *15* (2), 211−213.

(34) Matoug, I. O. M. Study of metals contamination in different filter papers. *IOSR J. Environ. Sci., Toxicol. Food Technol.* **2013**, *3* (5), 59−61.

(35) Gault-Ringold, M.; Stirling, C. H. Anomalous isotopic shifts associated with organic resin residues during cadmium isotopic analysis by double spike MC-ICPMS. *J. Anal. At. Spectrom.* **2012**, *27* (3), 449−459.

(36) Gault-Ringold, M.; Adu, T.; Stirling, C. H.; Frew, R. D.; Hunter, K. A. Anomalous biogeochemical behavior of cadmium in subantarctic surface waters: Mechanistic constraints from cadmium isotopes. *Earth Planet. Sci. Lett.* **2012**, *341−344*, 94−103.

(37) Abouchami, W.; Galer, S. J. G.; Horner, T. J.; Rehkamper, M.; Wombacher, F.; Xue, Z. C.; Lambelet, M.; Gault-Ringold, M.; Stirling,

C. H.; Schonbachler, M.; Shiel, A. E.; Weis, D.; Holdship, P. F. A common reference material for Cadmium isotope studies - NIST SRM 3108. *Geostand. Geoanal. Res.* **2013**, *37* (1), 5.

(38) Boyle, E. A.; John, S.; Abouchami, W.; Adkins, J. F.; Echegoyen-Sanz, Y.; Ellwood, M.; Flegal, A. R.; Fornace, K.; Gallon, C.; Galer, S.; Gault-Ringold, M.; Lacan, F.; Radic, A.; Rehkamper, M.; Rouxel, O.; Sohrin, Y.; Stirling, C.; Thompson, C.; Vance, D.; Xue, Z.; Zhao, Y. GEOTRACES IC1 (BATS) contamination-prone trace element isotopes Cd, Fe, Pb, Zn, Cu, and Mo intercalibration. *Limnol. Oceanogr.: Methods* **2012**, *10* (9), 653−665.

(39) Sun, F.; Xie, M.; Wu, C. Quick sequential procedure for speciation analysis of heavy metals in soils by supersonic extraction. *Chem. Speciation Bioavailability* **2005**, *17* (4), 137−146.

(40) Moore, J. W.; Semmens, B. X. Incorporating uncertainty and prior information into stable isotope mixing models. *Ecol. Lett.* **2008**, *11* (5), 470−480.

(41) Parnell, A. C.; Inger, R.; Bearhop, S.; Jackson, A. L. Source partitioning using stable isotopes: coping with too much variation. *PLoS One* **2010**, *5* (3), e9672.

(42) Sposito, G. *The Surface Chemistry of Soils*. Oxford University Press: New York, 1984.

(43) Lee, S. Z.; Allen, H. E.; Huang, C. P.; Sparks, D. L.; Sanders, P. F.; Peijnenburg, W. J. G. M. Predicting soil-water partition coefficients for cadmium. *Environ. Sci. Technol.* **1996**, *30* (12), 3418−3424.

(44) Conway, T. M.; Rosenberg, A. D.; Adkins, J. F.; John, S. G. A new method for precise determination of iron, zinc and cadmium stable isotope ratios in seawater by double-spike mass spectrometry. *Anal. Chim. Acta* **2013**, *793*, 44−52.

(45) Reiser, R.; Simmler, M.; Portmann, D.; Clucas, L.; Schulin, R.; Robinson, B. Cadmium concentrations in new zealand pastures: Relationships to soil and climate variables. *J. Environ. Qual.* **2014**, *43*, 917−925.

(46) Syers, J. K.; Mackay, A. D.; Brown, M. W.; Currie, L. D. Chemical and physical characteristics of phosphate rock materials of varying reactivity. *J. Sci. Food Agric.* **1986**, *37* (11), 1057−1064.

(47) Williams, C. H.; David, D. J. The effects of superphosphate on cadmium content of soils and plants. *Aust. J. Soil Res.* **1973**, *11*, 43−56.

(48) Wombacher, F.; Rehkämper, M.; Mezger, K.; Münker, C. Stable isotope compositions of cadmium in geological materials and meteorites determined by multiple-collector ICPMS. *Geochim. Cosmochim. Acta* **2003**, *67* (23), 4639−4654.

(49) Schmitt, A.-D.; Galer, S. J. G.; Abouchami, W. Mass-dependent cadmium isotopic variations in nature with emphasis on the marine environment. *Earth Planet. Sci. Lett.* **2009**, *277* (1−2), 262−272.

(50) Amalhay, M.; Roberts, T. L. SYMPHOS 2013 - 2nd International Symposium on Innovation and Technology in the Phosphate IndustryCadmium and Phosphorous Fertilizers: The Issues and the Science. *Procedia Eng.* **2014**, *83*, 52−59.

(51) Ballnace Agri-Nutrients *Cadmium in Fertilizers*; New Zealand. http://www.ballance.co.nz/~/media/BALLANCE-WEB/Our-Science/Fact-Sheets/pdf/Ballance-fact-sheet--Cadmium-in-fertilisers-O-15035.ashx?la=en (13 June 2017).

(52) Rothbaum, H. P.; Goguel, R. L.; Johnston, A. E.; Mattingly, G. E. G. Cadmium accumulation in soils from long-continued applications of superphosphate. *J. Soil Sci.* **1986**, *37* (1), 99−107.

(53) Fegley, B., Cosmochemistry. In *Encyclopedia of Planetary Science*; Springer Netherlands: Dordrecht, 1997; pp 169−177.

(54) Yang, J. L.; Li, Y. B.; Liu, S. Q.; Tian, H. Q.; Chen, C. Y.; Liu, J. M.; Shi, Y. L. Theoretical calculations of Cd isotope fractionation in hydrothermal fluids. *Chem. Geol.* **2015**, *391*, 74.

(55) Shiel, A. E.; Weis, D.; Orians, K. J. Evaluation of zinc, cadmium and lead isotope fractionation during smelting and refining. *Sci. Total Environ.* **2010**, *408* (11), 2357−68.

(56) Martinkova, E.; Chrastny, V.; Francova, M.; Sipkova, A.; Curik, J.; Myska, O.; Mizic, L. Cadmium isotope fractionation of materials derived from various industrial processes. *J. Hazard. Mater.* **2016**, *302*, 114−9.

(57) Standing Committee on Agriculture and Resource Management-Ruminants Subcommittee. *Feeding Standards for Australian Livestock: Ruminants*; CSIRO Publications: Australia, 1990.

(58) Loganathan, P.; Vigneswaran, S.; Kandasamy, J.; Naidu, R. Cadmium sorption and desorption in soils: A review. *Crit. Rev. Environ. Sci. Technol.* **2012**, *42* (5), 489−533.

(59) Wasylenki, L. E.; Swihart, J. W.; Romaniello, S. J. Cadmium isotope fractionation during adsorption to Mn oxyhydroxide at low and high ionic strength. *Geochim. Cosmochim. Acta* **2014**, *140*, 212−226.

(60) Horner, T. J.; Schönbächler, M.; Rehkämper, M.; Nielsen, S. G.; Williams, H.; Halliday, A. N.; Xue, Z.; Hein, J. R. Ferromanganese crusts as archives of deep water Cd isotope compositions. *Geochem., Geophys., Geosyst.* **2010**, *11*, 1−10.

(61) Wei, R.; Guo, Q.; Wen, H.; Liu, C.; Yang, J.; Peters, M.; Hu, J.; Zhu, G.; Zhang, H.; Tian, L.; Han, X.; Ma, J.; Zhu, C.; Wan, Y. Fractionation of Stable Cadmium Isotopes in the Cadmium Tolerant Ricinus communis and Hyperaccumulator Solanum nigrum. *Sci. Rep.* **2016**, *6*, 24309.

(62) Lacan, F.; Francois, R.; Ji, Y.; Sherrell, R. M. Cadmium isotopic composition in the ocean. *Geochim. Cosmochim. Acta* **2006**, *70* (20), 5104−5118.

(63) Yang, S.-C.; Lee, D.-C.; Ho, T.-Y. Cd isotopic composition in the suspended and sinking particles of the surface water of the South China Sea: The effects of biotic activities. *Earth Planet. Sci. Lett.* **2015**, *428*, 63−72.

(64) Zhang, Y.; Wen, H.; Zhu, C.; Fan, H.; Luo, C.; Liu, J.; Cloquet, C. Cd isotope fractionation during simulated and natural weathering. *Environ. Pollut.* **2016**, *216*, 9−17.

(65) Weinstein, C.; Moynier, F.; Wang, K.; Paniello, R.; Foriel, J.; Catalano, J.; Pichat, S. Isotopic fractionation of Cu in plants. *Chem. Geol.* **2011**, *286* (3−4), 266−271.

(66) Ryan, B. M.; Kirby, J. K.; Degryse, F.; Harris, H.; McLaughlin, M. J.; Scheiderich, K. Copper speciation and isotopic fractionation in plants: uptake and translocation mechanisms. *New Phytol.* **2013**, *199* (2), 367−78.

(67) Nicholson, F. A.; Jones, K. C.; Johnston, A. E. *Evidence for the Leaching of Surface Deposited Cadmium in Agricultural Soils*; Organisation for Economic Cooperation and Development: Paris, France, 1996; pp 218−231.

(68) Nriagu, J. O., Production, uses and properties of cadmium. In *Cadmium in the Environment: Part I: Ecological Cycling*; Nriagu, J. O., Ed.;John Willey and Sons: New York, 1980.