



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

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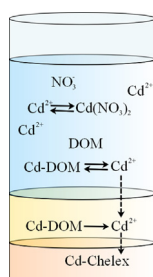
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HIGHLIGHTS

- 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.

GRAPHICAL ABSTRACT



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ABSTRACT

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

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1. Introduction

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

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

Recent work has shown the potential for different types of organic amendments to bind soil Cd in agricultural soils (Simmler et al., 2013b; Al Mamun et al., 2017), as well as other trace metals (e.g. Pb, Zn, As and Cu) in industrial contaminated soils (Bolan et al., 2014; Abad-Valle et al., 2017; Van Poucke et al., 2018). The ability for different organic amendments to influence trace metal bioavailability is informed by the characteristics of the organic matter that is employed (e.g. pH, CEC, humification degree) and the metal of concern (e.g. affinity for solid and solution phase complexing ligands), as well as the soil type (Albiach et al., 2000; Bolan et al., 2014).

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

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

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

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

2. Material and methods

2.1. Sample collection and pre-treatment

Ten different types of solid organic matter-rich substrates that are used as soil amendments, either by themselves, or as constituent parts, were selected for analysis. These were two types of peat, used coffee grounds, two types of biosolids and five different composts. Forthwith, these will be referred to as “amendments” for simplicity. The two types of peat were sampled from the Kopuatai ombrotrophic peat dome on the North Island of New Zealand, 37°24'45.79"S, 175°33'23.38"E (Sample ID: OP) and a peat formation on in the Canterbury region of NZ's South Island (43°40'38.22"S, 172°26'52.03"E) (Sample ID: EP). The peat samples underwent an initial screening upon collection using a 10 mm mesh to discard stones and larger plant material. The coffee grounds (Sample ID: CFF) were collected from ten different coffee shops around Christchurch, NZ. The biosolids were collected from two locations: the Kaikōura Regional Treatment Works in Kaikōura, NZ, (Sample ID: KBS) and Christchurch Wastewater Treatment Plant, Christchurch, NZ (Sample ID: CBS). KBS had undergone an initial treatment of sedimentation and anaerobic digestion in settlement ponds. CBS was thermally dried to <10% water content to eliminate pathogens and facilitate transport. Both sets of biosolids samples were provided by the plant operators. The composts were obtained from three locations. Three types of compost were purchased from Parkhouse Garden Supplies Ltd. (Christchurch, NZ). The company was only willing to provide general descriptions of their compositions, which were: (1) compost derived from commercial mushroom growing waste (Sample ID: PH), (2) fish waste and ocean botanicals (Sample ID: PHW), and (3) pig manure and sawdust (Sample ID: PHP); green waste is not used in any of these composts. Compost manufactured by Living Earth Ltd. (Sample ID: LE) is made from municipal green waste (includes: food and garden waste) collected as part of Christchurch city's kerbside waste collection program. The fifth type of compost was purchased from Oderings Nurseries Christchurch Ltd. (Sample ID: OD), the raw materials used to make this are unknown. All samples were air-dried, manually ground and sieved using a nylon sieve (2 mm mesh).

2.2. Sample analysis

All sample analyses and dilutions used high-purity water (HPW, 18.2 MΩ resistivity; Heal Force® SMART Series, SPW Ultra-pure Water system, Model-PWUV). pH (Mettler Toledo Seven Easy) and conductivity (Mettler Toledo Five Easy) of the sieved samples were determined in triplicate using a 1:10 solid:water ratio (w./vol.) and 24 h equilibration time (Blakemore et al., 1987). Total

carbon and nitrogen content of the amendments was measured using a Vario-Max CN Analyzer (Elementar Analysensysteme GmbH, Germany). Cold and hot water extractable carbon (C_{WEC} and H_{WEC}, respectively) were measured in all of the amendments following the method described by Ghani et al. (2003). Briefly, 3 g of each amendment was sequentially extracted, first with 30 mL HPW at ambient temperature for 30 min, after which the extractant was separated from the sample, filtered (0.45 µm pore diameter cellulose acetate filter) and analysed for total carbon (C_{WEC}) using a Shimadzu TOC-VCSH analyzer (Shimadzu Corporation, Kyoto, Japan). The remaining sample was then extracted with a further 30 mL of HPW at 80 °C for 16 h, after which the extractant was separated from the sample, filtered as before and analysed for total carbon (H_{WEC}) as before.

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

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

The different amendments' capacity to sorb Cd was analysed using previously developed sorption experiments using spiked solutions of 0.05 M of Ca(NO₃)₂ (Simmler et al., 2013b; Al Mamun et al., 2016). Briefly, 5 g batches of each amendment, except OP, were mixed with 30 mL of either 0.05 M Ca(NO₃)₂ (Sigma-Aldrich) extraction solution, or extraction solution that had been spiked to 2 mg L⁻¹ (18 µM) of Cd (salt: Cd(NO₃)₂·4H₂O, BDH, AnalaR). The mass of OP used was reduced to 2 g to ensure a sufficient separation between solid and solution phases. A vortex mixer was used to agitate the mixtures for 3 min, after which the pHs of replicate sets of each mixture were adjusted to 4.5.5, 6.5 (±0.02) using 2 M HNO₃ (BDH Aristar) or 2 M NaOH (BDH AnalaR). The mixtures were then placed in an end-over-end shaker for 2 h, after which they were centrifuged at 3000 rpm for 20 min. The supernatant was then filtered through Whatman no. 52 filter paper and analysed for the same analytes as the digests using ICP-OES.

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

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

$$= \frac{(C_{\text{spike}} - (C_{\text{eq}} - C_b)) \times (V_m)}{(C_{\text{eq}} - C_b)}$$

Where K_d describes the solid-solution phase partitioning of the analyte of interest, C_{spike} is the concentration of metal in the spike

Table 1
Chemical properties and elemental concentrations of the amendments considered.

	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 (µS/cm)	307 (±0.35)	296 (±6.09)	4060 (±1.23)	2370 (±0.54)	309 (±0.46)	1408 (±0.46)	2893 (±0.75)	3096 (±0.82)	4340 (±0.40)	6733 (±0.89)
CEC (me/100 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 (µg C g ⁻¹)	671	7939	3073	2196	428	2070	37017	1173	903	6531
Hot water-extractable C (µg C g ⁻¹)	3928	4690	5219	4538	1530	3536	5	2100	3860	11,265
P (mg kg ⁻¹)	836	241	7378	2786	836	2798	1158	2976	5369	17,760
S (mg kg ⁻¹)	2538	2347	6856	2360	837	3438	1496	3056	10,580	14,867
Ca (mg kg ⁻¹)	8350	1486	27,916	22,406	15,848	15,892	1140	10,899	11,200	30,320
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 (µg kg ⁻¹)	<0.21	<0.021	<0.021	0.1	<0.021	<0.021	0.01	<0.021	3	1
Zn (µg kg ⁻¹)	49	8	649	294	73	153	9.8	441	1356	1108
Ni (µg kg ⁻¹)	10.7	0.185	4.6	7.5	27.7	5.6	0.17	5.0	20.7	31.4
Cu (µg kg ⁻¹)	15.8	1.7	109.9	46.3	29.7	26.2	23.3	74.0	782.9	318.1
Pb (µg kg ⁻¹)	13.9	2.4	5.5	99.7	11.1	10.2	<0.21	7.6	135.0	60.7
Al (µg kg ⁻¹)	15,888	1364	6666	10,461	28,189	12,229	4	9840	19,008	15,605
Cr (µg 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.

solution, C_{eq} is the concentration in the spike solution after equilibration with the amendment, and C_b is the metal concentration in the unspiked extractant solution after equilibration. The volume of extractant (0.03 L) and mass of amendment used (0.002 or 0.005 kg) were V and m , respectively. Extraction samples C_{eq} and C_b were analysed in triplicate for each amendment-pH combination.

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

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

2.3. Dissolved organic matter quality

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

$$\text{SUVA}_\lambda = \frac{A_\lambda \times 1000}{b \times [\text{DOC}]} \quad (2)$$

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

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

2.4. Diffusive gradients in thin-films analysis

The lability of Cd, Ni and Zn in the extracts obtained from the sorption experiments on the four different amendments was

analysed by adapting the method used by Amery et al. (2010). A 1 mL gel layer containing 1 g Chelex-100 cation binding resin (200–400 mesh, Bio-Rad) in an agarose gel matrix (1.5%) (Total Lab Systems, molecular grade) was cast onto the bottom of a flat-base 30 mL sample vials (1.2 cm internal radius); henceforth, this is referred to as the *binding layer*. A 1.36 cm^3 agarose-only (1.5%) layer was cast on top of this: the *diffusive layer* forthwith. During casting it was observed that there was a small amount of even adhesion to the sides of the SV-DGT, resulting in a slightly concave diffusion layer surface. The vial containing the diffusion and binding layers was placed on a lab shaker with HPW for 24 h, during which the water was changed three times. The gels were then conditioned with 0.01 M NaNO_3 for at least 8 h before deployment. The use of diffusive and binding layers within a confined test vessel allowed the application of the underlying principles of the diffusive gradients in thin-films (DGT) technique, but in relatively small volumes; forthwith, these devices are referred to as *small volume-DGT* (SV-DGT) devices.

2.4.1. Theory of SV-DGT

When a simple solution containing trace metals, existing mainly as their hydrated (free) ion species, is deployed in an SV-DGT device, the metal ions diffuse through the diffusive layer and towards the binding layer, where they are rapidly bound by the chelating resin. Within approx. 60 min a linear concentration gradient is formed within the diffusive layer and a diffusive flux progressively depletes trace metal from the solution. When the diffusive flux into the binding layer is greater than the diffusive flux from the solution, a diffusive boundary layer (DBL) emerges perpendicular to diffusive layer. Using Fick's first law of diffusion, the flux, J ($\text{mol cm}^{-2} \text{s}^{-1}$), of metal from the solution at a given time (t) can be calculated using Equation (3):

$$J(t) = C_i(t) \left(\frac{D^{DL}}{\delta_{DL}} + \frac{D^w}{\delta_{DBL}} \right), 0 < t < T \quad (3)$$

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

In conventional DGT solution deployments, the volume of solution is large enough to allow an assumption to be made that the solute concentration in the solution does not change significantly during the deployment. Due to the small volume used here, this does not apply. If an assumption is made that the rate of diffusion of solute is the same in the diffusion layer and the surrounding solution, and that the flux of trace metal is directly proportional to the concentration at the edge of the DBL, then the change in the solution concentration can be modelled by including Eq. (3) into the expression for first order decay (Equation (4)).

$$C_t = C_0 \times e^{\left(-\frac{D^{DL} \times A}{(\delta_{DL} + \delta_{DBL}) \times V_{sol}} \times t \right)} \quad (4)$$

Where, C_0 and C_t are the metal concentrations in a solution with a known volume (V_{sol}) at the start of the deployment and at the end of the deployment, respectively, and the cross-sectional area of the SV-DGT device is given by A . Given the highly confined nature of the SV-DGT device, and the slightly concave gel-solution interface, accurate determination of δ_{DL} and δ_{DBL} is challenging. However, when C_t and C_0 are known, Equation (4) can be solved for the sum of $\delta_{DL} + \delta_{DBL}$. The sum of these two terms is referred to forthwith as the *apparent diffusion layer* (ADL, δ_A), which is an operationally-defined lumped parameter that integrates differences in rates of

diffusion between the DBL and the diffusion layer, as well as the average length of the diffusive path between the bulk solution in the SV-DGT and the resin layer-diffusion layer interface during the deployment.

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

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

Under conditions where the availability of trace metal to be bound by the resin layer is limited by the rate at which its complexed species can dissociate, the rate of trace metal depletion is reduced. In equation (4), this can be represented by increasing δ_A , given that all other variables can be constrained by careful experimental design and previously established diffusion coefficients in the agarose gels used here (Zhang and Davison, 1999; Wang et al., 2016). This concept is analogous to the 'apparent diffusive boundary layer thickness' developed by Warnken et al. (2007). By comparing $\delta_{A,C}$ measured in a control solution, where most of the metal exists as free metal ions, against $\delta_{A,T}$ that has been determined in test solutions deployed under identical deployment conditions, specifically: the same SV-DGT device physical characteristics, temperature, stirring rates and deployment time, it is possible to gain a semi-quantitative estimate of the differences in lability of the dissolved complexes in the test solutions. By using the diffusion coefficient of the free-metal ion in calculating $\delta_{A,T}$, the kinetic limitation imposed by the partially labile complex can be related to the metal availability in the well-defined control solution.

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

2.4.2. SV-DGT measurements

To enable more direct comparison of the specific ligands present in the different organic matter extracts, the extracts from the sorption experiments carried out for Cd, Ni and Zn at pH 5.5 were modified to achieve matching metal:DOC molar ratios in the solutions. Cadmium, Ni and Zn were added to their respective extract solutions to match the highest metal:DOC molar ratio in the extract solutions (Zn in the EP extract solution) (Table 2). The

conductivities of the extract solutions were measured and adjusted to 10.5 mS cm (± 2.0) using NaNO₃ to approximate a consistent ionic strength between solutions, while reducing the possible time within which microbial degradation might influence the DOM. The extracts were then equilibrated at 5 °C for 24 h, after which they were brought to room temperature and deployed in SV-DGT devices placed on a laboratory shaker for 24 h. A subsample of each test solution was then collected and analysed for Cd, Ni and Zn using ICP-OES.

The SV-DGT probes were also used to analyse the lability of Cd, Ni and Zn from complexes formed from two synthetic model ligands, nitrilotriacetic acid (NTA, Sigma-Aldrich) and ethylenediaminetetraacetic acid (EDTA, Titriplex III, MERCK). These were made in 0.05 M Ca(NO₃)₂ solutions and adjusted to pH 5.5, as before. The ligand concentrations used here were chosen to achieve consistent metal:ligand molar ratios (Table 2). The model ligand test solutions were allowed to equilibrate for 24 h before deployment. Each extract and model ligand solution was analysed in triplicate.

2.5. Speciation modelling

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

3. Results and discussion

3.1. Cadmium sorption capacity of the organic amendments

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

Peat and coffee grounds are often used as a growth amendment in soil-less growth media, as a bulking agent in composts, and peat

Table 2

Solution composition in the extract and test solutions analysed 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.

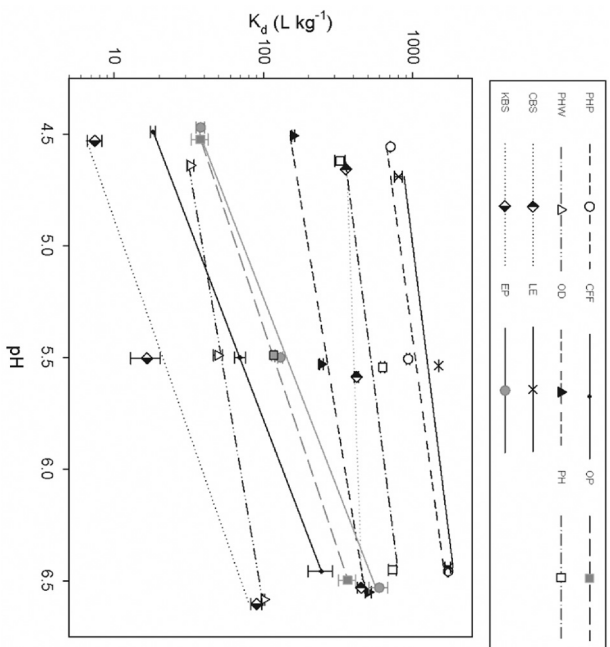


Fig. 1. Sorption of Cd at three different pHs by the organic amendments considered. The error bars show standard deviation ($n = 3$).

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

The two composts tested for Ni and Zn sorption bound more Cd than either of the two other metals, although the differences are only significant between Cd and Zn at pH 5.5 ($p < 0.05$) (Fig. 2). Simmler et al. (2013b) suggested that reduced organic sulphur-containing functional groups (soft Lewis bases) in lignite enable it to bind Cd effectively. Al Mamun et al. (2016) subsequently proposed that these functional groups may also be important in allowing composts to reduce the dissolved Cd concentrations, and

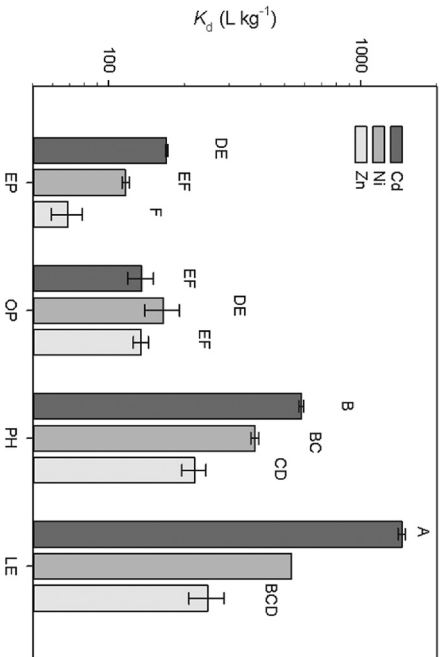


Fig. 2. Average K_d of Cd, Ni and Zn at pH 5.5 in two types of peat (OP and EP) and two composts (PH and LE). The error bars show standard error of the mean, different letters indicate significant differences between the means ($p < 0.05$, $n = 3$, except $K_{d,Ni}$ for LE where $n = 2$).

hence plant bioavailability of the metal. However, they also noted that the relatively high bioavailability of Zn in the compost-amended soils may have also affected the uptake of Cd by the plant. The stronger binding of Cd over Zn and Ni seen here provides further support for these both theories. There are few significant differences in the peats' capacity to sorb the different metals: their CECs are approximately a half those of the composts, which is reflected in differences in K_d values for each of the metals between the peats and the composts (Fig. 2; Table 1).

An important question regarding the use of organic amendments for managing the bioavailability of potentially hazardous trace metals in soils is the longevity of the effect, and the fate of the bound trace metals if the organic matter is degraded through microbial action. This is especially pertinent when considered in the context of predicted effects of forecasted changes in global temperature and rainfall patterns on organic matter stability in soils (e.g. Puissant et al. (2017)). The cold and hot-water extraction methods sample different pools of carbon from the amendments. Previous studies have shown that the CWEC fraction consists mostly of hydrophilic carbon (e.g. amino sugars, carbohydrates and low molecular weight organic acids, polysaccharides and high molecular weight fulvic acids) (Haynes, 2005; Said-Pullicino et al., 2007). The focus here is on the HWEC fraction, which has been associated with weakly adsorbed dissolved organic matter to mineral surfaces and humic acids, and has been used as a general indicator of the labile fraction of the organic carbon in soils (von Lützow et al., 2007). Out of the amendments considered here, the HWEC fraction of CBS was over twice as high as the next highest (PH) (Table 1) and between three to ten times higher than values measured in soils under different land uses (Ghani et al., 2003). While the K_d of CBS was relatively high ($\sim 400 \text{ L kg}^{-1}$ at pH 5.5, Fig. 1) compared to most other amendments here, its high Cd concentration, combined with the apparent vulnerability to microbial degradation, could be seen as valid reasons for restricting its use as a soil amendment. The two peats (EP, OP) and the municipal and mushroom-derived composts (LE and PH) had the next highest HWEC fractions, which prompts the subsequent investigation into the lability of Cd, Ni and Zn associated with the DOM extracted from them by the $0.05 \text{ M Ca(NO}_3)_2$ and the chemical characteristics of that DOM.

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

Geochemical modelling of the extracted solutions using WHAM VII suggested that over 99.4% of the total Cd, Ni and Zn was complexed by the DOM in all of the respective extracts (Table 2). This is considerably higher than seen in previous work when the WHAM VII model has been used to estimate trace metal speciation in soil extracts (Tipping et al., 2003; Cornu et al., 2011; Ren et al., 2015). This is almost certainly due to the very low metal:DOC ratios in the extracts, driven mainly by the large amount of DOM extracted from the organic amendments. With this in mind, it is important to acknowledge that the lability and speciation estimates carried out here are artificial and unlikely to be directly representative of most soil environments, where the amount of soil organic matter than can equilibrate with porewater is considerably less, and a proportion of the DOM is likely to be mineralized rapidly and/or sorb to soil solid interfaces (Lehmann and Kleber, 2015). It does however provide an opportunity to estimate conservatively whether complexed metals might become available for biological uptake or a chemical reaction, following a change in equilibrium. Kinetic limitations have been reported previously for trace metal uptake by plants (Degryse et al., 2006; Custos et al., 2014) and organisms native to

sediments (Amirbahman et al., 2013), and natural water (Jansen et al., 2002; Buffle et al., 2009; Shaked and Lis, 2012). These conditions are often identified when equilibrium-based methods fail to predict biological uptake (Zhao et al., 2016).

Amery et al. (2010) used a similar type of DGT design to the one employed here to show that the method can be used to analyse complex lability and obtain comparable kinetic information to the more conventionally used competitive ligand exchange method (CLEM) (Lam et al., 1999). In our work the SV-DGT analyses confirmed the previously observed kinetic limitation of Zn and Ni release from NTA and EDTA complexes and that Zn complexes were more labile than those of Ni, and a greater kinetic limitation of both metals' dissociation from EDTA complexes (Fig. 4) (Bowles et al., 2006). Analyses of the compost and peat extracts showed that the Zn and Cd complexes are relatively labile when compared to Ni, which agrees with previous measurements in natural waters (Warnken et al., 2007; Levy et al., 2012) and hints at relatively low solubility of organic matter containing reduced sulphur functional groups at this pH. Cadmium was relatively labile in the OP extracts, however significantly less so in the EP and compost extracts, especially LE (Fig. 4). This indicates that Cd-DOM complexes mobilized from soils where these composts had been used to manage Cd bioavailability may persist longer in soils before dissociation than when peat similar to OP was used. If composts

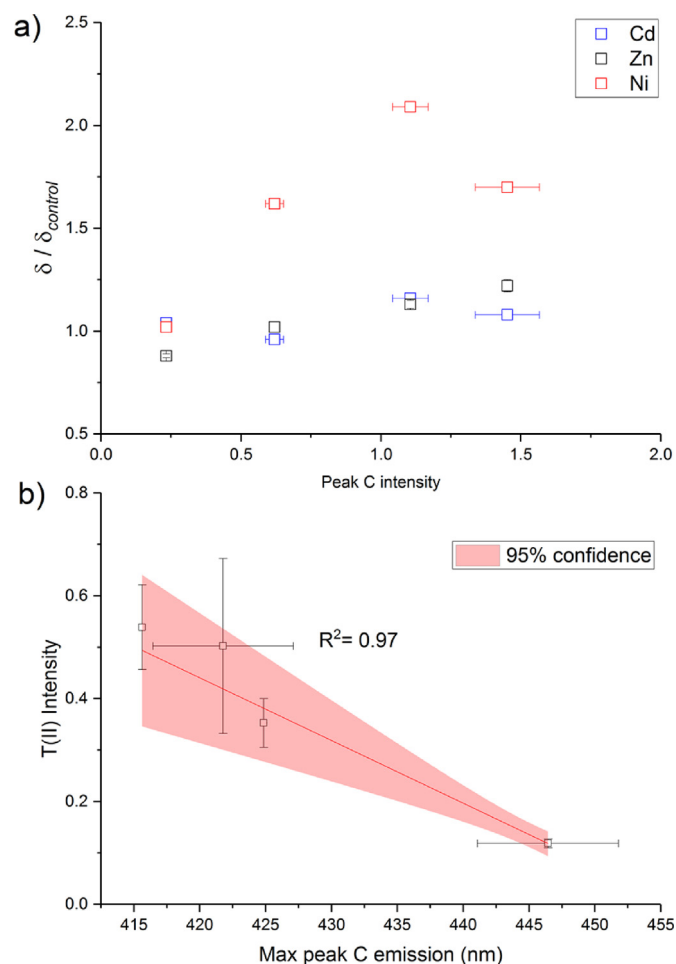


Fig. 3. The relationship between the relative kinetic restriction of DOM-metal complexes ($\delta/\delta_{\text{control}}$) and DOM aromaticity (Peak C Raman-normalized intensity) (a); and (b) negative correlation between DOM amino-acid fluorescence (peak T2; inferred biodegradability) and DOM aromaticity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

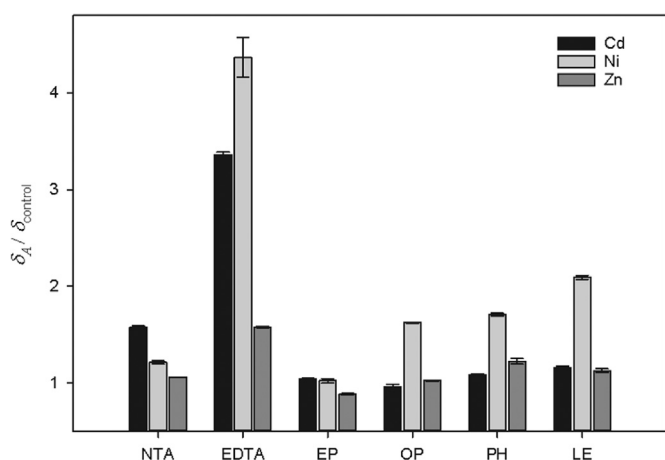


Fig. 4. The relative kinetic limitation of Cd, Ni and Zn in the extracted spiked 0.05 M $\text{Ca}(\text{NO}_3)_2$ solutions from the four organic amendments and two model ligands, NTA and EDTA. The error bars show standard error ($n = 3$).

were used to manage Ni contamination, under leaching conditions this could conceivably increase Ni mobility in the soil, more than a less labile complex, such as Zn, whose ability to participate in chemical reactions or be taken up by biota would be less kinetically limited.

3.3. Quality of the dissolved organic matter in the extracts

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

The Peak T fluorophore indicates of the proportion of bioavailable organic matter (Marschner and Kalbitz, 2003), and hence the potential for microbial activity in the sample (Hudson et al., 2008). Peak T fluorescence in our samples showed a declining relationship with the emission wavelength of maximum fluorescence intensity at Peak C (Fig. 3 b), which has been shown to increase in tandem with the degree of aromaticity and conjugation in soil organic matter (Senesi et al., 1991). DOM aromaticity (i.e. phenolic content) may diminish DOM biodegradability, whilst enhancing metal complexation strength (Baker et al., 2008). However, aromaticity will increase in DOM if biodegradation acts preferentially on aliphatic and low molecular weight DOM fractions (Hansen et al., 2016). Regardless of the precise mechanisms of causation, refractory amendments with higher metal binding strength are likely to exhibit lower protein-like fluorescence. This is consistent with the results of metal lability measurements in the studied extracts (Fig. 3 a) that show a positive trend between Ni and Zn kinetic limitation and the Peak C emission wavelength. These results are broadly supported by the SUVA_{254} measurements (Table 2). Shafaei Arvajeht et al. (2013) observed that Ni-HA complexes were less labile than Ni-FA complexes, which further suggests that the former

may be more abundant in the compost extracts. By contrast, Cd lability showed little change as a function of DOM aromaticity, probably indicating Cd complexation with non-phenolic moieties in DOM ligands. This suggests that microbial degradation of DOM may reduce the mobility of Cd-DOM complexes to a greater extent than Ni-DOM complexes. The work by Amery et al. (2008) provides further evidence to support this hypothesis. They showed a strong correlation between Cu:DOM concentration ratios and DOM aromaticity in 250 soil leachates, highlighting the role of DOM quality in determining metal-complex mobility in the environment.

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

As with the speciation modelling, it is important to recognize that the results herein are subject to certain caveats caused by the experimental approach used. We normalized the metal:DOC ratios across the different metal-amendment combinations after the extraction solutions had equilibrated with the amendments considered. We did this to enable comparison of the lability of the different DOM complexes and to elucidate whether the that could be related to the quality of the DOM from the different extracts. Previous studies have shown that the metal:ligand ratio is an important determinant when assessing the lability of a complex (Sekaly et al., 1999; Guthrie et al., 2003). This means that these measurements are likely to overestimate the lability of Cd in the extracts where a kinetic limitation is observed. It is also useful to note that, although numerous studies have shown that soil extractions carried out using 0.05 M $\text{Ca}(\text{NO}_3)_2$ can provide a good estimate of plant bioavailable fraction of soil Cd (Gray et al., 1999; Black et al., 2011, 2012; Reiser et al., 2014), the ionic strength of this extraction solution is higher than what is commonly observed in most soil porewaters (Edmeades et al., 1985). Dissolution of solute from the amendments will have contributed to this. While the high ionic strength is likely to have reduced the probability of solute binding to the agarose diffusion layer (Wang et al., 2016), it is also possible that there was a consequent increase in the perceived lability of the Ni complexes due to ligand-assisted dissociation in the resin gel (Puy et al., 2014). Further testing is needed to quantify this effect.

4. Conclusions

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

evidence that DOM quality likely to be an important factor.

Data availability statement

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Additional information

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

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2018.02.069>.

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