Isotope tracing of long-term cadmium fluxes in an agricultural soil

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Supplementary Methods 1 (sample preparation for Cd concentration and isotope analysis)

All samples were prepared for Cd isotopic analysis in the Centre for Trace Element Analysis, within the Department of Chemistry, University of Otago under Class 10 (ISO 4) laminar flow within a Class 100 (ISO 5) clean room. Ultra-high purity acids and deionized water (>18.2 MΩ) supplied by a Milli-Q Element purification system (Millipore, USA) were used for all reagent, equipment, and sample preparation. Teflon vials (Savillex, USA) were used throughout for the chemical preparation of samples. All sample processing equipment was rigorously acid cleaned before use following standard protocols. For each digest, a known amount of sample corresponding to ~50 ng Cd was transferred to a teflon vial for further processing. A $^{111}$Cd-$^{110}$Cd double spike, with a calibrated $^{110}$Cd/$^{111}$Cd ratio of 1.95193, was admixed to each sample before sample preparation to allow for reliable correction of instrumental mass bias and for any isotopic fractionation that occurred during chemical processing. Then, a two-stage ion exchange separation procedure was conducted using AG1-X8 and AG-MP1 to isolate and purify the Cd fraction from the remaining sample matrix (Table S1). Using this approach, the recovery of Cd was routinely >90 % and often exceeded 95%. The total procedural blank during chemical
preparation is typically less than 7 pg of Cd, which is negligible for all samples analysed with respect to both Cd isotopic composition and concentration.

**Table S1.** Chemical separation procedure for pre-concentration and purification of Cd from soil, fertilizer and rock phosphate samples

<table>
<thead>
<tr>
<th>Eluent</th>
<th>Volume (mL)</th>
<th>Eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG1-X8 anion-exchange resin</td>
<td>5.0</td>
<td>matrix</td>
</tr>
<tr>
<td>2 M HNO₃ (resin cleaning)</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>Mili-Q water (resin cleaning)</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>8 M HCl (conversion to Cl⁻ form, wash)</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>0.7 M HCl (resin conditioning, wash)</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>0.7 M HCl (sample solution)</td>
<td>5.5</td>
<td>matrix</td>
</tr>
<tr>
<td>0.7 M HCl</td>
<td>5.5</td>
<td>matrix</td>
</tr>
<tr>
<td>1 M HCl</td>
<td>5.5</td>
<td>matrix</td>
</tr>
<tr>
<td>2 M HCl</td>
<td>5.5</td>
<td>matrix</td>
</tr>
<tr>
<td>0.7 M HCl</td>
<td>5.5</td>
<td>matrix</td>
</tr>
<tr>
<td>8 M HCl</td>
<td>5.5</td>
<td>Ag</td>
</tr>
<tr>
<td>0.5 M HNO₃-0.1 M HBr</td>
<td>5.5</td>
<td>Zn and Sn</td>
</tr>
<tr>
<td>2 M HNO₃</td>
<td>5.5</td>
<td>Cd</td>
</tr>
<tr>
<td>evaporate to dryness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dissolve in 8M HCl/scratch for 24 hr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>evaporate to dryness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dissolve in 1 mL 0.7M HCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AG-MP1 resin</td>
<td>100 µL</td>
<td></td>
</tr>
<tr>
<td>2 M HNO₃ (resin cleaning)</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Mili-Q water (resin cleaning)</td>
<td>50 µL</td>
<td></td>
</tr>
<tr>
<td>8 M HCl (conversion to Cl⁻ form, wash)</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>0.7 M HCl (resin conditioning, wash)</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>0.7 M HCl (sample solution)</td>
<td>1.6</td>
<td>matrix</td>
</tr>
<tr>
<td>0.7 M HCl</td>
<td>1.6</td>
<td>matrix</td>
</tr>
<tr>
<td>2 M HNO₃-0.1 M HBr</td>
<td>1.6</td>
<td>Zn and Sn</td>
</tr>
<tr>
<td>2 M HNO₃</td>
<td>1.6</td>
<td>Cd</td>
</tr>
<tr>
<td>evaporate to dryness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>reflux in H₂O₂ for 24 hr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>evaporate to dryness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dissolve in 2% HNO₃</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure S1. Cadmium isotopic measurements of the NIST 3108 standard during a single analytical session. During this session, the average 2 SE uncertainty for individual measurements is ±0.049 δ and is comparable to the 2 SD external reproducibility (±0.044 δ) based on repeat measurements of this standard.
Supplementary Methods 2 (Sequential extraction)

3.0 g of air dried and sieved (< 2mm) soil sample was digested following the steps in Table S2. After each extraction, the samples were centrifuged (4000 rpm) for 10 minutes and the reagents were pipetted out of the tube without any filtration and transferred to clean tubes for ICP-MS analysis. Before each extraction step, the remaining solid residue from the previous step was washed using 10 mL deionized water and the washings were discarded after centrifugation at 4000 rpm for 10 minutes.

Table S2. Sequential extraction method procedure

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Reagent</th>
<th>Extraction method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>25 mL of 0.5 M MgCl₂ (pH 7)</td>
<td>1.5 h at 50°C</td>
</tr>
<tr>
<td>Bound to carbonates</td>
<td>25 mL of 0.5 M NaOAC (pH 5)</td>
<td>1.5 h at 50°C</td>
</tr>
<tr>
<td>Bound to Fe-Mn oxides</td>
<td>25 mL of 0.04 M Nh₂OH-Hcl in 25% (v/v) HOAC</td>
<td>1.5 h at 85°C</td>
</tr>
<tr>
<td>Bound to organic matter</td>
<td>4.5 mL of 0.02 M HNO₃ and 7.2 mL of H₂O₂ (pH 2 with HNO₃)</td>
<td>1.5 h at 85°C</td>
</tr>
<tr>
<td></td>
<td>Add 4.5 mL of H₂O₂ (pH 2 with HNO₃)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Add 8.8 mL of 3.2 M NH₄OAC in 20% (v/v) HNO₃</td>
<td>1.5 h at 85°C</td>
</tr>
<tr>
<td>Residual</td>
<td>4 mL Aqua Regia</td>
<td>30 min at room temperature</td>
</tr>
</tbody>
</table>

Figure S2. The percentage of Cd in different fractions of topsoil 2015
Supplementary Methods 3 (pH adsorption edge experiment)

Native (unfertilized) soil samples were air dried and sieved (< 2mm). 1 g of soil sample was added to a set of beakers containing 100 ml of 0.01 M NaNO$_3$ and then Cd(NO$_3$)$_2$ was added at the concentration of $1 \times 10^{-4}$ M. Eleven pH values were covered from 3.5-8.5 using NaOH or HNO$_3$. After shaking the samples at 150 rpm on a reciprocating shaker for 24 h at room temperature (20 °C), samples were filtered using a 0.45 µm membrane filters and then Cd concentration was measured using ICP-MS.

Figure S3. Adsorption of $1 \times 10^{-4}$ M Cd onto Winchmore soils
<table>
<thead>
<tr>
<th>Sample</th>
<th>Cd (mg kg(^{-1}))(^a)</th>
<th>(\delta^{114/116})Cd ± 2 SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native (unfertilized) subsoil-1</td>
<td>0.02</td>
<td>-0.36 ± 0.05</td>
</tr>
<tr>
<td>Native (unfertilized) subsoil-2</td>
<td>0.02</td>
<td>-0.31 ± 0.06</td>
</tr>
<tr>
<td>Topsoil 1959-1</td>
<td>0.16</td>
<td>0.23 ± 0.06</td>
</tr>
<tr>
<td>Topsoil 1959-2</td>
<td>0.15</td>
<td>0.31 ± 0.06</td>
</tr>
<tr>
<td>Topsoil 1961-1</td>
<td>0.21</td>
<td>0.09 ± 0.06</td>
</tr>
<tr>
<td>Topsoil 1961-2</td>
<td>0.23</td>
<td>0.10 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 1967-1</td>
<td>0.25</td>
<td>0.18 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 1967-2</td>
<td>0.22</td>
<td>0.22 ± 0.06</td>
</tr>
<tr>
<td>Topsoil 1974-1</td>
<td>0.23</td>
<td>0.15 ± 0.08</td>
</tr>
<tr>
<td>Topsoil 1974-2</td>
<td>0.23</td>
<td>0.26 ± 0.04</td>
</tr>
<tr>
<td>Topsoil 1979-1</td>
<td>0.25</td>
<td>0.20 ± 0.07</td>
</tr>
<tr>
<td>Topsoil 1979-2</td>
<td>0.25</td>
<td>0.25 ± 0.07</td>
</tr>
<tr>
<td>Topsoil 1986-1</td>
<td>0.30</td>
<td>0.11 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 1986-2</td>
<td>0.27</td>
<td>0.17 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 1993-1</td>
<td>0.34</td>
<td>0.15 ± 0.06</td>
</tr>
<tr>
<td>Topsoil 1993-2</td>
<td>0.46</td>
<td>0.09 ± 0.06</td>
</tr>
<tr>
<td>Topsoil 1999-1</td>
<td>0.35</td>
<td>0.19 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 1999-2</td>
<td>0.35</td>
<td>0.12 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 2002-1</td>
<td>0.38</td>
<td>0.19 ± 0.06</td>
</tr>
<tr>
<td>Topsoil 2002-2</td>
<td>0.31</td>
<td>0.14 ± 0.07</td>
</tr>
<tr>
<td>Topsoil 2004-1</td>
<td>0.28</td>
<td>0.09 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 2004-2</td>
<td>0.29</td>
<td>Not Reported(^b)</td>
</tr>
<tr>
<td>Topsoil 2009-1</td>
<td>0.29</td>
<td>0.11 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 2009-2</td>
<td>0.29</td>
<td>0.05 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 2015-1</td>
<td>0.30</td>
<td>0.19 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 2015-2</td>
<td>0.31</td>
<td>0.12 ± 0.04</td>
</tr>
<tr>
<td>Fertilizer 1980s-1</td>
<td>30.7</td>
<td>0.24 ± 0.05</td>
</tr>
<tr>
<td>Fertilizer 1980s-2</td>
<td>33.0</td>
<td>0.25 ± 0.05</td>
</tr>
<tr>
<td>Fertilizer 2000-1</td>
<td>26.9</td>
<td>0.19 ± 0.06</td>
</tr>
<tr>
<td>Fertilizer 2000-2</td>
<td>27.1</td>
<td>0.16 ± 0.06</td>
</tr>
<tr>
<td>Fertilizer 2007-1</td>
<td>23.3</td>
<td>-0.14 ± 0.06</td>
</tr>
<tr>
<td>Fertilizer 2007-2</td>
<td>23.4</td>
<td>-0.09 ± 0.05</td>
</tr>
<tr>
<td>Fertilizer 2015-1</td>
<td>8.34</td>
<td>-0.18 ± 0.05</td>
</tr>
<tr>
<td>Fertilizer 2015-2</td>
<td>8.20</td>
<td>-0.17 ± 0.04</td>
</tr>
<tr>
<td>Nauru phosphorite-2</td>
<td>92.2</td>
<td>0.28 ± 0.06</td>
</tr>
<tr>
<td>Nauru phosphorite-2</td>
<td>100</td>
<td>0.16 ± 0.05</td>
</tr>
<tr>
<td>Christmas Island phosphorite-1</td>
<td>35.2</td>
<td>0.06 ± 0.04</td>
</tr>
<tr>
<td>Christmas Island phosphorite-2</td>
<td>40.7</td>
<td>0.18 ± 0.06</td>
</tr>
</tbody>
</table>

\(^a\) Instrumental uncertainties are ±0.9 % (2 SE)\(^b\) Due to value exceeding 2σ from the centroid
Table S4. Input data for the CadBal model in our study and McDowell 3 for the dryland treatment of the Winchmore long-term irrigation trial

<table>
<thead>
<tr>
<th>Input</th>
<th>McDowell 3</th>
<th>This study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Farm type</td>
<td>Sheep/beef</td>
<td>Sheep/beef</td>
</tr>
<tr>
<td>Pasture yield (kg DM ha(^{-1}) y(^{-1}))</td>
<td>Annual data from Rickard and McBride 4,5 and Smith, et al. 6</td>
<td>6442 (average of pasture yield in dryland treatment from Rickard and McBride 4)</td>
</tr>
<tr>
<td>Sediment yield (erosion) (kg ha(^{-1}) y(^{-1}))</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Soil group</td>
<td>Yellow-grey earth (Silt loam)</td>
<td>Yellow-grey earth (Silt loam)</td>
</tr>
<tr>
<td>Bulk density (g cm(^{-3}))</td>
<td>1.01</td>
<td>1.01</td>
</tr>
<tr>
<td>Sample depth (m)</td>
<td>0.075</td>
<td>0.075</td>
</tr>
<tr>
<td>Initial soil Cd (mg kg(^{-1}))</td>
<td>0.06</td>
<td>0.02 (control soil Cd)</td>
</tr>
<tr>
<td>P fertilizer rate (kg P ha(^{-1}) y(^{-1}))</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>P fertilizer Cd (mg kg(^{-1}) P)</td>
<td>345 (1952-1968)</td>
<td>first scenario: input data same as McDowell 3</td>
</tr>
<tr>
<td></td>
<td>325 (1968-1975)</td>
<td>second scenario: this study and P fertilizer Cd</td>
</tr>
<tr>
<td></td>
<td>155 (1975-1983)</td>
<td>(mg kg(^{-1}) P) of:</td>
</tr>
<tr>
<td>Leaching loss (mg ha(^{-1}) y(^{-1}))</td>
<td>1600(^b)</td>
<td>third scenario: input data same as first scenario for pre-1998 AD fertilizers and second scenario for post-1998 AD fertilizers</td>
</tr>
<tr>
<td>Atmospheric accession (mg ha(^{-1}) y(^{-1}))</td>
<td>170</td>
<td>fourth scenario: input data same as first scenario for pre-1998 AD fertilizers and second scenario for post-1998 AD fertilizers and leaching loss rate of 3200 mg ha(^{-1}) y(^{-1}) for post-2000 AD soils</td>
</tr>
</tbody>
</table>

\(^a\) (mg Cd kg\(^{-1}\) P) × (P% in fertilizer) ÷ 100 = mg Cd/kg fertilizer (P% ≈ 9%) 7

\(^b\) Calculated using the method and data from McDowell 3,8 and Gray, et al. 9, leaching loss = 1080 (Cd leaching from Brown soil 9) × [40 (olsen P from Winchmore soil-dryland treatment 8) / 27 (olsen P for Brown soil 3)]
Supplementary Methods 4 (isotope mass balance)

The input and output terms in this mass balance were constrained using CadBal which generates loss terms for these vectors. This modelling utilized $\alpha$ values taken from Wiggenhauser, et al.\textsuperscript{10} which were selected on the basis of relevance (i.e. similarity to soil properties). Wiggenhauser, et al.\textsuperscript{10} showed that the isotope ratios of Cd ($\begin{array}{c}^{114}/^{110} \delta \end{array}$) in topsoil (Qen soil, Silt loam) and plant (wheat) root were 0.07‰ and 0.11‰, respectively and the fractionation of Cd between whole plant (wheat) and extractable Cd (extracted using Ca(NO$_3$)$_2$ was $\Delta_{\text{extract-wheat}} = -0.03$‰. Extractable Cd was introduced as available Cd (therefore available for leaching, plant uptake and erosion). Because erosion was considered negligible in our study (Plot 15, dryland treatment), the available Cd is considered to represent the Cd fraction available for plant uptake and leaching, and therefore $\Delta_{\text{extract-wheat}}$ defines the Cd isotope fractionation in leachate. Therefore:

$$\delta_{\text{plant-topsoil}} = \frac{\delta_{\text{plant}} + 1000}{\delta_{\text{soil}} + 1000} = \frac{0.11 + 1000}{0.07 + 1000} = 1.00004$$

And

$$\alpha_{\text{leaching-topsoil}} = \frac{\delta_{\text{leaching}} + 1000}{\delta_{\text{soil}} + 1000} = \frac{-0.03 + 1000}{0.07 + 1000} = 0.9999$$

We also examined the effect of using the entire Ca(NO$_3$)$_2$-extractable fraction (without plant uptake) to represent the leached Cd. This resulted in very large differences to composition of the leached fraction calculated using the CadBal outputs, and an unrealistically negative soil isotope composition. Using these $\alpha$ values and Equations 3 and 4 (in the main manuscript), we estimated the isotope ratios of Cd in topsoil and in soil leachate through the interval of the Winchmore field trial, and beyond (Figure 3). In addition, we applied the factor of 0.37 (the percentage of
available Cd in our soil samples based on the sequential extraction; Figure S2) to our mass
balance model. The results of this exercise also showed a negligible difference to the results from
using total Cd concentrations in the soil and are therefore not given herein.

Matalb code

Soil 1959-1993
>> %year=year of sampling
>> %concentration=Cd concentrations
>> %sa_ratio=isotope ratio of mixed sample
>> %n_ratio=isotope ratio of natural soil
>> %of_ratio=isotope ratio of old fertiliser
>> vals=csvread('3-pre2000-1.csv',1,0);
>> year=vals(:,1);
>> concentration=vals(:,2);
>> sa_ratio=vals(:,3);
>> n_ratio=vals(1,4);
>> of_ratio=vals(1,5);
>> %designated error for isotope ratios of sample
>> sigma_sa=0.2;
>> %N is number of model trial run
>> N=1e5;
>> sample_number=[1:size(vals,1)];
>> %fractions of source definitions
>> %fn=fraction of natural soil
>> %fof=fraction of old fertiliser
>> %designated errors for natural soil source
>> sigma_fn=0.2;
>> %designated errors for old fertiliser source
>> sigma_fof=0.18;
>> %arrays to keep the best outcomes or values with the highest likelihood of being true for fraction
contribution from end members
>> fn_best=zeros(size(concentration));
>> fof_best=zeros(size(concentration));
>> %arrays to keep the mean of posterior, or the average fraction contribution from end members
>> fn_mean=zeros(size(concentration));
>> fof_mean=zeros(size(concentration));
>> %arrays to keep the standard deviations of the posteriors
>> fn_std=zeros(size(concentration));
>> fof_std=zeros(size(concentration));
>> %arrays to keep the 2D correlation coefficients of the posteriors
>> fnof_corr=zeros(size(concentration));
>> %determines best outcomes or values with the highest likelihood of being true for isotope ratios
>> sa_ratiop_best=zeros(size(concentration));
>> for n=sample_number
%choose f so that sum(f)=1 -> use fn to find fof

fn_trial = unifrnd(0, 1, N, 1);
pos = find(fn_trial <= 1);
fn_trial = fn_trial(pos);
fof_trial = 1 - (fn_trial);

% generate random samples of sample ratio
n_ratio_trial = normrnd(n_ratio, sigma_fn, length(pos), 1);
of_ratio_trial = normrnd(of_ratio, sigma_fof, length(pos), 1);

% predicted sample isotope ratio
sa_ratio = (fn_trial .* n_ratio_trial) + (fof_trial .* of_ratio_trial);

% L2^2 norm
phi = (sa_ratio - sa_ratio(n)).^2 / sigma_sa.^2;

% determines best outcomes or values with the highest likelihood of being true
[best_phi, pos] = min(phi);
fn_best(n) = fn_trial(pos);
fof_best(n) = fof_trial(pos);

% isolates and determines accepted posteriors values for function
phi_post = phi(accept);
fn_post = fn_trial(accept);
fof_post = fof_trial(accept);

% isolates and determines accepted posterior values of isotope ratios of sources
n_ratio_post = n_ratio_trial(accept);
of_ratio_post = of_ratio_trial(accept);

% saves accepted values to folder
save(sprintf('Post_%02d.mat', n), 'phi_post', 'fn_post', 'fof_post', 'n_ratio_post', 'of_ratio_post');

fn_mean(n) = mean(fn_trial(accept));
fof_mean(n) = mean(fof_trial(accept));
Cmat = cov([fn_trial(accept) fof_trial(accept)]);
fn_std(n) = sqrt(Cmat(1, 1));
fof_std(n) = sqrt(Cmat(2, 2));

% determines covariance relationships between the posterior fraction contribution values from different sources
fnfof_corr(n) = Cmat(1, 2) / (fn_std(n) * fof_std(n));
end
Soil 1993

>> %year=year of sampling
>> %concentration=Cd concentrations
>> %sa_ratio=isotope ratio of mixed sample
>> %n_ratio=isotope ratio of natural soil
>> %of_ratio=isotope ratio of old fertiliser and fertiliser 1998
>> vals=csvread('3-pre2000-2.csv',1,0);
>> year=vals(:,1);
>> concentration=vals(:,2);
>> sa_ratio=vals(:,3);
>> n_ratio=vals(1,4);
>> of_ratio=vals(1,5);
>> %designated error for isotope ratios of sample
>> sigma_sa=0.2;
>> %N is number of model trial run
>> N=1e5;
>> sample_number=[1:size(vals,1)];
>> %fractions of source definitions
>> %fn=fraction of natural soil
>> %fof=fraction of fertilisers
>> %designated errors for natural soil source
>> sigma_fn=0.2;
>> %designated errors for two fertiliser sources
>> sigma_fof=0.15;
>> %arrays to keep the best outcomes or values with the highest likelihood of being true for fraction
>> contribution from end members
 >> fn_best=zeros(size(concentration));
 >> fof_best=zeros(size(concentration));
 >> %arrays to keep the mean of posterior, or the average fraction contribution from end members
 >> fn_mean=zeros(size(concentration));
 >> fof_mean=zeros(size(concentration));
 >> %arrays to keep the standard deviations of the posteriors
 >> fn_std=zeros(size(concentration));
 >> fof_std=zeros(size(concentration));
 >> %arrays to keep the 2D correlation coefficients of the posteriors
 >> fnfof_corr=zeros(size(concentration));
 >> %determines best outcomes or values with the highest likelihood of being true for isotope ratios
 >> sa_ratiop_best=zeros(size(concentration));
 >> for n=sample_number
 >> %choose f so that sum(f)=1 -> use fn to find fof
 >> fn_trial=unifrnd(0,1,N,1);
 >> pos=find(fn_trial<=1);
 >> fn_trial=fn_trial(pos);
 >> fof_trial=1-fn_trial;
 >> n_ratio_trial=normrnd(n_ratio,sigma_fn,length(pos),1);
 >> of_ratio_trial=normrnd(of_ratio,sigma_fof,length(pos),1);
 >> %predicted sample isotope ratio
 >> sa_ratiop=(fn_trial.*n_ratio_trial)+(fof_trial.*of_ratio_trial);
 >> %L2^2 norm
 >> phi=(sa_ratiop-sa_ratio(n)).^2./sigma_sa.^2;
determines best outcomes or values with the highest likelihood of being true

\[ \text{[best}_\phi,\text{pos]}=\min(\phi); \]
\[ \text{fn}_\text{best}(n)=\text{fn}_\text{trial}(\text{pos}); \]
\[ \text{fof}_\text{best}(n)=\text{fof}_\text{trial}(\text{pos}); \]
\[ \text{sa}_\text{ratiop}_\text{best}(n)=\text{sa}_\text{ratiop}(\text{pos}); \]
\[
\text{L} = \exp((-1/2) \cdot \phi); \quad \text{L} = \text{L}./\max(\text{L});
\]
\[ \text{accept} = \text{find}(\text{L} \geq \text{rand}(	ext{size}(\text{L}))); \]
\[
\text{fprintf}(1,\text{[}'\text{year }%y: \text{tried }%y \text{ samples of the prior, accepted }%y',\text{samples of the posterior; }%6.2f\%s
\text{ acceptance rate}'\text{n}],n,\text{length}(\text{fn}_\text{trial}),\text{length}(\text{accept}),100*\text{length}(\text{accept})/\text{length}(\text{fn}_\text{trial}),\text{char}(37));
\]
isolates and determines accepted posterior values for function

\[ \text{phi}_\text{post}=\phi(\text{accept}); \]
\[ \text{fn}_\text{post}=\text{fn}_\text{trial}(\text{accept}); \]
\[ \text{fof}_\text{post}=\text{fof}_\text{trial}(\text{accept}); \]
\[ \text{n}_\text{ratio}_\text{post}=\text{n}_\text{ratio}_\text{trial}(\text{accept}); \]
\[ \text{of}_\text{ratio}_\text{post}=\text{of}_\text{ratio}_\text{trial}(\text{accept}); \]
\[ \text{save}(\text{sprintf}'\text{Post}_{02d}.\text{mat}',n),\text{'phi}_\text{post'},\text{'fn}_\text{post'},\text{'fof}_\text{post'},\text{'n}_\text{ratio}_\text{post'},\text{'of}_\text{ratio}_\text{post'}); \]
\[ \text{fn}_\text{mean}(n)=\text{mean}(\text{fn}_\text{trial}(\text{accept})); \]
\[ \text{fof}_\text{mean}(n)=\text{mean}(\text{fof}_\text{trial}(\text{accept})); \]
\[ \text{Cmat}=\text{cov}([\text{fn}_\text{trial}(\text{accept}) \text{fof}_\text{trial}(\text{accept})]); \]
\[ \text{fn}_\text{std}(n)=\sqrt{\text{Cmat}(1,1)}; \]
\[ \text{fof}_\text{std}(n)=\sqrt{\text{Cmat}(2,2)}; \]
\[ \text{fnfof}_\text{corr}(n)=\text{Cmat}(1,2)/(\text{fn}_\text{std}(n)\times\text{fof}_\text{std}(n)); \]
end
Soil 2002 and 2004

%year=year of sampling
%concentration=Cd concentrations
%sa_ratio=isotope ratio of mixed sample
%n_ratio=isotope ratio of natural soil
%f2001_ratio=isotope ratio of fertiliser 2001
vals=csvread('2-post2000-1.csv',1,0);
year=vals(:,1);
concentration=vals(:,2);
sa_ratio=vals(:,3);
n_ratio=vals(1,4);
fpr2000_ratio=vals(1,5);
f2001_ratio=vals(1,6);
%designated error for isotope ratios of sample
sigma_sa=0.2;
%N is number of model trial run
N=1e5;
sample_number=[1:size(vals,1)];
%fractions of source definitions
fn=fraction of natural soil
ffpr2000=fraction of pre-2000 fertilisers
ff2001=fraction of fertiliser 2001
%designated errors for natural soil source
sigma_fn=0.2;
%designated errors for pre-2000 fertilisers
sigma_ffpr2000=0.18;
%designated errors for post 2000 fertilisers
sigma_ff2001=0.25;
%arrays to keep the best outcomes or values with the highest likelihood of being true for fraction
fn_best=zeros(size(concentration));
ffpr2000_best=zeros(size(concentration));
ff2001_best=zeros(size(concentration));
%arrays to keep the mean of posterior, or the average fraction contribution from end members
fn_mean=zeros(size(concentration));
ffpr2000_mean=zeros(size(concentration));
ff2001_mean=zeros(size(concentration));
%arrays to keep the standard deviations of the posteriors
fn_std=zeros(size(concentration));
ffpr2000_std=zeros(size(concentration));
ff2001_std=zeros(size(concentration));
%arrays to keep the 2D correlation coefficients of the posteriors
fntf2000_corr=zeros(size(concentration));
fnf2001_corr=zeros(size(concentration));
ffpr2000f2001_corr=zeros(size(concentration));
%determines best outcomes or values with the highest likelihood of being true for isotope ratios
sa_ratiop_best=zeros(size(concentration));
for n=sample_number
choose f so that sum(f)=1 -> use fn and ffpr2000 to find ff2001
fn_trial=unifrnd(0,1,N,1);
ffpr2000_trial=unifrnd(0,1,N,1);
pos=find(fn_trial+ffpr2000_trial<=1);
fn_trial=fn_trial(pos);
ffpr2000_trial=ffpr2000_trial(pos);
ff2001_trial=1-(fn_trial+ffpr2000_trial);


n_ratio_trial=normrnd(n_ratio,sigma_fn,length(pos),1);
fpr2000_ratio_trial=normrnd(fpr2000_ratio,sigma_ffpr2000,length(pos),1);
f2001_ratio_trial=normrnd(f2001_ratio,sigma_ff2001,length(pos),1);

Diese Anweisung erzeugt normale Zufallszahlen mit der angegebenen Mittelwert und Standardabweichung, die dann in n_ratio_trial, fpr2000_ratio_trial und f2001_ratio_trial gespeichert werden.

sa_ratiop=(fn_trial.*n_ratio_trial)+(ffpr2000_trial.*fpr2000_ratio_trial)+(ff2001_trial.*f2001_ratio_trial);


phi=(sa_ratiop5sa_ratio(n)).^2./sigma_sa.^2;

Dieser Ausdruck berechnet den L2-norm, der die Quadratsumme der Abweichungen von den theoretischen Werten zu den gemessenen Werten dividiert durch die quadratische Standardabweichung.

[best_phi,pos]=min(phi);
fn_best(n)=fn_trial(pos);
ffpr2000_best(n)=ffpr2000_trial(pos);
ff2001_best(n)=ff2001_trial(pos);


L=exp((-1/2).*phi); L=L./max(L);

Diese Anweisung berechnet die L-kurve, die im nächsten Schritt benötigt wird.

accept=find(L>=rand(size(L)));

Diese Anweisung sucht nach den Werten von L, die größer oder gleich einem zufällig generierten Wert sind.

fprintf(1,'year %y: tried %y samples of the prior, accepted %y% of the posterior; %6.2f% acceptance rate en',n,length(fn_trial),length(accept),100*length(accept)/length(fn_trial),char(37));

Diese Anweisung gibt eine Mitteilung in der Konsolenleiste aus, die die Übereinstimmung zwischen den Vorgabewerten und den akzeptierten Postern zeigt.

phi_post=phi(accept);
fn_post=fn_trial(accept);
ffpr2000_post=ffpr2000_trial(accept);
ff2001_post=ff2001_trial(accept);
n_ratio_post=n_ratio_trial(accept);
fpr2000_ratio_post=fpr2000_ratio_trial(accept);
f2001_ratio_post=f2001_ratio_trial(accept);

Diese Anweisung selektiert die akzeptierten Werte aus phi, fn_trial, ffpr2000_trial, ff2001_trial und n_ratio_trial.

save(sprintf('Post_%02d.mat',n),'phi_post','fn_post','ffpr2000_post','ff2001_post','n_ratio_post','fpr2000_ratio_post', 'f2001_ratio_post');

Diese Anweisung speichert die akzeptierten Werte in einem Dateinamen, der mit der Nummer n endet.

fn_mean(n)=mean(fn_trial(accept));
ffpr2000_mean(n)=mean(ffpr2000_trial(accept));
ff2001_mean(n)=mean(ff2001_trial(accept));
Cmat=cov([fn_trial(accept) ffpr2000_trial(accept) ff2001_trial(accept)]);
fn_std(n)=sqrt(Cmat(1,1));
ffpr2000_std(n)=sqrt(Cmat(2,2));
ff2001_std(n)=sqrt(Cmat(3,3));

Diese Anweisung berechnet die Mittelwerte und die Kovarianzmatrix der akzeptierten Werte und berechnet die Standardabweichung.

fnffpr2000_corr(n)=Cmat(1,2)/(fn_std(n)*ffpr2000_std(n));
fnff2001_corr(n)=Cmat(1,3)/(fn_std(n)*ff2001_std(n));
ffpr2000ff2001_corr(n)=Cmat(2,3)/(ffpr2000_std(n)*ff2001_std(n));
end
>> %year=year of sampling
>> %concentration=Cd concentrations
>> %sa_ratio=isotope ratio of mixed sample
>> %n_ratio=isotope ratio of natural soil
>> vals=csvread('2-post2000-2.csv',1,0);
>> year=vals(:,1);
>> concentration=vals(:,2);
>> n_ratio=vals(1,4);
>> fpr2000_ratio=vals(1,5);
>> fpo2000_ratio=vals(1,6);
>> %designated error for isotope ratios of sample
>> sigma_sa=0.2;
>> %N is number of model trial run
>> N=1e5;
>> sample_number=[1:size(vals,1)];
>> %fractions of source definitions
>> %fn=fraction of natural soil
>> %ffpr2000=fraction of pre-2000 fertilisers
>> %ffpo2000=fraction of post 2000 fertilisers
>> %designated errors for natural soil source
>> sigma_fn=0.2;
>> %designated errors for pre-2000 fertilisers
>> sigma_ffpr2000=0.18;
>> %designated errors for post 2000 fertilisers
>> sigma_ffpo2000=0.20;
>> %arrays to keep the best outcomes or values with the highest likelihood of being true for fraction
>> fn_best=zeros(size(concentration));
>> ffpr2000_best=zeros(size(concentration));
>> ffpo2000_best=zeros(size(concentration));
>> %arrays to keep the mean of posterior, or the average fraction contribution from end members
>> fn_mean=zeros(size(concentration));
>> ffpr2000_mean=zeros(size(concentration));
>> ffpo2000_mean=zeros(size(concentration));
>> %arrays to keep the standard deviations of the posteriors
>> fn_std=zeros(size(concentration));
>> ffpr2000_std=zeros(size(concentration));
>> ffpo2000_std=zeros(size(concentration));
>> %arrays to keep the 2D correlation coefficients of the posteriors
>> fnfpr2000_corr=zeros(size(concentration));
>> fnffpo2000_corr=zeros(size(concentration));
>> ffpr2000ffpo2000_corr=zeros(size(concentration));
>> %determines best outcomes or values with the highest likelihood of being true for isotope ratios
>> sa_ratiop_best=zeros(size(concentration));
>> for n=sample_number
  %choose f so that sum(f)=1 -> use fn and ffpr2000 to find ffpo2000
  fn_trial=unifrnd(0,1,N,1);
ffpr2000_trial = unifrnd(0,1,N,1);
pos = find(fn_trial+ffpr2000_trial<=1);
fn_trial = fn_trial(pos);
ffpr2000_trial = ffpr2000_trial(pos);
ffpo2000_trial = 1-(fn_trial+ffpr2000_trial);

% generate random samples of sample ratio
n_ratio_trial = normrnd(n_ratio, sigma_fn, length(pos), 1);
fpr2000_ratio_trial = normrnd(fpr2000_ratio, sigma_ffpr2000, length(pos), 1);
fpo2000_ratio_trial = normrnd(fpo2000_ratio, sigma_ffpo2000, length(pos), 1);

% predicted sample isotope ratio
sa_ratiop = (fn_trial.*n_ratio_trial)+(ffpr2000_trial.*fpr2000_ratio_trial)+(ffpo2000_trial.*fpo2000_ratio_trial);

% L2^2 norm
phi = (sa_ratiop - sa_ratio(n)).^2./sigma_sa.^2;

% determines best outcomes or values with the highest likelihood of being true
[best_phi, pos] = min(phi);
fn_best(n) = fn_trial(pos);
ffpr2000_best(n) = ffpr2000_trial(pos);
ffpo2000_best(n) = ffpo2000_trial(pos);

% isolates and determines accepted posterior values for function
% contributions from natural soil, and old fertiliser
phi_post = phi(accept);
fn_post = fn_trial(accept);
ffpr2000_post = ffpr2000_trial(accept);
ffpo2000_post = ffpo2000_trial(accept);
n_ratio_post = n_ratio_trial(accept);
fpr2000_ratio_post = fpr2000_ratio_trial(accept);
fpo2000_ratio_post = fpo2000_ratio_trial(accept);

% saves accepted values to folder

fn_mean(n) = mean(fn_trial(accept));
ffpr2000_mean(n) = mean(ffpr2000_trial(accept));
ffpo2000_mean(n) = mean(ffpo2000_trial(accept));
Cmat = cov([fn_trial(accept) ffpr2000_trial(accept) ffpo2000_trial(accept)]);
fn_std(n) = sqrt(Cmat(1,1));
ffpr2000_std(n) = sqrt(Cmat(2,2));
ffpo2000_std(n) = sqrt(Cmat(3,3));

% determines covariance relationships between the posterior fraction contribution values from different sources
fnffpr2000_corr(n) = Cmat(1,2)/(fn_std(n)*ffpr2000_std(n));
fnffpo2000_corr(n) = Cmat(1,3)/(fn_std(n)*ffpo2000_std(n));
ffpr2000ffpo2000_corr(n) = Cmat(2,3)/(ffpr2000_std(n)*ffpo2000_std(n));
end
Soil 2015

>> %year=year of sampling
>> %concentration=Cd concentrations
>> %sa_ratio=isotope ratio of mixed sample
>> %n_ratio=isotope ratio of natural soil
>> vals=csvread('2-post2000-3.csv',1,0);
>> year=vals(:,1);
>> concentration=vals(:,2);
>> n_ratio=vals(1,4);
>> fpr2000_ratio=vals(1,5);
>> fpo2000_ratio=vals(1,6);
>> %designated error for isotope ratios of sample
>> sigma_sa=0.2;
>> %N is number of model trial run
>> N=1e5;
>> sample_number=[1:size(vals,1)];
>> %fractions of source definitions
>> %fn=fraction of natural soil
>> %ffpr2000=fraction of pre-2000 fertilisers
>> %ffpo2000=fraction of post 2000 fertilisers
>> %designated errors for natural soil source
>> sigma_fn=0.2;
>> %designated errors for pre-2000 fertilisers
>> sigma_fpr2000=0.18;
>> %designated errors for post 2000 fertilisers
>> sigma_fpo2000=0.29;
>> %arrays to keep the best outcomes or values with the highest likelihood of being true for fraction contribution from end members
>> fn_best=zeros(size(concentration));
>> fpr2000_best=zeros(size(concentration));
>> fpo2000_best=zeros(size(concentration));
>> %arrays to keep the mean of posterior, or the average fraction contribution from end members
>> fn_mean=zeros(size(concentration));
>> fpr2000_mean=zeros(size(concentration));
>> fpo2000_mean=zeros(size(concentration));
>> %arrays to keep the standard deviations of the posteriors
>> fn_std=zeros(size(concentration));
>> fpr2000_std=zeros(size(concentration));
>> fpo2000_std=zeros(size(concentration));
>> %arrays to keep the 2D correlation coefficients of the posteriors
>> fnfpr2000_best=zeros(size(concentration));
>> fnfpo2000_best=zeros(size(concentration));
>> fpr2000fpo2000_best=zeros(size(concentration));
>> %determines best outcomes or values with the highest likelihood of being true for isotope ratios
>> sa_ratiop_best=zeros(size(concentration));
>> for n=sample_number
%choose f so that sum(f)=1 -> use fn and fpr2000 to find fpo2000
fn_trial=unifrnd(0,1,N,1);
ffpr2000_trial = unifrnd(0,1,N,1);
pos = find(fn_trial+ffpr2000_trial<=1);
fn_trial = fn_trial(pos);
ffpr2000_trial = ffpr2000_trial(pos);
ffpo2000_trial = 1-(fn_trial+ffpr2000_trial);

% generate random samples of sample ratio
n_ratio_trial = normrnd(n_ratio,sigma_fn,length(pos),1);
fpr2000_ratio_trial = normrnd(fpr2000_ratio,sigma_ffpr2000,length(pos),1);
fpo2000_ratio_trial = normrnd(fpo2000_ratio,sigma_ffpo2000,length(pos),1);

% predicted sample isotope ratio
sa_ratiop = (fn_trial.*n_ratio_trial)+(ffpr2000_trial.*fpr2000_ratio_trial)+(ffpo2000_trial.*fpo2000_ratio_trial);

% L2^2 norm
phi = (sa_ratiop-sa_ratio(n)).^2./sigma_sa.^2;

% determines best outcomes or values with the highest likelihood of being true
[best_phi,pos] = min(phi);
fn_best(n) = fn_trial(pos);
ffpr2000_best(n) = ffpr2000_trial(pos);
ffpo2000_best(n) = ffpo2000_trial(pos);
sa_ratiop_best(n) = sa_ratiop(pos);

% GaussianDataError
L = exp((51/2).*phi); L = L./max(L);
accept = find(L>=rand(size(L)));

fprintf(1,
 ['year %y: tried %y samples of the prior, accepted %y samples of the posterior; %6.2f\%
 acceptance rate\n'],n,length(fn_trial),length(accept),100*length(accept)/length(fn_trial),char(37));

% isolates and determines accepted posteriors values for function
phi_post = phi(accept);
fn_post = fn_trial(accept);
ffpr2000_post = ffpr2000_trial(accept);
ffpo2000_post = ffpo2000_trial(accept);

% isolates and determines accepted posterior values of isotope ratios of sources
n_ratio_post = n_ratio_trial(accept);
fpr2000_ratio_post = fpr2000_ratio_trial(accept);
fpo2000_ratio_post = fpo2000_ratio_trial(accept);

% saves accepted values to folder
save(sprintf('Post_%02d.mat',n),'phi_post','fn_post','ffpr2000_post','ffpo2000_post','n_ratio_post','fpr2000_ratio_post','fpo2000_ratio_post');

fn_mean(n) = mean(fn_trial(accept));
ffpr2000_mean(n) = mean(ffpr2000_trial(accept));
ffpo2000_mean(n) = mean(ffpo2000_trial(accept));

Cmat = cov([fn_trial(accept) ffpr2000_trial(accept) ffpo2000_trial(accept)]);
fn_std(n) = sqrt(Cmat(1,1));
ffpr2000_std(n) = sqrt(Cmat(2,2));
ffpo2000_std(n) = sqrt(Cmat(3,3));

% determines covariance relationships between the posterior fraction contribution values from different sources
fn_ffpr2000_corr(n) = Cmat(1,2)/(fn_std(n)*ffpr2000_std(n));
fn_ffpo2000_corr(n) = Cmat(1,3)/(fn_std(n)*ffpo2000_std(n));
ffpr2000_ffpo2000_corr(n) = Cmat(2,3)/(ffpr2000_std(n)*ffpo2000_std(n));
end
References