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1 Cadmium isotope fractionation during complexation with 2 humic acid

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11 Keywords

12 cadmium isotopes; humic acid; carboxylic groups; non-specific binding; electrostatic attractions; cadmium
13 hydration complexes

14 Abstract

15 Cadmium (Cd) isotopes are known to fractionate during complexation with various
16 environmentally relevant surfaces and ligands. Our results, which were obtained using a combination of
17 various techniques and approaches, highlight the preferential enrichment of light Cd isotopes bound to
18 humic acid (HA), leaving preferentially the heavier Cd pool in the solution ($\Delta^{114/110}\text{Cd}_{\text{HA-Cd(aq)}}$ of $-0.15 \pm$
19 0.01%). At high ionic strengths, Cd isotope fractionation mainly depends on its complexation with
20 carboxylic sites. Outer-sphere complexation occurs at equilibrium together with inner-sphere
21 complexation as well as with the change of the first Cd coordination and its hydration complexes in
22 solution. At low ionic strengths, non-specific Cd binding induced by electrostatic attractions plays a
23 dominant role and promotes Cd isotope fractionation during complexation. This significant outcome

24 elucidates the mechanisms involved in HA-Cd interactions. The results can be used during (i)
25 fingerprinting the available Cd in soil solution after its complexation with solid or soluble natural organic
26 matter and (ii) evaluate the contribution of Cd complexation with organic ligands and phytoplankton-
27 derived debris vs. Cd assimilation by phytoplankton in seawater.

28 **1. Introduction**

29 Besides other “non-traditional” isotopes that have been studied increasingly during the last couple
30 of decades, Cd has drawn much interest as the knowledge of Cd isotope systematics is crucial for a
31 thorough understanding of the Earth’s Cd geochemistry cycle. Pilot studies involving Cd isotopes date
32 back to the 1970s, when large variations were measured in meteoritic and extraterrestrial materials.^{1,2}
33 Cadmium has six stable isotopes (¹⁰⁶Cd, ¹⁰⁸Cd, ¹¹⁰Cd, ¹¹¹Cd, ¹¹²Cd, ¹¹⁴Cd) and its isotope systematics can
34 be used in different fields: (i) marine biogeochemistry and oceanography, given the nutrient-like behavior
35 of Cd and its close correlation with algal nutrients, e.g., nitrate and phosphate,³⁻⁶ (ii) Cd plant uptake in the
36 soil-plant system influenced by the applications of mineral P fertilizers containing Cd and the risk of Cd
37 transfer into the food chain,⁷⁻¹¹ and (iii) natural and anthropogenic source tracking based on the large
38 isotope fractionation induced by evaporation and condensation processes during industrial Cd
39 emissions.¹²⁻¹⁵

40 Despite these numerous environmental studies, there is a surprising lack of a fundamental
41 understanding of Cd isotope fractionation at specific conditions. Bioavailability, mobility, and toxicity of
42 Cd depend on its speciation in the natural system. Cadmium does not undergo natural redox reactions in
43 such natural settings, so the most likely processes affecting its mobility are precipitation and
44 adsorption/complexation with mineral or organic particles. Only four laboratory experiments have been
45 conducted to quantify Cd isotope fractionation during adsorption¹⁶ and (co)precipitation.¹⁷⁻¹⁹ The results
46 showed that lighter Cd isotopes are preferentially adsorbed to Mn-oxyhydroxides¹⁶ ($\Delta^{114/110}\text{Cd}_{\text{solid-Cd(aq)}} = -$
47 0.54 to -0.24 ‰) and precipitated to calcite¹⁷ ($\Delta^{114/110}\text{Cd}_{\text{CaCO}_3\text{-Cd(aq)}} \approx -0.45\%$) or as CdS¹⁸ (closed-system
48 Rayleigh fractionation model $1.00028 < \alpha_{\text{Cd(aq)-CdS}} < 1.00052$ for ¹¹⁴Cd/¹¹⁰Cd).

49 The mobility of Cd and its inherent toxicity to living organisms and humans²⁰⁻²² has motivated the
50 scientific community to understand its sources and behavior in the environment.²³ By the end of the 1980s,
51 Cd mobilization from anthropogenic sources (mining, metal smelting, manufacturing, and fertilizer use)
52 was more than 5,000 times higher than from natural weathering.²⁴ Therefore, significant Cd amounts were
53 remobilized in the biosphere resulting in an enrichment in the atmosphere, soils, sediments, and aquatic
54 environments relative to its concentration in the continental crust.^{25,26} Organo-Cd complexes are usually
55 the primary chemical Cd species at different biogeochemical interfaces, i.e., soil-plants, sediment-surface
56 waters-ocean, and strongly influence its behavior and fate in the environment.^{10,27,28} The principal
57 components of natural organic matter (NOM) are humic substances, i.e., fulvic acids, humin, and humic
58 acids (HA), the latter being a heterogeneous high-molecular-weight organic material, which is ubiquitous
59 in terrestrial (soil, peat) and aquatic environments (sediment, ocean, and freshwater), in both soluble and
60 insoluble forms.²⁹⁻³¹ The physical, chemical, and microbiological transformations of plant, animal, algal,
61 and microbial material³² lead to the formation of HA through different humification processes,³⁰
62 generating variable and complex organic molecules. Humic acids are an important source of dissolved
63 complexing organic ligands, such as carboxylic and phenolic hydroxyl groups³³ and these complexes
64 affect the speciation of metal ions, together with their bioavailability, mobility, and toxicity.³⁴⁻³⁷
65 Therefore, Cd complexation by HA is a crucial process influencing the biogeochemical cycling of Cd in
66 the ocean, in the soil-plant system, or in general, during its remobilization in the environment.

67 The first objective of this study is to examine Cd complexation with a commonly used
68 representative HA, i.e., leonardite humic acid, at different experimental conditions (Cd concentration,
69 ionic strength, pH). The second objective is to determine the Cd isotope fractionation occurring during Cd
70 complexation with HA under the same experimental conditions by measuring both dissolved (aqueous Cd)
71 and complexed (Cd bound to HA) phases. Finally, combining Fourier transformation infrared (FTIR), X-
72 ray absorption spectroscopy (XAS), and modeling, our study highlights the complexation mechanisms
73 leading to Cd isotope fractionation during its complexation with HA.

74 **2. Materials and Methods**

75 **2.1. Sorption experiments**

76 **2.1.1. Leonardite humic acid**

77 Leonardite (humic acid) was chosen due to its high potential for complexation of metal(loid)s in
78 aqueous solutions (As, Cd, Cu, Pb, Ni, etc.) and because it is commonly used as a NOM proxy.^{38–40}
79 Leonardite is a coal-like substance and is believed to be derived from lignitic coal *via* natural oxidation.⁴¹
80 Leonardite has a greater oxygen content than lignite due to a larger number of carboxylic groups.
81 Leonardite is composed of phenolic and carboxylic OH groups, aliphatic CH groups, and carbonyl groups
82 together with conjugated carbonyl or aromatic groups⁴¹. In this study, leonardite HA was obtained from
83 the International Humic Substances Society (IHSS) (C = 63.8%, O = 31.3%, H = 3.70% and N = 1.23%,
84 HA/DOC = 1.57) and characterized by infrared spectroscopy (Fig. S1). For Fourier transform infrared
85 spectroscopy (FTIR) analysis, samples were grounded with KBr at a 1/100 mass ratio and then pressed
86 into disks. FTIR spectra were recorded using a FTIR spectrometer (Perkin Elmer) between 5000 and 400
87 cm^{-1} at a resolution of 0.5 cm^{-1} .

88 Leonardite was solubilized at pH between 9 and 10 (adding 1 mol L^{-1} NaOH) to ensure complete
89 dissolution.⁴² Then, any possibly present HA molecules $<10 \text{ kDa}$ were removed using the Labscale TFF
90 system equipped with a Pellicon XL membrane⁴³ (PLCGC10, Millipore). The dissolved organic carbon
91 (DOC) concentrations were measured by the Carbon Analyzer (TOC-L CPH, Shimadzu). Further in this
92 work, humic acid (HA) denotes leonardite for simplification purposes.

93 **2.1.2. Cd adsorption edges**

94 Adsorption edges were obtained using batch experiments in opaque plastic bottles to avoid any
95 photoluminescence process. All plastic containers were acid-washed, and all reagents used were of reagent
96 grade. Adsorption experiments with Cd ICP standard (Merck standard) were performed under N_2
97 atmosphere at three different initial metal concentrations (10^{-6} , 10^{-5} , and $10^{-4} \text{ mol L}^{-1}$) and three ionic
98 strengths (10^{-1} , 10^{-2} , and $10^{-3} \text{ mol L}^{-1}$ with NaNO_3 as a background electrolyte). The DOC concentration

99 was fixed for each batch experiment at 60 mg L⁻¹. A volume of 60 to 75 mL was used for each batch
100 experiment, and the pH was buffered by adding a controlled volume of HNO₃ (10⁻¹, 10⁻², and 10⁻³ mol L⁻¹)
101 and NaOH (10⁻¹, 10⁻², and 10⁻³ mol L⁻¹) ranging from 2 to 11 pH units. Each bottle was then closed and
102 agitated for 24h. After equilibration, the pH was measured, and an aliquot of the sample (12 mL) was
103 centrifuged using a centrifugal filter device at 6600 rpm for 45 minutes (Amicon[®] Ultra-15 centrifugal
104 filter devices 3kDa). Before the ultrafiltration, the centrifugal filter device was washed with NaOH 0.05
105 mol L⁻¹ and MilliQ[®] water to remove trace amounts of glycerin that could have interfered with the
106 measurements. The filtrate was analyzed for Cd concentration using inductively coupled plasma optical
107 emission spectroscopy (ICP OES; 720 Series, Agilent Technologies) or inductively coupled plasma mass
108 spectroscopy (ICP-MS; iCAP Q, Thermo Fisher Scientific), depending on Cd concentrations. Cadmium
109 bound to HA was calculated as the difference between the initial Cd concentration and the final Cd
110 concentration in the filtrates.

111 **2.1.3. Complexation modeling**

112 The datasets of the adsorption edges were used further for the modeling using Visual MINTEQ
113 software.⁴⁴ The NICA-Donnan model was used for our purpose, which results in a combination of non-
114 ideal competitive adsorption (NICA) to a heterogeneous material, coupled with a Donnan electrostatic
115 sub-model, describing the electrostatic attractions between ions and the humic material.⁴⁵⁻⁴⁷ The
116 distribution between the low adsorption sites (LAS, i.e., carboxylic sites) and high adsorption sites (HAS,
117 i.e., phenolic sites) was calculated using the HH-10, i.e., leonardite HA, binding parameters⁴⁸ and the
118 generic NICA-Donnan model parameters for Cd-ion binding by humic acids.⁴⁹ In our study, the
119 thermodynamic NICA-Donnan model parameters for Cd-ion binding to HA were slightly modified (Table
120 S1).

121 **2.2. Cd isotope analysis**

122 **2.2.1 Batch experiments**

123 Adsorption experiments with a Cd isotope standard (NIST SRM 3108 Cd) were performed under
124 N₂ atmosphere at three fixed pH values (4, 5, and 6), three different initial metal concentrations (2×10^{-6} ,
125 2×10^{-5} , and 2×10^{-4} mol L⁻¹), five ionic strengths (10^{-1} , 5×10^{-2} , 10^{-2} , 5×10^{-3} , and 10^{-3} mol L⁻¹ with NaNO₃ as
126 the background electrolyte). The DOC concentration (120 mg L⁻¹) was increased two times from previous
127 batch experiments in order to obtain a sufficient amount of material for performing FTIR and XAS
128 measurements. The initial concentration of Cd was also doubled to maintain the same Cd/HA ratio. In the
129 case of 10^{-6} mol L⁻¹ Cd, only two fixed pH values were used (4 and 5) as pH 6 did not allow us to analyze
130 the small amount of Cd in the solution. The batch experiment conditions were similar to those used for the
131 determination of the adsorption edges and HA was separated from the solution through a series of
132 ultrafiltrations (five times 12 mL on the same centrifugal filter device 3 kDa) at 6600 rpm for 45 minutes.
133 Cadmium concentrations and isotope compositions were measured in the solution samples. The HA
134 fraction was recovered, freeze-dried, and used for EXAFS and FTIR measurements and for Cd isotope
135 analysis (nine HA samples) to determine the isotopic mass balance. Kinetic batch complexation
136 experiments were conducted to monitor the equilibration time of Cd isotope fractionation with HA at high
137 (10^{-1} mol L⁻¹ NaNO₃) and low (10^{-3} mol L⁻¹ NaNO₃) ionic strengths with a Cd concentration of 10^{-5} mol L⁻¹
138 and DOC concentration of 120 mg L⁻¹.

139 **2.2.2. Cadmium isotopes measurements**

140 Cadmium isotope ratios were measured using thermal ionization mass spectrometry (TIMS;
141 Triton, ThermoFisher), and Cd isotopic compositions are reported as $\delta^{114/110}\text{Cd}$, relative to the NIST SRM
142 3108, with Eq. 1:

$$143 \quad \delta^{114/110}\text{Cd} = \left(\frac{\left(\frac{^{114}\text{Cd}}{^{110}\text{Cd}} \right)_{\text{sample}}}{\left(\frac{^{114}\text{Cd}}{^{110}\text{Cd}} \right)_{\text{NIST SRM 3108}}} - 1 \right) \times 1,000 \quad (1)$$

144 Raw measurements were corrected for potential Cd isotope fractionation during the Cd
145 purification procedure and the analysis, the double-spike (DS) method based on the nested iteration
146 method was used. The DS was prepared by mixing two enriched Cd isotopes spikes: ^{106}Cd (97%) and
147 ^{116}Cd (99 %) purchased from IsoFlex, USA. The DS was added to the sample before the Cd separation
148 process and was composed of ^{106}Cd (35%) and ^{116}Cd (65%). The natural/DS ratio was 5.6 for $^{106}\text{Cd}/^{110}\text{Cd}$
149 and 10.8 for $^{116}\text{Cd}/^{110}\text{Cd}$.

150 Before the Cd separation process, liquid samples were evaporated and transferred to bromide
151 form, whereas HA samples were firstly dissolved in a mixture of concentrated HNO_3 and H_2O_2 and then
152 transferred to bromide form. Chromatographic separation of Cd was performed following the analytical
153 methods previously published by Schmitt et al.^{50,51} and Abouchami et al.^{4,52} This technique was inspired
154 by Pb separation and is promising because it is fast and requires only small amounts of acid. In
155 comparison with Cd isotope measurements by MC-ICP MS, there were no isobaric interferences due to Sn
156 and Pd isotopes,⁵¹ allowing us to skip the chemical separation of Sn using a second anion-exchange
157 chromatography. This protocol was adapted in our laboratory using 400 μL of the BioRad AG1-X8 anion
158 exchange resin (100-200 mesh) in bromide form.

159 After Cd recovery, the sample was evaporated entirely on a hot plate (110-120°C) to the last drop.
160 After cooling, an activator was added to the sample depending on the amount of Cd. For 500 ng of Cd, the
161 activator was composed of 50 μL of H_3PO_4 0.1 N and 100 μL of silica gel (100 mg L^{-1} of Si). Then, the
162 sample was evaporated to dryness and 10 μL of 2% HNO_3 was added and treated by ultrasonication. The
163 volume was loaded stepwise onto outgassed single Re filaments. Peak emission of Cd ions occurs in the
164 temperature range from 1150 to 1200 °C with this activator. The signal varied between 0.2 to 0.5 V (^{112}Cd ,
165 central cup) for the sample, and three complete measurements were feasible: 10 blocks of 20 cycles giving
166 600 measured values for the $^{114}\text{Cd}/^{110}\text{Cd}$ ratio.

167 Additionally, in order to evaluate the Cd purification procedure and the analysis, the full
168 purification procedure was applied for standard solutions (BAM-I012 and NIST SRM 3108) and

169 international soil standard (NIST SRM 2711a Montana soil II). During the experiment and purification,
170 the procedure blank was 4 pg of Cd, having a negligible impact on Cd isotopic composition. International
171 reference standard solutions BAM I012 and NIST SRM 3108 were analyzed, and the long-term external
172 precision was found to be $\pm 0.08\%$ (2SD, n=12) and $\pm 0.02\%$ (2SD, n=3), respectively. The measured
173 $\delta^{114/110}\text{Cd}$ value, relative to the NIST SRM 3108, was $-1.32 \pm 0.08\%$ for BAM I012 (n=12, mean
174 published value⁵³: $-1.33 \pm 0.43\%$) and $0.57 \pm 0.02\%$ for NIST 2711a Montana soil II (n=10, mean
175 published value⁵⁴⁻⁵⁶: $0.55 \pm 0.03\%$).

176 **2.3. Cd EXAFS measurements**

177 The Cd XAS spectra were collected on the SAMBA beamline (SOLEIL Synchrotron, France) at
178 the Cd K-edge (26.7 keV). The energy was calibrated by setting the first inflection point of a Cd metallic
179 foil XANES. The reference (CdO) and samples were prepared as pellets of finely ground and
180 homogenized powder with boron nitride (15 mg of sample + 45 mg of BN) and then sealed with Kapton
181 tape and mounted in sample holders. The data were collected under vacuum at 20 K using a He cryostat to
182 avoid modification in Cd speciation and sample damage due to beam exposure. Spectra were collected in
183 transmission (using an ionization chamber) and fluorescence modes. According to the spectrum quality,
184 several spectra (up to 30) were collected over the 26.65-27.70 keV energy range. Each raw bulk-XAS
185 spectrum of Cd K-edge was merged and normalized, and the background was subtracted with a spline
186 fitting function to obtain the extended X-ray absorption fine structure (EXAFS) function using Athena
187 software.⁵⁷ Fourier transforms were generated on k^3 -weighted spectra over k -ranges of 1.5-15 Å and 2-10
188 Å using the Hanning window for the reference (CdO) and samples, respectively. Theoretical
189 backscattering-amplitude (S_0^2) and phase-shift (ΔE_0) values were calculated using FEFF 6.0 (IFEFFIT
190 package) based on the crystal structure of CdO. The S_0^2 factor was set to 1.14159. The known structure of
191 Cd acetate dihydrate⁵⁸ was used to find the structural parameters that best fit the observed spectrum for the
192 HA samples. The goodness of fit was characterized by two parameters: the XAFS reliability factor R,

193 which measures how close the fit is to the experimental data, and the reduced χ^2 factor, which considers
194 the number of floating parameters and noise in the data.

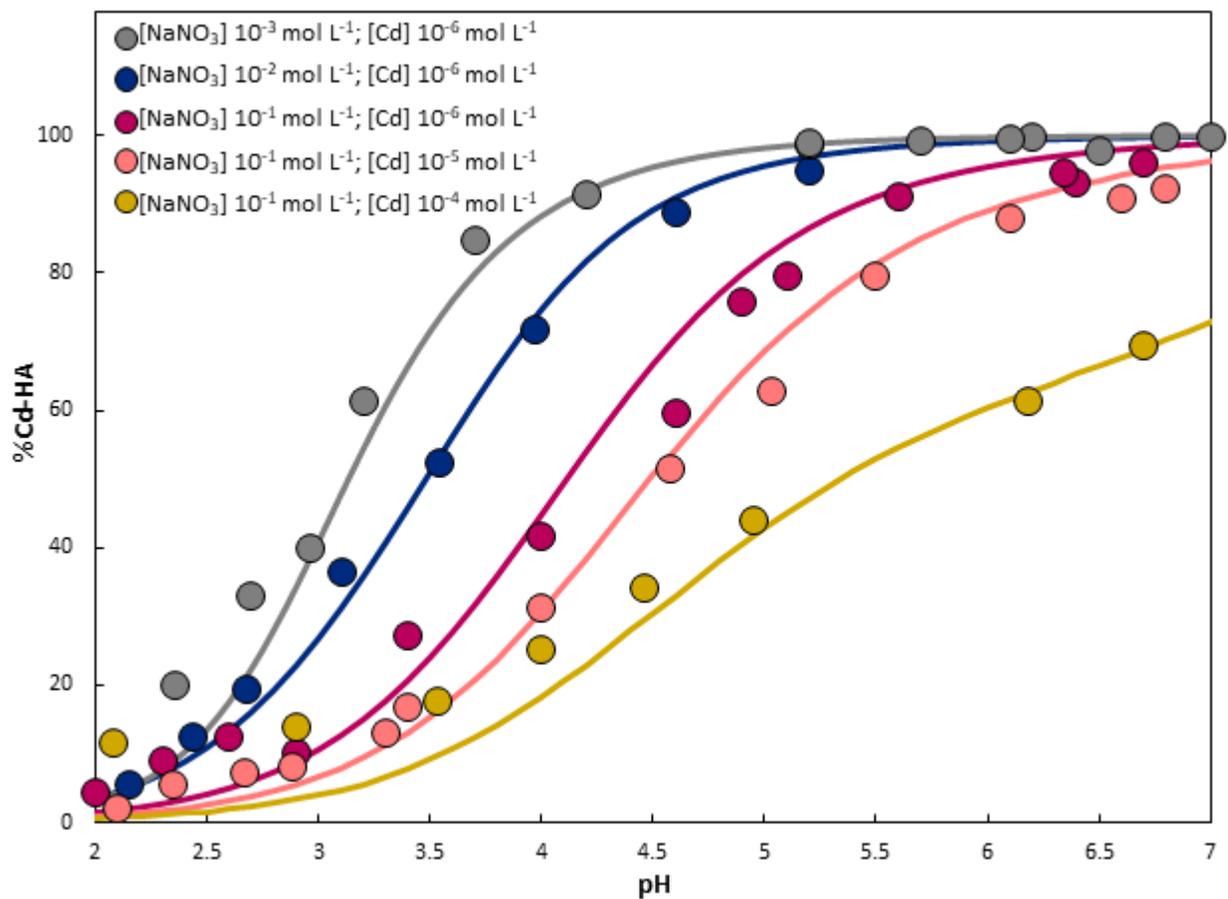
195 **3. Results and discussion**

196 **3.1. Cadmium complexation with HA**

197 Cadmium complexation with HA depends on the pH and ionic strength and is complete in the pH
198 range of 3 to 7 (Fig. 1 and S2). At low ionic strength, low competition between Na^+ and Cd^{2+} leads to a
199 complete Cd complexation in acidic and neutral conditions. On the other hand, at high ionic strength,
200 strong competition between Na^+ and Cd^{2+} led to a complete Cd complexation only in neutral and alkaline
201 conditions. Additionally, the influence of the Cd/DOC ratio highlights the diversity of HA binding groups,
202 which are present in various proportions and cover a large range of affinity constants for Cd. The presence
203 of few high-affinity sites and many weaker sites resulted in complete Cd complexation at lower pH levels
204 for low Cd/DOC than for high Cd/DOC ratios (Fig. 1). Complexation of Cd-HA was investigated using
205 150 batch experiments under different experimental conditions (Cd concentration, ionic strength, and pH).
206 This large experimental data set allowed us to precisely investigate and model Cd complexation with HA
207 using the NICA-Donnan model.^{45,47,59,60}

208 **3.2. Cadmium speciation during complexation with HA**

209 The NICA-Donnan model described four main Cd species (Fig. 2, S3, and S4): Cd^{2+} in solution
210 ($\text{Cd}^{2+}_{\text{aq}}$), non-specifically bound Cd^{2+} (i.e., accumulated in the Donnan volume via electrostatic attractions,
211 $\text{Cd}^{2+}_{\text{D}}$), Cd complexed with carboxylic groups (COO-Cd), and Cd complexed with phenolic groups (PhO-
212 Cd). Furthermore, inorganic complexes, other than Cd^{2+} in solution, were only minor components of Cd
213 aqueous speciation with contributions lower than 0.01% ($\text{Cd}(\text{OH})^+$, CdNO_3^+ , etc.).



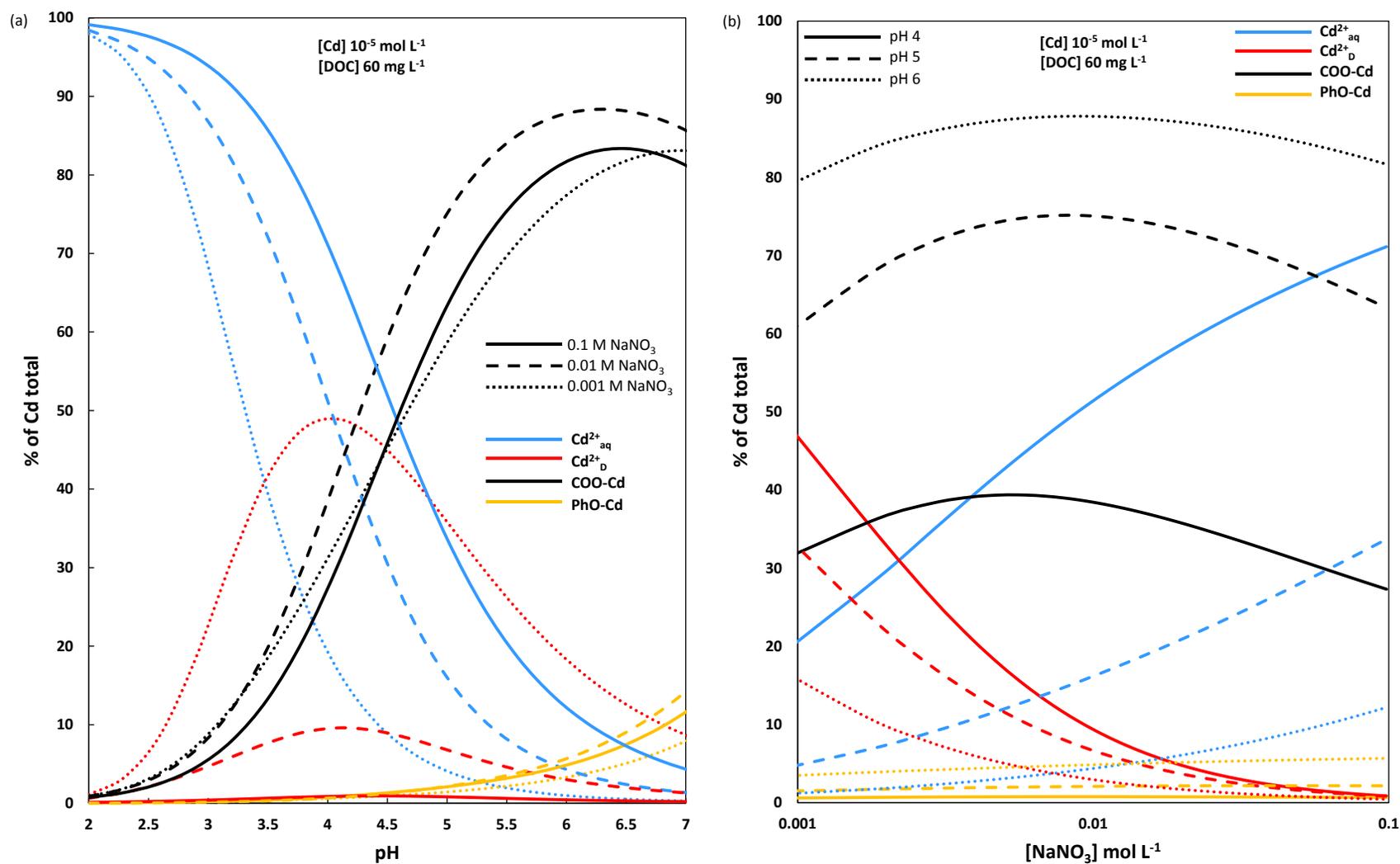
214
 215 **Figure 1:** Cadmium complexation with HA (60 mg L⁻¹ DOC) at different Cd concentrations and ionic
 216 strengths (NaNO₃ as background electrolyte) and as a function of pH. Scatter plots express experimental
 217 data, solid lines represent modeling by Visual MINTEQ (NICA-Donnan model). The ionic strength effect
 218 on Cd complexation is highlighted at 10⁻⁶ mol L⁻¹ Cd. The effect of the Cd concentration on the Cd
 219 complexation is expressed at 10⁻¹ mol L⁻¹ NaNO₃. The remaining complexation dataset is shown in Figure
 220 S2.

221 First, the formation of Cd(II)-carboxyl complexes⁶¹ occurred in acidic and neutral conditions
 222 because of the larger deprotonation of carboxylic groups compared with phenolic groups at low pH values
 223 (Fig. 2a, S3a, and S4a). At low Cd concentrations (10⁻⁶ and 10⁻⁵ mol L⁻¹), carboxylic groups complexed at
 224 least 80% of total Cd, while at a higher Cd concentration (10⁻⁴ mol L⁻¹), Cd complexation was limited to
 225 60% due to (i) site saturation, (ii) charge neutralization of HA which led to less favorable electrostatic
 226 attractions, and (iii) conformational changes of HA that limited the site availability for Cd
 227 complexation^{62,63} (Fig. 2a, S3a, S4a). Although phenolic groups are high-affinity sites for cations,⁴⁹ PhO-

228 Cd complexation was limited by the protonation of phenolic groups at pH levels between 2 and 7.
229 Therefore, most of Cd complexation in the environment will occur at this pH range from 3 to 7 and will be
230 mainly controlled by the carboxylic sites.

231 Secondly, ionic strength had a small effect on Cd complexation to carboxylic groups (Fig. 2b,
232 S3b, S4b), but it strongly affected non-specific binding of Cd with HA. Indeed, due to its amphiphilic
233 character, HA forms micelle-like structures⁶⁴ acting as electrically neutral phases with a consistent
234 negative electrostatic potential (Donnan potential) compared to the solution.⁶⁵ On the other hand, the
235 electrostatic potential is “neutralized” by the counterions from the background electrolyte Na^+_{aq} and $\text{Cd}^{2+}_{\text{aq}}$
236 in solution.^{45,66} As a result, the highest effect of electrostatic attractions between Cd and HA was observed
237 at pH around 4 and at low ionic strength. In these conditions, the carboxylic sites are weakly deprotonated
238 and the competition between Cd^{2+} and Na^+ in the Donnan volume is low (Fig. 2). That led to a prevalence
239 of non-specific Cd binding (up to 50% of total Cd, 60% of the total complexed Cd) due to electrostatic
240 attractions. Furthermore, non-specific binding is almost absent in alkaline conditions, where phenolic and
241 carboxylic groups are deprotonated and ionic strength too high. However, at high Cd concentrations, there
242 are not enough deprotonated sites to bind all the Cd in solution and non-specific binding is still important
243 at pH 6-7 corresponding to 35% of total Cd due to the saturation of the binding sites (Fig. S3).

244 Finally, thermodynamic modeling allowed us to specify Cd speciation. Over the pH range from 3
245 to 7, Cd speciation is explained by the relative proportions of complexation with carboxylic groups (COO-
246 Cd), non-specific Cd binding in the Donnan volume ($\text{Cd}^{2+}_{\text{D}}$), and the free Cd species in solution ($\text{Cd}^{2+}_{\text{aq}}$).
247 Consequently, the isotopic approach was designed to determine the Cd isotopic signature ($\delta^{114/110}\text{Cd}$) in
248 the same experimental conditions (Table 1) and to characterize the Cd isotope fractionation associated
249 with Cd binding to carboxylic groups or by electrostatic attractions.



250

251 **Figure 2:** Cadmium speciation as a function of (a) pH and (b) ionic strength (NaNO₃). The data were determined using the NICA-Donnan model
 252 for $10^{-5} \text{ mol L}^{-1}$ Cd and 60 mg L^{-1} DOC. Cd²⁺_{aq} refers to the aqueous Cd free in solution, Cd²⁺_D to the Cd bound to HA by electrostatic attractions,
 253 COO-Cd to the Cd complexed with carboxylic sites, and PhO-Cd to the Cd complexed with phenolic sites.

254 **Table 1:** Detailed experimental conditions and Cd isotope measurements in solution and in the HA fraction. The isotopic mass balance was
 255 calculated for 9 samples and did not exceed 0.03%. The amount of Cd bound to HA by electrostatic attractions ($f(\text{Cd}^{2+D})$) and with the carboxylic
 256 groups ($f(\text{COO-Cd})$) and aqueous Cd in solution $f(\text{Cd}^{2+aq})$ were calculated based on the NICA-Donnan chemical speciation modeling (n.d.: not
 257 determined).

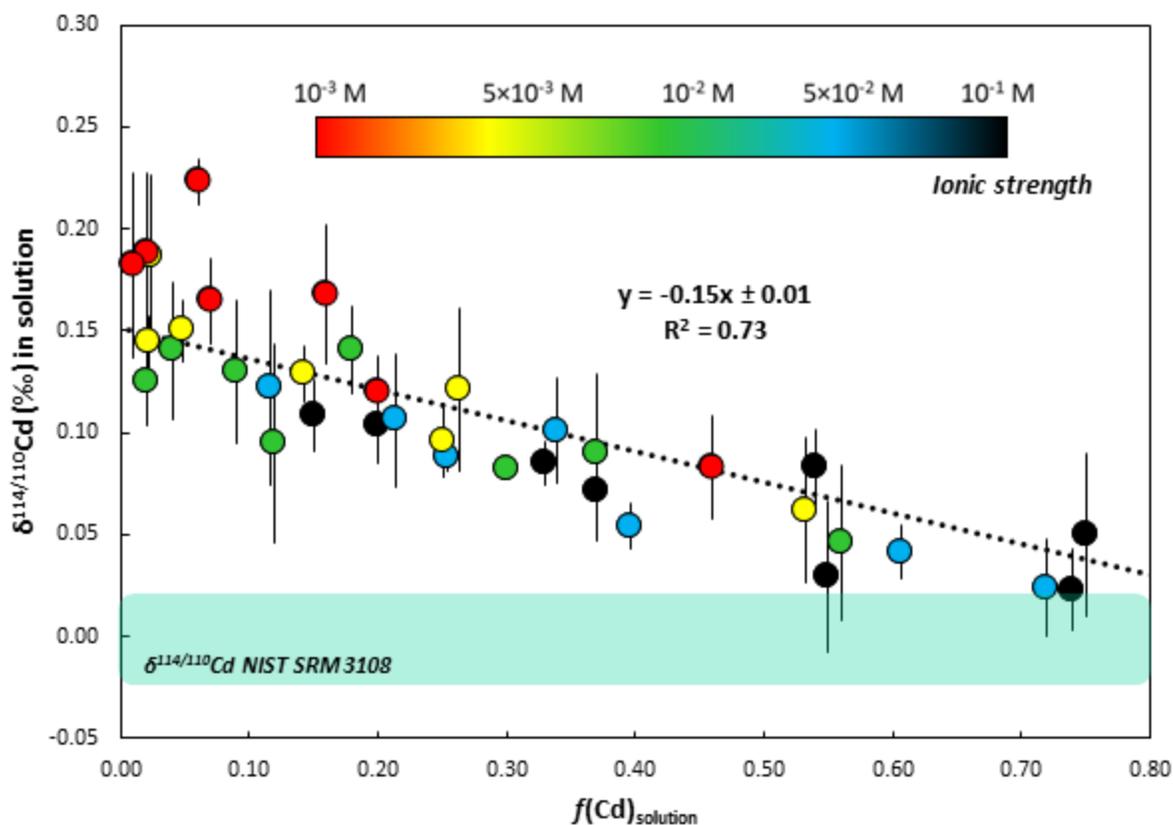
	pH solution	[NaNO ₃] mol L ⁻¹ solution	$f(\text{Cd})$ in solution	$f(\text{Cd}^{2+aq})$ model.	$f(\text{Cd}^{2+D})$ model	$f(\text{COO-Cd})$ model	$\delta^{114/110}\text{Cd}$ solution (‰)	2 SD	$\delta^{114/110}\text{Cd}$ solid (‰)	2 SD	Isotopic balance
[Cd] 2×10^{-4} mol L ⁻¹ ; [DOC] 120 mg L ⁻¹	4.2	1.0E-01	0.74	0.73	0.02	0.25	0.02	± 0.02	-0.06	± 0.01	0.00
	4.0	4.8E-02	0.72	0.74	0.03	0.23	0.02	± 0.02			
	4.0	9.8E-03	0.56	0.61	0.12	0.26	0.05	± 0.04			
	3.9	5.1E-03	0.53	0.57	0.19	0.24	0.06	± 0.04			
	4.0	1.1E-03	0.46	0.39	0.39	0.22	0.08	± 0.03	-0.04	± 0.04	0.02
	5.0	1.0E-01	0.55	0.53	0.02	0.44	0.03	± 0.04			
	5.0	4.7E-02	0.40	0.48	0.03	0.48	0.05	± 0.01			
	4.9	1.0E-02	0.30	0.37	0.12	0.50	0.08	± 0.00			
	4.9	5.3E-03	0.25	0.31	0.19	0.49	0.10	± 0.02			
	4.9	1.1E-03	0.20	0.17	0.42	0.41	0.12	± 0.02			
	6.2	1.0E-01	0.33	0.36	0.01	0.57	0.08	± 0.01	-0.01	± 0.03	0.02
	5.9	4.8E-02	0.25	0.34	0.03	0.59	0.09	± 0.01			
	6.0	9.5E-03	0.12	0.21	0.11	0.64	0.09	± 0.05			
	5.4	4.5E-03	0.14	0.21	0.20	0.57	0.13	± 0.01			
	5.8	1.1E-03	0.07	0.07	0.38	0.53	0.16	± 0.02			
[Cd] 2×10^{-5} mol L ⁻¹ ; [DOC] 120 mg L ⁻¹	4.0	1.0E-01	0.75	0.59	0.01	0.39	0.05	± 0.04	-0.10	± 0.03	0.01
	4.0	4.6E-02	0.61	0.51	0.03	0.45	0.04	± 0.01			
	4.0	1.1E-02	0.37	0.37	0.13	0.49	0.09	± 0.04	-0.01	± 0.08	0.03
	4.1	5.7E-03	0.26	0.27	0.21	0.52	0.12	± 0.04			
	4.0	1.2E-03	0.16	0.12	0.52	0.35	0.17	± 0.03			
	5.1	1.0E-01	0.37	0.20	0.01	0.76	0.07	± 0.02			
	5.1	5.1E-02	0.21	0.15	0.02	0.80	0.11	± 0.03			
	5.1	1.1E-02	0.09	0.09	0.07	0.82	0.13	± 0.04			
	5.0	4.9E-03	0.05	0.06	0.14	0.78	0.15	± 0.02			
	5.0	1.1E-03	0.02	0.02	0.36	0.61	0.19	± 0.04	0.01	± 0.09	0.01
	6.0	9.9E-02	0.15	0.07	0.00	0.87	0.11	± 0.02			
	6.0	5.2E-02	0.09	0.05	0.01	0.88	n.d.				
	6.0	1.0E-02	0.02	0.02	0.03	0.90	0.13	± 0.02			
	6.1	4.9E-03	0.02	0.01	0.05	0.89	0.14	± 0.01			
	6.0	1.2E-03	0.01	0.00	0.18	0.78	0.18	± 0.05	0.01	± 0.05	0.01
[Cd] 2×10^{-6} mol L ⁻¹ ; [DOC] 120 mg L ⁻¹	4.1	1.0E-01	0.54	0.36	0.01	0.61	0.08	± 0.02	-0.07	± 0.01	0.01
	4.1	4.6E-02	0.34	0.30	0.02	0.66	0.10	± 0.03			
	4.1	9.8E-03	0.18	0.18	0.08	0.71	0.14	± 0.02			
	4.2	4.7E-03	0.10	0.11	0.14	0.72	n.d.				
	4.2	9.8E-04	0.06	0.04	0.41	0.54	0.22	± 0.01			
	5.2	1.0E-01	0.20	0.08	0.00	0.86	0.10	± 0.02	0.00	± 0.04	0.02
	5.2	5.1E-02	0.12	0.06	0.01	0.88	0.12	± 0.05			
	5.2	9.9E-03	0.04	0.03	0.03	0.90	0.14	± 0.03			
	5.1	5.3E-03	0.02	0.02	0.05	0.88	0.19	± 0.04			
	5.2	9.5E-04	0.01	0.01	0.22	0.75	n.d.				

258 3.3. Cd isotope fractionation during complexation with HA

259 The amount of Cd complexed with HA ranged from 25 to 99% of total Cd in solution (Table 1).
260 After experiments, the $\delta^{114/110}\text{Cd}$ values in solution varied from $0.02 \pm 0.02\text{‰}$ to $0.22 \pm 0.01\text{‰}$, showing
261 preferentially enrichment in light Cd isotopes in the complexed form. The kinetic experiments
262 demonstrated that the Cd isotopic composition was constant throughout the experiment at high ionic
263 strength and that a plateau was rapidly reached after 5 hours at low ionic strength (Fig. S5). Therefore, we
264 can assume that Cd complexation with HA reached isotopic equilibrium in the experimental conditions
265 (Fig. 3). The overall Cd isotope fractionation was defined as $\Delta^{114/110}\text{Cd}_{\text{HA-Cd(aq)}}$ of $-0.15 \pm 0.01\text{‰}$.
266 Oppositely, previous research on the complexation of other metals belonging to the first row transition
267 (Cu, Fe, and Zn) showed an enrichment in heavy isotopes bound to HA. These observations were
268 attributed to their stronger binding in organocomplexes than in aqueous solution at equilibrium.⁶⁷⁻⁷⁰
269 Cadmium does not undergo natural redox reactions in such settings, leading us to hypothesize that the
270 isotope fractionation was driven by differences in Cd coordination chemistry between the dissolved
271 species and the complexed species. In our case, Cd complexation is driven by carboxylic sites and the
272 electrostatic attractions, which may cause different Cd isotope fractionations as demonstrated for Cu with
273 HA,⁶⁹ and in other systems for Zn.^{71,72}

274 Consequently, this study highlights the importance of modeling to set up the experimental
275 conditions, which included: (i) pH variations from 4 to 6, (ii) ionic strengths variations from $10^{-3} \text{ mol L}^{-1}$
276 to $10^{-1} \text{ mol L}^{-1}$, and (iii) Cd concentrations in solution varying from $10^{-6} \text{ mol L}^{-1}$ to $10^{-4} \text{ mol L}^{-1}$. By
277 including all of these conditions, we had enough controlled data to determine Cd isotope fractionation
278 associated with its complexation with carboxylic groups ($\Delta^{114/110}\text{Cd}_{(\text{COO-Cd})-\text{Cd(aq)}}$) and that of the
279 electrostatic attractions ($\Delta^{114/110}\text{Cd}_{(\text{Cd}^{2+})-\text{Cd(aq)}}$).

280



281
 282 **Figure 3:** $\delta^{114/110}\text{Cd}$ values (‰) in solution as a function of the remaining Cd in solution ($f(\text{Cd})$) at
 283 different ionic strengths and Cd concentrations ($10^{-6} \text{ mol L}^{-1}$, $10^{-5} \text{ mol L}^{-1}$ and $10^{-4} \text{ mol L}^{-1}$) after 24 h of
 284 equilibration. Error bars on the y axis refer to 2SD. The graphical estimation gives an overall $\Delta^{114/110}\text{Cd}_{\text{HA-}}$
 285 $\text{Cd}_{(\text{aq})} = -0.15 \pm 0.01\text{‰}$ for the samples, with a linear regression set to 0.00‰ for $f(\text{Cd})$ value of 1 (black
 286 dashed line). The slope uncertainty (± 0.01) was determined by the least-squares method. The green
 287 shading shows the isotopic range of the bulk starting composition (NIST SRM 3108).

288 3.3.1. Specific Cd complexation: carboxylic sites

289 The proportion of Cd complexed with carboxylic sites was determined based on the NICA-
 290 Donnan thermodynamic modeling (Table 1). At high ionic strengths, Cd complexation was primarily
 291 dependent on the carboxylic groups ($\text{Cd}^{2+}_{\text{D}}$ lower than 3% of the total Cd and a ratio $\text{Cd}^{2+}_{\text{D}}/\text{COO-Cd}$ lower
 292 than 0.07 (16 samples). In these conditions, fifteen $\delta^{114/110}\text{Cd}$ values in solution were related to Cd
 293 complexation with the carboxylic sites, which represents a preferential enrichment in light isotopes bound
 294 to HA following a linear regression (slope: -0.13 ± 0.01 , $R^2=0.80$, Fig. S6). Therefore, the $\Delta^{114/110}\text{Cd}_{(\text{COO-}}$

295 $\Delta^{114/110}\text{Cd}_{(\text{COO-Cd})-\text{Cd}(\text{aq})}$ was estimated to $-0.13 \pm 0.01\%$. As an alternative to the graphical evaluation,⁶⁹ $\Delta^{114/110}\text{Cd}_{(\text{COO-Cd})-$
296 $\text{Cd}(\text{aq})$ can be calculated with Eq. 2 and 3

297
$$\Delta^{114/110}\text{Cd}_{\text{final solution-starting solution}} = \delta^{114/110}\text{Cd}_{\text{final solution}} - \delta^{114/110}\text{Cd}_{\text{starting solution}} \quad (2)$$

298
$$\Delta^{114/110}\text{Cd}_{(\text{COO-Cd})-\text{Cd}(\text{aq})} = - \frac{\Delta^{114/110}\text{Cd}_{\text{final solution-starting solution}}}{\%(\text{COO-Cd})} \times 100 \quad (3)$$

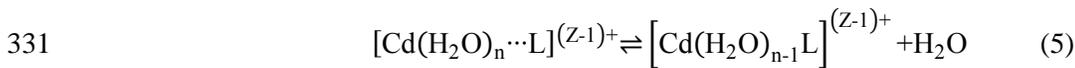
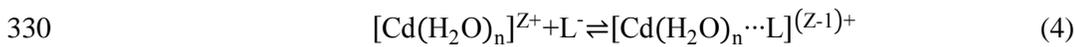
299 where $\delta^{114}\text{Cd}_{\text{starting solution}}$ is the measured isotope composition of the starting solution. The $\delta^{114}\text{Cd}_{\text{final solution}}$ is
300 the measured isotope composition of the solution at the end of the complexation experiment, and $\%(\text{COO-}$
301 $\text{Cd})$ is the percentage of the Cd complexed with carboxylic groups. The calculation resulted in a mean
302 $\Delta^{114/110}\text{Cd}_{(\text{COO-Cd})-\text{Cd}(\text{aq})}$ value of $-0.12 \pm 0.03\%$ (2SD, n=16).

303 As a consequence, the preferential enrichment in light Cd isotopes bound to HA demonstrated that
304 the dominant species of dissolved Cd likely have more stable bonds than those in the complexed form.^{73,74}
305 The calculated Cd-O distances for the most common aqueous form ($\text{Cd}(\text{H}_2\text{O})_6^{2+}$), either using the density
306 functional theory,⁷⁵ X-ray diffraction,⁷⁶ or RHF/DZP,⁷⁷ range from 2.29 to 2.34 Å. Moreover, the Cd-O
307 distances in perchlorate or nitrate solution vary from 2.28 to 2.31 Å with an octahedral geometry and
308 depend on the thermal effect during XAS measurements.^{76,78-81} In our study, the Cd K-edge EXAFS
309 spectra for Cd bound to HA were successfully fitted with first shell coordination of the Cd complexed to
310 HA with an average Cd-O length of 2.29 Å (Fig. S7). Therefore, based on the numerous studies dealing
311 with Cd in solution, we agree that a slight change of the Cd-O first coordination does not permit to
312 confirm that carboxylic groups might express longer and thus weaker bonds than in an aqueous solution.

313 According to Koopal et al.⁴⁷, the thermodynamic parameter “nCd/nH” is interpreted as the
314 stoichiometry of the binding reaction (Table S1). The ratio of 0.9 indicates that the average stoichiometry
315 of Cd binding with carboxylic groups^{82,83} (with respect to the proton reaction) is mainly monodentate.
316 Therefore, the obtained value (2.29 Å), which represents the average value of six Cd-O in the first Cd
317 coordination shell, does not differ from the established Cd-O lengths obtained from Cd solution
318 species.^{76,78-81} In contrast, S ligands leading to significant coordination changes^{84,85} induce an apparent Cd

319 isotope fractionation.^{81,86} As a consequence, the coordination of carboxylic groups to Cd in monodentate
 320 fashion led to similar bond distances to water oxygens than in solution. Therefore, a significant isotopic
 321 shift would be observed as a result of a bidentate or multidentate Cd complex. Based on the fact that bond
 322 strength is related to bond length^{87,88}, the preferential presence of heavier Cd isotopes in the solution
 323 cannot be explained only by their smaller Cd-O length than those bound to HA.

324 Monodentate binding to negatively-charged oxygen donor atoms (phenolic and carboxylic
 325 functional groups) and the associated linear free energy relationships (LFER) for metal-ligand
 326 complexation led to a different behavior for Cd than for metals of the first transition row.⁸⁹ Contrary to the
 327 metals from the first row transition, Cd²⁺ may be subjected to a larger extent to outer-sphere complex prior
 328 formation with a ligand in an aqueous solution.^{90,91} Indeed, Cd-ligand (L⁻) overall complexation can be
 329 described by the following two equilibrium reactions:



332 where $[\text{Cd}(\text{H}_2\text{O})_n \cdots \text{L}]^{(Z-1)^+}$ denotes an outer-sphere complex, in which the ligand forms hydrogen-
 333 bonds with water molecules in the first coordination sphere of Cd²⁺, and $[\text{Cd}(\text{H}_2\text{O})_{n-1} \text{L}]^{(Z-1)^+}$ is the inner-
 334 sphere complex in which one water molecule is replaced by the ligand in the first coordination sphere of
 335 Cd²⁺. Therefore, Cd bound to carboxylic groups includes $[\text{Cd}(\text{H}_2\text{O})_{n-1} \text{L}]^{(Z-1)^+}$ and $[\text{Cd}(\text{H}_2\text{O})_n \cdots \text{L}]^{(Z-1)^+}$.

336 Moreover, theoretical calculations showed that the reduced partition function ratio (RPFR) $10^3 \ln$
 337 $(\beta_{114-110})$ of the Cd hydration complexes increased with the increase of the number of water molecules,
 338 suggesting that the change in the hydration complexes (4, 5, or 6) may be a significant factor for isotope
 339 fractionation in solution.⁷⁵ The isotopic offsets in $\delta^{114/110}\text{Cd}$ ($\Delta^{114/110}\text{Cd}_{\text{hydration complexes}}$) can be estimated
 340 using the subtraction of one RPFR from another⁷⁵ (Eq. 6).

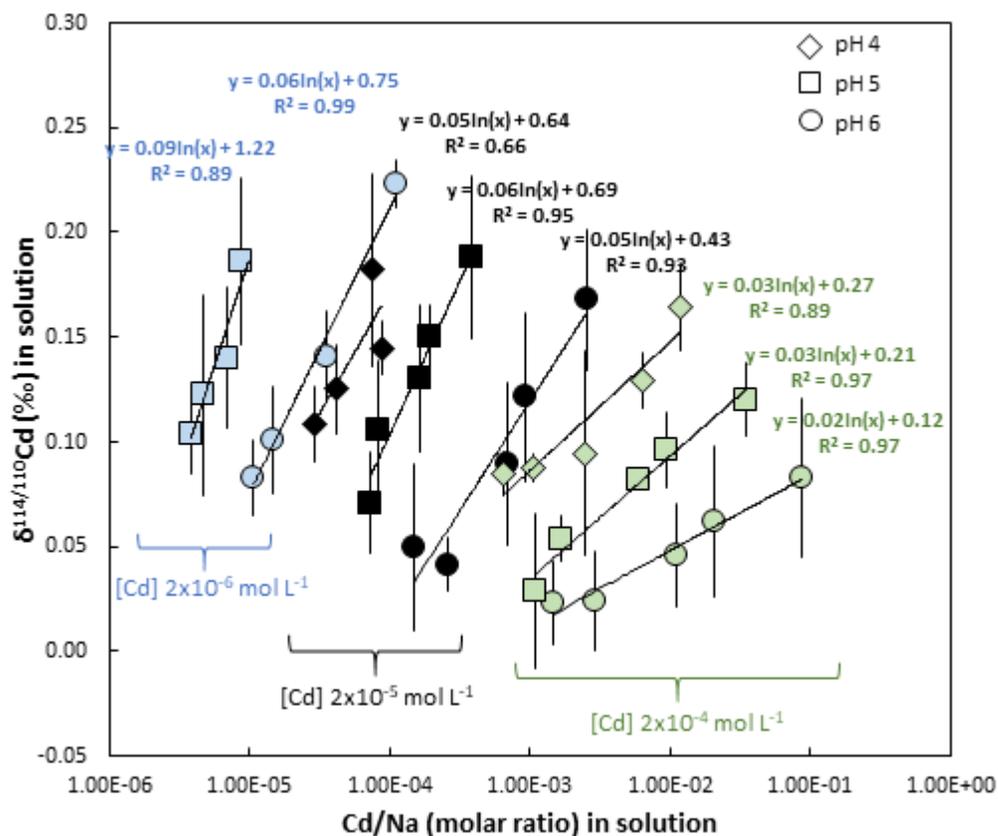
341
$$\Delta^{114/110}\text{Cd}_{\text{hydration complexes}} = \delta^{114/110}\text{Cd}(\text{H}_2\text{O})_{n-1} - \delta^{114/110}\text{Cd}(\text{H}_2\text{O})_n = 10^3 \ln \beta_{114-110} \text{Cd}(\text{H}_2\text{O})_{n-1} - 10^3 \ln \beta_{114-110} \text{Cd}(\text{H}_2\text{O})_n$$

342 (6)

343 The isotopic Cd shift is more pronounced at low temperatures. At 25°C, the RPFR exhibited
344 2.299, 2.261, and 2.167 for $\text{Cd}(\text{H}_2\text{O})_6^{2+}$, $\text{Cd}(\text{H}_2\text{O})_5^{2+}$, $\text{Cd}(\text{H}_2\text{O})_4^{2+}$, respectively.⁷⁵ These results
345 demonstrated that the lighter Cd isotopes were less stable and thus more susceptible to release a water
346 molecule (inner-sphere complex) leading to the preferential enrichment of lighter Cd isotopes in the HA
347 fraction. Moreover, X-ray absorption spectroscopy (XAS) studies on Cd coordination in solution revealed
348 that Cd^{2+} could primarily occur as a $\text{Cd}(\text{H}_2\text{O})_7^{2+}$ aqueous complex.⁹²⁻⁹⁴ Therefore, Cd hydration complex
349 in the aqueous solution is crucial in deciphering the isotope fractionation during its complexation and for
350 Cd isotope systematics in environmental studies in general.

351 **3.3.2. Non-specific Cd binding: electrostatic attractions**

352 In addition to the role of carboxylic groups in Cd complexation, the electrostatic attractions also
353 played a major role in the total Cd complexation with HA, especially at low ionic strengths and low pH
354 values (Fig. 2, S3, and S4). Cadmium isotope fractionation plotted as a function of the Cd/Na molar ratio
355 in solution followed a logarithmic regression exhibiting slopes increasing from 0.02 to 0.09 with
356 decreasing Cd/Na molar ratio, with the R^2 factor ranging from 0.66 to 0.99 (Fig. 4).



357
 358 **Figure 4:** Cadmium isotopic composition ($\delta^{114/110}\text{Cd}$ expressed in ‰) in solution as a function of Cd/Na
 359 (molar ratio) in solution at the beginning of the experiment. At each pH and each [Cd] in solution, the
 360 experimental data follows a logarithmic regression expressed by the equation and the R^2 factor. The error
 361 bars represent the analytical error (2SD).

362 Prior to this study, the exact influence of non-specific binding induced by electrostatic attractions
 363 on metal isotope fractionation has never been studied during metal complexation with HA. The
 364 complexation of Zn with HA, despite a low ionic strength ($2 \times 10^{-3} \text{ mol L}^{-1}$), has shown that electrostatic
 365 attractions represent only a small proportion of Zn bound to HA and therefore not capable to cause a
 366 measurable isotope fractionation.⁶⁸ The same observation has been noted for Cu at high ionic strength (10^{-1}
 367 mol L^{-1}), where electrostatically adsorbed Cu represented only a minor part (0.1-1%) of total Cu bound
 368 to HA.⁶⁹ However, our results showed that the proportion of Cd complexed by electrostatic attractions
 369 reached up to 50% of the total Cd, corresponding to 60% of the total complexed Cd (Fig. 2). Based on the
 370 Cd isotopic composition measured in solution and the Cd isotope fractionation attributed to the carboxylic

371 complexation, an isotopic mass balance calculation can be used to estimate the effective fractionation
 372 coefficient induced by electrostatic attractions with Eq. 7 and 8:

$$373 \quad \Delta^{114/110}\text{Cd}_{x-y} = \delta^{114/110}\text{Cd}_x - \delta^{114/110}\text{Cd}_y = 1,000 \ln(\alpha_{x-y}) \quad (7)$$

$$374 \quad \alpha_{x-y} = \frac{\delta^{114/110}\text{Cd}_x + 1,000}{\delta^{114/110}\text{Cd}_y - 1,000} \quad (8)$$

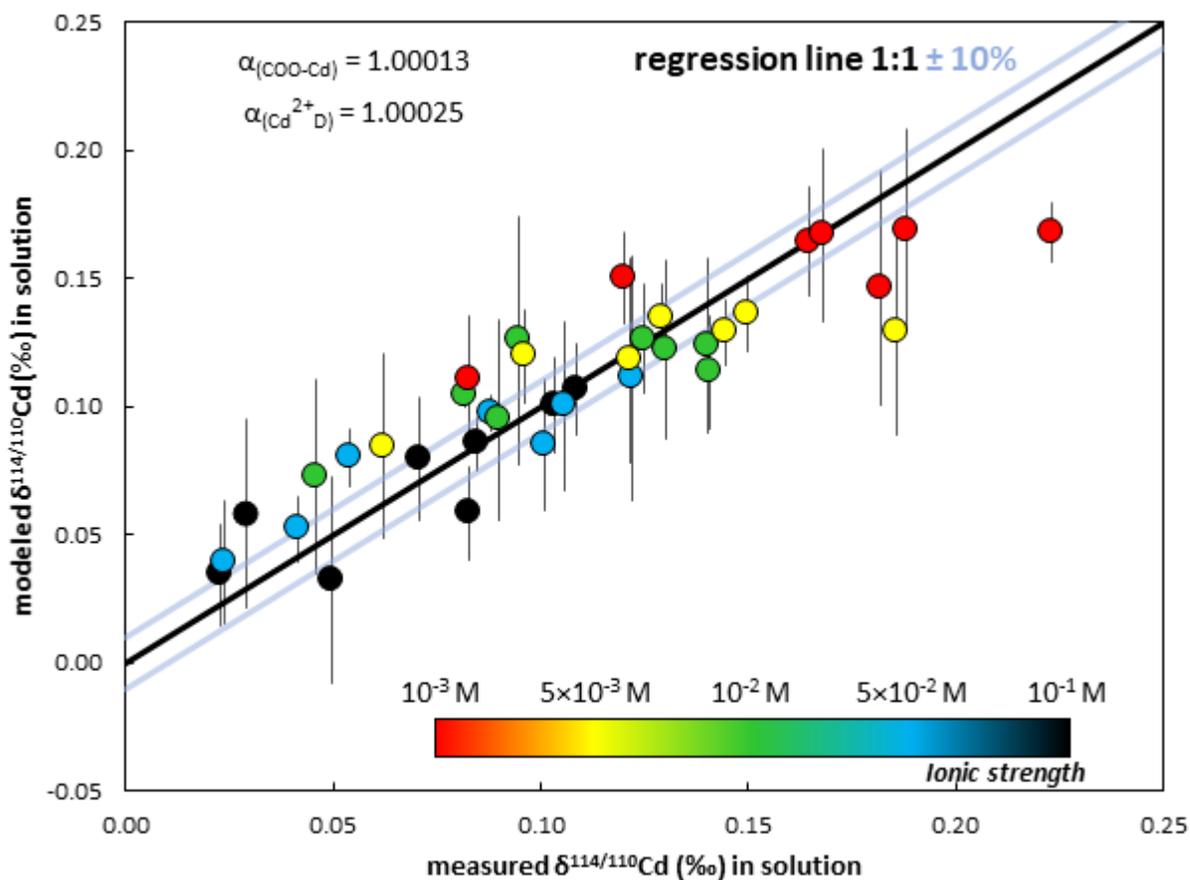
375 where x represents $\text{Cd}^{2+}_{\text{aq}}$ and y represents COO-Cd and $\text{Cd}^{2+}_{\text{D}}$; with their associated fractionation
 376 coefficient $\alpha_{(\text{COO-Cd})}$ and $\alpha_{(\text{Cd}^{2+}_{\text{D}})}$, respectively. According to our previous results, we defined $\alpha_{(\text{COO-Cd})}$ as
 377 1.00013 and the $\alpha_{(\text{Cd}^{2+}_{\text{D}})}$ was determined by the least-squares method to model the $\delta^{114/110}\text{Cd}$ values in
 378 solution with Eq 9:

$$379 \quad \delta^{114/110}\text{Cd}_{\text{modeled solution}} = -1,000f \left[\frac{P_{\text{COO-Cd}} \times (\alpha_{(\text{COO-Cd})} - 1)}{1 - f + (f \times \alpha_{(\text{COO-Cd})})} + \frac{P_{\text{Cd}^{2+}_{\text{D}}} \times (\alpha_{(\text{Cd}^{2+}_{\text{D}})} - 1)}{1 - f + (f \times \alpha_{(\text{Cd}^{2+}_{\text{D}})})} \right] \quad (9)$$

380 where f is the total fraction complexed with HA, $P_{\text{COO-Cd}}$ and $P_{\text{Cd}^{2+}_{\text{D}}}$ are the proportions of each site in total
 381 complexed Cd, and $\alpha_{(\text{COO-Cd})}$ and $\alpha_{(\text{Cd}^{2+}_{\text{D}})}$ are their respective fractionation coefficients.

382 Therefore, the best agreement between the measured $\delta^{114/110}\text{Cd}$ values in solution and modeled
 383 $\delta^{114/110}\text{Cd}$ values determined an $\alpha_{(\text{Cd}^{2+}_{\text{D}})}$ of 1.00025, giving a $\Delta^{114/110}\text{Cd}_{\text{Cd}^{2+}_{\text{D-Cd(aq)}}$ of -0.25‰ (Fig. 5).
 384 Surprisingly, the electrostatic attractions induced more extensive isotope fractionation than Cd
 385 complexation with carboxylic groups. However, when Cd complexation with carboxylic groups led to an
 386 inner-sphere complex, the electrostatic attractions were likely caused by a dipole-ion attraction between
 387 the Cd cation and the dipole of the oxygen from the OH responsible for an outer-sphere interaction.

388 Under such conditions, the electrostatic bonds are weak, and the Cd coordination number
 389 (complexation or hydration complexes) or Cd-HA bond lengths will not be modified relatively to the
 390 aqueous form of Cd. Therefore, there is no reason that such process induces Cd isotope fractionation. We
 391 also show the modeled $\delta^{114/110}\text{Cd}$ values in solution with a value of $\alpha_{(\text{Cd}^{2+}_{\text{D}})}$ set to 1, signifying that
 392 electrostatic attractions do not produce measurable Cd isotope fractionation (Fig. S8), which led to an
 393 underestimation of the measured $\delta^{114/110}\text{Cd}$ values at lower ionic strengths.



394
 395 **Figure 5:** Comparison between measured $\delta^{114/110}\text{Cd}$ in solution and modeled $\delta^{114/110}\text{Cd}$ through isotopic
 396 mass balance calculation (Eq. 8) for $\alpha_{(\text{COO-Cd})}$ of 1.00013, and $\alpha_{(\text{Cd}^{2+}_{\text{D}})}$ of 1.00025. The $\alpha_{(\text{Cd}^{2+}_{\text{D}})}$ was
 397 determined by the least-squares method. The black line represents the linear regression 1:1 with a range of
 398 10% (grey lines). The error bars represent the analytical error (2SD).

399 Therefore, a $\Delta^{114/110}\text{Cd}_{\text{Cd}^{2+}_{\text{D-Cd(aq)}}}$ of -0.25‰ has to be applied to Cd isotopes fractionation during
 400 the complexation with HA. Humic acids are large and negatively charged polyelectrolytes, which results
 401 in the accumulation of cations in the vicinity of HA binding sites, leading to different chemical conditions
 402 between the solution and the vicinity of HA. Electrostatic models⁹⁵ (Nica Donnan, Donnan-EV, Donnan-
 403 EDL model, etc.) aim at converting the dissolved cation concentration in the bulk solution ($[\text{C}]_i$) to a local
 404 dissolved cation concentration ($[\text{C}]_{\text{loc},i}$) that occurs adjacent to the HA site, calculated according to the
 405 Boltzmann's law with Eq. 10:

406
$$[C]_{Cd_D^{2+}} = [C]_{Cd_{aq}^{2+}} \times \exp\left(-\frac{z(Cd^{2+})F\Psi}{RT}\right) \quad (10)$$

407 where $z(Cd^{2+})$ is the valence of Cd, F is the Faraday constant, Ψ is the electrostatic potential of HA
 408 particles, R is the gas constant, and T is the absolute temperature. This effect is calculated using the
 409 Boltzmann factor (Bf) with Eq. 11:

410
$$Bf = \frac{[C]_{Cd_D^{2+}}}{[C]_{Cd_{aq}^{2+}}} \quad (11)$$

411 The $\Delta^{114/110}Cd_{HA-Cd(aq)}$ calculated (Eq. 12), based on measured $\delta^{114/110}Cd$ value and the verified
 412 isotopic mass balance (Table 1), was expressed as a function of the Bf (Fig. 6).

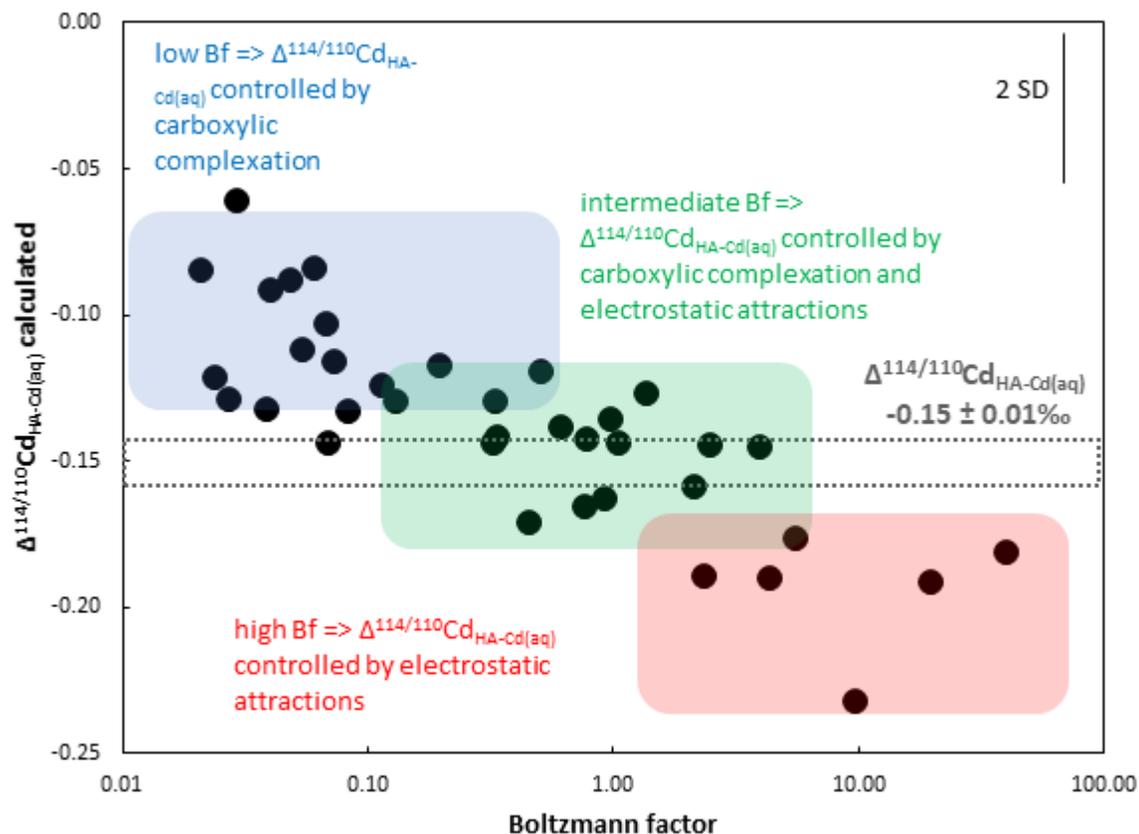
413
$$\Delta^{114/110}Cd_{HA-Cd(aq) \text{ calculated}} = (\delta^{114/110}Cd_{\text{initial}} - f(Cd_{aq}) \times \delta^{114/110}Cd_{\text{solution}}) / (1 - f(Cd_{aq})) - (\delta^{114/110}Cd_{\text{solution}})$$

 414
$$(12)$$

415 where $f(Cd_{aq})$ is the proportion of Cd in the aqueous form in solution and $\delta^{114/110}Cd_{\text{initial}}$ is set to 0‰.

416 At low Bf, isotope fractionation is limited, and the $\Delta^{114/110}Cd_{HA-Cd(aq)}$ is controlled by carboxylic
 417 complexation. However, at high Bf, the strongest isotope fractionation is observed, related to the non-
 418 specific Cd binding during electrostatic attractions. As a result, these must play a significant role in Cd
 419 isotope fractionation during complexation with HA. As previously observed for Zn sorption onto
 420 kaolinite,⁷² the mechanism leading to preferential lighter Cd isotope enrichment during outer-sphere
 421 complexation formation *via* electrostatic attractions remains unclear and additional studies are required to
 422 explain the effect of electrostatic attractions on metal isotope fractionation.

423 In general, Cd isotope fractionation is controlled by pH and ionic strength and occurs throughout
 424 specific complexation processes with the carboxylic sites and non-specific Cd binding induced by
 425 electrostatic attractions. Based on our large experimental dataset, the overall Cd isotope fractionation due
 426 to Cd complexation with HA can be set for future studies as a $\Delta^{114/110}Cd_{HA-Cd(aq)}$ of $-0.15 \pm 0.01\%$.



427
 428 **Figure 6:** $\Delta^{114/110}\text{Cd}_{\text{HA-Cd(aq)}}$ calculated as a function of the Boltzmann factor (Bf). The error bar represents
 429 the highest analytical error observed for one measured $\delta^{114/110}\text{Cd}$ value (2SD). The grey rectangle
 430 represents the overall Cd isotope fractionation due to Cd complexation with HA as $\Delta^{114/110}\text{Cd}_{\text{HA-Cd(aq)}} = -$
 431 $0.15 \pm 0.01\text{‰}$.

432 4. Environmental implications

433 Our study is an important contribution to Cd isotope systematics focusing on Cd complexation
 434 with HA, an important constituent in soils, sediments and waters. Information on Cd isotope fractionation
 435 after complexation with natural organic matter is crucial to fully understand the biogeochemical processes
 436 in the Cd-soil-aqueous solution-plant continuum and for contamination tracing. The introduction of Cd to
 437 the soil environment and its initial solubilization is followed by numerous biogeochemical reactions with
 438 soil components. Modeling Cd speciation in soil solution revealed that dissolved Cd is present either
 439 bound to dissolved organic matter (DOM) or as free Cd^{2+} .⁸⁶ Based on our data on Cd isotope fractionation

440 after complexation with the carboxylic sites and bound to HA by electrostatic attractions, we show that
441 free Cd^{2+} , which is the main form taken up by the plants,⁹⁶ should be preferentially enriched with the
442 heavier isotopes compared to Cd bound to soil organic matter, as assumed in a previous study.⁸⁶ These
443 findings are in accordance with the heavier Cd isotope pool available for crops and Cd hyper-
444 accumulating plant species.^{8-11,86} However, when environmental factors change, e.g., pH and Eh due to
445 flooding, contaminants input, soil organic matter quantity and quality, ionic strength of the soil solution,
446 etc., changes of Cd sorption/desorption occurs as a result of the competition of negatively charged sites,
447 and the Cd isotope composition may thus be strongly modified. In order to completely understand Cd
448 behavior in the soil environment, studies involving other soil constituents, and their affinity to Cd, are
449 required. Moreover, a comparison of our study with HA analogs (plants, phytoplankton, diatoms, etc.)
450 would allow explaining simple complexation mechanisms, although we are aware of the fact that limiting
451 the conclusions to these simple processes might be a simplification.

452 Cadmium is mainly coordinated with O atoms^{97,98} in plant tissues of Cd hyperaccumulators, as
453 determined by Cd K-edge EXAFS spectroscopy. Additionally, Ueno et al.⁹⁹ and Tian et al.¹⁰⁰ found that in
454 Cd hyperaccumulators leaves, Cd was present in an octahedral coordination with O ligands, possibly due
455 to the presence of malate and citrate. Therefore, the complexation of Cd with malate and citrate in the
456 leaves, i.e., carboxylic ligands, might be responsible for the preferential enrichment in light isotopes.
457 Recent development of Cd isotope measurements in the ocean provides new clues for identifying the key
458 mechanisms controlling the Cd biogeochemical cycle in surface ocean. While the effect of uptake by
459 phytoplankton on $\delta^{114/110}\text{Cd}$ signatures has been shown in nutrient repleted regions,^{4,101} the impact of
460 organic complexation is still debated, namely for its buffering effect on the $\delta^{114/110}\text{Cd}$ measured in
461 nutrient-depleted waters.¹⁰² In surface seawater, Cd aqueous speciation is dominated by Cd-organic
462 complexes.¹⁰³⁻¹⁰⁵ Thus, the dissolved $\delta^{114/110}\text{Cd}$ is similar to those complexes. Previous research has shown
463 that Cd organic complexation only occurs via surface complexation since the 0.5 mol L^{-1} mean ionic
464 strength of seawater prevents any electrostatic attractions. Louis et al.¹⁰⁶ showed that dissolved organic
465 matter sampled in the Mediterranean Sea off the coast of France is composed of 60% carboxylic and 40%

466 phenolic sites, in agreement with the overall binding site composition of the HA used in this study.
467 Therefore, based on the relatively small value of $\Delta^{114/110}\text{Cd}_{(\text{COO-Cd})-\text{Cd}(\text{aq})} = -0.13\text{‰}$ determined in our study,
468 only a minor change of dissolved oceanic $\delta^{114/110}\text{Cd}$ can be associated with organic complexation. The
469 isotopic shift is even smaller than the Cd isotope partitioning between Cd inorganic species ($\Delta^{114/110}\text{Cd}$ of
470 0.3‰ for $\text{Cd}^{2+}/\text{CdCl}_2$).¹⁸

471 In addition to organic ligands, phytoplankton-derived debris found as particles in the surface
472 ocean can act as a Cd sink via surface complexation. After diatom remineralization, Cd adsorption
473 occurring on the remineralization-resistant *Dunaliella tertiolecta* surface leads to a limited $\Delta^{114/110}\text{Cd}$
474 fractionation of $-0.1 \pm 0.1\text{‰}$.⁵ Furthermore, Pokrovsky et al.¹⁰⁷ and Gélabert et al.¹⁰⁸ have shown that
475 carboxyl functional groups are responsible for more than 90% of total bound Zn and the behavior of Cd is
476 similar to Zn since these two metals share the same geochemical traits. Therefore, our observations of
477 limited Cd isotope fractionation during complexation with carboxylic groups is totally consistent with
478 previous studies and strengthens the limited impact of Cd scavenging on the distribution of Cd isotopes
479 during diatom mineralization.

480 As a conclusive remark, in nutrient-rich regions, the impact of organic complexation on $\delta^{114/110}\text{Cd}$
481 in surface oceanic waters is secondary with respect to Cd uptake by phytoplankton, which tends to enrich
482 the dissolved $\delta^{114/110}\text{Cd}$ with preferentially heavier isotopes ($\Delta^{114/110}\text{Cd}_{\text{surface-deepwater}}$ up to 2.5‰).^{4,52,101}
483 However, in oligotrophic environments, stable and light $\delta^{114/110}\text{Cd}$ were measured at picomolar Cd
484 concentrations.^{102,109} As reported before, due to the predominance of the Cd-organic complexes in the
485 dissolved fraction, dissolved $\delta^{114/110}\text{Cd}$ is directly driven by the Cd-organic fraction. The absence of
486 heavier $\delta^{114/110}\text{Cd}$ linked with Cd biological uptake in such context indicates a buffering effect of the Cd-
487 organic complexes in solution as proposed recently by Xie et al.¹⁰² and Guinoiseau et al.⁶ for the Atlantic
488 Ocean transects. So, even if a small isotope fractionation is observed during Cd organic complexation, the
489 importance of these organic complexes on the Cd oceanic cycle in metal-depleted water masses can be
490 indirectly indicated using Cd isotopes.

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504 **Author Contributions**

505 M.K., V.C. and G.R. conceived the idea. G.R. designed the global experiment and developed the
506 Cd isotopes determination with contributions of V.C. and Z.V. (Cd separation and TIMS measurements).
507 R.M. and G.R. performed the modelling and the interpretation. G.R. drafted the manuscript with inputs
508 from all authors with extended participation of D.G., specifically on the ocean discussion part. M.K. was
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