



Soil cadmium mobilisation by dissolved organic matter from soil amendments

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HIGHLIGHTS

- Cd mobilisation from soils treated with organic matter-rich substrates was tested.
- Mobilisation was reduced by the treatments at soil pH 5.6 and by liming to 7.4
- Treating soils with compost and peat at pH 6.4 increased Cd mobilisation.
- Dissolved organic matter quality can determine extent of Cd mobilisation.

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ABSTRACT

Dissolved organic matter (DOM) release from Cd contaminated soils been linked to mobilisation of the metal as Cd-DOM complexes and this may be exacerbated by organic matter-rich soil amendments. The quantity and quality of the DOM can determine the proportion of dissolved Cd that partitions to mobile complexes and their stability and, thus, the potential for Cd transport from contaminated soils. The aim of this work was to examine differences in Cd mobilisation from soils to which different types of soil amendments/conditioners have been applied and the importance of DOM characteristics in determining the extent to which this can happen. Three soils were spiked with Cd to 2 mg kg⁻¹, allowed to equilibrate and then treated with compost and peat. These soils and an untreated subsample of each soil were then adjusted to three different pHs: 5.6, 6.4 and 7.4, using lime. The amount of Cd mobilised from each soil was tested using a column leaching experiment. Ultrafiltration and speciation modelling were used to determine amounts of Cd as DOM-complexed, “truly” dissolved (<5 kDa) and colloidal species, while DOM quality was assessed using UV–Vis and fluorescence spectroscopy. Most colloidal Cd was mobilised from the compost treated soils (50%–60%), followed by the peat treated soils (20–44%). The relationships between colloidal Cd, DOC concentration and soil pH, together with the spectroscopic and modelling results showed that structural properties of DOM are an important factor in mobilising Cd from contaminated soils.

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1. Introduction

Cadmium (Cd) is a biologically non-essential trace metal that is relatively toxic to living organisms. It is a naturally occurring impurity in many phosphorus fertilizers, whose intensive use has

been identified as an important contributor to the accumulation of the metal in agricultural soils (Chaney, 2010). High concentrations of Cd in soils can increase Cd uptake by plants (McLaughlin et al., 2011), causing exceedances of food safety standards. It may also mobilise to other environmental compartments, such as ground water (Salmanzadeh et al., 2017; Kubier et al., 2019). Plant uptake of the metal can be reduced by various low-cost inorganic and organic matter-rich soil amendments (Bolan and Duraisamy, 2003; Bolan et al., 2014) while improving soil fertility (Al Mamun et al., 2016;

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Khan et al., 2017; Gı̇b et al., 2018). However, organic matter amendments can also increase concentrations of dissolved organic matter (DOM) in soils (Kalbitz et al., 2000; Hernandez-Soriano et al., 2013) and that can serve as a potential vector for transporting the metal from soils to other parts of the biosphere (Welikala et al., 2018). The ability of soil amendments that are rich in organic matter (OM) to retain Cd in the soil is variable (Welikala et al., 2018; Liu et al., 2019) and the key factors that determine the extent to which they can achieve this are not well understood (Shuman, 1998; Houben et al., 2013; Bolan et al., 2014). Developing further insight into these mechanisms can help inform better application of OM amendments to prevent plant Cd uptake while minimizing mobilisation of the metal.

The extent to which organic matter is solubilised in soils, and its subsequent mobility, is determined by the physical, chemical and biological characteristics of the soil (e.g. texture, pH, microbial activity) and soil management practices (Ghani et al., 2010; Bolan et al., 2011). When OM-rich substrates are applied to soils, the characteristics of the substrate (e.g. parent material, maturity) are another important determinant in the quantity of DOM released (Tapia et al., 2010; Liu et al., 2019) and its quality (Huang et al., 2016; Guo et al., 2019).

Dissolved organic matter has been shown to solubilise Cd in soils through complexation as Cd-DOM complexes and ligand-assisted dissolution of solid binding phases (namely metal (oxyhydr)oxides) (Collins et al., 2003). Others have shown DOM to be an important vector for transport of other trace metals cations, such as Cu in soils and the surrounding environment (Amery et al., 2008). Welikala et al. (2018) proposed that the extent to which Cd can move through soils as DOM complexes could be regulated by the rates at which Cd-DOM complexes can release Cd to be (re)adsorbed onto solid phases by dissociation and biodegradation. They showed that the quantity and characteristics (or 'quality') of the DOM can help inform the rate of Cd dissociation from DOM complexes, while others have shown DOM quality to also be an important determinant in how fast it can be degraded by microorganisms (Kalbitz et al., 2003; Liu et al., 2019; Vujinović et al., 2019).

Dissolved organic matter is a heterogeneous mixture of organic molecules (e.g. humic-like, protein, lignin, polysaccharides) with various functional groups (e.g. carboxylic, phenolic, amine and thiol groups) that can show different affinities for complexing Cd (Kaschl et al., 2002; Karlsson et al., 2007; Laborda et al., 2009; Bai et al., 2018). These organic molecules in DOM are often fractionated depending on their molecular weight, polarity, acidity and humic or non-humic characteristics. The association of Cd with different fractions of DOM can vary depending on the provenance of DOM (e.g. soil solution, surface and groundwater, compost extracts) and the resulting DOM characteristics and environmental variables (e.g. soil texture and pH) (Laborda et al., 2008; Ren et al., 2015; Kozyatnyk et al., 2016; Bai et al., 2018). Kaschl et al. (2002) and Bai et al. (2018) found that Cd has a strong affinity for high molecular weight humic-like compounds that are abundant in colloidal DOM derived from aged OM (e.g. compost and peat) frequently used to amend soils (Laborda et al., 2008, 2009; bib_Laborda_et_al_2008; bib_Laborda_et_al_2009). Kalbitz et al. (2003) showed that DOM emerging from aged OM sources is less susceptible to biodegradation, thus Cd associated with this DOM may exist in these species for longer and travel further.

The pernicious nature of soil Cd in the environment means that further insight is urgently needed to understand how sensitive the mobilisation of Cd may be to the characteristics of DOM in different soils. Therefore, the aim of this work was to examine differences in the magnitude of Cd-DOM complexes' release from contaminated

soils treated with different types of organic matter-rich substrates and elucidate important characteristics of the DOM that may inform the extent to which this happens.

2. Materials and methods

2.1. Sample collection and preparation

Topsoils (<0.25 m depth) from three New Zealand (NZ) soil orders (Hewitt, 2010) were collected from New Zealand's South Island in January 2018. The 'Craigieburn' soil is an *Allophanic Brown* soil, collected from Craigieburn area (43° 20' 21" S, 171° 37' 54" E); the 'Templeton' soil is an *Immature Pallic* soil, collected from near Lincoln University (43° 38' 54" S, 172° 39' 39" E). These two soils are generally representative of soils used for agriculture in parts of NZ. The 'Waikari' soil is a *Rhendzic Melanic* soil, collected from Waikari (42° 58' 2" S, 172° 38' 22" E) and was chosen to expand the range of soil chemical and physical characteristics considered in this study. Large stones and roots were removed manually, after which the soils were sieved through a 2 mm nylon mesh. Subsamples of each soil were air-dried for characterisation (see below). Cadmium was added as Cd(NO₃)₂ solution to increase the total Cd concentration by 2 mg Cd kg⁻¹ (expressed as oven-dried at 105 °C). The soil moisture content of each soil was increased to field capacity (FC), after which the soils were left to equilibrate at room temperature (20–25 °C) for four months while being regularly mixed to ensure aeration. Subsamples of the spiked soils were collected at various intervals and tested for pH (not shown) and 0.05 M Ca(NO₃)₂ extractable Cd (see section 2.2 for method description) (Fig. S1).

Commercially produced compost and naturally formed peat were used as the OM substrates. The compost was made from municipal green waste by Living Earth Ltd, Christchurch. Peat is a component part of some commercially produced composts and soil conditioners. The peat used here was sampled from a formation near Lincoln, New Zealand (43° 40' 37" S, 172° 26' 52" E) and used to provide distinct source of organic matter to the soils to compare to the compost. Both substrates were sieved through a 2 mm nylon mesh and air-dried. Subsets of each of the three Cd-spiked and equilibrated soils were treated with a combination of one of three organic matter treatments and three lime (laboratory grade Calcium carbonate, VETEC™, Sigma-Aldrich, India) rates. The OM substrates were applied at a rate of 2.5% (total organic carbon (TOC) wt/soil wt, air-dried mass basis). Subsets of the three treated soils and untreated control soils were then limed at different rates to achieve a final pH of 5.5, 6.5 or 7.5 (±0.2 pH units) and the moisture content was adjusted to 60% of FC. This was followed by further 12 weeks of incubation at 25 °C, during which the pHs in the treatments stabilised; forthwith, the soil pHs are categorised into three groups: 5.6, 6.4 and 7.4 according to the median pHs at the time of the experiment.

2.2. Soil and organic matter analysis

Soil pH and conductivity were measured at 2:5 and 1:5 soil:water ratios, respectively (Blakemore et al., 1987). The pH of the organic substrates was measured using 1:5 solid:water ratio. Total C and N were determined using a CN element analyser (Elementar Vario MAX CN Elemental Analyser, Elementar®, Germany). Total organic carbon in the soil and substrates was analysed by pre-digesting inorganic carbon with 0.5–0.8 mL of 3% HCl prior to total C measurement. The soil and OM were prepared for pseudo-total element content analysis using microwave digestion (MARS XPRESS, CEM Corporation, USA) as described by Kovács et al. (2000). Cation exchange capacity (CEC) of the soils and OM

Table 1
Chemical properties and element concentrations of soils and organic matter substrates.

	Craigieburn	Templeton	Waikari	Compost	Peat
clay/silt/sand%	10/50/40	4/22/74	7/36/57	nd	Nd
pH (H ₂ O)	5.62	5.51	6.05	6.49	4.69
Conductivity ($\mu\text{S cm}^{-1}$)	23.5(0.2)*	41.7(0.2)*	48.6(0.3)*	5347(24)*	560(12)*
CEC $_{\text{AgTu}}$ (cmol kg ⁻¹)	6.5(0.1)*	7.5(0.2)*	15.2(0.4)*	62.0(2.6)*	37.9(2.2)*
BS%	58.4(4.3)*	89.7(9.5)*	83.2(2.0)*	136.3(6.4)*	103.5(6.4)*
TOC%	1.96(0.02)*	1.99(0.05)*	3.57(0.03)*	18.85(0.93)*	18.25(0.39)*
N%	0.24(0.01)	0.19(0.003)	0.30(0.004)	2.28(0.02)	1.95(0.02)
P (mg kg ⁻¹)	575(7)	405(8)	858(45)	2996(84)	1635(27)
S (mg kg ⁻¹)	281(5)	225(3)	398(28)	2579(11)	3765(10)
Mn (mg kg ⁻¹)	637(24)	256(18)	698(56)	293(2)	384(29)
Al (g kg ⁻¹)	40.7(0.8)	18.5(0.6)	23.0(0.8)	7.3(0.6)	13.3(0.2)
Fe (g kg ⁻¹)	26.1(0.1)	13.7(0.3)	16.5(0.4)	7.9(0.1)	140.3(0.1)
Cd (mg kg ⁻¹) [†]	<0.001 ϵ	<0.001 ϵ	<0.001 ϵ	0.5(0.003)	0.34(0.007)
Cd (mg kg ⁻¹) [‡]	1.70	1.47	1.85		
Cu (mg kg ⁻¹)	8.2 (0.1)	3.4 (0.1)	9.0 (0.1)	49.2 (0.1)	28.5 (0.1)
Pb (mg kg ⁻¹)	21.0 (0.2)	8.1 (0.02)	9.0 (0.1)	109.5 (1.1)	32.7 (0.5)

Standard error (SE) of the mean of replicates is given in bracket. (n = 3, except when * indicated n = 2). ϵ below the detection limit. nd = not determined. [†] Pseudo-total Cd concentration in unspiked soil and organic substrate. [‡] Total Cd concentration in Cd-spiked soil. CEC is the cation exchange capacity and BS is the base saturation.

substrates was measured using the silver thiourea (AgTu)(-Blakemore et al., 1987) (results are shown in Table 1).

After six weeks of incubation following the OM and lime treatment (15 weeks after spiking), extractable Cd (as determined by a 0.05 M Ca(NO₃)₂ solution) was determined using the method reported by Gray et al. (1999). Briefly, 5.00 g of air-dried soil was mixed with 30 mL of 0.05 M Ca(NO₃)₂·4H₂O (ACS reagent, Sigma-Aldrich) solution and equilibrated in an end-over-end shaker for 2 h. The mixture was then centrifuged at 2000 rpm for 20 min followed by filtration (Whatman 52 filter paper). The filtrate was stored at -20 °C prior to analysis for extracted trace metals and other elements, forthwith this shall be referred to as 'extractable Cd'.

2.3. Column leaching

After a further six weeks of incubation the moist soils were packed into cylindrical PVC leaching columns (height: 50 mm, internal ϕ : 44 mm) to a uniform bulk density of 1 g cm⁻³. The bottom of each column was underlaid with a nylon mesh (mesh size of 20 μm) and the top of the soil was protected from water droplet impact using a filter membrane, which also helped to ensure an even distribution of water across the surface. The soil moisture content in each column was then increased to FC and left to equilibrate for 24 h. Leaching was induced by dripping synthetic rainwater (Zhao et al., 2007) at a constant rate of 0.3 mL min⁻¹ onto the soil until a volume of leachate equal to four soil porewater volumes was collected at the bottom of the column. The use of moist soils aimed to reduce the release of additional DOM by OM mineralisation following a soil drying-rewetting event (Vujinović et al., 2019).

The leachates were collected into acid-cleaned containers on ice baths (<4 °C) to minimize microbial activity. Samples were filtered through 0.45 μm syringe filters (GPA/CA Membrane, Phenex™, phenomenex®, USA) and divided into subsamples within 12 h of the end of leachate collection. The filtered leachates were analysed for pH and conductivity, dissolved organic and inorganic carbon (DOC and DIC, respectively), cations and anions (section 2.7). Sub-samples for dissolved cation analysis were preserved by acidifying with high purity 1 M HNO₃ (pH < 2) (PrimarPlus-Trace Analysis grade, Fisher Scientific, UK) and DIC samples were preserved with saturated mercuric chloride (0.02% V/V; HgCl₂, BDH laboratory reagent, England). Forthwith, cadmium (and other solutes) in these

samples will be referred to as having been 'mobilised'.

Filtered samples were also allocated for ultrafiltration (section 2.4), organic matter quality indices analysis (section 2.5) and tested using Small Volume Diffusive Gradient in Thin-Films (SV-DGT) (section 2.6). Samples allocated to organic matter quality indices were stored at -80 °C, all the other samples were stored at -20 °C before analysis.

2.4. Ultrafiltration: the 'truly' dissolved fraction

The <5 kDa size fraction of Cd in the leachates of OM treated and untreated soils at pHs 5.6 and 6.4 was isolated using a 200 mL polycarbonate stirred cell (Amicon® stirred cell, Merck Millipore, USA) where, 50 mL of leachate was filtered through 5 kDa regenerated cellulose membrane (ϕ : 63.5 mm, Merck Millipore, USA). The pressure of N₂ (oxygen-free) was set at 250 kPa to get a continuous flow rate. The filtrate was then acidified to pH < 2 with high purity 1 M HNO₃ for subsequent Cd analysis. Forthwith, this will be referred to as the "truly dissolved" fraction. The "colloidal Cd" was estimated as the difference between the total dissolved (<0.45 μm) and truly dissolved Cd.

2.5. Dissolved carbon analyses

The DOC concentration in the leachates was measured using a TOC analyser (Vario TOC-cube, elemental, Germany). UV-VIS spectrophotometry (UVmini-1240, SHIMADZU corporation, Kyoto, Japan) was used to elucidate certain qualitative characteristics of DOM: specific absorbance measured at 254 nm (SUVA₂₅₄) was used to estimate the aromaticity of the DOM (Weishaar et al., 2003), while the ratio of absorbance measured at 465 and 665 nm (E₄/E₆) was considered to reflect the degree of aromatic condensation of the substance in the DOM (Kleber and Johnson, 2010). The ratio of the absorbance measured at 254 and 365 nm (A₂₅₄/A₃₆₅) was calculated to estimate the relative molecular weight of the DOM (Dahlén et al., 1996).

Fluorescence excitation-emission matrices (EEMs) for the leachates were obtained by measuring fluorescence emission intensities 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). For all samples, fluorescence intensities were normalised using ultra-pure water Raman peak intensity (350 nm excitation, 398 nm

emission) at the same analytical setting as the samples. Common DOM quality indices (Fluorescence index, Humification index, and Biological index) were calculated for DOM leached using the EEMs (Parlanti et al., 2000; Wilson and Xenopoulos, 2009; Gao et al., 2017).

The fraction of humic acid in the leachate was determined using the method described by Van Zomeren and Comans (2007). Briefly, 30 mL of leachate was acidified to pH < 1 with 6 M HCl (AnalaR NORMAPUR, VWR International S.A.S, France) and centrifuged at 2000 rpm for 10 min. The supernatant was carefully extracted and analysed for DOC, with the proportion of DOC as humic acids in the leachates being the difference in concentration between the initial non-acidified and the acidified leachate. The low amount of DOM mobilised from some of the untreated soils resulted in low DOC concentrations (<10 mg L⁻¹) and a large uncertainty in the percentage of HA. The concentration of humic acids in those cases was assumed to be zero.

2.6. Kinetic limitation measurement

The kinetic limitation of Cd leached from the OM treated and untreated soils at pH 5.6 and 6.4 was evaluated using an adapted DGT: SV-DGT. The operating principles of the technique and preparation of SV-DGT vials are described elsewhere (Welikala et al., 2018) and summarised in the supplementary information (Section S1.). Briefly, the SV-DGT comprise a 30 mL cylindrical vial with a 3 mm thick agarose gel cast over a layer into which a cation binding resin (Chelex® 100 Resin, BIO-RAD, USA) is embedded. A 10 mL control solution of 0.077 µM Cd (Cd(NO₃)₂·4H₂O, BDH, AnalaR®, England) is deployed in the SV-DGT vial and the diffusion rate of labile Cd species into the binding resin is measured by monitoring the rate at which the Cd concentration in the solution is depleted over 24 h. The depletion rate in the control is then compared against the rate in 10 mL of a sample solution, where the Cd may be bound by inert or partially labile complexes, deployed in an identical vessel simultaneously. Comparison of the two rates allows a semi-quantitative estimate of the extent to which the rate of dissociation of free Cd²⁺ ions from complexes in the sample solution is limited. Forthwith, this is referred to as 'relative kinetic limitation'. Here the ionic strength of the control solutions and samples were normalised by adjusting the electrical conductivity of the solution to 2 mS cm⁻¹ with 0.1 M NaNO₃ (TraceSELECT®, Sigma-Aldrich, Germany).

2.7. Cation and anion analyses

The concentration of Cd in 0.05 M Ca(NO₃)₂ extracts and elemental concentrations in acid digests were analysed using Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES; Varian 720 ES – USA). These are expressed on a mass element per mass air-dried soil basis. The leachates were analysed for cations (Ca, Mg, Na, K, Zn, Cu, Cd, Ni) and anions (Cl⁻, NO₃⁻, PO₄³⁻, SO₄²⁻) using a ICP- Mass Spectrometry (ICP-MS, Agilent 7500cx, USA) and a DIONEX (ICS-2100, Thermo Scientific, USA), respectively. The filtrates from the ultrafiltration and the solutions from SV-DGT experiment were analysed only for Cd using the same ICP-MS. All sample treatments and dilutions used high purity water (18.2 MΩ resistivity; Heal Force® SMART Series Ultra-pure water system, Model-PWUV), acid (HNO₃, PrimarPlus-Trace Analysis grade, Fisher Scientific UK) and reagents. The equipment used to handle, contain, and/or analyse samples was thoroughly acid-washed before analysis. Blank extracts, filtrates, and solutions were analysed regularly to confirm low contamination levels.

2.8. Speciation modelling

The speciation of Cd in leachates collected from OM treated and treated soils at pH 5.6 and 6.4 was modelled using the Windermere Humic Acid Model (WHAM) VII (Tipping et al., 2011). The concentration ratio of DOM: DOC was assumed to be 2 (Cornu et al., 2011). The DOM was considered to consist of 25% fulvic acid (Laborda et al., 2009; Ren et al., 2015) and experimentally determined concentrations of humic acid were used. Overall, <30% of the mobile DOM was found to exist in the humic acid fraction.

2.9. Statistical analysis

Data analysis and visualization were carried out using R (R core Team, 2018). Data were analysed using ANOVA, with Tukey's post-hoc test to compare means. Linear models were fitted to understand the statistical significance of the soil order, type of OM treatment and soil pH and their interactions for the observed variation for the leached Cd. The correlations among the amount of Cd leached, DOC quantity and quality, and kinetic limitation were tested using Spearman's rho (ρ) using log-transformed data. The normality of residuals was assessed using QQ-plots. Significance was assumed at the 0.05 confidence level throughout, unless stated otherwise.

3. Results and discussion

3.1. Cadmium mobilisation from soils

Soil type, pH and OM treatment, and the interactions between these three factors, significantly affected the amount of Cd mobilised from the soils ($P < 0.001$). As indicated by the leaching experiment, most Cd was mobilised from the untreated soils at pH 5.6 (7.5–12.2 µg kg⁻¹ soil) and decreased in the order: Templeton > Craigieburn > Waikari, with significant differences between the soils ($P < 0.05$) (Fig. 1). Treating the soils with compost at pH 5.6 reduced Cd mobilisation significantly in the Templeton and Craigieburn soils (49–70%), while peat only reduced the mobilisation in the Craigieburn soil (17%; $P < 0.05$) (Fig. 1). Across all soils, 56% of the variation in Cd mobilisation was explained by soil pH ($P < 0.001$). Increasing soil pH from 5.6 to 6.4 reduced the average amounts of Cd mobilised from the untreated soils by 76% and the peat treated soils by 65%. The amount of Cd mobilised was further reduced between pH 6.4 and 7.4 ($P < 0.05$) (Fig. 1). Increasing the pH of the compost treated soils from 5.6 to 6.4 reduced Cd mobilisation from the Templeton and Waikari soils ($P < 0.05$). Moreover, treating the soil with compost increased Cd mobilisation from the Templeton and Waikari soils at pH 6.4 ($P < 0.05$; no significant differences at pH 7.4). The 0.05 M Ca(NO₃)₂-extractable Cd concentration plateaued four weeks after spiking (Fig. S1) and subsequent changes under the constant incubation conditions were considered unlikely. Adding peat and compost to the soils and raising the pH reduced the amount of 0.05 M Ca(NO₃)₂- extractable Cd from each soil significantly, with the effect of compost being greater than peat (Fig. S2). The amount of Cd extracted from the soil was between 2- to 99-fold higher than what was mobilised; the correlation between the two was not significant.

The rate of organic matter application to the soils here (equivalent areal rate of ~134 t/ha) is ca. 3–5 times higher than in most agronomic situations (e.g. Horrocks et al. (2016)). However, high rates can be used to ensure longer term nutrient supply to plants (Sullivan et al., 2003). Applying at a higher rate could arguably also sequester soil Cd into less plant available forms for longer and help reduce the frequency with which fresh compost needs to be applied

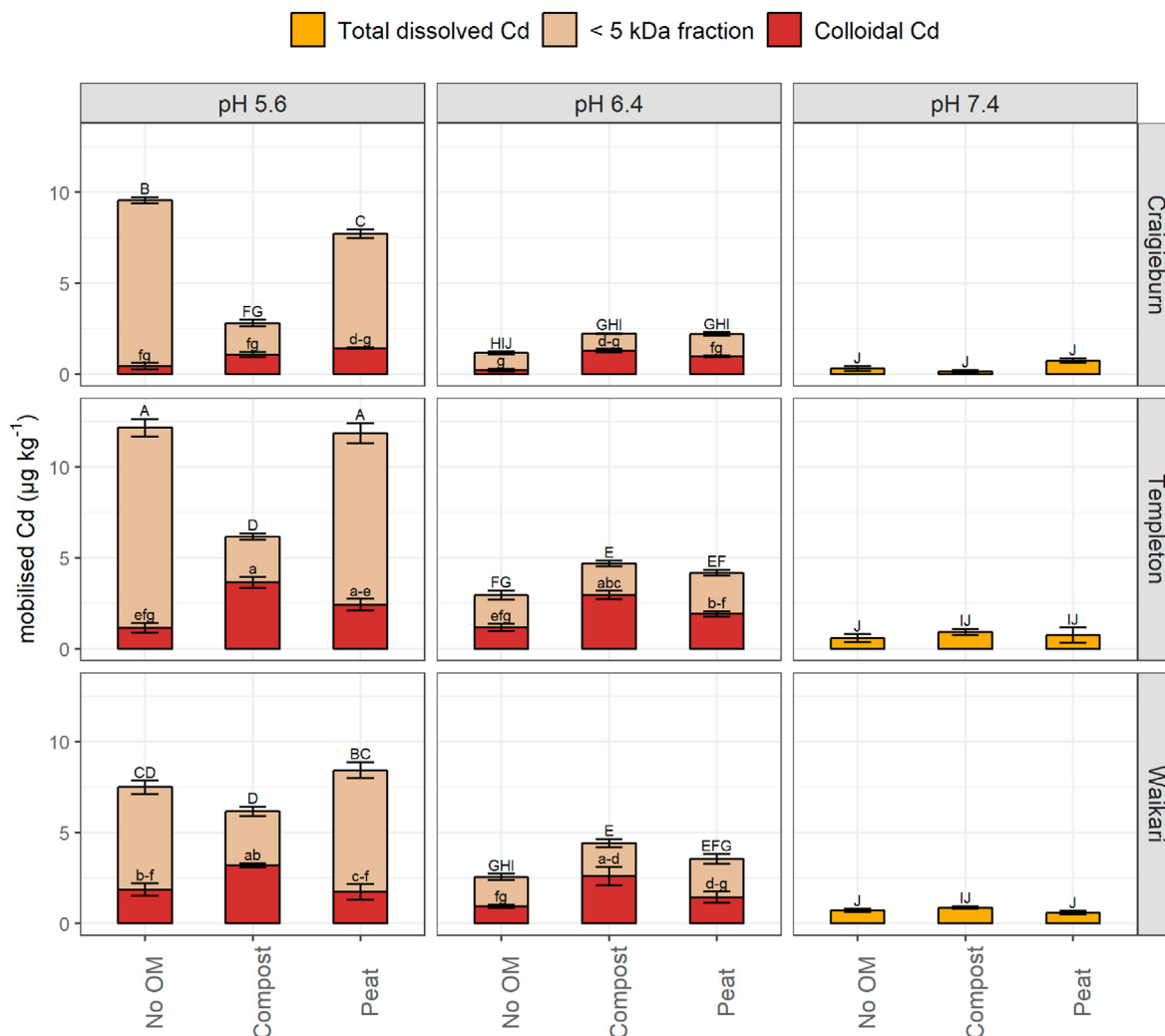


Fig. 1. Cadmium mobilised during column experiments, as “truly dissolved” (<5 kDa fraction) and “colloidal” (total dissolved – truly dissolved). Only the total dissolved amount of Cd was measured at pH 7.4. The amount mobilised is expressed relative to the mass of soil. Error bars represent the standard error of the mean ($n = 3$). The uppercase letters indicate the significant difference in the total dissolved Cd and lowercase letters indicates the significant differences for colloidal Cd only.

and mixed in, thus potentially reducing mineralisation of existing OM, however these effects on Cd have not been systematically tested. The overall contribution of Cd that was already in the compost and peat (Table 1) to the total amounts mobilised is unlikely to have been significant. Adding Cd with the OM substrates will have only increased the total soil Cd by <5% and the low amounts of mobilised Cu and Pb (not shown) –also readily transported by DOM (Amery et al., 2007; Okkenhaug et al., 2018)—suggest that the greater Cd mobilisation observed in OM treated soils at pH 6.4 is likely to be driven by the increased complexation of soil Cd by the DOM (Naidu and Harter, 1998).

Given the short measurement period and relatively low volume of leachate collected, these results can be best used to describe the initial mobilisation of solute and colloids from these soils and should be considered in that context. Therefore, the mobilised Cd here is likely to be representative of a combination of (i) the initial concentration of Cd species in the soil solution, (ii) Cd released from relatively labile solid-phase species into soil solution species during leaching and (iii) Cd bound to organic matter solid phases that dissolve during the experiment. The advantage of the experimental procedure employed here is that it allows a relatively rapid and systematic means by which to examine the role of quality of DOM

in mobilising soil Cd across three different soils.

3.2. Mobile colloidal-cadmium and its relation with quantity and characteristics of dissolved organic matter

The colloidal fraction is thought to consist of large (high molecular weight) humic acids and organo-minerals that have a strong affinity for binding Cd (Kaschl et al., 2002; Pokrovsky et al., 2005; Chen et al., 2019). In this experiment, the colloidal fraction of mobilised Cd correlated strongly with mobilised DOM ($\rho = 0.771$, $P < 0.0005$), but showed a poor relationship with soil pH ($\rho = 0.053$, $P > 0.05$) (Table 2). The opposite was seen for truly dissolved Cd (<5 kDa size fraction), where pH was strongest explanatory variable for this fraction ($\rho = -0.751$, $P < 0.0005$) (Table 2). This agrees with Tang et al. (2020) who showed a significant decrease in dissolved Cd release from a clay soil following an increase in pH from 5.9 to 6.8 using lime, with a concomitant increase in colloidal Cd. The strong negative correlation between pH and truly dissolved Cd may be explained by the preferential sorption of free Cd^{2+} ions to solid phases. This also helps to explain the relatively low binding of Cd to the soil matrix in the relatively sandy Templeton soil that is likely to feature lower numbers of variable charge sorption sites (McLaren,

Table 2
Spearman correlation matrix for the relationship among Cd mobilised, soil pH, kinetic limitation, and quantity and quality of DOM.

	<5 kDa Cd ^e ($\mu\text{g kg}^{-1}$)	colloidal Cd ^f ($\mu\text{g kg}^{-1}$)	soil pH	DOC (mg kg^{-1})	SUVA ₂₅₄	E ₄ /E ₆	A ₂₅₄ /A ₃₆₆	Kinetic Limitation
soil pH	-0.751****	0.053						
DOC (mg kg^{-1})	-0.115	0.771****	0.434***					
SUVA ₂₅₄	0.166	-0.479****	-0.298*	-0.654****				
E ₄ /E ₆	-0.522****	0.229	0.711****	0.61****	-0.398****			
A ₂₅₄ /A ₃₆₆	0.069	-0.688****	0.157	-0.518****	0.398****	-0.086		
kinetic limitation	-0.541****	-0.373**	0.502***	-0.006	-0.152	0.329**	0.122	
Cd-HA ^{a,d} (M)	0.219	0.625**	0.148	0.571**	-0.482*	0.251	-0.456*	-0.067
Cd-FA ^{b,d} (M)	0.449	0.876****	-0.254	0.734****	-0.433	0.136	-0.739***	-0.447
Cd-DOM ^{c,d} (M)	0.389	0.820****	-0.024	0.697***	-0.485*	0.214	-0.625**	-0.300

$P < 0.0005$ **** 0.001 *** 0.01 ** 0.05 * 0.9 "

^a Concentration of Cd complexes with HA (mol L^{-1}).

^b Total concentration of Cd complexes with FA (mol L^{-1}).

^c Concentration of Cd complexes with both HA and FA (mol L^{-1}).

^d Correlations are calculated with average results for each parameter for each treatment.

^e Considered to be "truly dissolved" Cd.

^f Calculated as total dissolved - truly dissolved.

1996; McLaughlin et al., 1996) and reduced sensitivity in Cd immobilisation to changes in pH (Naidu et al., 1994, 1997; bib_Naidu_et_al_1994; bib_Naidu_et_al_1997). The higher amounts of Fe and Al in the Craigieburn and Waikari soils (Table 1) may also be indicative of the presence of oxide minerals that can bind Cd. On the other hand, the reasons behind the poor relationship between pH and colloidal Cd appears to extend beyond simply the relationship between pH and DOM ($\rho = -0.434$, $P < 0.001$) (Table 2). The characteristics of the mobilised DOM are likely to be an important contributing factor.

The average proportion of colloidal Cd mobilised from the compost treated soils increased from 50% to 60% between pH 5.6 and 6.4 across all three soils, the corresponding increase in the peat treated soils was from 20% to 44% (Fig. 1). In the untreated soils the proportion of colloidal Cd increased between pH 5.6 and 6.4 in the three soils as follows: Craigieburn (5%–20%), Templeton (9%–40%) and Waikari (25%–37%) soils. The increase in Cd mobilisation from compost treated Templeton and Waikari soils at pH 6.4 can therefore be linked to the mobilisation of colloidal Cd. The generally lower mobilisation of colloidal Cd from the Craigieburn soil is likely to be due to the relatively small amount of mobilised DOM from that soil (Fig. 2), probably driven by the abundance of strongly DOM-binding iron oxide minerals in that soil (Kaiser et al., 1996) and, by extension, an increased metal sorption capacity (Arias et al., 2002; Chen et al., 2019).

The amount of DOC mobilised ranged between 0.4 and 7.9 mg DOC g^{-1} TOC which agrees with Vujinović et al. (2019) who reported a range of 1.5–5.5 mg DOC g^{-1} TOC (assuming all soil C was organic C) mobilised from a laboratory leaching experiment with another group of soils. The mobilisation from the peat treated soils was more sensitive to pH than from the soils treated with compost (Fig. 2). The DOM from these soils also had a generally proportion of aromatic moieties and were lower in molecular weight (Table 3). Increase in DOM mobilisation with pH is well recognized (Kalbitz et al., 2000). In this case the increase in Ca^{2+} through the lime application is likely to have reduced the total amount of DOM mobilised, when compared what might be seen if the pH is elevated along with the addition of Na^+ or K^+ , due to changes in the intermolecular attraction between DOM moieties (Lieferring and McLay, 1996; Curtin et al., 2016).

Across pH 5.6 and 6.4 the average proportions of humic acid in the DOM mobilised from compost ($20.5 \pm 5.2\%$) and peat ($24.1 \pm 5.7\%$) treated soils agree with those found in compost extracts by Laborda et al. (2009), but are lower than those reported by Klinkert and Comans (2020). Bai et al. (2018) showed that high molecular weight humic acid molecules bind Cd strongly, which is

supported here by the correlation between colloidal Cd and the A₂₅₄/A₃₆₆ index (inversely related to molecular weight of the DOM (Dahlén et al., 1996)) (Table 2). However, the amount of mobilised colloidal Cd correlated negatively with the aromaticity index, SUVA₂₅₄ ($P < 0.0005$; Table 2), indicating that Cd binding ligands in large DOM moieties tend to occur predominantly in aliphatic moieties. This is further supported by negative correlations between SUVA₂₅₄ and the amount of Cd complexed with humic and fulvic acid (Table 2), and aligns with the suggestions that non-phenolic moieties and reduced sulphide groups on non-aromatic humic acid structures are important Cd-binding ligands in DOM (Chen et al., 2018; Welikala et al., 2018).

Colloidal DOM may be formed through breakdown of larger OM aggregates or the polymerising or aggregating of small organic molecules, which can show more resistivity for biodegradation than the DOM in the smaller fractions (Kleber and Johnson, 2010; Lehmann and Kleber, 2015). Moreover, due to its generally larger size and stability, colloidal DOM may not bind to soil solid mineral surfaces to a large extent (Kleber and Johnson, 2010). Therefore, colloidal Cd-DOM species may persist in the soil solution for longer and have the potential to transport Cd in the surrounding environment. Kalbitz et al. (2003) measured high proportions (>75%) of stable DOM from humified OM (humified layer from Spruce forest) and agricultural soil and reported their half-lives as 8.6 and 2.3 years, respectively. Given the higher humification degree of DOM mobilised from the compost and peat treated soils than DOM from the untreated soils (Fig. S3), it is possible that Cd associated with DOM-released from compost or peat treated soils may persist as complexes in soils and able to be transported from their point of origin. The quality of the DOM here is, again, only reflective of what was initially mobilised from these soils, but this should serve as a basis from which to investigate the role of DOM quality in Cd mobilisation further.

3.3. Kinetic limitation and speciation of cadmium in the leachates

The total fraction of mobilised Cd that was bound by either humic or fulvic acid ranged widely between pH 5.6 and 6.4 in the untreated (4–21%) soils and soils treated with compost (30–62%) and peat (32–77%), with greater proportions complexed by these fractions at pH 6.4 (Table 3). The proportions of Cd complexes identified here are in line with estimates of Cd bound by soil DOM by Ren et al. (2015) (<28%) and by Cornu et al. (2011) (34–77%). Various authors have emphasised the importance using an experimentally determined F-value, (i.e.) the ratio of active to total DOM that is both metal and DOM specific and, therefore, appropriate for

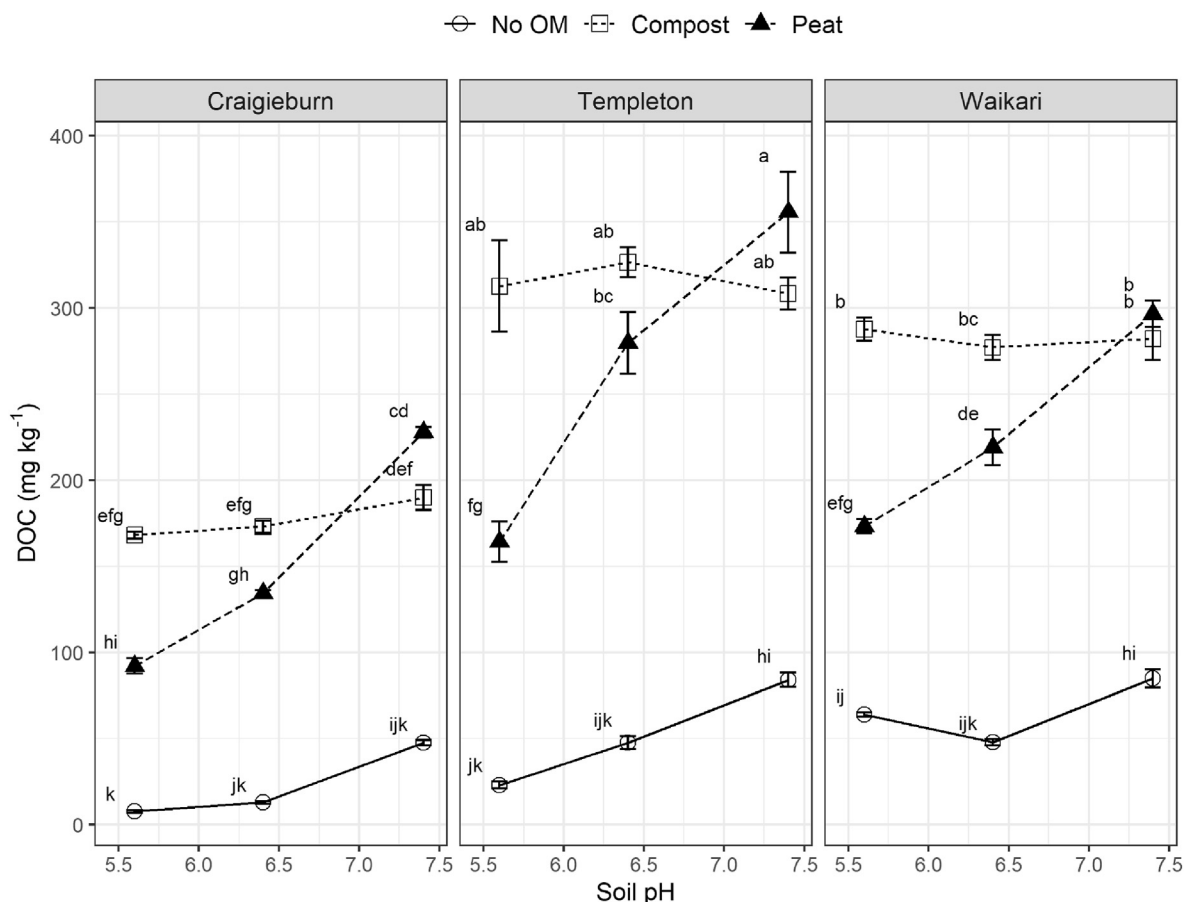


Fig. 2. Dissolved organic carbon (DOC) mobilisation from OM treated and untreated soils between pH 5.5 and 7.5, expressed as the mass of DOC mobilised either from the mass of soil or soil + OM substrate, as applicable. Error bars represent the standard error of the mean ($n = 3$). Values sharing the same letter are not significantly different ($p > 0.05$).

modelling the speciation of specific trace metals across a range of diverse soil solutions and natural waters (Groenenberg et al., 2010; Djae et al., 2017; Chen et al., 2018). In absence of specific measurements, an F-value of 1.3 is commonly used (Tipping et al., 2011); however, the F-values determined here ranged between 0.5 and 1.2, which agrees with the optimum range of values 0.3 to 1.1 for modelling Cd speciation reported by Chen et al. (2018).

The kinetic limitation of Cd in the leachates correlated negatively with Cd measured in the <5 kDa fraction ($P < 0.0005$; Table 2), which suggests that the non-colloidal Cd was generally more labile. The lack of significant correlation between Cd-DOM complexes and Cd in the truly dissolved fraction ($P > 0.05$) suggests that the metal in that fraction could be present as free Cd^{2+} and complexed to inorganic or smaller organic molecules. The correlation between kinetic limitation and pH (Table 2) is likely to be due to a combination of increasing amounts of complexation by DOM and reduced competition for binding ligands by H^+ ions. The kinetic limitations for Cd estimated for dissolved Cd from OM treated soils here (Fig. 3) are higher than the kinetic limitations for Cd observed by Welikala et al. (2018), which can be attributed to the generally lower Cd:DOC ratio (10^{-3} - 10^{-6}), here. As the metal:ligand ratio increases, the strong metal-binding sites in heterogeneous substrates like DOM become increasingly saturated and remaining metal starts to bind to the weaker ligands, resulting in more labile metal (Guthrie et al., 2003). However, it is important to recognize that in three cases the theoretical maximum kinetic limitation value that could be measured for Cd using SV-DGT (4.13) (Welikala et al., 2018) was exceeded (Fig. 3). The range of ionic

strengths in the leachates (2.3–27 mM) agrees with previously reported values for soil solutions (Schofield and Taylor (1955); Edmeades et al., 1985). To reduce the effect that differences in ionic strength may have on the diffusion rates of the Cd-DOM complexes (Wang et al., 2016), the conductivity of all leachates was normalised to 2 mS cm^{-1} (the conductivity of leachates from compost treated soils at all pHs tested). The possibility Cd-DOM complexes aggregating following the increase in solution ionic strength (Cincotta et al., 2019; Mosley and Liss, 2019) cannot be discounted and this may have reduced the rate of Cd diffusion into the agarose gel and thus confounding the interpretation of kinetic limitations in these cases. Future studies employing SV-DGT to measure kinetic limitation should seek to identify whether such effects are likely by testing different ionic strength solutions.

4. Conclusions

The amount of Cd that is (im)mobilised by the addition of OM to soil in the short term varied widely (between -70% and +73%) depending on the soil, the nature of the OM and other physico-chemical conditions. Mobilisation of colloidal-Cd increased with OM treatments, where Cd can be bound to the mobile and high molecular weight DOM released by the substrates. While increasing pH from 5.6 to 6.4 can significantly reduce the Cd in <5 kDa dissolved fraction, mobilisation of colloidal-Cd species was less affected by changes in pH and could conceivably sustain losses of Cd from soils, within the pH range tested here. It follows that the potential for continued mobilisation Cd as organic species, despite

Table 3

WHAM VII speciation modelling results and DOM quality indices via SUVA₂₅₄ and E₄/E₆. Humic and fulvic acids are represented by HA and FA, respectively. Cd²⁺:DOC is the ratio of concentrations (mol L⁻¹) of free Cd²⁺ and DOC. For SUVA₂₅₄ and E₄/E₆, the values are expressed as mean ± standard error of the mean (n = 3).

soil	treatment	soil pH group	leachate pH	Total [DOC] (mg C L ⁻¹)	[HA] ^a (mg C L ⁻¹)	WHAM speciation modelling results			SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)	E ₄ /E ₆	A ₂₅₄ /A ₃₆₅		
						total dissolved Cd (µg L ⁻¹)	Cd bound by colloidal HA (%) ^a	Cd bound by colloidal FA (%)					
Craigieburn	non	5.6	5.61	3.15	0	3.83	0	4	4	1.3	5.37 ± 0.17	2.6 ± 0.1	6.00 ± 0.18
	compost	5.6	6.88	69.09	19.4	1.16	16	27	43	0.02	2.92 ± 1.13	5.9 ± 0.4	5.58 ± 0.09
	peat	5.6	5.59	37.86	14.5	3.17	14	18	32	0.09	2.65 ± 0.17	2.9 ± 0.1	5.65 ± 0.07
	non	6.4	6.75	5.28	0	0.48	0	9	9	0.1	5.06 ± 0.51	5.3 ± 0.7	5.90 ± 0.17
	compost	6.4	7.13	71.13	36	0.92	28	26	54	0.01	1.75 ± 0.18	8.0 ± 0.5	5.49 ± 0.02
	peat	6.4	6.78	55.19	22	0.91	25	30	54	0.02	2.61 ± 0.08	5.4 ± 0.5	5.82 ± 0.01
Templeton	non	5.6	5.44	9.42	0	4.99	0	5	5	0.57	2.77 ± 0.23	3.3 ± 0.5	6.29 ± 0.07
	compost	5.6	6.38	128.49	0	2.54	0	30	30	0.02	2.59 ± 0.18	6.5 ± 0.03	6.27 ± 0.04
	peat	5.6	5.36	67.51	28.7	4.87	15	18	33	0.08	2.70 ± 0.16	3.6 ± 0.2	6.18 ± 0.03
	non	6.4	6.74	19.6	12	1.21	24	20	44	0.07	2.61 ± 0.04	4.1 ± 0.2	6.04 ± 0.17
	compost	6.4	7.13	134.2	48.2	1.93	24	33	57	0.02	1.85 ± 0.15	6.4 ± 0.4	5.21 ± 0.01
	peat	6.4	6.68	114.97	76.6	1.72	45	32	77	0.02	2.11 ± 0.22	6.4 ± 0.2	5.55 ± 0.03
Waikari	non	5.6	5.81	26.24	11.5	3.07	13	15	28	0.12	3.04 ± 0.33	4.2 ± 0.1	5.84 ± 0.04
	compost	5.6	6.46	118.22	59	2.54	28	27	55	0.02	2.09 ± 0.32	8.0 ± 0.3	5.10 ± 0.06
	peat	5.6	5.47	67.51	31.4	3.46	19	22	41	0.05	2.83 ± 0.41	5.1 ± 0.3	5.65 ± 0.22
	non	6.4	6.9	19.6	1.1	1.05	2	19	21	0.06	4.98 ± 0.28	7.3 ± 1.1	5.75 ± 0.03
	compost	6.4	7.2	134.2	56.7	1.81	32	31	62	0.01	2.34 ± 0.17	15.9 ± 0.8	5.26 ± 0.06
	peat	6.4	6.9	114.97	52.2	1.45	38	32	70	0.01	2.61 ± 0.21	10.8 ± 0.9	5.81 ± 0.03

^a Where concentrations of DOC were low (<10 mg L⁻¹), the HA fraction could not be measured reliably and was assumed to be zero.

changes in pH, should be considered when estimating Cd leaching losses, especially from OM-amended contaminated soils. In the larger DOM fractions, Cd may be bound by the ligands in non-

aromatic structures, where its lability is likely to depend on the source of the DOM, pH, and Cd:DOC ratio. Dissolved OM emerged from OM treated soils may persist in soil solution for longer than

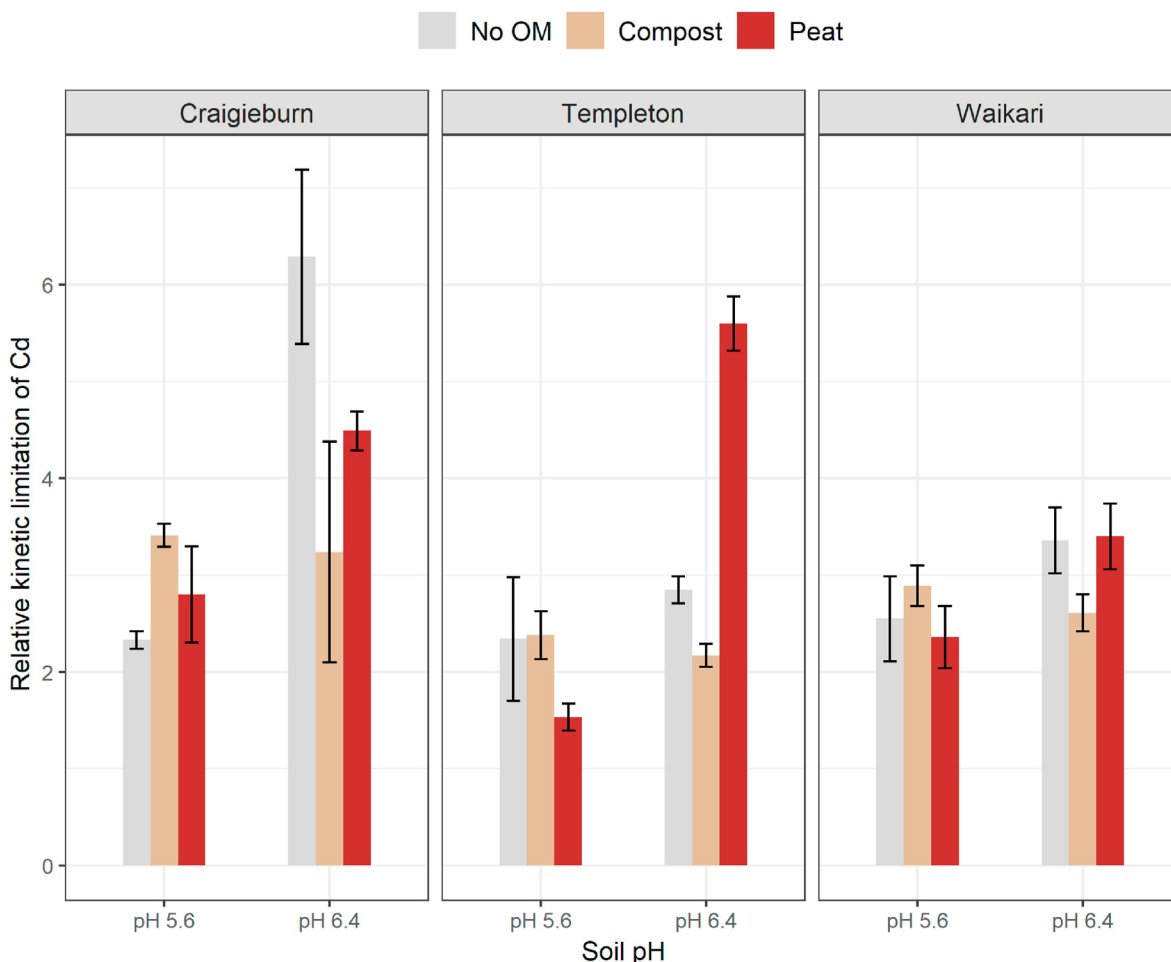


Fig. 3. Relative kinetic limitation (arbitrary units) of Cd in OM untreated and treated soils at pH 5.6 and 6.4. Error bars represent the standard error of the mean (n = 3).

the DOM from soil itself. Future work should examine its biodegradability and differences in DOM release rates at other amendment application rates and longer time frames to further understand the potential for DOM-facilitated transport of Cd in soils and surrounding environments.

Author contributions

Dharshika Welikala: Conceptualisation, Methodology, Investigation, Formal analysis, Visualization, Writing – original draft and revisions; **Brett H. Robinson:** Supervision, Writing – review & editing; **Elena Moltchanova:** Formal analysis; **Adam Hartland:** Resources, Writing – review & editing; **Niklas J. Lehto:** Supervision, Conceptualisation, Methodology, Writing – review & editing and revisions

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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