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Trace metal mobilization by organic soil amendments: Insights gained from analyses of solid and solution phase complexation of cadmium, nickel and zinc

Dharshika Welikala, Cameron Hucker, Adam Hartland, Brett H. Robinson, Niklas J. Lehto



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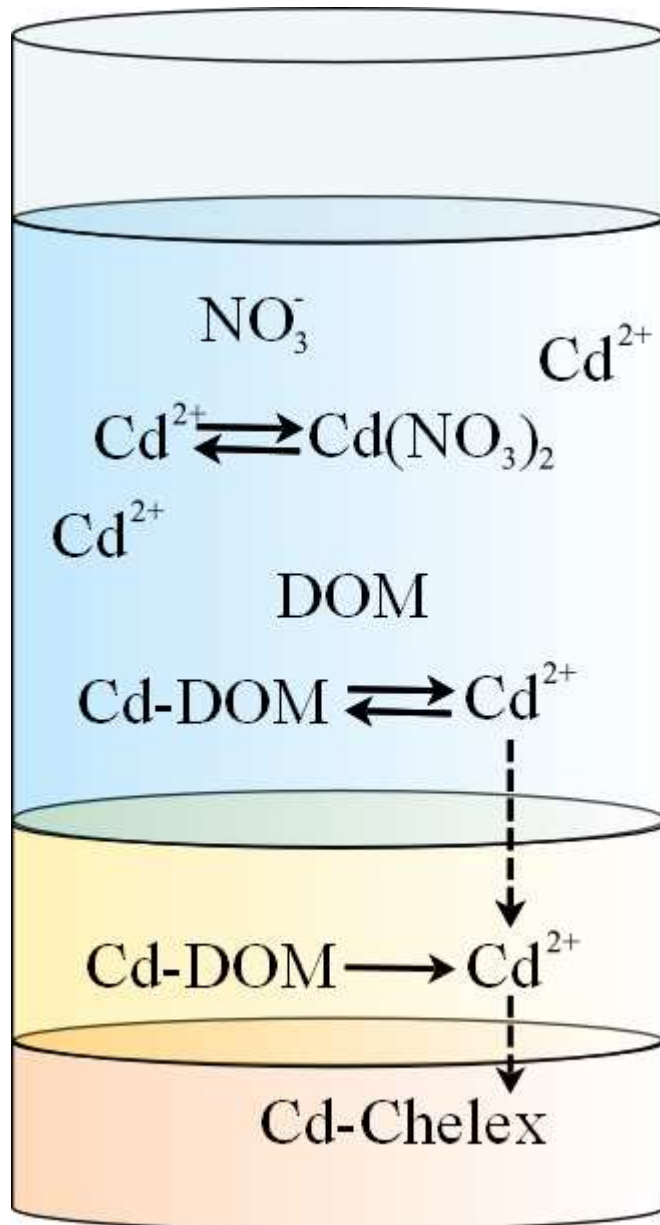
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1 **Trace metal mobilization by organic soil amendments:**
2 **insights gained from analyses of solid and solution phase**
3 **complexation of cadmium, nickel and zinc.**

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5 Dharshika Welikala¹, Cameron Hucker¹, Adam Hartland², Brett H. Robinson³ and Niklas J.
6 Lehto^{1,*}

7
8 ¹ Department of Soil and Physical Sciences, Lincoln University, Lincoln 7647, Christchurch,
9 New Zealand

10 ² Environmental Research Institute, School of Science, University of Waikato, Private Bag
11 3105, Hamilton 3240, New Zealand

12 ³ School of Physical and Chemical Sciences, University of Canterbury

13
14
15 *Corresponding author: N.J. Lehto, Tel: +64 3 423 0796, Fax: +64 3 325 3607, Email:
16 Niklas.Lehto@lincoln.ac.nz

17 **Keywords:** trace metals; organic matter quality; lability; speciation; diffusive gradients in
18 thin-films; soils.

19

20 **Abstract**

21 The accumulation of Cd in soils worldwide has increased the demand for methods to reduce
22 the metal's plant bioavailability. Organic matter rich soil amendments have been shown to be
23 effective in achieving this. However, it is not known how long these amendments can retain
24 the Cd, and whether dissolved organic matter (DOM) released from them can enhance the
25 metal's mobility in the environment. In this study we sought to test the Cd binding capacity
26 of various organic soil amendments, and evaluate differences in characteristics of the DOM
27 released to see if they can explain the lability of the Cd-DOM complexes. We collected ten
28 organic soil amendments from around New Zealand: five different composts, biosolids from
29 two sources, two types of peat and spent coffee grounds. We characterised the amendments'
30 elemental composition and their ability to bind the Cd. We then selected two composts and
31 two peats for further tests, where we measured the sorption of Ni or Zn by the amendments.
32 We analysed the quality of the extracted DOM from the four amendments using 3D
33 Excitation Emission Matrix analysis, and tested the lability of the metal-DOM complexes
34 using an adapted diffusive gradients in thin-films (DGT) method. We found that composts
35 bound the most Cd and that the emergent Cd-DOM complexes were less labile than those
36 from the peats. Ni-DOM complexes were the least labile. The aromaticity of the extracted
37 DOM appears to be an important factor in determining the lability of Ni complexes, but less
38 so for Zn and Cd.

39 1. Introduction

40 Cadmium is a non-essential trace metal that has accumulated in soils worldwide (Kabata-
41 Pendias, 2007). Its relatively high availability for plant uptake allows it to be transported
42 from soils, through the food chain and eventually pose a potential risk to humans and animals
43 (Kabata-Pendias, 2007; Gall et al., 2015). The accumulation of Cd in soils has been linked to
44 sustained application of phosphorous fertilizers, where it is a naturally occurring contaminant
45 (Loganathan et al., 2003; Kelliher et al., 2017; Salmanzadeh et al., 2017). Cadmium can also
46 enter soils through road runoff, industrial emissions and land application of biosolids and
47 effluents (Kabata-Pendias, 2007). There are no low-cost means of removing Cd from soils,
48 and consequently, there has been an increasing focus on options for reducing the
49 bioavailability of Cd instead (e.g. Simmler et al. (2013a); Al Mamun et al. (2016)).

50 Various types of soil amendments have been considered as potential means by which to
51 reduce the uptake of Cd by plants (Bolan and Duraisamy, 2003; Valentinuzzi et al., 2015; Al
52 Mamun et al., 2017; Shaheen et al., 2017). The ideal amendments should reduce Cd uptake,
53 but not impact on the availability of important macro or micronutrients, such as P, Fe or Zn.
54 (Beesley and Marmiroli, 2011; Valentinuzzi et al., 2015), or introduce other contaminants
55 (Beesley et al., 2011; Paramashivam et al., 2017). Moreover, they should be readily available
56 and affordable to allow for their widespread use (Al Mamun et al., 2016).

57 Recent work has shown the potential for different types of organic amendments to bind soil
58 Cd in agricultural soils (Simmler et al., 2013b; Al Mamun et al., 2017), as well as other trace
59 metals (e.g. Pb, Zn, As and Cu) in industrial contaminated soils (Bolan et al., 2014; Abad-
60 Valle et al., 2017; Van Poucke et al., 2017). The ability for different organic amendments to
61 influence trace metal bioavailability is informed by the characteristics of the organic matter

62 that is employed (*e.g.* pH, CEC, humification degree) and the metal of concern (*e.g.* affinity
63 for solid and solution phase complexing ligands), as well as the soil type (Albiach et al.,
64 2000; Bolan et al., 2014).

65 Zinc and nickel can accumulate in soils through a variety of means, including: atmospheric
66 deposition and application of sewage sludge, animal manure and phosphate fertilizers. Both
67 metals are essential to biota at low concentrations (Gonnelli and Renella, 2013; Mertens and
68 Smolders, 2013). Moreover, Zn deficiency in plants has been linked to increased plant uptake
69 of soil Cd (Chaney, 2010). On the other hand, elevated concentrations of Ni and Zn can also
70 have deleterious effects on biota throughout terrestrial food chains (Gall et al., 2015). Both of
71 these metals are intermediate Lewis acids, and are therefore expected to show a greater
72 affinity to intermediate and hard Lewis acids (*e.g.* carboxylic and phenolic functional groups)
73 than Cd, which is a soft Lewis acid. Cadmium is expected to bind strongly to soft Lewis
74 bases in organic matter (*e.g.* reduced sulphur functional groups). By comparing the binding of
75 these metals by a range of organic amendments, we can discover which amendments are
76 suited for optimal management of soils used for food production, and gain insight into the
77 chemical characteristics of the amendments that allow them to best serve this function. This
78 comparison can also be extended to examine the potential mobilization of these metals from
79 the amended soils.

80 Organic matter-based amendments that have been used to immobilize contaminants in soils
81 may be destabilized, resulting in the release of any associated trace metals back into the soil
82 (Grybos et al., 2007; Huang et al., 2016). Moreover, several studies have shown that
83 dissolved organic matter (DOM) can induce metal mobilization through the formation of
84 metal-DOM complexes (see: Bolan et al. (2011) and references therein). Although DOM
85 represents a labile energy source for soil microbes, the readily mineralizable fraction has been

86 found to be often less than 40% of the total (Kalbitz et al., 2000; Haynes, 2005). This makes
87 it a potentially powerful vector for mobilizing otherwise immobile trace metals in the
88 environment and raises the question of what potential risks may be associated with metal-
89 DOM complexes that are transported from contaminated soils.

90 We aimed to determine the trace metal (Cd, Ni and Zn) sorption capacities of different types
91 of organic matter, with a particular focus on Cd. We also sought to elucidate whether the
92 DOM released from these substances show different qualities for enabling the transport and
93 subsequent release of these metals for biological uptake. We used a combination of targeted
94 chemical analyses of soil organic matter stability and capacity to bind trace metals,
95 spectroscopic analyses of DOM quality and novel measurements of trace metal complex
96 lability to achieve these aims.

97 **2. Material and Methods**

98 **2.1. Sample collection and pre-treatment**

99 Ten different types of solid organic matter-rich substrates that are used as soil amendments,
100 either by themselves, or as constituent parts, were selected for analysis. These were two types
101 of peat, used coffee grounds, two types of biosolids and five different composts. Forthwith,
102 these will be referred to as “amendments” for simplicity. The two types of peat were sampled
103 from the Kopuatai ombrotrophic peat dome on the North Island of New Zealand,
104 37°24'45.79"S, 175°33'23.38"E) (Sample ID: OP) and a peat formation on in the Canterbury
105 region of NZ's South Island (43°40'38.22"S, 172°26'52.03"E) (Sample ID: EP). The peat
106 samples underwent an initial screening upon collection using a 10 mm mesh to discard stones
107 and larger plant material. The coffee grounds (Sample ID: CFF) were collected from ten
108 different coffee shops around Christchurch, NZ. The biosolids were collected from two

109 locations: the Kaikōura Regional Treatment Works in Kaikōura, NZ, (Sample ID: KBS) and
110 Christchurch Wastewater Treatment Plant, Christchurch, NZ (Sample ID: CBS). KBS had
111 undergone an initial treatment of sedimentation and anaerobic digestion in settlement ponds.
112 CBS was thermally dried to <10% water content to eliminate pathogens and facilitate
113 transport. Both sets of biosolids samples were provided by the plant operators. The composts
114 were obtained from three locations. Three types of compost were purchased from Parkhouse
115 Garden Supplies Ltd. (Christchurch, NZ). The company was only willing to provide general
116 descriptions of their compositions, which were: (1) compost derived from commercial
117 mushroom growing waste (Sample ID: PH), (2) fish waste and ocean botanicals (Sample ID:
118 PHW), and (3) pig manure and sawdust (Sample ID: PHP); green waste is not used in any of
119 these composts. Compost manufactured by Living Earth Ltd. (Sample ID: LE) is made from
120 municipal green waste (includes: food and garden waste) collected as part of Christchurch
121 city's kerbside waste collection program. The fifth type of compost was purchased from
122 Oderings Nurseries Christchurch Ltd. (Sample ID: OD), the raw materials used to make this
123 are unknown. All samples were air-dried, manually ground and sieved using a nylon sieve (2
124 mm mesh).

125 **2.2. Sample Analysis**

126 All sample analyses and dilutions used high-purity water (HPW, 18.2 M Ω resistivity; Heal
127 Force® SMART Series, SPW Ultra-pure Water system, Model-PWUV). pH (Mettler Toledo
128 Seven Easy) and conductivity (Mettler Toledo Five Easy) of the sieved samples were
129 determined in triplicate using a 1:10 solid:water ratio (w./vol.) and 24 h equilibration time
130 (Blakemore et al., 1987). Total carbon and nitrogen content of the amendments was measured
131 using a Vario-Max CN Analyzer (Elementar Analysensysteme GmbH, Germany). Cold and
132 hot water extractable carbon (CWEC and HWEC, respectively) were measured in all of the

133 amendments following the method described by Ghani et al. (2003). Briefly, 3g of each
134 amendment was sequentially extracted, first with 30 mL HPW at ambient temperature for 30
135 mins, after which the extractant was separated from the sample, filtered (0.45 μm pore
136 diameter cellulose acetate filter) and analysed for total carbon (CWEC) using a Shimadzu
137 TOC-VCSH analyzer (Shimadzu Corporation, Kyoto, Japan). The remaining sample was
138 then extracted with a further 30mL of HPW at 80°C for 16 hours, after which the extractant
139 was separated from the sample, filtered as before and analysed for total carbon (HWEC) as
140 before.

141 Cation exchange capacity (CEC) of the amendments was measured using the silver thiourea
142 (AgTU) method (Blakemore et al., 1987). Briefly, 0.70 g of amendment was equilibrated
143 with 35 mL of 0.01 M AgTU in an end-over-end shaker for 16 h. Samples were then
144 centrifuged at 2000 rpm for 10 min, after which the supernatant was filtered through a
145 Whatman no. 40 filter and analysed using Inductively Coupled Plasma-Optical Emission
146 Spectrometry (ICP-OES) (Varian 720 ES - USA).

147 Pseudo-total elemental content of the amendments was determined by microwave digestion
148 (MARSXPRESS, CEM Corp.) of 0.5 g of sample in 8 mL of Aristar nitric acid ($\pm 69\%$). The
149 digest was then filtered through Whatman no. 52 filter paper (pore size: 7 μm) and diluted
150 with HPW to a volume of 25 mL (Kovács et al., 2000). Certified Reference Materials for soil
151 and plant matter (International Soil analytical Exchange- ISE 921, and International Plant
152 analytical Exchange IPE 100; Wageningen University, The Netherlands) were also analysed
153 to confirm acceptable recovery of the analytes. The digests were analysed for Cd, P, S, Ca,
154 Mg, K, Cd, Zn, Ni, Cu, Pb, Al and Cr using ICP-OES and showed acceptable recoveries for
155 the analytes. The physical and chemical properties of the amendments are shown in Table 1.

156 The different amendments' capacity to sorb Cd was analysed using previously developed
 157 sorption experiments using spiked solutions of 0.05 M of $\text{Ca}(\text{NO}_3)_2$ (Simmler et al., 2013b;
 158 Al Mamun et al., 2016). Briefly, 5 g batches of each amendment, except OP, were mixed
 159 with 30 mL of either 0.05 M $\text{Ca}(\text{NO}_3)_2$ (Sigma-Aldrich) extraction solution, or extraction
 160 solution that had been spiked to 2 mg L^{-1} ($18 \text{ }\mu\text{M}$) of Cd (salt: $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, BDH,
 161 AnalaR). The mass of OP used was reduced to 2 g to ensure a sufficient separation between
 162 solid and solution phases. A vortex mixer was used to agitate the mixtures for 3 min, after
 163 which the pHs of replicate sets of each mixture were adjusted to 4.5, 5, 6.5 (± 0.02) using 2 M
 164 HNO_3 (BDH Aristar) or 2 M NaOH (BDH AnalaR). The mixtures were then placed in an
 165 end-over-end shaker for 2 h, after which they were centrifuged at 3000 rpm for 20 min. The
 166 supernatant was then filtered through Whatman no. 52 filter paper and analysed for the same
 167 analytes as the digests using ICP-OES.

168 The metal adsorption coefficients (K_d) for the different soil amendments were determined at
 169 each pH as described by Simmler et al. (2013b) (Eq. 1):

$$170 \quad K_d \left(\text{L kg}^{-1} \right) = \frac{\text{Metal sorbed by substrate } \left(\text{mg kg}^{-1} \right)}{\text{Metal in solution } \left(\text{mg L}^{-1} \right)}$$

$$171 \quad = \frac{\left(C_{\text{spike}} - \left(C_{\text{eq}} - C_b \right) \right) \times \left(V/m \right)}{\left(C_{\text{eq}} - C_b \right)} \quad (\text{Eq. 1})$$

172 Where K_d describes the solid-solution phase partitioning of the analyte of interest, C_{spike} is the
 173 concentration of metal in the spike solution, C_{eq} is the concentration in the spike solution
 174 after equilibration with the amendment, and C_b is the metal concentration in the unspiked
 175 extractant solution after equilibration. The volume of extractant (0.03 L) and mass of

176 amendment used (0.002 or 0.005 kg) were V and m , respectively. Extraction samples C_{eq} and
177 C_b were analysed in triplicate for each amendment-pH combination.

178 The results of the sorption experiment were used to select four amendments for further
179 analysis. These were the two peat samples (OP and EP), Parkhouse mushroom-derived
180 compost and Living Earth municipal composts (PH and LE).

181 A further sorption experiment using 0.05 M $\text{Ca}(\text{NO}_3)_2$ spiked with Cd, Ni and Zn (salts used:
182 $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (BDH, AnalaR)) was carried out on
183 these amendments at pH 5.5 as before. The molar concentrations of the metals in the spike
184 solution were the same as those of Cd (18 μM) in the previous sorption experiment. The
185 extracted solutions from the four amendments were divided into subsets. Three subsets were
186 allocated for DGT analysis (see below). The other subsets were analysed in triplicate for
187 dissolved Cl^- , SO_4^{2-} , NO_3^- and NH_4^+ using a Shimadzu Ion Chromatograph (Thermo
188 Scientific, DIONEX, ICS-2100), total organic carbon (measured as non-purgeable organic
189 carbon, NPOC) and dissolved inorganic carbon (DIC) using the Shimadzu TOC-VCSH
190 analyser. Differences between the mean K_d values measured for Ni, Cd and Zn in the four
191 amendments were tested by ANOVA with Tukey's post-hoc test using Minitab® 17 (Minitab
192 Inc, State College, Pennsylvania, USA) at the 0.05 level of significance.

193 **2.3. Dissolved Organic Matter Quality**

194 The Ultra-Violet Absorbance of the dissolved organic matter in the extracts was measured at
195 254, 270 and 350 nm using a UV-VIS spectrophotometer (UVmini-1240, SHIMADZU)
196 (Carter et al., 2012). The specific UV-absorbance for the dissolved organic matter (DOM) at
197 the set wavelengths was calculated using Equation 2.

$$198 \quad SUVA_{\lambda} = \frac{A_{\lambda} \times 1000}{b \times [DOC]} \quad (\text{Eq. 2.})$$

199 Where, λ is the wavelength (nm) at which the absorbance (A_{λ}) is measured, b is the path
200 length through quartz cell (cm) and $[DOC]$ is the dissolved organic carbon concentration (mg
201 L^{-1}).

202 Fluorescence excitation-emission matrices (EEMs) for organic matter extractions were
203 obtained by measuring fluorescence emission intensity across excitation wavelengths ranging
204 from 240-600 nm and emission wavelengths ranging from 245-820 nm using a Horiba
205 Aqualog fluorescence spectrophotometer (Kyoto, Japan). All sample fluorescence intensities
206 were normalized using the pure water Raman peak intensity (350 nm excitation, 398 nm
207 emission) at the same analytical settings as the sample. Parallel factor analysis (PARAFAC)
208 for EEM results was conducted to identify statistically independent components within the
209 EEM set, and their relative contributions to the sample EEMs (Fellman et al., 2010).
210 PARAFAC analysis was carried out in MATLAB using the N-way toolbox and DOMFlour
211 toolbox for MATLAB (Stedmon and Bro, 2008) following sample screening for outliers. The
212 optimal number of components was selected in order to minimise the residual sum of squares
213 and maximise model core consistency (Murphy et al., 2013). On the basis of these criteria a
214 two-component model was adopted.

215 **2.4. Diffusive gradients in thin-films analysis**

216 The lability of Cd, Ni and Zn in the extracts obtained from the sorption experiments on the
217 four different amendments was analysed by adapting the method used by Amery et al. (2010).
218 A 1 mL gel layer containing 1 g Chelex-100 cation binding resin (200-400 mesh, Bio-Rad) in
219 an agarose gel matrix (1.5%)(Total Lab Systems, molecular grade) was cast onto the bottom

220 of a flat-base 30 mL sample vials (1.2 cm internal radius); henceforth, this is referred to as
221 the *binding layer*. A 1.36 cm³ agarose-only (1.5%) layer was cast on top of this: the *diffusive*
222 *layer* forthwith. During casting it was observed that there was a small amount of even
223 adhesion to the sides of the SV-DGT, resulting in a slightly concave diffusion layer surface.
224 The vial containing the diffusion and binding layers was placed on a lab shaker with HPW for
225 24 h, during which the water was changed three times. The gels were then conditioned with
226 0.01 M NaNO₃ for at least 8 h before deployment. The use of diffusive and binding layers
227 within a confined test vessel allowed the application of the underlying principles of the
228 diffusive gradients in thin-films (DGT) technique, but in relatively small volumes; forthwith,
229 these devices are referred to as *small volume-DGT* (SV-DGT) devices.

230 2.4.1. Theory of SV-DGT

231 When a simple solution containing trace metals, existing mainly as their hydrated (free) ion
232 species, is deployed in an SV-DGT device, the metal ions diffuse through the diffusive layer
233 and towards the binding layer, where they are rapidly bound by the chelating resin. Within
234 approx. 60 minutes a linear concentration gradient is formed within the diffusive layer and a
235 diffusive flux progressively depletes trace metal from the solution. When the diffusive flux
236 into the binding layer is greater than the diffusive flux from the solution, a diffusive boundary
237 layer (DBL) emerges perpendicular to diffusive layer. Using Fick's first law of diffusion, the
238 flux, J (mol cm⁻² s⁻¹), of metal from the solution at a given time (t) can be calculated using
239 Equation 2:

$$240 \quad J(t) = C_i(t) \left(\frac{D^{DL}}{\delta_{DL}} + \frac{D^w}{\delta_{DBL}} \right), 0 < t < T \quad (\text{Eq. 2})$$

241 where, C_i is the trace metal concentration at the edge of the DBL, D^{DL} and D^w are the
 242 diffusion coefficients of the metal in the diffusive layer and the solution, respectively, and
 243 δ_{DL} and δ_{DBL} are the length of the diffusive pathway through the diffusive layer and the DBL
 244 respectively.

245 In conventional DGT solution deployments, the volume of solution is large enough to allow
 246 an assumption to be made that the solute concentration in the solution does not change
 247 significantly during the deployment. Due to the small volume used here, this does not apply.
 248 If an assumption is made that the rate of diffusion of solute is the same in the diffusion layer
 249 and the surrounding solution, and that the flux of trace metal is directly proportional to the
 250 concentration at the edge of the DBL, then the change in the solution concentration can be
 251 modelled by including Eq. 2 into the expression for first order decay (Equation 3).

$$252 \quad C_t = C_0 \times e^{\left(-\frac{D^{DL} \times A}{(\delta_{DL} + \delta_{DBL}) \times V_{sol}} \times t \right)} \quad (\text{Eq. 3})$$

253 Where, C_0 and C_t are the metal concentrations in a solution with a known volume (V_{sol}) at the
 254 start of the deployment and at the end of the deployment, respectively, and the cross-sectional
 255 area of the SV-DGT device is given by A . Given the highly confined nature of the SV-DGT
 256 device, and the slightly concave gel-solution interface, accurate determination of δ_{DL} and δ_{DBL}
 257 is challenging. However, when C_t and C_0 are known, Equation 3 can be solved for the sum of
 258 $\delta_{DL} + \delta_{DBL}$. The sum of these two terms is referred to forthwith as the *apparent diffusion layer*
 259 (ADL, δ_A), which is an operationally-defined lumped parameter that integrates differences in
 260 rates of diffusion between the DBL and the diffusion layer, as well as the average length of
 261 the diffusive path between the bulk solution in the SV-DGT and the resin layer-diffusion
 262 layer interface during the deployment.

263 When partially labile trace metal complexes are present, the depletion of the free metal ions
264 perturbs the equilibrium between the free metal ion and the metal complexes, and the
265 complexes begin to dissociate to re-establish the equilibrium. Under these conditions, the rate
266 at which the trace metal concentration in the test solution is depleted is determined by:

- 267 (1) the concentration of free metal ions in the solution
- 268 (2) the length of the diffusive pathway between the solution and the binding layer, under
269 well stirred conditions this is closely approximated by the thickness of the diffusive layer
- 270 (3) the diffusive characteristics of the metal ion species present in the solution
- 271 (4) the concentrations of the metal-ligand complexes present and the rates at which they
272 diffuse and dissociate.

273 Under conditions where the availability of trace metal to be bound by the resin layer is
274 limited by the rate at which its complexed species can dissociate, the rate of trace metal
275 depletion is reduced. In equation 3, this can be represented by increasing δ_A , given that all
276 other variables can be constrained by careful experimental design and previously established
277 diffusion coefficients in the agarose gels used here (Zhang and Davison, 1999; Wang et al.,
278 2016). This concept is analogous to the ‘apparent diffusive boundary layer thickness’
279 developed by Warnken et al. (2007). By comparing $\delta_{A,C}$ measured in a *control solution*,
280 where most of the metal exists as free metal ions, against $\delta_{A,T}$ that has been determined in *test*
281 *solutions* deployed under identical deployment conditions, specifically: the same SV-DGT
282 device physical characteristics, temperature, stirring rates and deployment time, it is possible
283 to gain a semi-quantitative estimate of the differences in lability of the dissolved complexes
284 in the test solutions. By using the diffusion coefficient of the free-metal ion in calculating
285 $\delta_{A,T}$, the kinetic limitation imposed by the partially labile complex can be related to the metal
286 availability in the well-defined control solution.

287 In test solutions where the complexes are highly labile and/or the majority of the metals exist
288 as free metal ion species, the ratio $\delta_{A,T}/\delta_{A,C}$ will be close to unity. In solutions where the
289 complexes are not labile within the timescale of the deployment, the complexes can diffuse
290 into the resin layer (Lehto et al., 2006; Shafaei Arvajeh et al., 2013; Galceran and Puy, 2015).
291 This results in a ‘dilution’ effect where metal concentration is still depleted in the test
292 solution. This provides a theoretical maximum for $\delta_{A,T}/\delta_{A,C}$ which is metal-specific and
293 determined by the relative volumes of the deployment solution and the total volume within
294 the SV-DGT where the complex can dissociate (*i.e.* the sum of the resin layer, diffusion layer
295 and deployment solution volumes). For the SV-DGT devices used to analyse Cd, Ni and Zn
296 here, where the ratio of V_{sol} to total available volume is 0.81, therefore the theoretical
297 maximum values of $\delta_{A,T}/\delta_{A,C}$ are 4.13 (Cd), 4.17 (Ni) and 4.26 (Zn). The differences between
298 the metals are determined by their respective diffusion coefficients in agarose.

299

300 2.4.2. SV-DGT measurements

301 To enable more direct comparison of the specific ligands present in the different organic
302 matter extracts, the extracts from the sorption experiments carried out for Cd, Ni and Zn at
303 pH 5.5 were modified to achieve matching metal:DOC molar ratios in the solutions.
304 Cadmium, Ni and Zn were added to their respective extract solutions to match the highest
305 metal:DOC molar ratio in the extract solutions (Zn in the EP extract solution) (Table 2). The
306 conductivities of the extract solutions were measured and adjusted to 10.5 mS·cm (± 2.0)
307 using NaNO₃ to approximate a consistent ionic strength between solutions, while reducing the
308 possible time within which microbial degradation might influence the DOM. The extracts
309 were then equilibrated at 5 °C for 24 h, after which they were brought to room temperature

310 and deployed in SV-DGT devices placed on a laboratory shaker for 24 h. A subsample of
311 each test solution was then collected and analysed for Cd, Ni and Zn using ICP-OES.

312 The SV-DGT probes were also used to analyse the lability of Cd, Ni and Zn from complexes
313 formed from two synthetic model ligands, nitrilotriacetic acid (NTA, Sigma-Aldrich) and
314 ethylenediaminetetraacetic acid (EDTA, Titriplex III, MERCK). These were made in 0.05 M
315 $\text{Ca}(\text{NO}_3)_2$ solutions and adjusted to pH 5.5, as before. The ligand concentrations used here
316 were chosen to achieve consistent metal:ligand molar ratios (Table 2). The model ligand test
317 solutions were allowed to equilibrate for 24 h before deployment. Each extract and model
318 ligand solution was analysed in triplicate.

319

320 **2.5. Speciation modelling**

321 The speciation of the metals in the model ligand solutions was modelled using Visual
322 MINTEQ ver. 3.1 (Gustafsson, 2016). The speciation in the organic matter extracts was
323 estimated using the Windermere Humic Acid Model (WHAM) VII (Tipping et al., 2011).
324 The proportion of DOM as fulvic acid (FA) in the peat extracts was assumed to be 25%, with
325 the rest as humic acid (HA) (Tipping et al., 2003). Laborda et al. (2008) found that almost all
326 of the DOM in compost extracts was FA at pH 5, given the slightly higher pH used in this
327 work, the proportion of DOM as FA in the PH and LE extracts was set at 95%.

328

329

330 3. Results and Discussion

331 3.1. Cadmium sorption capacity of the organic amendments.

332 The results from the batch sorption experiments confirmed the previously observed high
333 capacity of composts to sorb Cd (Figure 1.) (Ulmanu et al., 2003; Al Mamun et al., 2016). Al
334 Mamun et al. (2016) suggested that the high CEC of certain composts could be an important
335 feature of these amendments' capacity to bind Cd. This is further supported by the results
336 from these experiments. A regression analysis found that CEC correlated positively with the
337 $\log K_d$ measured in these amendments and explained 64% of the variation at pH 5.5 ($p < 0.01$,
338 $n = 10$; not shown), which may explain why the compost derived from fish waste and ocean
339 botanicals (PHW) did not appear to sorb Cd as well as the other composts. This can also be
340 seen in KBS, CFF and OP. The contrasting abilities of CBS and KBS biosolids to sorb Cd
341 may also be related to their CECs. Fard et al. (2011) showed a positive relationship between
342 pH and Cd sorption capacity of biosolids and a similar pattern is seen here. The low pH KBS
343 did not sorb much Cd at pH 4.5, while the K_d of CBS was over ten times higher than that of
344 KBS at around pH 4.5; however, at pH 6.5 CBS's K_d only increased ~20% from the K_d at pH
345 4.5. On the other hand, the K_d of KBS increased twelve-fold across the same pH range, which
346 suggests that Cd adsorption onto variable charge binding sites may be a significant
347 component of the overall binding of Cd to KBS. These results suggest that careful pH
348 management of biosolids amended soil is an important consideration when managing the
349 trace metal uptake from those soils. This is especially important given the relatively high Cd
350 concentrations in KBS (3 mg kg^{-1}) and CBS (1 mg kg^{-1}) (Table 1).

351 Peat and coffee grounds are often used as a growth amendment in soil-less growth media, as
352 a bulking agent in composts, and peat has been proposed as a potential medium for treating

353 wastewater (Brown et al., 2000; Barreto et al., 2007; Farrell and Jones, 2010), which
354 informed the decision to their use them in this study. Despite the marked difference in their
355 provenance, the two peat samples showed almost an identical capacity to sorb Cd, while the
356 coffee grounds bound relatively little Cd. The two peats' CECs are very similar, while CFF
357 had the lowest CEC of the amendments considered and that is reflected in the amendments'
358 ability to bind Cd (Table 1).

359 The two composts tested for Ni and Zn sorption bound more Cd than either of the two other
360 metals, although the differences are only significant between Cd and Zn at pH 5.5 ($p < 0.05$)
361 (Figure 2.). Simmler et al. (2013b) suggested that reduced organic sulphur-containing
362 functional groups (soft Lewis bases) in lignite enable it to bind Cd effectively. Al Mamun et
363 al. (2016) subsequently proposed that these functional groups may also be important in
364 allowing composts to reduce the dissolved Cd concentrations, and hence plant bioavailability
365 of the metal. However, they also noted that the relatively high bioavailability of Zn in the
366 compost-amended soils may have also affected the uptake of Cd by the plant. The stronger
367 binding of Cd over Zn and Ni seen here provides further support for these both these theories.
368 There are few significant differences in the peats' capacity to sorb the different metals: their
369 CECs are approximately a half those of the composts, which is reflected in differences in K_d
370 values for each of the metals between the peats and the composts (Figure 2; Table 1).

371

372 An important question regarding the use of organic amendments for managing the
373 bioavailability of potentially hazardous trace metals in soils is the longevity of the effect, and
374 the fate of the bound trace metals if the organic matter is degraded through microbial action.
375 This is especially pertinent when considered in the context of predicted effects of forecasted

376 changes in global temperature and rainfall patterns on organic matter stability in soils (e.g.
377 Puissant et al. (2017)). The cold and hot-water extraction methods sample different pools of
378 carbon from the amendments. Previous studies have shown that the CWEC fraction consists
379 mostly of hydrophilic carbon (e.g. amino sugars, carbohydrates and low molecular weight
380 organic acids, polysaccharides and high molecular weight fulvic acids) (Haynes, 2005; Said-
381 Pullicino et al., 2007). The focus here is on the HWEC fraction, which has been associated
382 with weakly adsorbed dissolved organic matter to mineral surfaces and humic acids, and has
383 been used as a general indicator of the labile fraction of the organic carbon in soils (von
384 Lützow et al., 2007). Out of the amendments considered here, the HWEC fraction of CBS
385 was over twice as high as the next highest (PH) (Table 1) and between three to ten times
386 higher than values measured in soils under different land uses (Ghani et al., 2003) . While the
387 K_d of CBS was relatively high ($\sim 400 \text{ L kg}^{-1}$ at pH 5.5, Figure 1) compared to most other
388 amendments here, its high Cd concentration, combined with the apparent vulnerability to
389 microbial degradation, could be seen as valid reasons for restricting its use as a soil
390 amendment. The two peats (EP, OP) and the municipal and mushroom-derived composts (LE
391 and PH) had the next highest HWEC fractions, which prompts the subsequent investigation
392 into the lability of Cd, Ni and Zn associated with the DOM extracted from them by the 0.05
393 M $\text{Ca}(\text{NO}_3)_2$ and the chemical characteristics of that DOM.

394

395 **3.2. Speciation and lability of cadmium, nickel and zinc in the organic matter** 396 **extracts**

397 Geochemical modelling of the extracted solutions using WHAM suggested that over 99.4%
398 of the total Cd, Ni and Zn was complexed by the DOM in all of the respective extracts (Table

399 2). This is considerably higher than seen in previous work when the WHAM model has been
400 used to estimate trace metal speciation in soil extracts (Tipping et al., 2003; Cornu et al.,
401 2011; Ren et al., 2015). This is almost certainly due to the very low metal:DOC ratios in the
402 extracts, driven mainly by the large amount of DOM extracted from the organic amendments.
403 With this in mind, it is important to acknowledge that the lability and speciation estimates
404 carried out here are artificial and unlikely to be directly representative of most soil
405 environments, where the amount of soil organic matter than can equilibrate with porewater is
406 considerably less, and a proportion of the DOM is likely to be mineralized rapidly and/or sorb
407 to soil solid interfaces (Lehmann and Kleber, 2015). It does however provide an opportunity
408 to estimate conservatively whether complexed metals might become available for biological
409 uptake or a chemical reaction, following a change in equilibrium. Kinetic limitations have
410 been reported previously for trace metal uptake by plants (Degryse et al., 2006; Custos et al.,
411 2014) and organisms native to sediments (Amirbahman et al., 2013), and natural water
412 (Jansen et al., 2002; Buffle et al., 2009; Shaked and Lis, 2012). These conditions are often
413 identified when equilibrium-based methods fail to predict biological uptake (Zhao et al.,
414 2016).

415 Amery et al. (2010) used a similar type of DGT design to the one employed here to show that
416 the method can be used to analyse complex lability and obtain comparable kinetic
417 information to the more conventionally used competitive ligand exchange method (CLEM)
418 (Lam et al., 1999). In our work the SV-DGT analyses confirmed the previously observed
419 kinetic limitation of Zn and Ni release from NTA and EDTA complexes and that Zn
420 complexes were more labile than those of Ni, and a greater kinetic limitation of both metals'
421 dissociation from EDTA complexes (Bowles et al., 2006). Analyses of the compost and peat
422 extracts showed that the Zn and Cd complexes are relatively labile when compared to Ni,

423 which agrees with previous measurements in natural waters (Warnken et al., 2007; Levy et
424 al., 2012) and hints at relatively low solubility of organic matter containing reduced sulphur
425 functional groups at this pH. Cadmium was relatively labile in the OP extracts, however
426 significantly less so in the EP and compost extracts, especially LE. This could indicate that
427 Cd-DOM complexes mobilized from soils where these composts had been used to manage
428 Cd bioavailability may persist longer in soils before dissociation than when peat similar to
429 OP was used. If composts were used to manage Ni contamination, under leaching conditions
430 this could conceivably increase Ni mobility in the soil, more than a less labile complex, such
431 as Zn, whose ability to participate in chemical reactions or be taken up by biota would be less
432 kinetically limited.

433

434 **3.3. Quality of the dissolved organic matter in the extracts**

435 Excitation-emission matrix (EEM) fluorescence of the extracts was characterised by
436 fluorophores consistent with aromatic (humic-like) organic acids (peaks C and A), proteins
437 and amino acids (tryptophan- and tyrosine-like; peaks T1 and T2) that are common features
438 of humic extracts (see: Supporting Information) (Senesi et al., 1991). Steady-state
439 fluorescence EEMs integrate information on the mixture of compounds present in DOM
440 which have been shown to consist of fluorophores with multiple excitation peak centres for
441 both proteins and humic substances (Li et al., 2013). Despite the complexity of EEM
442 fluorescence, previous workers have shown the applicability of this method for understanding
443 both DOM metal binding properties (Luster et al., 1996; Baker et al., 2008; Ohno et al., 2008)
444 and biodegradability (Hudson et al., 2008; Hansen et al., 2016).

445 The Peak T fluorophore indicates of the proportion of bioavailable organic matter (Marschner
446 and Kalbitz, 2003), and hence the potential for microbial activity in the sample (Hudson et
447 al., 2008). Peak T fluorescence in our samples showed a declining relationship with the
448 emission wavelength of maximum fluorescence intensity at Peak C (Figure 3 b), which has
449 been shown to increase in tandem with the degree of aromaticity and conjugation in soil
450 organic matter (Senesi et al., 1991). DOM aromaticity (i.e. phenolic content) may diminish
451 DOM biodegradability, whilst enhancing metal complexation strength (Baker et al., 2008).
452 However, aromaticity will increase in DOM if biodegradation acts preferentially on aliphatic
453 and low molecular weight DOM fractions (Hansen et al., 2016). Regardless of the precise
454 mechanisms of causation, refractory amendments with higher metal binding strength are
455 likely to exhibit lower protein-like fluorescence. This is consistent with the results of metal
456 lability measurements in the studied extracts (Figure 3 a) that show a positive trend between
457 Ni and Zn kinetic limitation and the Peak C emission wavelength. These results are broadly
458 supported by the $SUVA_{254}$ measurements (Table 2). Shafaei Arvajeh et al. (2013) observed
459 that Ni-HA complexes were less labile than Ni-FA complexes, which further suggests that the
460 former may be more abundant in the compost extracts. By contrast, Cd lability showed little
461 change as a function of DOM aromaticity, probably indicating Cd complexation with non-
462 phenolic moieties in DOM ligands. This suggests that microbial degradation of DOM may
463 reduce the mobility of Cd-DOM complexes to a greater extent than Ni-DOM complexes. The
464 work by Amery et al. (2008) provides further evidence to support this hypothesis. They
465 showed a strong correlation between Cu:DOM concentration ratios and DOM aromaticity in
466 250 soil leachates, highlighting the role of DOM quality in determining metal-complex
467 mobility in the environment.

468 The relatively simple mathematical solution and well constrained system used to assess the
469 lability of the metal:ligand complexes here makes the SV-DGT method an attractive option
470 for measuring the dissociation rate constants of complexes. Previous work has shown that
471 when the kinetic window of a DGT device is changed by using different diffusion layer
472 thicknesses, it is possible to estimate complex dissociation rate constants (Scally et al., 2003;
473 Warnken et al., 2007). This method could be adapted to the SV-DGT device; however,
474 measuring these rate constants was not an objective of this work. The greatest advantage of
475 the method is that enables the analysis of trace metal complexes under circumstances where
476 extensive dilution of sample is would normally be required, such as those from soil or
477 sediment porewaters.

478 As with the speciation modelling, it is important to recognize that the results herein are
479 subject to certain caveats caused by the experimental approach used. We normalized the
480 metal:DOC ratios across the different metal-amendment combinations after the extraction
481 solutions had equilibrated with the amendments considered. We did this to enable
482 comparison of the lability of the different DOM complexes and to elucidate whether the that
483 could be related to the quality of the DOM from the different extracts. Previous studies have
484 shown that the metal:ligand ratio is an important determinant when assessing the lability of a
485 complex (Sekaly et al., 1999; Guthrie et al., 2003). This means that these measurements are
486 likely to overestimate the lability of Cd in the extracts where a kinetic limitation is observed.
487 It is also useful to note that, although numerous studies have shown that soil extractions
488 carried out using 0.05 M $\text{Ca}(\text{NO}_3)_2$ can provide a good estimate of plant bioavailable fraction
489 of soil Cd (Gray et al., 1999; Black et al., 2011; Black et al., 2012; Reiser et al., 2014), the
490 ionic strength of this extraction solution is higher than what is commonly observed in most
491 soil porewaters (Edmeades et al., 1985). Dissolution of solute from the amendments will have

492 contributed to this. While the high ionic strength is likely to have reduced the probability of
493 solute binding to the agarose diffusion layer (Wang et al., 2016), it is also possible that there
494 was a consequent increase in the perceived lability of the Ni complexes due to ligand-assisted
495 dissociation in the resin gel (Puy et al., 2014). Further testing is needed to quantify this effect.

496 **4. Conclusions**

497 Our results provide further evidence to suggest that composts are well-suited to managing
498 soil Cd bioavailability, without inducing Zn deficiency in plants. However, they also indicate
499 there may be an associated risk of Cd being transported from the location of the
500 contamination, especially under conditions where the organic matter is destabilized. The risk
501 of metal transport will probably be greater if compost was used to manage Ni contaminated
502 soils, owing to its apparently greater affinity for DOM with a high aromaticity and the likely
503 stability of the Ni-DOM complexes that emerged. While it should be recognized that this
504 work only considered four types of organic amendments, and further work is needed to gauge
505 whether leaching of Cd (or other trace metals) from compost amended soils is significant,
506 there is increasing evidence that DOM quality likely to be an important factor.

507

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728 **Data Availability Statement:** The datasets generated during and/or analysed during the
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730

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735

736 **Additional information**

737 Competing financial interests: The authors declare no competing financial interests

738

739 **Tables**740 **Table 1.** Chemical properties and elemental concentrations of the amendments considered

741

	EP	OP	PH	LE	PHW	PHP	CFF	OD	KBS	CBS
pH	7.13 (± 0.00)	3.25 (± 0.02)	6.92 (± 0.08)	7.65 (± 0.07)	5.55 (± 0.02)	6.26 (± 0.00)	4.89 (± 0.06)	5.30 (± 0.00)	3.68 (± 0.01)	6.49 (± 0.03)
Conductivity ($\mu\text{S}/\text{cm}$)	307 (± 0.35)	296 (± 6.09)	4060 (± 1.23)	2370 (± 0.54)	309 (± 0.46)	1408 (± 0.46)	2893 (± 0.75)	3096 (± 6.82)	4340 (± 0.40)	6733 (± 0.89)
CEC ($\text{me}/100\text{g}$)	26.4	21.4	42	44.8	36.1	42.2	16.8	37.9	17.4	30.9
C (%)	15.7	46.9	34.5	22.0	16.1	25.5	50.2	30.4	26	nd
N (%)	1.20	1.56	1.58	1.93	0.45	1.63	2.30	1.03	2.6	nd
Water extractable C ($\mu\text{g C g}^{-1}$)	671	7939	3073	2196	428	2070	37017	1173	903	6531
Hot water-extractable C ($\mu\text{g C g}^{-1}$)	3928	4690	5219	4538	1530	3536	5	2100	3860	11265
P (mg kg^{-1})	836	241	7378	2786	836	2798	1158	2976	5369	17760
S (mg kg^{-1})	2538	2347	6856	2360	837	3438	1496	3056	10580	14867
Ca (mg kg^{-1})	8350	1486	27916	22406	15848	15892	1140	10899	11200	30320
Mg (mg kg^{-1})	2326	699	3965	4510	9168	3008	1682	2931	4043	5842
K (mg kg^{-1})	2684	833	6020	5363	3000	5019	4526	4843	3379	3354
Cd ($\mu\text{g kg}^{-1}$)	<0.21	<0.021	<0.021	0.1	<0.021	<0.021	0.01	<0.021	3	1
Zn ($\mu\text{g kg}^{-1}$)	49	8	649	294	73	153	9.8	441	1356	1108
Ni ($\mu\text{g kg}^{-1}$)	10.7	0.185	4.6	7.5	27.7	5.6	0.17	5.0	20.7	31.4
Cu ($\mu\text{g kg}^{-1}$)	15.8	1.7	109.9	46.3	29.7	26.2	23.3	74.0	782.9	318.1
Pb ($\mu\text{g kg}^{-1}$)	13.9	2.4	5.5	99.7	11.1	10.2	<0.21	7.6	135.0	60.7
Al ($\mu\text{g kg}^{-1}$)	15888	1364	6666	10461	28189	12229	4	9840	19008	15605
Cr ($\mu\text{g kg}^{-1}$)	17.9	1.2	10.2	25.3	33.7	39.5	0.0	23.9	41.9	153.2

Where values are averages, standard errors are given in brackets ($n=3$). nd: not determined

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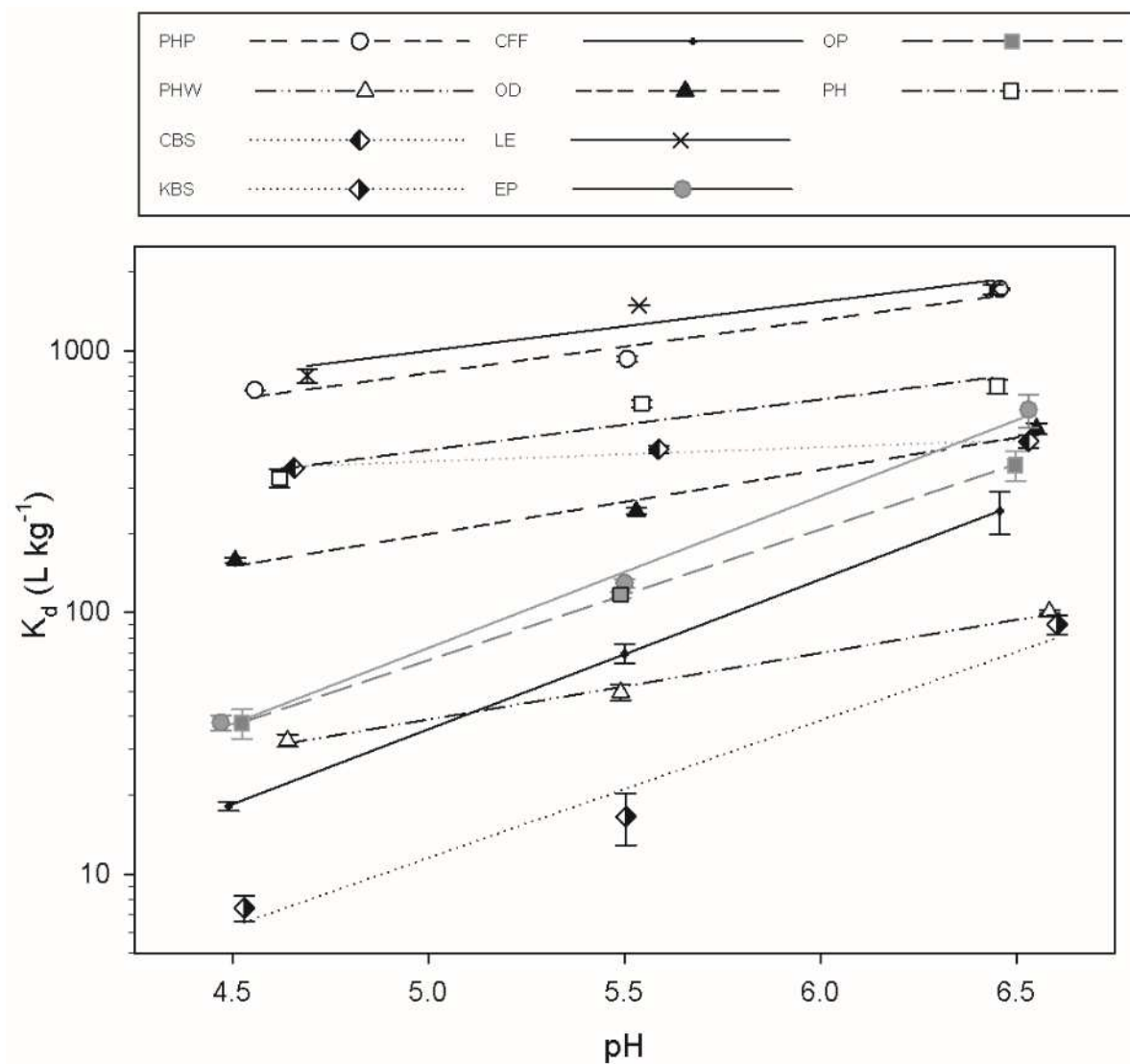
745 **Table 2.** Solution composition in the extract and test solutions analyzed using SV-DGT.

Metal	Sample	Initial [Me] (μM)	Initial [DOC] or [ligand] (mM)	Conductivity (mS cm)	pH	[Me] in test solution (μM)	[DOC] or [ligand] in test solution (mM)	Free ion activity (nM)	% complexed	SUVA ($\text{L g}^{-1} \text{cm}^{-1}$)
Cd	NTA	-	-	10.51	5.49	1.537 (± 0.005)	5.0	2.38	99.6	nd
	EDTA	-	-	10.06	5.59	1.362 (± 0.004)	5.0	0.007	99.9	nd
	EP	0.658 (± 0.008)	185.6 (± 4.9)	9.37	5.6	3.92	13.92	5.41	99.6	17.84
	OP	1.16 (± 0.01)	841.6 (± 4.3)	9.50	5.5	17.77	63.06	6.36	99.9	10.31
	PH	0.35 (± 0.02)	452.6 (± 16.8)	11.93	5.6	9.56	33.91	10.96	99.5	16.41
	LE	0.102 (± 0.002)	378.6 (± 9.1)	12.02	5.6	8.12	28.82	11.45	99.4	24.33
Ni	NTA	-	-	10.54	5.47	1.141 (± 0.008)	5.0	0.03	>99.9	nd
	EDTA	-	-	10.40	5.62	1.185 (± 0.009)	5.0	6×10^{-5}	>99.9	nd
	EP	0.95 (± 0.01)	185.6 (± 4.9)	9.69	5.6	3.92	13.92	6.08	99.5	17.84
	OP	1.08 (± 0.11)	841.6 (± 4.3)	9.39	5.5	17.77	63.06	7.17	99.9	10.31
	PH	0.18 (± 0.02)	452.6 (± 16.8)	12.28	5.6	9.56	33.91	14.68	99.5	16.41
	LE	0.24 (± 0.02)	378.6 (± 9.1)	12.39	5.6	8.12	28.82	15.67	99.4	24.33
Zn	NTA	-	-	10.56	5.51	1.106 (± 0.003)	5.0	0.29	99.5	nd
	EDTA	-	-	10.10	5.53	1.152 (± 0.002)	5.0	9×10^{-3}	99.6	nd
	EP	4.36 (± 0.15)	185.6 (± 4.9)	9.38	5.6	3.92	13.92	3.23	99.8	17.84
	OP	2.47 (± 0.10)	841.6 (± 4.3)	9.48	5.5	17.77	63.06	3.61	99.9	10.31
	PH	7.33 (± 0.08)	452.6 (± 16.8)	11.89	5.6	9.56	33.91	6.25	99.8	16.41
	LE	2.29 (± 0.09)	378.6 (± 9.1)	12.02	5.6	8.12	28.82	6.75	99.7	24.33

The concentration of DOC is given as mmol C L^{-1} , while the concentrations of NTA and EDTA are based on their molecular weight. Where values are averages, standard errors are given in brackets ($n=3$). n.d.: not determined.

746 **Figures**

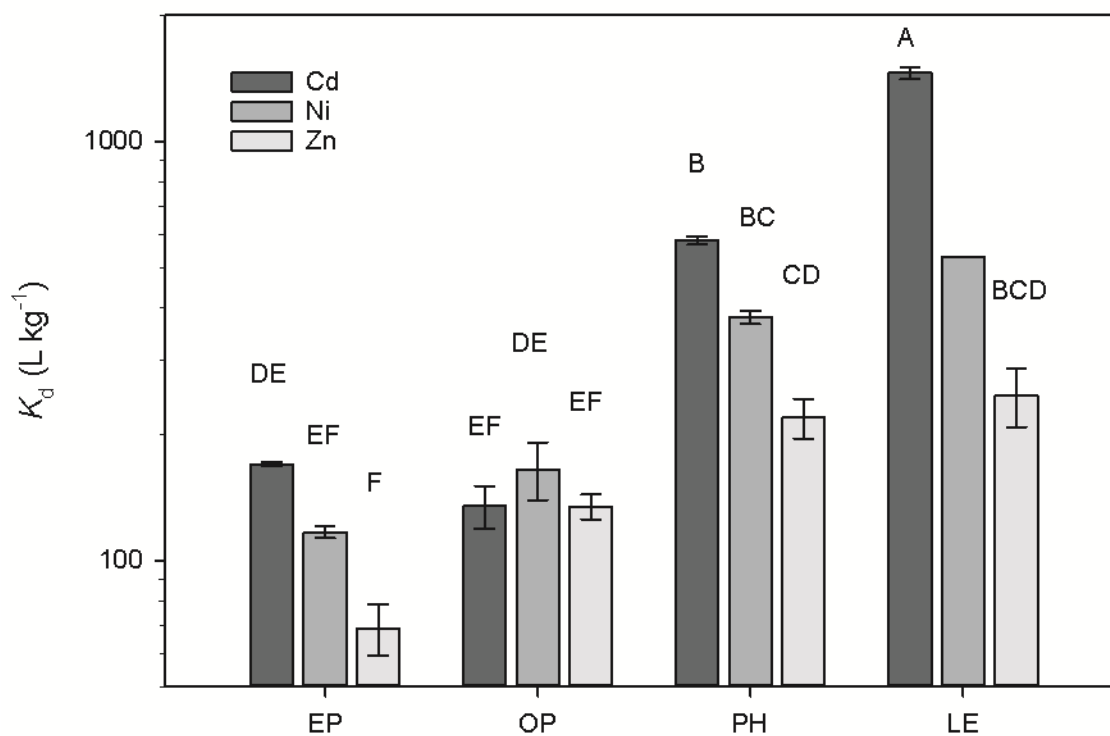
747 **Figure 1.** Sorption of Cd at three different pHs by the organic amendments considered. The
 748 error bars show standard deviation ($n=3$).



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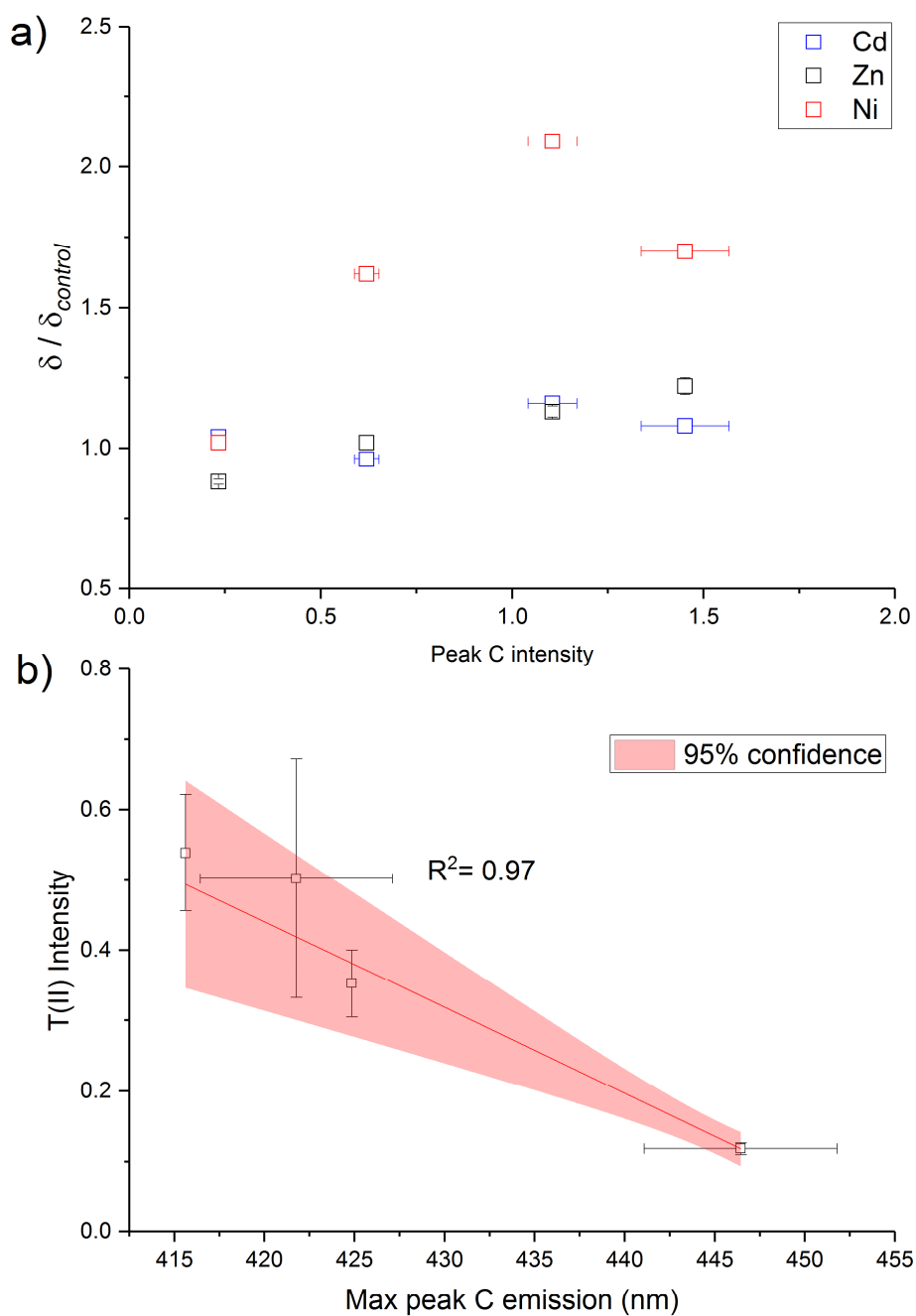
750

751 **Figure 2.** Average K_d of Cd, Ni and Zn at pH 5.5 in two types of peat (OP and EP) and two
752 composts (PH and LE). The error bars show standard error of the mean, different letters
753 indicate significant differences between the means ($p < 0.05$, $n = 3$, except $K_{d,Ni}$ for LE where
754 $n = 2$).



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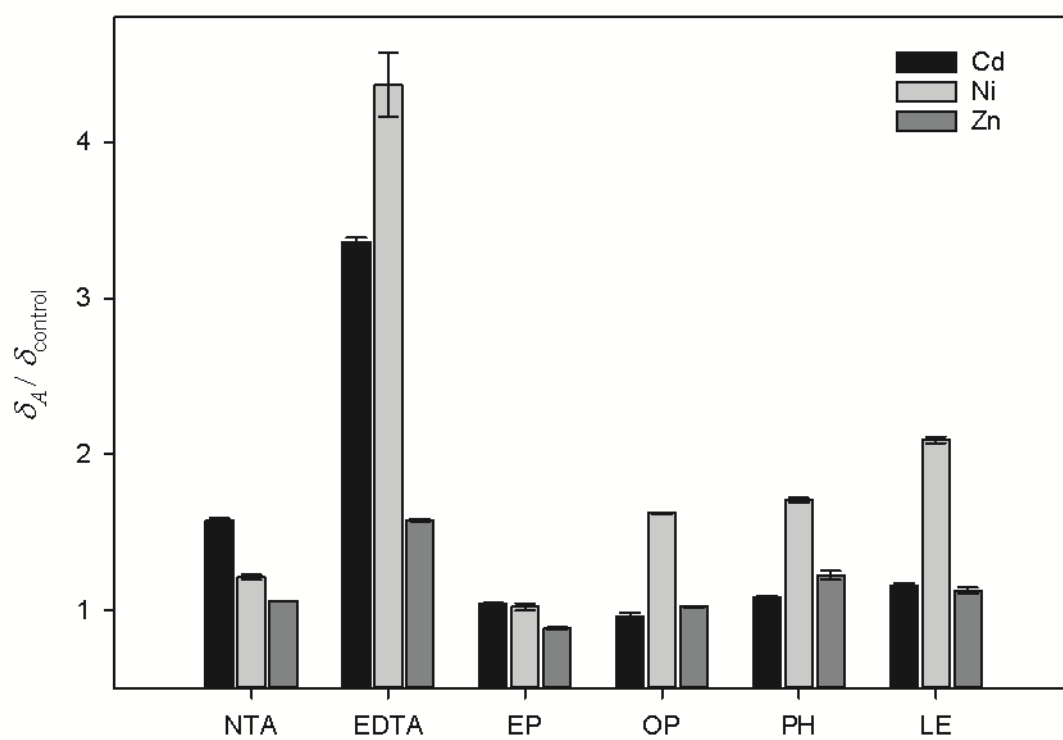
756 **Figure 3.** The relationship between the relative kinetic restriction of DOM-metal complexes
757 ($\delta/\delta_{control}$) and DOM aromaticity (Peak C Raman-normalised intensity) (a); and (b) negative
758 correlation between DOM amino-acid fluorescence (peak T2; inferred biodegradability) and
759 DOM aromaticity (emission wavelength of maximum Peak C fluorescence intensity).



760

761 **Figure 4.** The relative kinetic limitation of Cd, Ni and Zn in the extracted spiked 0.05 M
762 $\text{Ca}(\text{NO}_3)_2$ solutions from the four organic amendments and two model ligands, NTA and
763 EDTA. The error bars show standard error ($n = 3$).

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Highlights

- Adapted DGT method measures complex lability in small volumes
- Composts bind Cd effectively, but may mobilize trace metals via DOM-complexes.
- Nickel complexes are less labile than Cd or Zn complexes in compost extracts
- Aromatic DOM reduce lability of Ni complexes, and Zn to a lesser extent.