The effects of organic matter, pH, and dissolved ligands on the mobility of cadmium in soils

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Dharshika Welikala

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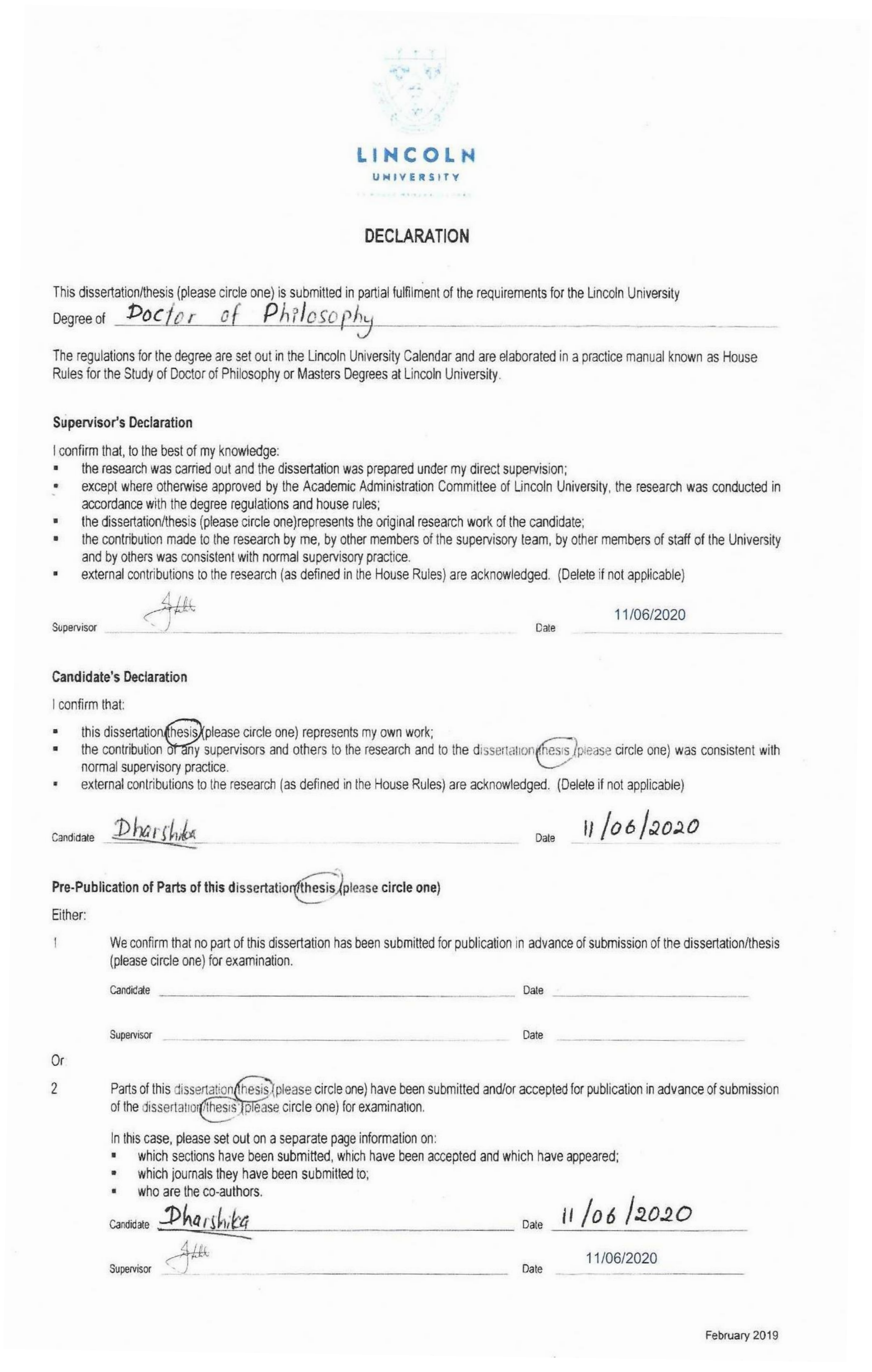

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The effects of organic matter, pH, and dissolved ligands on the mobility of cadmium in soils

by
Dharshika Welikala

The fate of cadmium (Cd) in soil is important because of its toxicity even at low concentrations. Mobilisation of Cd to soil below the root zone can decrease Cd accumulation in topsoil where plants take up available Cd. However, this mobilisation may ultimately result in groundwater contamination. The majority of Cd in soil usually occurs in the solid phase, with only small amounts present in soil solution, which are the most mobile. The partitioning of Cd between matrix and soil solution is affected by soil pH, organic matter content, and dissolved ligands in porewater. The aim of this study was to investigate how these factors may affect the potential mobility of Cd in soils.

Experiment (1): Ten soil amendments that are rich in organic matter (OM), but with different provenances, were tested for their ability to sorb Cd across a pH range of 4.5 to 6.5. These amendments included five different composts, two peats, two biosolids and spent coffee grounds. By using an adapted diffusive gradient thin-film (DGT) method, the lability of Cd associated with dissolved organic matter (DOM) emergent from two of the above composts and two peats were tested and related to the quality of DOM. The retention of Cd varied between the OM amendments and was generally reflected by the cation exchange capacity (CEC) of each amendment. The Cd sorption capacity increased with pH, implying that variable charge sites play an important role in Cd sorption to OM. The Cd-DOM species emergent from the composts appeared to be more kinetically limited than that from the peats and the aromaticity of DOM was a less important factor in determining this lability of Cd-DOM complexes.

Experiment (2): To explore the ability of OM to immobilise the soil Cd, a compost and a peat which showed high and moderate Cd sorption capacities, respectively were amended with three different soils spiked to about 2 mg kg^{-1} Cd at three pHs (5.6, 6.4 and 7.2). A short-term column leaching experiment was carried out to investigate the potential mobility of Cd in these OM amended soils and

how that was related to quality and quantity of DOM leached. The "truly" dissolved (<5 kDa) Cd fraction from the mobilised dissolved Cd (<0.45 µm) was separated by ultrafiltration. The quality of DOM mobilised was assessed with ultraviolet absorbance measured at various wavelengths and fluorescence excitation-emission matrices. At relatively low pH (5.6) the compost was more effective in immobilising Cd than the peat, which consistent with the first sorption experiment. However, regardless of the high capability of soil solid phases (including OM amended) to bind Cd, mobilisation at higher pH (6.4) was linked to DOM mobilisation. Approximately 50% of Cd mobilised from OM amended soils existed in the dissolved colloidal fraction (5 kDa-0.45 µm). This mobile colloidal-Cd was highly correlated with the mobilised DOM (r=0.77, p=1.74 X 10^{-11}), in which Cd binding ligands in non-aromatic structures in the high molecular weight DOM may have played a major role in Cd complexation. The mobilised DOM from the compost and the peat amended soils had a greater humification index than the DOM mobilised from the soil itself and, therefore mobile Cd-DOM from those OM amended soils may persist in soil for a longer period. Cadmium mobility was also affected by physicochemical differences between soils. Sorption of Cd or OM to mineral surfaces in an allophanic clay-rich soil may have decreased Cd-DOM mobility compared to more sandy soils.

Experiment (3): Investigated potential soil Cd mobilisation from soils treated with cow urine, also in a column leaching experiment, employing different three soils to before. This experiment revealed the potential mobility of Cd species in soil solution and Cd released to soil solution from readily exchangeable sites. Here, top 1/3 of columns was packed with Cd isotopes (^{108}Cd and ^{116}Cd) spiked soil while the rest of 2/3 was unspiked soil. Cadmium isotope ratio ($^{116/108}$Cd) was used to investigate the extent of mobilisation of Cd-originated from the spiked soil and Cd speciation in the leachates. Overall, 17 to 60% of total Cd leached originated from the top spiked soil layer across three soils, which did not receive urine. The fractional contribution of Cd from spiked soil for total Cd leached increased with pH. Cow urine increased dissolved chloride (Cl^-) and DOM in soils. While 7-10% of Cd mobilised was as Cd-chloro complexes, Cl^- concentration alone could not explain Cd mobilisation. This was attributed to the higher affinity of Cd for colloidal DOM, where mobilised Cd from urine treated soils had a strong positive correlation with the mobilised high molecular weight DOM (humic acid-like: r=0.73, p=7.2 X 10^{-7}). Consistent with the first leaching experiment, more Cd mobilised from coarser soils than from soils with low sand content.

Experiment (4): The size of labile Cd pool and resupply kinetics for three stable Cd isotopes (^{108}Cd,^{112}Cd and ^{116}Cd) in the soils from the third experiment was explored through a combination of experimental measurements using DGT and numerical modelling the DGT-Induced Fluxes in Soils model (DIFS). The labile Cd pool size for ^{108}Cd and ^{116}Cd isotopes were similar but larger than for ^{112}Cd within soils, which appeared to be affected by the contact time of each isotope. Desorption kinetics of ^{108}Cd and ^{116}Cd isotopes in same soil were similar. The labile pool size and resupply kinetics for each isotope were

different between soils. The labile pools of the three Cd isotopes were relatively smaller in the allophanic clay-rich soil, which also had a greater sand content than the other two soil.

This study found that the amount of Cd transported in OM amended soils depends on the type of the OM used, and the extent to which this happens is controlled by the interaction between the type of OM, soil type, and its pH. Further, the relative contribution of Cd^{2+}, Cd-DOM and Cd-chloro species towards Cd transport depends on properties of soil, pH, OM content, DOM and Cl^- concentrations. Finally, this work provides new insights for the use of stable Cd isotopes in tracing the transport of topsoil Cd to subsoil and/or groundwater.

Keywords: Cadmium, trace metals, mobility, speciation, soil amendments, compost, peat, dissolved organic matter, colloids, diffusive gradient thin-films (DGT), ultrafiltration, stable isotope ratio analysis, fluorescence excitation-emission spectroscopy, DGT-induced fluxes in soil (DIFS).

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Chapter 1

Introduction

Cadmium (Cd) is a naturally occurring trace metal. It is non-essential for biota and toxic to humans and animals at low concentrations due to its long biological half-life (Smolders et al., 2013). In non-smoking populations, Cd enters the human body mainly through food that originated from plants that bioaccumulate Cd in their edible parts. The potential for Cd toxicity in humans and animals is increased when edible plants are grown on soils where the availability of the metal for plant uptake is high. Cadmium contamination in water sources is another risk, where it can be toxic to humans if Cd concentrations in drinking water exceed the maximum permitted levels, while it is also likely to be toxic to aquatic lifeforms (Qu et al., 2013; World Health Organization, 2011).

Soils are polluted with Cd via natural and anthropogenic sources. Main natural inputs of Cd to soil are weathering of zinc ores, volcanic emission and forest fires (Adriano, 2001). In general, soil can become contaminated with Cd anthropogenically mainly through mining, processing non-ferrous materials, fossil fuel combustion, and incineration of municipal waste (Adriano, 2001; Kabata-Pendias, 2007). For agricultural soils, primary Cd inputs are phosphate fertilizer, biosolids and atmospheric deposition (Bramley, 1990; Kabata-Pendias, 2007). High level of Cd accumulation in grains and vegetables grown in soils having elevated Cd concentration has been demonstrated worldwide (Kabata-Pendias, 2007; Rizwan et al., 2017; Shahid et al., 2017), and a key factor informing this accumulation is the physicochemical behaviour of Cd in the soil (Hooda, 2010).

Cadmium entering the soil undergoes several chemical and physical processes, which determines the chemical species in which Cd exists (henceforth, ‘Cd speciation’). Cadmium speciation is a key determinant of the proportion of the total Cd in soil or water that can be internalised by an organism, such as plant or micro-organism, from the solution phase. This fraction is referred to as being ‘bioavailable’ (Kim et al., 2015). The processes that affect Cd speciation include sorption to organic and inorganic surfaces on the soil solid phases, formation of metal-colloidal complexes in soil solution, precipitation, biological uptake and leaching to groundwater (Hooda, 2010). The ‘species’ found in soils include the ‘free’ ion, dissolved organic and inorganic complexes, Cd sorbed to solid constituents, and Cd precipitated as carbonates (Hooda, 2010; Templeton et al., 2000). The distribution of Cd between these different species is dynamic. ‘Labile’ Cd species are henceforth considered as the those can participate in reaction (e.g. sorption and desorption) and/or are bioavailable within a specific period of time; the free Cd^{2+} ion is often the most labile and bioavailable species. Other less labile Cd species include Cd complexed or sorbed to soil organic matter or mineral phases and Cd complexes formed with dissolved organic matter or inorganic ligands. These species can replenish free Cd^{2+} ions to the solution by desorption and/or dissociation to replace the Cd^{2+} lost through biological uptake or leaching. Dissolved Cd species are also considered to be the 'mobile' species that can be transported with water movement. Therefore, processes governing the soil solid-solution partitioning of Cd ultimately control the species of Cd that may be mobilised. Understanding the kinetics of Cd interchange between species in soils will, therefore, inform both its lability and mobility.

In agricultural soil, Cd accumulates in topsoil due to the aforementioned processes, and so has a restricted mobility (Salmanzadeh et al., 2016). However, some dissolved ligands (chloride and dissolved organic matter) and soil management practices (e.g. irrigation, fertiliser application) can enhance the mobility and thus transport Cd down through the soil profile (Gray et al., 2017; Liu et al., 2019; McDowell, 2019; Salmanzadeh et al., 2017b). Therefore, there is increasing concern on anthropogenic Cd mobilisation in agricultural soils that may be a potential threat for groundwater contamination.

Various immobilising agents have been employed to reduce the plant uptake of Cd by affecting the mobility of Cd accumulated in the topsoil (Abad-Valle et al., 2017; Hamid et al., 2019; Huang et al., 2016; Shaheen et al., 2017). These immobilisation agents include organic (e.g. compost, peat, lignite) and inorganic (e.g. lime) amendments, which redistribute the labile Cd in the solid phases through sorption, complexation and precipitation (Al Mamun et al., 2016; Bolan et al., 2003a; Simmler et al., 2013; Van Poucke et al., 2018). Cadmium binds strongly to organic ligands (e.g. carboxylic, phenolic, reduced sulphur groups), thus organic matter (OM) rich soil amendments like compost can be a cost-effective method to immobilise the labile Cd in contaminated soils (Al Mamun et al., 2016; Karlsson et al., 2007; Kaschl et al., 2002a; Laborda et al., 2009). The extent of Cd immobilisation by these amendments depends on the chemical and physical characteristics of the amendment (e.g. cation exchange capacity, functional groups, molecular weight of the organic components, resistivity for biodegradation, and pH) and the soil (e.g. pH, Fe, Al and Mn oxides, and texture), to which they are applied (Al Mamun et al., 2016; Bolan et al., 2014; Huang et al., 2016; Liu et al., 2019). Such interactions are poorly understood, making the expected effects of Cd immobilising agents uncertain.

Increasing trace metal mobility using chelating ligands which are then extracted by hyper-accumulating plants or flushed to deep down the soil profile (soil washing) are also popular remediation methods for reducing bioavailable trace metals in contaminated soils (Bolan et al., 2014; Leštan et al., 2008). Generally, chelating ligands like EDTA, EDDS, and NTA are used for this purpose (Leštan et al., 2008). However, OM rich amendments could also be a cost effective and environment friendly method for remediating Cd contaminated soils via increasing its mobility through chelation with organic ligands

(Wu et al., 2012c), unless it may not become a threat for contaminating groundwater through leaching (Shuman, 1998; Wu et al., 2012b).

Organic matter-rich amendments may directly or indirectly enhance the mobility of Cd in soil. By acting as a source of dissolved organic matter (DOM) or by promoting solubilisation of soil organic matter (SOM) or by changing soil pH (Hernandez-Soriano et al., 2013), OM-rich amendments may enhance the concentration of DOM in the soil solution. Consequently, this DOM can reduce Cd sorption to solid surfaces either by forming soluble Cd-DOM complexes or by preferential adsorption to solid sorption sites over Cd (Naidu et al., 1998). As trace metal-DOM complexes are potentially mobile (Grybos et al., 2007; Xie et al., 2019), the introduced DOM may have the potential to transport Cd in the environment.

However, extent of Cd transport as Cd-DOM complexes partly depends on the stability of Cd-ligand association in those complexes and the resistivity of DOM complexes for biodegradation. For instance, one can hypothesise that Cd complexed to DOM by formation of strong Cd-ligand bonds has a greater potential to transport Cd in the soil as Cd-DOM complexes than Cd complexed with weaker Cd-ligand bond, where latter can readily release free Cd^{2+} ions to the solution than the former. Released Cd^{2+} can be taken up by biota if they remain in soil solution or adsorbed to solid phase making it immobile. Similar fate can happen to Cd^{2+} released into the soil solution due to the (bio)degradation of DOM in Cd-DOM complexes; therefore, DOM having a higher resistivity for biodegradation may have greater potential to transport Cd via Cd-DOM complexes. In other words, the quality of DOM that determines the affinity for Cd binding by different ligands and influences the resistance for biodegradation matters; such as the various organic compounds in DOM (e.g. polysaccharides, protein, lignin), aromaticity, molecular weight, and aggregate stability. While the aforementioned research has looked at OM as an immobilisation agent for soil Cd, the effect of DOM emerging from those OM amended soils, for mobilising soil Cd is uncertain.

1.1 Aims and objectives

The overall aim of this thesis is to investigate how the mobility of Cd is influenced by organic matter, dissolved ligands, and pH in agricultural soils.

I seek to address that aim by fulfilling the following specific objectives:

Objective 1: To investigate the effect of OM-rich amendments on partitioning of Cd between solid and dissolved phases and the influence of the quality of DOM emerging from these amendments on complexing Cd.

Objective 2: To investigate the mobility of Cd in soils that have been treated with OM-rich amendments.

Objective 3: To explore the use of stable isotopes to study the mobility of Cd in soils, as affected by soil pH, DOM, and chloride species.

Objective 4: To investigate the lability of stable isotopes of Cd sorbed to soil solid phases in a dynamic non-equilibrium soil system.

1.2 Structure of the thesis

This thesis is organised in seven chapters as follows:

Chapter 1 introduces the topic of interest focusing on the importance of speciation of Cd for its potential mobilisation in soil and specifically how soil organic matter may affect this.

Chapter 2 reviews the known factors that may affect the speciation of Cd, thereby influencing the extent of Cd mobility, and summarise the previous work showing the mobilisation of Cd in various New Zealand soils. Also, this chapter introduces methods that are used for the thesis to investigate the speciation and lability of Cd in soil.

Chapter 3 is a journal article that I published in *Chemosphere* that demonstrating the ability of various OM-rich amendments to bind Cd and the influence of DOM quality derived from the amendments on complexing Cd.

Chapter 4 reports the effects of two types of OM rich amendments (compost and peat) on mobilising Cd in soils with respect to characteristics of the soil (pH, texture, and minerals) and the influence of DOM quality on Cd speciation and mobility.

Chapter 5 evaluates the influence of chloride and DOM on mobilising Cd following cow urine application and explore the use of stable Cd isotopes to study the Cd mobility.

Chapter 6 reports experimental and modelling research exploring the lability of three different Cd isotopes in different soil orders

Chapter 7 summarises the research and provides a synthesis, conclusions, and suggestions for future studies.

Chapter 2

Background

2.1 Introduction

The risk assessment of soil cadmium (Cd) for plants and animals is concerned with the fraction of total Cd that is soluble, mobile, and bioavailable. The mobility of trace metals (TMs), in the soil is affected by: (1) physicochemical processes (sorption and desorption, solubility and precipitation, partitioning and complexation) and (2) biological processes (microbial activity) (Carrillo-González et al., 2006). In soil, Cd is distributed in both the solid and solution phases. The 'mobile species' are generally considered to be the soil solution phase species while solid phase species are immobile but could contribute to solution phase Cd via various physicochemical processes. Therefore, the species of Cd in soil solution and as part of the solid phase are equally important in determining the extent to which Cd can be mobilised from soil to the surrounding environment.

The distribution of TMs in various soil constituents (solid and solution) is known as the 'speciation'. The global definition for speciation is "the distribution of an element among defined chemical species within a system", where a chemical species is a "specific form of an element as to isotopic composition, electronic or oxidation state and/or complex or molecular structure" (Templeton et al., 2000). Figure 2.1 illustrates a general speciation of TMs in soil solid-solution phases and key processes governing the extent of mobility of the TMs.

Chemical species of TMs in soil solid phase and soil solution phase can be defined as follows (Hooda, 2010):

- Soil solid-phase species: exchangeably bound to a charged surface, complexed with or occluded within organic matter, adsorbed or occluded in hydrated oxides of iron, aluminium, and manganese, adsorbed or occluded in carbonates, precipitated as carbonates, phosphates, and sulphides and, bound within structural components in minerals.

- Soil solution-phase species: free ion, inorganic complexes, organic complexes and bound to suspended colloids (clay, organic matter).

Several factors affecting the speciation of TMs in soil can enhance the transport of Cd through the soil profile and in the surrounding environment. This chapter reviews the known factors, which influence the speciation and therefore the mobility of Cd in agricultural soils.

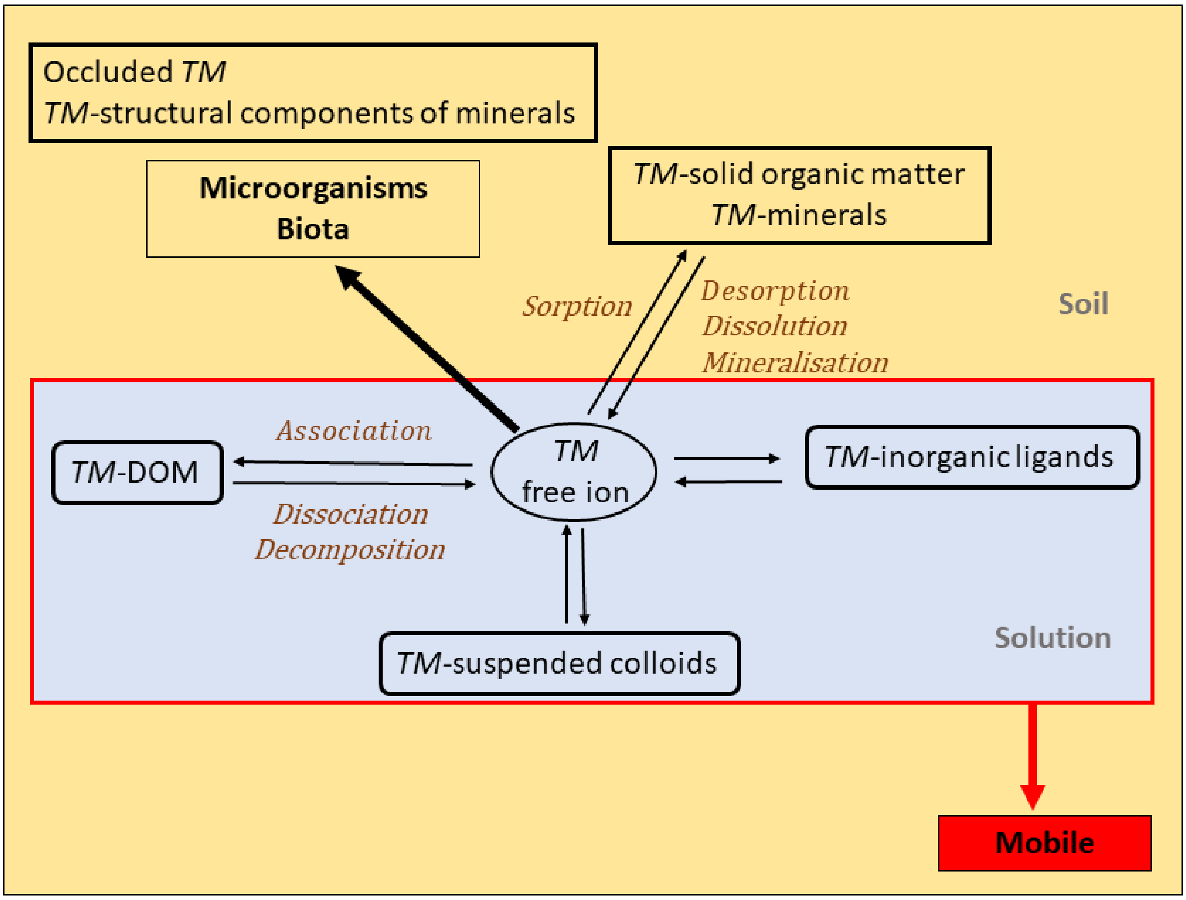

Figure 2.1: Various trace metal (TM) species in soils and key processes governing the interchange between the species and their mobility.

2.2 Distribution of Cd between solid and solution phase

In soil, Cd is distributed over different chemical species, but mainly associated with the soil solid phase (99%), thus a small percentage is dissolved in soil solution (Kabata-Pendias, 2007). Soil pH, soil composition, dissolved ligands, other TMs, and total Cd concentration mainly influence the speciation of Cd between the solid and solution phases.

Sorption-desorption reactions are the most important process in the soil for speciation of Cd (or other TM) and they dominate when Cd concentration is relatively low (Loganathan et al., 2012). Sorption is the removal of species from solution and succeeding association with soil solid phase, while desorption is the reverse process of sorption where species are released from the soil particle to the solution (Roberts et al., 2005). Trace metal sorption onto soil solid phases may occur in two well-defined mechanisms. The first mechanism is cation exchange, which is also known as 'non-specific adsorption' or 'outer-sphere complexation'. The negative charge on the soil solid surface can hold cations through electrostatic attractions and these adsorbed cations can exchange with other cations in the soil solution (McLaren, 1996; Roberts et al., 2005). The equilibrium between exchangeable cations and those in the solution depends on their relative activities and affinities for the adsorbing site. The cation in the solution which exchanges with another cation bound to the soil surface will form an outer-sphere complex with the adsorption site (Loganathan et al., 2012). In this outer-sphere complexation, the bound ion exists as a hydrated species, and one or two water molecules are in between the binding surface and the bound ion. The second mechanism of TM sorption to soil solid phase is 'specific sorption' or 'inner-sphere complexation'. There are no water molecules present in between the sorption site and the sorbed cation when an inner-sphere complex is formed. During inner-sphere complexation, cations form coordination or other types of chemical bonds between adsorbing sites; these bonds are stronger than the electrostatic bonds, formed during outer-sphere complexation (Bolan et al., 1999; Naidu et al., 1994a; Roberts et al., 2005). Hence, compared to specifically adsorbed TMs, TMs adsorbed to the soil as outer-sphere complexes generally desorb easily, and so are more available for uptake by biota or complexation with dissolved ligands.

The mechanism of Cd binding to soil solid phase varies with the binding sites in different soil constituents. Further, other physicochemical factors (e.g. pH, ionic strength, and other cations) can influence the sorption and desorption of Cd (Loganathan et al., 2012; Naidu et al., 1994; Naidu et al., 1998).

2.2.1 Types of solid phases

2.2.1.1 Soil minerals

In soil mineralogy, phyllosilicates and the soil components which are intimately associated with the phyllosilicates, such as metal oxides, hydroxides and (oxyhydr)oxides of iron (Fe), manganese (Mn) and aluminium (Al) are classified as clay minerals (Essington, 2004). These clay minerals consist of large specific surface areas and high surface reactivities. Phyllosilicates are layer silicates that are composed of various combinations of tetrahedral silica sheets and octahedral alumina sheets (McLaren, 1996). These clay minerals can have two types of charges: permanent and pH-dependent (variable) (Figure 2.2). Permanent charge is specifically seen in phyllosilicates by isomorphic substitution of Si^{4+} or Al^{3+} in tetrahedral sheets or octahedral sheets, respectively by another cation, whereas the pH-dependent charges are developed from protonation and deprotonation of surface hydroxyl groups (Essington, 2004).

Cadmium can sorb on to permanent and variable charge surfaces in various clay minerals by cation exchange or specific adsorption depending on various soil physicochemical factors such as pH, ionic strength, presence of various dissolved ligands, and other competing TMs. In kaolinite Cd is adsorbed onto permanent charge sites by ion exchange reactions at low pHs while, at relatively high pH, Cd is specifically adsorbed onto variable charges on crystal edges and octahedral alumina faces via bidentate inner-sphere complexes (Srivastava et al., 2005). While the formation of outer-sphere complexes with Cd is predominant in kaolinite, bidentate-binuclear inner-sphere complexes are dominant in gibbsite

(Grafe et al., 2007). Cadmium can also form stable inner-sphere complexes with goethite; however, the affinity for surface complexation with goethite is less for Cd compared to other TMs such as Zn (Forbes et al., 1976; Tiller et al., 1984). According to the model by Lackovic et al. (2003), goethite forms outer-sphere complexes with Cd at pH<6 (illustrated as SOH--Cd^{2+} species, where SOH represents a surface hydroxyl group); inner-sphere surface complexes at pH>6 (SOCd^{+} at intermediate pH (~6 to 8) and SOCdOH at pH>8, where SO is the ionised surface hydroxyl group).

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Figure 2.2: Cadmium sorption sites in different soil solid constituents. (Loganathan et al., 2012)

2.2.1.2 Soil organic matter

Soil organic matter (SOM), is a reservoir of metabolic energy for soil microorganisms and contributes to soil physical and chemical characteristics such as aggregate stability, water retention capacity, soil pH buffering, cation exchange capacity (CEC), and retention of TM and organic pollutants. The chemical characteristics of SOM may vary depending on its parent material (e.g. protein, lignin, polysaccharides), while the dynamics of SOM is affected by soil physical and chemical characteristics (e.g. soil texture), climate variables (e.g. temperature and rainfall), vegetation and soil organisms (Harrison, 2008; Kleber et al., 2010; Puissant et al., 2017; Zaccone et al., 2018). The SOM can be considered as a heterogeneous mixture of organic compounds derived from plant and animal residuals, which are in various stages of decomposition process (Kleber et al., 2010; Lehmann et al., 2015). The pathways and rates of decomposition of SOM may be controlled by, (1) the SOM's polymeric nature and/or aggregation stability and, (2) adsorption and/or co-precipitation on/by mineral surfaces (Essington, 2004; Kleber et al., 2010).

Soil organic matter consists of a large number of ionisable functional groups, which are responsible for its high CEC, typically ranging between 60-300 cmol kg^{-1} at pH 7 (Essington, 2004). The functional groups that lie on the solid-solution interface develop pH dependent charges that can retain cations and anions through electrostatic attractions (Figure 2.2). Other than electrostatic attractions, the functional groups residing in the soil-solution interface can retain TM through chelation or by the formation of covalent bonds (Fan et al., 2016; Roberts et al., 2005). Therefore, these functional groups in SOM can serve as metal binding ligands. The most common functional groups in SOM like carboxylic, hydroxyl and phenolic groups can develop negative charges by deprotonating, thereby binding Cd through electrostatic attractions (outer-sphere complexation). However, these groups and other functional groups like amine, amide and reduced sulphide groups can also bind Cd through chelation (inner-sphere complexation) (Karlsson et al., 2007; Karlsson et al., 2005; Kaschl et al., 2002b).

Organic reduced sulphur (Org-S_{red}) ligands in SOM may form strong Cd-ligand bonds due to its higher affinity for Cd than affinity of other ligands like carboxylic and phenolic for Cd (Karlsson et al., 2005; Skyllberg et al., 2006). This phenomenon can be explained by the Hard and Soft Lewis Acid-Base (HSAB) theory. Lewis base is a neutral or negatively charged ligand (atom, molecule, or ion) that has at least one pair of valence electrons that are not already being shared in a covalent bond. Lewis acid is a unit; at least one atom has a vacant orbital in which a pair of electrons can be accommodated, for example, a positively charged metal or ligand. Lewis acids and bases can be categorised as 'soft' and 'hard' according to their polarizability, size, and charge (Essington, 2004). According to this categorization, Cd^{2+} is a soft acid, which can show a higher affinity to bind to soft bases, such as Org-S_{red} ligands. Karlsson et al. (2005) showed that Cd forms inner-sphere complexes with Org-S_{red} ligands in SOM collected from organic soils. They also stated that SOM strongly binds Cd at low Cd concentrations, which can be the case in 'low-polluted' soils, meaning that Org-S_{red} ligands in SOM are involved in the complexation of Cd even at native Cd concentrations in organic matter-rich soils.

Due to the strong affinity of TMs to bind with SOM, recent research has focused on amending Cd contaminated soils with organic matter (OM)-rich amendments to immobilise the soil Cd thereby making them less available for plant uptake. Most of these OM amendments are also biowastes, which makes their re-use attractive, from a waste minimisation point of view. Bolan et al. (2003a) added biosolid compost manufactured from green waste in the presence of a small amount of sewage sludge to two different soil orders in New Zealand. They found that biosolid compost enhanced Cd retention in soils by increasing the negative surface charge. Further, by fractionation of the solid phase, they revealed that, in amended soils, concentrations of soluble Cd and extractable Cd decreased while organic bound-Cd increased. In a recent study, Al Mamun et al. (2016) was able to reduce the Cd concentration in onions, spinach, and lettuce, grown in two soils up to 60% by immobilizing plant-available soil Cd with municipal compost (2.5% (dry w w^{-1})). They analysed soils that had elevated Cd concentrations of 1.45 and 0.47 mg kg^{-1} while most other studies have used highly contaminated or Cd spiked soils (Ciecko et al., 2001; Tapia et al., 2010), which is not representative of most agricultural soils.

Organic matter-rich amendments of various provenance have been shown to variably retain Cd, which may be attributed to the different functional groups present in those amendments and their relative proportions. For example, Tapia et al. (2010) reported that composted spent mushroom waste and pruning waste + bio-solid had a higher affinity for Cd adsorption than composted pine bark, which they attributed to the presence of more carboxylic groups in the composted spent mushroom waste and the pruning waste + bio-solid than in the composted pine bark. Further, they showed that in the composted pine bark, more Cd is associated with the soluble fraction that has a comparatively large number of phenolic groups than in the other two amendments. In soils amended with lignite, Cd retention at relatively low Cd concentrations can be explained by the affinity of Cd for Org-S_{red} ligands. From a sorption study, Simmler et al. (2013) suggested that a large percentage of Cd adsorbed to lignite at pH 3.4 might be due to binding to Org-S_{red} ligands while the concomitant increase in Cd sorption with pH is associated with Cd binding to carboxylic groups.

It is important to note that the longevity of SOM or OM amendments to retain Cd (or other TM), depends on their resistivity for biodegradation and/or decomposition, where those processes can eventually release free TM ions to the soil solution.

2.2.2 Factors affecting solid-solution Cd distribution

2.2.2.1 pH

Soil pH is generally the dominant factor in the solubility and sorption-desorption mechanism of Cd in soils, and thereby controlling the mobility of Cd (Loganathan et al., 2012). At low pH, the increased Cd solubility is attributed to the competition for binding sites between Cd^{2+} and H^+ (or Al^{3+}) (Strobel et al., 2001). While at high pH, Cd in solution phase decreases due to increased sorption to the solid phase. The pH dependent sorption of Cd to the solid phase is often attributed to three mechanisms: (1) hydrolysed Cd complexes ($CdOH^+$) can be preferentially bound by soil solid surface over free Cd^{2+} ions at elevated pHs (Hodgson et al., 1964; James et al., 1972), (2) the electric potential of the variable charge surface can decrease with increasing pH making the solid surface more negative, and facilitating more Cd^{2+} sorption (Barrow, 1984; Naidu et al., 1994), (3) with increasing pH, H^+ sorbed to the solid phase can exchange with Cd^{2+} in the solution (Boekhold et al., 1993). Outside of sorption processes, greater pH may dissolve SOM (Andersson et al., 2001; Curtin et al., 2016; Guggenberger et al., 1994; Lambie et al., 2012b), which may release SOM-bound Cd to soil solution as free Cd ions or Cd-organic complexes.

2.2.2.2 Other cations

Other cations (Ca, Mg, Na and K) and TMs (Zn, Pb, Ni and Cu), which can compete with Cd for binding sites, can affect Cd speciation in the soil solid phase. However, the competition for binding may depend on pH, affinity of the cation for binding sites, and solid phase mineralogy. The presence of Ca in the solution is more effective in decreasing the Cd sorption to solid phases than other cations like Na, Mg and K (Fotovat et al., 1998). For example, Naidu et al. (1994) found that the sorption of Cd to several soils with variable and permanent charges approximately doubled when Na was the index cation rather than Ca of the background electrolyte solution with the same ionic strength. This competition of Ca and Cd for exchangeable sites is problematic in agricultural soils where fertilisers like superphosphate contain about 20% Ca, while having Cd as a natural contaminant (Bramley, 1990); the predominant adsorption of Ca may enhance the solubility of Cd. Additionally, soil amendments for increasing pH (e.g. lime ($CaCO_3$)) and, therefore, increasing Cd immobilisation via sorption or precipitation, may unintentionally mobilise Cd if Ca competition for sorption sites overrides the benefit of a greater pH (Loganathan et al., 2012).

Other than major cations, TMs also compete with Cd for soil sorption sites. In general, affinities of different TMs for sorption sites follow the Irving-Williams order (Kim et al., 2009).

Irving-Williams order: $Hg^{2+} > Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} \approx Co^{2+} > Cd^{2+}$

That is, metals' affinity for sorption decreases from Hg^{2+} to Cd^{2+}, making Cd^{2+} the least competitive sorbate among the TMs. However, it should be noted that there are exceptions depending on other factors affecting the TM sorption (Tiller et al., 1984).

Serrano et al. (2009) reported that the retention of Cd by Fe-OH sites significantly decreased in the presence of Pb, while Pb did not show any change in its occupancy at these sites with the presence of Cd. In the same system, Cd had a higher affinity for ion exchange sites than Pb, while Pb showed higher affinity for specific sorption to hydroxyl sites than Cd. Among the TMs, Zn is considered Cd's greater competitor for binding sites due to the chemical similarity between the two metals (Adriano, 2001; Hooda, 2010). Tiller et al. (1979) found that, at low concentration, Zn has no effect on non-specifically bound (exchangeably bound) Cd, while Zn significantly decreased the specific adsorption of Cd in some clay soils. Zinc may have a higher affinity for those binding sites than Cd in clay minerals, where the specific adsorption is dominant at low metal concentrations. The adsorption affinities of Cd, Ni and Zn were reported as Zn> Ni> Cd for binding sites on surfaces where adsorption is dominated by Fe-oxide and followed the order of Cd, Ni> Zn, for binding sites on surfaces with high organic matter (Tiller et al., 1984).

2.2.2.3 Dissolved ligands

Dissolved inorganic ligands may variably affect Cd sorption, but their more dramatic role is in formation of Cd-inorganic complexes in soil solution. Chloride (Cl^-), sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}) anions play important roles in controlling the solubility of Cd. Sorption of phosphate ions can increase soil surface negative charge; resulting in increased Cd sorption capacity unlike sulphate, nitrate, and chloride present in the soil solution (Bolan et al., 1999). Conversely, Cl^- decreases Cd sorption, possibly due to the formation of soluble $CdCl^+$ complexes (Bolan et al., 1999), so total Cd concentration in soil solution typically increased with increasing Cl^- concentration (Kamewada et al., 2011). Indeed, when Cd forms Cl^- complexes, it becomes more soluble, thus more mobile, and more available for uptake by plants (Smolders et al., 1996; Wang et al., 2019a). If this increased mobility is coupled with sufficient vertical water flow, Cl^- addition to agricultural soils can promote Cd leaching to subsoil: plant uptake of Cd is reduced but at the environmental cost of losing Cd to groundwater (Gray et al., 2017; McDowell, 2019).

Dissolved organic ligands can reduce Cd sorption to the soil solid phase either by complexing with Cd and forming stable soluble organic complexes or by competing with Cd for binding sites. Various low molecular weight organic acids (acetate, citrate, fumarate, and malate) can enhance the solubility of Cd in soils; these organic acids may enhance Cd solubility by affecting pH, soil surface charge, cation exchange and solution TM-complexation (Collins et al., 2003; Naidu et al., 1998). Notably, such organic acids are prevalent in the soil environment as they are excreted by various microorganisms and as root exudates (Jones, 1998). In particular, organic acid release may be pronounced in the rhizosphere, leading to decreased Cd sorption with the increase in dissolved organic matter (Li et al., 2011). Conversely, high molecular weight dissolved organic molecules can enhance Cd binding by clay minerals such as kaolinite and goethite (Arias et al., 2002; Chen et al., 2019; Lai et al., 2002). These organic molecules may increase the adsorption onto Fe-(oxyhydr)oxide moieties in mineral colloids by stabilizing those minerals and providing more binding sites to retain Cd (Chen et al., 2019).

2.2.2.4 Soil texture and mineralogy

Soil composition is crucial for determining the extent of Cd sorption by the soil solid surface as variable constituents have different sorption affinities for Cd. In soils with high clay content, Cd is less soluble, due to the higher surface area and surface charge of clay particles than for sand and silt (Eriksson, 1989). The soil clay fraction consists of clay minerals (e.g. kaolinites, montmorillonite, illite), organic matter, and Fe, Mn and Al oxides, which contribute to Cd sorption (as discussed above) (McLaren, 1996). Kim et al. (1992) studied Cd sorption by various soil components such as whole soil, clay, silt and sand fractions, soil without Fe-Mn oxides and soil without organic matter. They found that the greatest amount of Cd was adsorbed to the clay fraction (particle size < 3.9 µm) compared to the other components. Further, they showed that removal of organic matter from soil reduced the amount of sorbed Cd from 87.3 % to 37.3 %, while removal of Fe-Mn oxide reduced the amount of Cd sorbed only to 80.4 %. By analysing Cd sorption for 29 different soils having a range of textures, organic matter, and Fe-Mn oxide content Gray et al. (1999) found that there was a positive correlation between Cd sorption and organic matter content but no significant relation to either Fe-Mn oxide content or texture.

Soils with greater composition of allophanic minerals have taken special attention for Cd sorption, because allophane minerals contain variable charge, therefore have the ability to retain Cd between pH 5-7 (Parfitt, 1990). There have been contrasting effects shown by allophane minerals rich soil for Cd sorption. While Bolan et al. (2013) found greater Cd accumulation in allophane-rich soils than in the soils that did not have allophane minerals in a laboratory sorption experiment, Salmanzadeh et al. (2016) reported no significant difference in the amount of Cd accumulated in two Allophanic soils and a Gley soil that had the same phosphate fertiliser history. Under field conditions, if the soil pH is less than the point zero charge (PZC; the pH where net surface charge change from negative to positive) of the allophane minerals, those mineral surfaces can develop a net positive to neutral charge. In that case, allophane minerals may not show greater affinity for retaining Cd, while the other solid phases, such as organic matter and metal-oxides may show greater affinity for Cd sorption (Salmanzadeh et al., 2016).

2.2.3 Numerical description of distribution coefficients

The TM lability and mobility largely depend on its partitioning between soil solid and solution phase, where the extent of TM mobilisation is affected by the amount of TM that is distributed between the soil solution and the labile solid phase, the phase that can replenish TM to soil solution. This partitioning of TM in soil is frequently quantified by a distribution coefficient (K_d) that, indicates the distribution of an element between the solid and solution phase (equation 2.1):

$$K_d = \frac{TM_{solid}}{TM_{solution}} \tag{2.1}$$

where, TM_{solid} is the solid phase concentration (expressed on soil-weight basis), $TM_{solution}$ is the solution phase concentration (expressed on solution volume basis) of the metal of interest. K_d is expressed in L kg^{-1} (Degryse et al., 2009).

The partitioning of TM between the solid and solution phase can also be presented as Langmuir (equation 2.2) and Freundlich (equation 2.3) sorption isotherms.

$$q = \frac{Q_{\max} b C_e}{(1 + bC_e)} \tag{2.2}$$

$$q = K_F C_e^{1/n} \tag{2.3}$$

where, q is the amount of Cd sorbed (mg g^{-1}), C_e is the equilibrium Cd solution concentration (mg g^{-1}), Q_{max}, b, K_F are isotherm fitting parameters.

This generally represents a system, where with greater metal loading, sorption sites become saturated and K_d progressively decreases. However, in a soil-solution system at low equilibrium concentration, such as those seen usually for TMs, the sorption sites are far from saturation, thus a constant K_d can be assumed. Therefore, Langmuir and Freundlich isotherms can be modified and applied to estimate the K_d at low equilibrium concentrations.

In this condition, $(1 + bC_e) \approx 1$ and $n \approx 1$, so that:

$$K_d = \frac{q}{C_e} = Q_{\max} b \tag{2.4}$$

and, $K_d = \frac{q}{C_e} = K_F$ (2.5)

Therefore, by measuring the equilibrium Cd concentration and calculating the amount of Cd sorbed to the solid phase of interest (soil, organic matter or mineral), the extent of Cd partitioning in that solid-solution system can be estimated. The K_d value for the same TM can vary depending on the method used to specify the solid and solution pool (described below).

2.2.4 Kinetics of sorption-desorption

The sorption of TM to soil solid phases may happen in two steps: (1) initial rapid sorption to reach to pseudo-equilibrium at the soil-solution interface, and (2) sorption at a slower rate for a period of days to years. The extent of desorption depends on the strength of sorption (Trivedi et al., 2006). Cadmium sorption to the solid phase is studied using batch experiments, where soil is equilibrated with dilute salt solution spiked with Cd salt (Loganathan et al., 2012). For Cd desorption, two methods are typically used. One brings soils up to its maximum sorption capacity first by equilibrating with Cd spiked salt solution, and then the soil is allowed to equilibrate with Cd-free salt solution to evaluate the extent of

Cd desorption. The second method is the extraction of soil with a Cd free dilute salt solution to determine the Cd desorption capacity of soil-borne Cd; this method is generally employed to assess Cd desorption from contaminated soils.

Studies on sorption-desorption kinetics of Cd in various soils and soil minerals have shown that Cd sorption-desorption from exchangeably bound sites is reversible (Backes et al., 1995; Christensen, 1984; Naidu et al., 1997). For example, Backes et al. (1995) found that, after sorption to goethite over a week, >96% of Cd could desorb with 0.01 M $Ca(NO_3)_2$ within 5 h. However, Cd desorption may be irreversible in calcareous soils where Cd can be precipitated with carbonate under high metal loading (Buekers et al., 2007). Sorption-desorption hysteresis (the phenomena where sorption-desorption is not reversible) has also been observed for different soil minerals at high pH (Shirvani et al., 2006), and high temperatures (Srivastava et al., 2007). Since sorption-desorption is an equilibrium process, the hysteresis observed in long-term contaminated soils can be explained by slow desorption from the non-labile pool compared to the fast desorption of labile Cd for the time scale considered (Loganathan et al. (2012) and references therein).

There can be various solid pools of Cd, where associated Cd may vary from labile to inert depending on the method used to extract the Cd. Therefore, different K_d values can be defined depending on the soil solid phase of interest (Degryse et al., 2009). For example, digestion of soil with hot acid determines the partition of Cd in the total solid phase, including some solid phase Cd species that are likely inert. However, extraction with dilute salts such as $CaCl_2$ and isotope extraction are better able to estimate the exchangeable Cd in soil. Likewise, extraction with a chelating ligand (e.g. EDTA) at low concentrations can reasonably estimate non-exchangeably bound labile Cd (Gäbler et al., 2007; Gray et al., 2003b; Tongtavee et al., 2005; Young et al., 2000). It is important to note that these extractions are performed at high soil to solution ratio and the soil-solution system is mechanically disturbed for hours to days; therefore, relating these measurements to field conditions needs to be done with care.

In the past two decades, a numerical method combined with diffusive gradient in thin-films (DGT) has been successfully used to determine the distribution coefficients for labile Cd species in soil under minimum disturbance and ~150% of soil field capacity. This numerical model is known as DGT-induced metal fluxes in soil and sediments (DIFS). Harper et al. (1998) introduced the DIFS model to understand the resupply of free ions from sediments to solution via diffusive flux measurements using DGT. Subsequently, Ernstberger et al. (2002), Ernstberger et al. (2005), Lehto et al. (2006a) and Lehto et al. (2012) have applied and adapted the DIFS model to determine distribution coefficients for 'DGT-labile TM' and the kinetics of TM desorption in soils. Given the differences in operational characteristics, this technique likely provides an estimate for the labile pool of Cd that is more representative of natural soil conditions than using extraction solutions with variable ionic composition and concentrations and high soil to solution ratios, as described above.

2.3 Cadmium speciation within soil solution

In soil solution, Cd can be found as Cd^{2+} free ion, associated with inorganic ions, complexed with dissolved organic matter (Kabata-Pendias, 2007; Sauve et al., 2000) and associated with colloidal organo-mineral complexes. The free Cd^{2+} ion is the most reactive species of Cd (labile), which is most available for biological uptake or for binding with the solid phase. The non-labile solution species of Cd may show greater potential for being mobilised in the soil environment, as they do not react with solid phases or biota.

The speciation of Cd in soil solution varies depending on the ligands present and the pH. Sauve et al. (2000) analysed soil solution extracted from 64 samples of soils collected from 18 different sites with varying soil pH, OM, and dissolved organic matter (DOM) concentration and found increased free Cd^{2+} and inorganic Cd species at low pH (pH<4), while Cd-DOM complexes were most abundant at pH 6. Further, they found an increase in the solution Cd inorganic pool at pH 8 than at pH 7, which was attributed to the hydrolysis and formation of carbonate ion-pairs. Using speciation modelling, Tahervand et al. (2016) found that Cd^{2+} and $CdCl^{+}$ were the dominant Cd species in soil solution of a calcareous soil at pH<8, while the percentage of $CdCO_3$ and $CdOH^{+}$ only increased after pH 7 and 8 respectively. While the Cd-DOM species are relatively low in soil solution, speciation of Cd within the DOM is complex because DOM is a heterogeneous mixture of various organic molecules, where Cd may be associated with these organic molecules to different extents (Cornu et al., 2011; Ren et al., 2015b).

2.3.1 Role of dissolved organic matter

Dissolved organic matter in soil and natural waters mainly originates from solubilisation of SOM, plant litter and root exudates (Bolan et al., 2011; Kalbitz et al., 2000). Biological waste materials such as poultry manure, animal manure, and sewage sludge are sources of DOM and can enhance the solubilisation of SOM by increasing soil pH (Hernandez-Soriano et al., 2013). Dissolved organic matter consists of a mixture of organic molecules, which can form Cd-DOM complexation via chelation. While most of the studies on TM binding to DOM are performed on chemically extracted humic substances from SOM depending on their solubility in acidic and basic solvents- namely ‘humic acid’ and ‘fulvic acid’ (Bai et al., 2018; Kaschl et al., 2002a; Ren et al., 2015b)- the existence of these organic molecules in nature is unlikely (Kleber et al., 2010). However, this operational definition allows us to identify the chemical properties of organic molecules in DOM important for determining the binding capacities for various TMs. The humic substances, also known as the hydrophobic fraction are responsible for 20-

60% of organic constituents in DOM (Amery et al., 2009; Groenenberg et al., 2010). Non-humic substances, which include aliphatic acids, amino acids, and carbohydrates, contribute 40-70% of the DOM pool (Croue et al., 2003; Pernet-Coudrier et al., 2011).

Qualities of DOM like the composition of various organic molecules (e.g. humic-like, fulvic-like and protein-like), aromaticity, and age (humification degree) can vary depending on its provenance. Various organic molecules in DOM are important in determining the affinity of DOM to bind different TMs and therefore, affect TM mobility in soil (Amery et al., 2010; Chen et al., 2018b; Ren et al., 2015b). For instance, Wu et al. (2012a) reported the affinity for DOM to bind different TM appeared to be determined by the various organic molecules (humic-like or protein-like) in the DOM, rather than the molecular weight of DOM. In a subsequent study, Wu et al. (2012b) found that in DOM collected from landfill leachates, the protein-like molecules were responsible for Cd binding, while both protein-like and humic-like compounds were responsible for Cu binding. This suggests that different functional groups (ligands) present in each organic molecule have different binding affinities for different TMs. The affinity for TMs to be bound by the different ligands in DOM determines the stability of TM-ligand association which affects the lability of the DOM-bound TM. For example, in DOM extracted from municipal solid waste, humic acids had the greatest Cd binding capacity, with stability constants (pK_a values) for Cd-ligand association decreasing from 10.05 (humic acid) to 6.8 (fulvic acid) and ranging from 6.9 to 8.11 for non-humic compounds (Kaschl et al., 2002a).

The aromatic nature of DOM is also an important quality that determines the affinity of DOM for some TM such as Cu and Pb (Amery et al., 2008; Amery et al., 2010; Chen et al., 2018b). For example, the Cu toxicity in water decreases with increasing DOM's aromaticity (De Schamphelaere et al., 2004), which can be attributed to the greater affinity of Cu for more aromatic DOM (Amery et al., 2008). However, for Cd, it is uncertain whether Cd mobilisation and lability may be affected by aromaticity of the DOM. For instance, Chen et al. (2018b) reported that while Cd may be bound by the aromatic moieties of DOM collected from natural waters, it might be bound to the ligands that are in the non-aromatic structure of the purified humic acid.

Recently, DOM size fractionation and DOM quality in each size fraction have been related to TM speciation in soil solution. Cadmium has a strong affinity for high molecular weight (Mw) DOM, such as humic-like molecules (Bai et al., 2018; Kaschl et al., 2002a), which are numerous in colloidal DOM derived from humified OM, e.g. aged compost and peat commonly used as soil amendments. By size fractionation of extracted humic acids from soils, Bai et al. (2018) found Cd binding affinity for the organic molecules present differed by Mw fractions in the order of: less than 5 kDa > 5 to 10 kDa > higher than 30 kDa > 10 to 30 kDa. The affinity for Cd association with different size fractions of DOM may be controlled by the structural factors of the DOM (e.g. steric hindrances), while Cd binding capacity by different size fraction is determined by the amount of ligands like carboxylic and phenolic groups (Bai et al., 2018; Kaschl et al., 2002a).

The quality of DOM is also important for informing DOM's stability against microbial degradation and, thus the longevity of TM-DOM complexes. Kalbitz et al. (2003) found that DOM released from less humified materials (e.g. stew, litter) were more susceptible for biodegradation, while an intermediate effect was shown by DOM from agricultural soil and DOM from peat was the most stable. Apart from its provenance, the aggregate stability of DOM also determines its resistivity to biodegradation (Kleber et al., 2010). The colloidal DOM and DOM present in soil solution that are associated with minerals (organo-minerals) are generally more resistant for mineralisation than low Mw DOM. This suggests that when TM is associated with DOM which is resistant to biodegradation (DOM from aged OM or more humified DOM), the TM may persist in the soil for a longer period and may have greater potential to be mobilised in the surrounding environment (Wu et al., 2012b).

2.3.2 Kinetics of trace metal-ligand complex association and dissociation

The lability of Cd in inorganic and organic complexes are determined by the association and dissociation rate constants. The stable Cd-inorganic complexes, slowly dissociating Cd-DOM complexes and Cd associated with organo-mineral colloids in soil solution may be considered as the important solution species in the transport of Cd in soil (Degryse et al., 2009). These species have potential to transport Cd deep down the soil profile with sufficient water flow and, thus contaminate groundwater unless the complex itself is retained by solid phases.

The association and dissociation of TM-ligand complexes can be described simply by equations 2.6 and 2.7 (Shafaei-Arvajeh et al., 2013) (charge of species are removed for simplicity):

$$TM + {}^{I}L \underset{k_{diss,I}}{\overset{k_{a,I}}{\rightleftarrows}} TM\,{}^{I}L \tag{2.6}$$

$$TM + {}^{O}L \underset{k_{diss,O}}{\overset{k_{a,O}}{\rightleftarrows}} TM\,{}^{O}L \tag{2.7}$$

Where, ${}^{I}L$ is an inorganic ligand, ${}^{O}L$ is an organic ligand, and $TM^{I}L$, and $TM^{O}L$ are TM-ligand complexes. $k_{a,I}$, $k_{a,O}$, $k_{diss,I}$, $k_{diss,O}$ are association and dissociation rate constants for the inorganic and organic metal-ligand complexes. These rate constants define rates of interconversion among TM, ${}^{I}L$, ${}^{O}L$, $TM^{I}L$, and $TM^{O}L$. Hence, the stability constants K_I, K_O for $TM^{I}L$, and $TM^{O}L$ can be defined as:

$$\frac{\left[TM\,{}^{I}L\right]}{[TM][{}^{I}L]} = K_I = \frac{k_{a,I}}{k_{diss,I}} \tag{2.8}$$

$$\frac{\left[TM\,^{O}L\right]}{[TM][^{O}L]} = K_O = \frac{k_{a,O}}{k_O} \tag{2.9}$$

Note that square brackets denote the species concentration.

As noted above, DOM may consist of different organic components with a large variety of functional groups whose individual role in TM binding kinetics is difficult to analyse accurately. With this in mind, ^{O}L and $M^{O}L$ are 'lumped variables' that represent the sum of the available binding sites in DOM (Shafaei-Arvajeh et al., 2013).

The dissociation kinetics of TM solution complexes have been studied with various techniques. These methods include isotope exchange, competitive ligand exchange (CLEM) and DGT techniques (Amery et al., 2010; Chakraborty et al., 2014; Shafaei-Arvajeh et al., 2013). However, studies on dissociation kinetics of Cd-DOM complexes are scarce, with most TM-DOM complex studies performed on TM-DOM complexes in natural water with Cu and Ni, which are known for their higher affinity for DOM (Amery et al., 2010; Shafaei-Arvajeh et al., 2013; Warnken et al., 2008; Warnken et al., 2007). Even Cd has comparatively low affinity for DOM, an increasing DOM concentration, can increase the ligand availability for Cd binding significantly, therefore according to equation (2.9) there will be more Cd-DOM complex formation.

2.4 Physical factors driving cadmium mobility in soils

The mobile TM species discussed above can migrate deep down the soil profile through advection and hydraulic dispersion (Hooda, 2010; McLaren, 1996). Their transport largely depends on the water movement through the soil profile, which in turn is determined by the soil's hydraulic conductivity. The hydraulic conductivity depends on the soil texture, which decreases in the order of sand, silt, and clay. Therefore, potential for TMs transport to groundwater is greater in coarse soils than in clay soils (Hooda, 2010).

Soil macropores also have a large impact on TM transport (Carrillo-González et al., 2006). In this case, solute transport will follow preferential flow paths, which can bypass the majority of the soil matrix and result in greater leaching of TMs. Kim et al. (2008) reported that the Cd follows a preferential flow path under different rainfall intensities, where the amount of mobilised Cd was greater with higher rainfall. However, Laboratory scale determination of TM leaching in homogenized soil columns can underestimate the leaching behaviour of TMs, where added TMs are adsorbed by soil particles and solute transport more often follows a matrix flow rather than preferential flow (Camobreco et al., 1996). Given that the matrix flow allows better buffering of species from solid to solution due to the increase in residence time, Cd leaching in homogenised soil columns may inform the extent of resupply of Cd to the soil solution from labile solid phase when the Cd in soil solution is progressively leached.

2.5 Cadmium mobilisation in agricultural soils in New Zealand

The behaviour (accumulation and leaching) of Cd in New Zealand soils varies depending on the land use, soil characteristics, Cd inputs, weather and climate (Cadmium Working Group, 2008; Gray et al., 2003a). In New Zealand 45% of the total land is used for agriculture (pasture, crop and horticulture) and from that 88% (40% of total land) is used for pastoral farming (dairy, beef and sheep) (Statistics New Zealand, 2016). The highest amount of soil Cd is found in pasture lands in intensively farmed areas as a result of continuous phosphate fertiliser application, leaching of Cd from these lands may be a potential threat for local groundwater contamination (Bramley, 1990; Loganathan et al., 2003; Reiser et al., 2014; Taylor et al., 2017; Taylor et al., 2007).

Nationwide analysis carried out by Nokes et al. (2014) reported that Cd level in groundwater is currently not a threat for drinking-water quality standards in New Zealand. However, high groundwater Cd concentrations in intensively farmed areas indicates a potential issue for groundwater contamination with continuous phosphate fertiliser application (Nokes et al., 2014; Taylor et al., 2017). Nokes et al. (2014) reported that the Cd concentration in 87% of sample analysed in their survey were below the method detection and found that in 1283 samples, none of the samples exceed the maximum permitted value for Cd concentration in drinking water in New Zealand (4 $\mu g\ L^{-1}$), while only three sample exceed 50% of the maximum permitted value. The groundwater samples that had high Cd concentrations were collected from the high intensity farming areas (Nokes et al., 2014; Taylor et al., 2017).

In New Zealand, soil pH is influenced more by the type of the land use (31%) than the soil order (20%) (NZ Soil Bureau., 1968). The pH ranges recommended for different crops are listed in the Table 2.1. Most of New Zealand pasture soils are acidic in their natural states, and hence continuous lime application is required to reach the recommended pH levels. There is a possibility to increase the Cd mobility if pasture lands were to concert for other purposes (horticultural, residential), where reduced liming is required, resulting in greater Cd solubilisation at the lower pH (Strobel et al., 2001). Monitoring of Cd mobility and leaching in such areas may be required.

Table 2.1: Preferred pH ranges for selected crops, vegetables and Fruits grown in New Zealand (NZ Institute of Chemistry).

pH range	Field Crop/ Vegetable	Fruit
4.0-5.5		Blueberry
4.5-6.0	Potato	
5.0-6.5	Oats, Parsley	
5.5-6.5	Barley, Capsicum, Kumara, Ryegrass, Wheat	Apple, Avocado, Cranberry, Strawberry
5.5-7.0	Carrot, White clover	
5.5-7.5	Corn, Pumpkin, Tomato	Rhubarb
6.0-7.5	Asparagus, Broccoli, Broad Bean, Cabbage, Onion, Spinach	Apricot, Cherry, Grape, Hazelnut, Pear

Transport of Cd to deeper soil layers under irrigation has been reported and therefore suggests that water movement plays an important role in transporting Cd in agricultural soils in New Zealand (McDowell, 2012; Salmanzadeh et al., 2017b). In these soils, the soil texture appeared to be important in controlling the mobility of Cd. For instance, in four soil orders in New Zealand (Pumice, Allophanic, Brown and Pallic) that have received superphosphate fertilizer with Cd concentrations of 280 mg Cd kg^{-1} P, the extent of Cd leaching was controlled by soil sorption capacity, leachate pH and total volume of drainage, which were determined by soil texture and water flow (Gray et al., 2003a). The total Cd concentrations of these soils varied between 0.19-0.44 mg Cd kg^{-1} and the amount of Cd leached for 24 months ranged between 0.54 to 1.71 g ha^{-1}, with the greatest leaching in Allophanic soil and the least in Pallic soil. However, the leached Cd loss accounted only for 5 – 15 % of Cd added from fertilizer, suggesting that added Cd was mainly accumulating in the topsoil and less susceptible to leaching. As soil organic matter strongly binds Cd, Gray et al. (2016) stressed that Cd adsorbed to soil organic phases may later enhance the mobility of Cd by desorption at low pHs. They found that Cd leaching from an Organic soil at pH 4.5 (0.39 g ha^{-1}) was relatively higher than at pHs 5.5 and 6.5 (< 0.25 g ha^{-1}) which have been amended with more than 100 kg P ha^{-1}. However, the total Cd loss was <1% of added Cd, indicating that even at low pH (4.5), organic soil has high Cd retention capacity. Clearly, these studies were focused on leaching losses of anthropogenic Cd in different soils, not the effect of different solution species of Cd (free ions, Cd-DOM, Cd-inorganic complexes) for Cd mobility in those soils.

Recent studies have shown that the DOM and chloride inputs can increase the Cd mobilisation in agricultural soils to a greater extent. Carrick et al. (2014) studied the Cd leaching in stony soils treated with cow urine under irrigation. They found a marked increase in Cd and dissolved organic carbon (DOC) leaching under cow urine application, thus indicating that urine, by increasing the soil pH, solubilised SOM, which may have increased the mobility of Cd as Cd-DOM complexes. However, urine is also considered as a source of Cl^{-}. Taking this fact into account Gray et al. (2017) also studied the effect of cow urine on Cd mobility in stony soils under irrigation and found a positive significant relationship between the concentrations of Cd and Cl^- leached. However, they did not observe a significant change in the concentration of DOC leaching under urine application. Both studies are done on stony soils, where stony soils are known for low sorption capacity and high permeability. Recently McDowell (2019) investigated soil Cd mobility as affected by chloride applied as KCl fertiliser, which is frequently applied to maintain the K concentration in grazed pasture. They found that chloride significantly increases the Cd loss from topsoil to subsoil, with greater losses associated with higher chloride rates and higher rainfall. Further, they reported that this Cd leaching loss of Cd was 29-41% of added Cd from phosphate fertiliser. They concluded that the application of chloride as KCl reduced the Cd accumulation in topsoil by mobilising it to deeper soil layers, without showing a change in Cd concentration in plants compared to the control soil.

These studies suggest that changes in Cl^- and DOM concentrations in soil solution have a potential to transport Cd to groundwater given sufficient water flow. However, it is unclear what might be the extent of mobilisation of Cd as influenced by these solution species with respect to the characteristics of the soil such as texture, minerals and organic matter.

2.6 Methods for investigating cadmium speciation and lability

2.6.1 Solid phase speciation

Sequential extractions are widely used to fractionate the TM in soil depending on their reactivity. This method provides detailed information about the origin, mode of occurrence, mobility, biological and physicochemical availability of TMs in soils (Hooda, 2010; Roberts et al., 2005). Sequential extraction procedures are used to fractionate TM species into (1) soluble in water, (2) exchangeable and/or acid soluble, (3) reducible or those associated with Fe and Mn oxides, (4) oxidizable or those associated with organic matter and sulphides and (5) residual or those associated with silicates (Hooda, 2010; Roberts et al., 2005). Isotope dilution methods can also be coupled with sequential extractions to measure the labile pool of Cd in soils (Ahnstrom et al., 2001; Ren et al., 2015a). However, sequential extraction procedures should be carefully related to natural soil conditions because of the use of highly concentrated chemicals. This is especially the case when trying to understand the potential mobility and bioavailability of TM in soils where such conditions are unlikely to occur in the presence of biota in natural soils conditions.

A wide range of single extraction procedures have been used to measure the soluble and labile TM fraction in soils, with methods varying in the chemical nature and concentration of leaching solutions, solution/soil ratio, operational pH, and extraction time (Hooda, 2010). Unbuffered metal salt solutions are often used to extract the exchangeably bound trace metals, which are the most labile species of TMs bound to the solid phase. Frequently used extractant are 0.1, 0.05, 0.005 M $CaCl_2$, 0.05 M

$Ca(NO_3)_2$, 0.1 M $NaNO_3$ and 1 M NH_4NO_3 (Al Mamun et al., 2016; Gray et al., 1999; Hooda, 2010; Kim et al., 2009; Naidu et al., 1998). Divalent Ca ion is known as the most effective cation to extract the exchangeably bound TMs, due to its high affinity for the soil solid phase (Hooda, 2010). Chloride may not be a suitable counter anion for extraction of exchangeable Cd, as it may desorb other Cd ions than those are exchangeably bound (Loganathan et al., 2012), therefore, NO_3^- is a better counter ion (Bolan et al., 1999). Stable isotopes of Cd also have been used to determine labile Cd in soil and organic matter amended soils (Ahnstrom et al., 2001; Gray et al., 2003b; Young et al., 2000). In this method, an enriched Cd isotope with known concentration is equilibrated with soil suspended in a dilute salt and the labile fraction of Cd defined as the fraction of soil Cd that is readily exchangeable with the spiked Cd isotope.

2.6.2 Solution phase speciation

Aqueous concentrations of TMs are often measured in soil porewater collected by centrifuging of wet soil sample or using a sample tool such as Rhizon samplers or in dilute salt solution extractions. Cadmium concentration in soil porewater and in dilute salt extracts are relatively similar. Common analytical techniques for analysis of free ion concentrations in solution include ion-exchange resins, ion-selective electrodes, anodic stripping voltammetry, and Donnan membrane systems (Hooda, 2010). However, measuring free metal ion concentration using these techniques are challenging due to poor detection limits, interference from other species, and disturbance in the chemical equilibrium, so often speciation models are used to estimate free ion concentrations as well as concentrations of inorganic and organic complexes of TM of interest in soil solution (Sauvé et al., 2005).

2.6.3 Chemical speciation modelling

Different chemical species and their concentrations and composition in a given environment can be characterised by speciation models. These models use well-established databases of stability constants and electrostatic relationships in aqueous solution to calculate the formation of ion pairs, complexes, chelates, pH of the medium, oxidation-reduction status of the medium and formation-dissolution from the solid phase when modelling the speciation of a system. Quality of output from these models depends on the accuracy of the analytical input parameters such as pH, concentration of DOC, cations and anions and also the environmental conditions of the system (temperature and atmospheric pressure) (Sauvé et al., 2005). Popular speciation modelling programmes are MINTEQA2, MINEQL+, GEOCHEM-PC and WHAM-VII (Sauvé et al., 2005; Tipping et al., 2011).

2.6.4 Size fractionation of the soil solution

Soil solution particles are size-fractionated to determine the TM distribution in ‘truly dissolved’, colloidal and particulate fractions. Traditionally, the total dissolved fraction of TM species is separated by filtering the solution through 0.45 µm filter. However, the TM may be distributed in the colloidal fraction (1 nm-0.1 µm). Therefore, techniques like size exclusion chromatography, ultrafiltration and field flow filtration are applied to separate the TM species associated with various size fractions of the total dissolved fraction (Hooda, 2010).

Ultrafiltration is a convenient method to size fractionate TMs and DOM in natural water, sediment pore water and soil solution by using molecular weight cut-off membranes (Dabrin et al., 2013; Pokrovsky et al., 2005; Wen et al., 1996). There are three well-known ultrafiltration techniques: tangential, cross-flow and frontal filtration in which molecular weight cut-off membranes ranging from 500 kDa to 1 kDa are used for filtering. Often, species in the <5 kDa fraction is considered as the 'truly' dissolved fraction, which may contain free TM ions and low molecular weight organic molecules (Dabrin et al., 2013; Gangloff et al., 2016).

2.6.5 Dissolved organic matter quality analysis

2.6.5.1 Ultraviolet-visible spectroscopy

The ultraviolet-visible absorbance measured at single or multiple wavelengths is used for qualitative and quantitative characterization of DOM collected from soil and natural water (Carter et al., 2012; Chen et al., 2018b; Weishaar et al., 2003). Ultraviolet-visible (UV-VIS) spectroscopy measures the absorption of radiation by certain molecules in the UV-VIS region due to the excitation of an electron from a bonding or non-bonding orbital to an anti-bonding orbital. The absorption radiation is largely affected by the presence of chromophores in the solution, which are parts of a molecule that can absorb the radiation in the UV-VIS region. Chromophores may consist of several functional groups such as conjugated double bonds, carbonyl, aromatic rings, thiocarbonyl, nitro, and nitrozo groups. Dissolved organic matter collected from soils and freshwaters consists of a large range of organic molecules containing these functional groups, thus adsorbs the light in UV-VIS region.

The Beer-Lambert law expresses the absorption (A) of radiation by a species, where, $\mathcal{E}$ is the molar absorption coefficient, c is the concentration of the analyte and l is the optical path length of the light (equation 2.10). The molar absorption coefficient is an intrinsic property of the attenuating species which depends on the combination of solvent, species, and the wavelength.

$$A = \xi cl \tag{2.10}$$

The absorbance of DOM measured at 254 nm (A_{254}) with a 1 cm path length (b) and normalised to total DOC ($[DOC]$, units: $mg\ L^{-1}$) concentration indicates the average aromaticity of organic molecules existing in the DOM ($SUVA_{254nm}$) ((Weishaar et al., 2003), equation 2.11. The absorption ratio of DOM measured at 465 and 665 nm (E_4/E_6) can be used as an indicator for the condensation of aromatic moieties in DOM (Kleber et al., 2010). Further, the ratio of absorbance measured at 254 and 365 nm have been employed to estimate the relative molecular weight of the DOM (A_{254}/A_{365}) (Dahlén et al., 1996).

$$SUVA_{254}(Lg^{-1}cm^{-1}) = \frac{A_{254} \times 1000}{b \times [DOC]} \tag{2.11}$$

2.6.5.2 Fluorescence excitation-emission matrix

Fluorescence excitation-emission spectroscopic measurements are extensively used to characterize the DOM and to identify the source of DOM in natural water and DOM collected from soil and composts (Bai et al., 2018; Baker et al., 2008; Coble et al., 1990; Gao et al., 2017). The fluorescence excitation-emission matrices (EEMs) are mapped by combining fluorescence emission spectra measured from a range of excitation wavelengths. Fluorescence occurs when an electron, which has been excited to a higher energy level by absorbing energy, is returning back to the ground state by losing energy as light. For fluorescence to occur, there should be chromophores; the chromophores which produce fluorescence are called fluorophores. The humic substances and protein-like substances are mostly responsible for the fluorescence observed in DOM (Hudson et al., 2007).

The fluorescence excitation (ex) and emission (em) energies (i.e., the wavelengths) are characteristics for certain molecules or for a group of molecules. Therefore, EEMs of samples collected from soil or water enables the identification of different organic molecular groups in DOM. This interpretation of EEMs to characterise the components in DOM commonly relies on either peak picking or PARAFAC analysis (Baker et al., 2008; Ohno et al., 2008; Stedmon et al., 2008). The peak picking method allows one to identify four main components: peaks A and C (Humic-like) and peaks T1 and T2 (Tyrosine and Tryptophan like) (Coble et al., 1990; Fellman et al., 2010). When there is a mixture of fluorophores in a sample, the peak maxima are affected by the contribution to the fluorescence intensity by each fluorophore and so their respective concentrations. PARAFAC analysis is a multiway data analysis method used to decompose the mixture of components responsible for overall EEM into individual underlying fluorescent phenomena (Stedmon et al., 2008). The ex/em wavelengths resulting for these individual fluorescent phenomena may be compared with literature to identify the individual chemical components in the sample.

Other than peak identification there are various fluorescence indices used to elucidate the quality of DOM. The Fluorescence Index (FI) is the ratio of fluorescence intensities at em at 450 and 500 nm obtained at ex at 370 nm (McKnight et al., 2001). The FI determines the source of DOM as either microbial (high FI ~ 1.8) or terrestrial (low FI~1.2) derived. The extent of humification of DOM is derived from the Humification Index (HIX), the sum of the peak area under the em spectra from 435-480 nm divided by the sum of the peak area under 300-345 nm and 435-480 at ex 254 nm (Ohno, 2002). Higher

HIX indicates a higher degree of humification. The Biological Index (BIX) reflects the freshness of the DOM (recently derived to more decomposed DOM); BIX is the ratio of em intensity at 380 nm divided by the emission maximum observed between 420 and 435 nm, obtained at ex 310 nm (Wilson et al., 2009).

2.6.6 Diffusive gradients in a thin-films technique for estimating the labile and mobile cadmium in soil and solution

The diffusive gradients in a thin-films (DGT) technique used as a tool for analysing TM speciation, bioavailability, and kinetics of dissociation of TM complexes in soils, sediments, soil solution, and natural water (Zhang et al., 2015). A DGT sampler, at a basic level is an ion selective resin that only binds free trace metal ions and is overlain by a hydrogel and a protective filter membrane, all contained within a protective plastic case (Figure 2.3). Hydrogels are used as the diffusion layer in the DGT device. A chelating ion-exchange resin such as Chelex 100, which is incorporated into gel matrix as polyacrylamide, is used as the binding layer for trace metals (Davison, 2016).

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Figure 2.3: The DGT probe. (Knutsson et al., 2014).

In a simple solution, without significant trace metal complexation, strong binding of trace metal to the resin results in an effective zero trace metal concentration in the resin layer. This creates a diffusive flux of trace metal from the deployment medium, through the diffusive layer and into the resin (Davison, 2016). Within a short period of time (usually < 1h, depending on temperature and thickness of the diffusive layer), steady state conditions are established, resulting in a linear concentration gradient between the resin-diffusive layer interface and the interface between the diffusive layer and deployment medium (the filter is considered as part of the diffusive layer (Figure 2.4)).

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Figure 2.4: The concentration gradients of free ion (M^{2+}) and its labile complex (ML) through DGT device. The dotted line represents the situation when there is a fast dissociation of complex (ML) releasing free ions (Scally et al., 2003).

When the TM is present as a TM-ligand complex, the amount of TM measured by DGT reveals the kinetic limitation (lability) of TM in that particular complex, which is determined by the strength of the TM-ligand association. The lability of various metals in natural water and synthetic metal-ligand solutions have been investigated with conventional DGT samplers, but these samplers are limited in investigating the lability of TM species in soil solution as about 5L of solution is required (Shafaei-Arvajeh et al., 2013; Warnken et al., 2008; Zhang et al., 2000, 2015). However, there has been an attempt to adapt the DGT theory to estimate the lability of Cu-DOM complexes in a small volume (5 mL) of soil solution by Amery et al. (2010), which could be further refined to estimate the kinetic limitation of other TM-DOM complexes in soil solution.When a DGT device is deployed in a soil, continuous removal of free ions from the soil solution by binding to resin induces trace metal dissociation from labile complexes as well as desorption from soil the solid labile phase (Davison, 2016) (sometimes referred to as “buffering”). Hence, the mass accumulated in the resin layer during a given deployment time will be determined by the sum of: (1) TM present as free ions, (2) TM that can dissociate from labile complexes and (3) TM that can desorb from solid phases and diffuse into the resin gel during that time. Because the amount of trace metal measured by DGT is determined by these processes, the measurement can give an operationally defined measurement of a TM’s lability and, by extension, a measure of bioavailability, in a certain environment. Therefore, the DGT technique has been identified as a tool for in situ measurement of labile and bioavailable TMs species in soils, sediments and natural waters (Davison, 2016; Zhang et al., 2000, 2001).

For DGT deployments in soils (or sediments) for a given period of time, the index R (equation 2.12) is used as an indicator for the soils capacity to supply solute to the DGT (Ernstberger et al., 2002; Gao et al., 2018; Xu et al., 2019).

$$R = \frac{C_{DGT}}{C^{soln}} \tag{2.12}$$

where, c_{DGT} is the DGT labile metal concentration and c^{soln} is the metal concentration in soil solution. For 24 h deployment period, three modes of solute supply to DGT device (with common diffusive layer thickness: 0.093 cm) are defined (Figure 2.5)(Lehto, 2016);

“(a) $R > 0.8$, sustained case: solute is continuously supplied from the solid and solution phase at a rate almost equal to the flux into the DGT,

(b) $0.2 < R > 0.8$, partially sustained case: solute is supplied from the solution phase but is insufficient to sustain R, and

(c) $R < 0.2$, diffusive case: diffusion is the major process supplying solute to the DGT.”

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Figure 2.5: Concentrations of free ions of TMs in the soil adjacent to the DGT interface for the (a) sustained case, (b) partially sustained case, and (c) diffusive case. The wavy grey arrow represents the diffusive path for mobile species (Lehto, 2016)

R rapidly increases and reaches its maximum value, followed by a gradual decrease with the deployment time (Lehto, 2016). The initial rapid increase of R is due to the diffusion of solute close to the DGT and soil interface (Lehto, 2016). As the deployment time increases, labile species near the interface become depleted, and solute begins to diffuse to the DGT from further away. The extent to which R decreases with increasing deployment time is an indication of the soil’s capacity to resupply solute to the DGT-soil interface during the deployment.

2.6.6.1 DGT-DIFS modelling

The DGT-induced fluxes in soils (DIFS) model has been used to investigate the extent of TM resupply from the soil when free ion species are removed from soil by DGT (Ernstberger et al., 2005). The DIFS model provides a numerical simulation of diffusion of dissolved ion into the DGT probe considering the resupply of ions to the solution from the solid phase (Lehto, 2016). To describe the sorption and desorption kinetics of TM in soil, DIFS uses the distribution coefficient based on labile solid phase components that can exchange with the solution phase (K_{dl}, equation 2.13), and response time, the characteristic time for the C_{ls} and C_{sol} to approach 63.2 % of its equilibrium solid-solution partitioning values, if C_{sol} was diminished to zero (T_c, equation 2.14) (Honeyman et al., 1988; Lehto, 2016).

$$K_{dl} = \frac{C_{ls}}{C_{so\ln}} \tag{2.13}$$

$$T_c = \frac{1}{k_1 + k_{-1}} \tag{2.14}$$

where, C_{ls} is the labile ion concentration of analyte bound to soil solid phase, C_{soln} is the ion concentration in solution phase, and k_1 and, k_{-1} are rate constants for adsorption and desorption in solid phase, respectively. In DIFS, different combinations of k_1 and k_{-1} are employed to determine the best fit for experimental *R*-values.

The DIFS model can be used to distinguish the lability of Cd in various soils, which depends on the characteristics of the soil (texture, minerals, and organic matter).

2.6.7 Isotope tracing of cadmium in soil

Isotope fingerprinting is a useful tool for studying the fate and mobility of TMs in soil (Prohaska et al., 2005; Sun et al., 2018; Wiederhold, 2015) and is increasingly applied for understanding the behaviour and source identification of Cd in soils with known sources of Cd (Cloquet et al., 2006; Imseng et al., 2018, 2019; Salmanzadeh et al., 2017a; Wiggenhauser et al., 2019; Wiggenhauser et al., 2016). Cadmium has eight stable isotopes in the environment with varying natural abundances: ^{106}Cd (1.3%), ^{108}Cd (0.9%), ^{110}Cd (12.5%), ^{111}Cd (12.8%), ^{112}Cd (24.1%), ^{113}Cd (12.2%), ^{114}Cd (28.7) and ^{116}Cd (7.5%) (Rosman et al., 1998). These isotopes enable the study of various Cd isotope ratios to understand the behaviour of Cd in soils (Ahnstrom et al., 2001; Salmanzadeh et al., 2017a; Wiggenhauser et al., 2019; Wiggenhauser et al., 2016).

For source identification, mixing models can be used, assuming that end members (different sources) are isotopically distinguishable (so, have distinct isotope ratios), therefore the fractional contribution from each Cd source (e.g. unfertilised soil and fertiliser) can be calculated for a given Cd pool (e.g. in fertilised soils, groundwater, plant) (Salmanzadeh et al., 2017a; Wiggenhauser et al., 2019). Use of mixing models can be challenging if physicochemical processes in the system interfere with the isotope fractionation. These processes may include, sorption to solid surfaces (organic matter and minerals), redox reactions, chemical weathering and biological cycling (plant uptake) (Imseng et al., 2018; Wasylenki et al., 2014; Wiederhold, 2015; Wiggenhauser et al., 2016; Zhang et al., 2016). Therefore, to use these mixing models, either isotope fractionation caused by physicochemical processes should be known or it should be insignificant compared to the difference in the isotope fractions between the sources.

The isotope fractionation in soil can also be used for predicting speciation in solid and solution phases. Often, Cd isotopes fractionate to lighter isotopes in solid phase and to heavier isotopes in solution phase (Imseng et al., 2018, 2019; Wasylenki et al., 2014). This fractionation is attributed to the difference in the bond lengths between the isotopes and the bonding atom (Wiederhold, 2015). Molecules containing heavier isotopes bond with lower zero-point energies than those containing lighter isotopes of the same element. Therefore bonds formed by heavier isotopes are stronger bonds resulting in shorter bond lengths (Wiederhold, 2015). For Cd in its natural abundance, the bond length between Cd and O atoms in aqueous solution ranges between 2.24 -2.30 °A, which is slightly shorter than that in the Cd-O bond length in goethite (2.30-2.33 °A), while Cd-S bond lengths in soil organic matter are even longer (around 2.5 °A) (Bochatay et al., 2000; Fulda et al., 2013; Karlsson et al., 2005; Ohtaki et al., 1981). Therefore, heavier Cd isotopes may preferentially form aqueous complexes resulting in fractionation to heavier isotopes in solution; likewise, solid phase Cd may be enriched with lighter Cd isotopes.

2.7 Summary

Cadmium is comparatively immobile in soil. However, agricultural practices such as irrigation, fertiliser application and soil amendments may enhance the mobility of Cd in soil, thus providing a potential risk to contaminate groundwater. The speciation of Cd and the factors controlling the speciation of Cd ultimately govern Cd mobility in soil. The mineral clay and organic solid phases play an important role in immobilising the Cd is soil, thus making them less available for plant uptake and leaching. However, sorption and desorption control the extent of resupply of free Cd ions to solution, making for a dynamic system where equilibrium conditions do not exist.

The extent of Cd sorption by SOM depends on the various organic compounds and functional groups involved in Cd complexation and their affinity for Cd binding; therefore, the provenance of SOM is important. Moreover, the longevity of Cd retention by SOM depends on the resistivity of the SOM for decomposition and mineralization, meaning that the quality of SOM (e.g. composition of various organic compounds and aggregate stability) and the climate variables are also considerably important.

The mobility of Cd in soil depends on what soil solution species of Cd are present. Dissolved organic ligands in soil solution, which can form labile to non-labile complexes with Cd, may be considered as an important species affecting Cd mobility in soil. The lability of Cd in those complexes is determined by the stability of the Cd-DOM complexes. Here the quality of DOM is important for both complex stability as well as its resistivity to biodegradability. Formation of soluble Cd-chloride complexes may decrease the Cd accumulation in the topsoil, but may mobilise Cd in soil, and so potentially threatens groundwater contamination in fields with high chloride inputs through fertiliser and urine.

The movement of Cd species with water flow will be controlled by the soil texture, rates of sorption and desorption of Cd from solid phase, rates of association and dissociation of Cd from Cd-ligand complexes in solution, and the rate of water flow. Novel techniques such as DGT and isotope ratio tracing can be used to investigate the lability and mobility of Cd in soil accounting for the above reactions.

Chapter 3

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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My contribution to this article: I designed, set up and conducted the experiments with advice from my co-authors. I collected and analysed the results and used those to identify the main findings of the work and prepared the initial drafts of the manuscript.

3.1 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). The accumulation of Cd in soils has been linked to sustained application of phosphorus fertilizers, where the trace metal is a naturally occurring contaminant (Kelliher et al., 2017; Loganathan et al., 2003; Salmanzadeh et al., 2017a), land application of biosolids and industrial effluents (Kabata-Pendias, 2007). The removal of Cd from soils is not only challenging owing to its close association with various soil components, the large area of land that has been affected precludes most options from a practical and an economic point of view. Consequently, there has been an increasing focus on options for reducing the plant bioavailability of soil Cd instead.

Various types of soil amendments have been considered as potential means by which to reduce the uptake of Cd by plants (Al Mamun et al., 2017; Bolan et al., 2003b; Shaheen et al., 2017; Valentinuzzi et al., 2015). 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 et al., 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 (Al Mamun et al., 2017; Simmler et al., 2013), as well as other trace metals (*e.g.* Pb, Zn, As and Cu) in industrial contaminated soils (Abad-Valle et al., 2017; Bolan et al., 2014; Van Poucke et al., 2018). The ability for different organic amendments to influence trace element bioavailability is informed by the characteristics of the organic matter that is employed (*e.g.* pH, CEC, humification degree) as well as the soil type and the trace element (Albiach et al., 2000; Bolan et al., 2014). However, organic matter that has 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 (Haynes, 2005; Kalbitz et al., 2000). This makes it a potentially powerful vector for mobilizing otherwise immobile trace elements in the environment and raises the question of what potential risks may be associated with metal-DOM complexes that are transported from contaminated soils.

The objectives of this work are to investigate the Cd sorption capacity of different types of organic matter, and then elucidate whether the DOM released from these substances show different qualities for enabling the transport and subsequent release of Cd for biological uptake. These objectives will be met by employing a combination of novel measurements of trace metal complex lability, spectroscopic analyses of DOM quality and targeted chemical analyses of soil organic matter stability and capacity to bind trace metals.

3.2 Materials and Methods

3.2.1 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. 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 (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).

3.2.2 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, 1987). Total carbon and nitrogen content of the solid substrates was measured using a Vario-Max CN Analyzer (Elementar Analysensysteme GmbH, Germany). Cold and hot water extractable carbon (CWEC and HWEC, respectively) were measured in all of the substrates following the method described by (Ghani et al., 2003). Briefly, 3 g of each substrate sample was sequentially extracted, first with 30 mL HPW at ambient temperature for 30 mins, after which the extractant was separated from the sample, filtered (0.45 µm pore diameter cellulose acetate filter) and analysed for total carbon (CWEC) 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 hours, after which the extractant was separated from the sample, filtered as before, and analysed for total carbon (HWEC) as before.

Cation exchange capacity (CEC) of the substrates was measured using the silver thiourea (AgTU) method (Blakemore, 1987). Briefly, 0.70 g of substrate 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 substrates 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 organic substrates are shown in Table 3.1.

The different substrates' capacity to sorb Cd was analysed using previously developed sorption experiments using spiked solutions of 0.05 M of $Ca(NO_3)_2$ (Al Mamun et al., 2016; Simmler et al., 2013). Briefly, 5 g batches of each substrate, except OP, were mixed with 30 mL of either 0.05 M $Ca(NO_3)_2$ (Sigma-Aldrich) extraction solution, or extraction solution that had been spiked to 2 mg L^{-1} (18 µM) of Cd (salt: $Cd(NO_3)_2{\cdot}4H_2O$, 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 HNO_3 (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. (2013)(equation 3.1):

$$K_d\,(L\,kg^{-1}) = \frac{Metal\,sorbed\,by\,substrate\,(mg\,kg^{-1})}{Metal\,in\,solution\,(mg\,L^{-1})} = \frac{(C_{spike} - (C_{eq} - C_b)) \times (V/m)}{(C_{eq} - C_b)} \tag{3.1}$$

where K_d describes the solid-solution phase partitioning of the analyte of interest, C_{spike} is the concentration of metal in the spike solution, C_{eq} is the concentration in the spike solution after equilibration with the substrate, and C_b is the metal concentration in the unspiked extractant solution after equilibration. The volume of extractant (0.03 L) and mass of substrate 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 substrate-pH combination.

The results of the sorption experiment were used to select four substrates 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 $Ca(NO_3)_2$ spiked to 18 µM Ni and Zn (salts used: $Ni(NO_3)_2{\cdot}6H_2O$, and $Zn(NO_3)_2{\cdot}6H_2O$ (BDH, AnalaR)) was carried out on these substrates at pH 5.5 as before. The extracted solutions from the four substrates 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 substrates 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.

3.2.3 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 3.2.

$$SUVA_{\lambda} = \frac{A_{\lambda} \times 1000}{b \times \left[DOC\right]} \tag{3.2}$$

Where, λ is the wavelength (nm) at which the absorbance (A_{λ}) is measured, *b* is the path length through quartz cell (cm) and *[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 240-600 nm and emission wavelengths ranging from 245-820 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 et al., 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.

3.2.4 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 substrates 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 diffusive 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.

3.2.4.1 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 minutes 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 the diffusive layer. Using Fick's first law of diffusion, the flux, J (mol cm^{-2} s^{-1}), of metal from the solution at a given time (t) can be calculated using equation 3.3:

$$J(t) = C_i(t)\left[\frac{D^{DL}}{\delta_{DL}} + \frac{D^{W}}{\delta_{DBL}}\right], 0 < t < T \tag{3.3}$$

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 lengths 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 diffusive 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 equation 3.3 into the expression for first order decay (equation 3.4).

$$C_t = C_0 \times e^{\left[-\frac{D^{DL}\times A}{(\delta_{DL}+\delta_{DBL})\times V_{SOL}}\times t\right]} \tag{3.4}$$

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 3.4 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 3, 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 (Wang et al., 2016; Zhang et al., 1999). 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 (Galceran et al., 2015; Lehto et al., 2006a; Shafaei-Arvajeh et al., 2013). 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 4.27 (Cd), 4.38 (Ni) and 4.06 (Zn). The differences between the metals are determined by their respective diffusion coefficients in agarose.

3.2.5 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 3.2). The conductivities of the extract solutions were measured and adjusted to 10.5 mS cm^{-1} (± 2.0) using $NaNO_3$ 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 $Ca(NO_3)_2$ solutions and adjusted to pH 5.5, as before. The ligand concentrations used here were chosen to achieve the same metal:DOC molar ratio as in the organic matter extracts (Table 3.2). The model ligand test solutions were allowed to equilibrate for 24 h before deployment. Each extract and model ligand solution were analysed in triplicate.

3.2.6 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%.

Table 3.1: Chemical properties and elemental concentrations of the substrates 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 (±6.82)	4340 (±0.40)	6733 (±0.89)
CEC (me/100g)	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	16.1	25.5	50.2	30.4	26	nd
N (%)	1.2	1.56	1.58	1.93	0.45	1.63	2.3	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	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 (mg kg^{-1})	<0.21	<0.021	<0.021	0.1	<0.021	<0.021	0.01	<0.021	3	1
Zn (mg kg^{-1})	49	8	649	294	73	153	9.8	441	1356	1108
Ni (mg kg^{-1})	10.7	0.185	4.6	7.5	27.7	5.6	0.17	5	20.7	31.4
Cu (mg kg^{-1})	15.8	1.7	109.9	46.3	29.7	26.2	23.3	74	782.9	318.1
Pb (mg kg^{-1})	13.9	2.4	5.5	99.7	11.1	10.2	<0.21	7.6	135	60.7
Al (mg kg^{-1})	15888	1364	6666	10461	28189	12229	4	9840	19008	15605
Cr (mg kg^{-1})	17.9	1.2	10.2	25.3	33.7	39.5	0	23.9	41.9	153.2

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

3.3 Results and Discussion

3.3.1 Cadmium sorption capacity of the different organic substrates

The results from the batch sorption experiments confirmed the previously observed high capacity of composts to sorb Cd (Figure 3.1) (Al Mamun et al., 2016; Ulmanu et al., 2003). 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 log K_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 biosolid 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 3.1). Peat and coffee grounds are often used as a growth substrate in soil-less growth media, as a bulking agent in composts, and peat has been proposed as a potential medium for treating wastewater (Barreto et al., 2008; Brown et al., 2000; Farrell et al., 2010), which informed the decision to 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 were similar, while CFF had the lowest CEC of the substrates considered and that is reflected in the substrates' ability to bind Cd (Table 3.1).

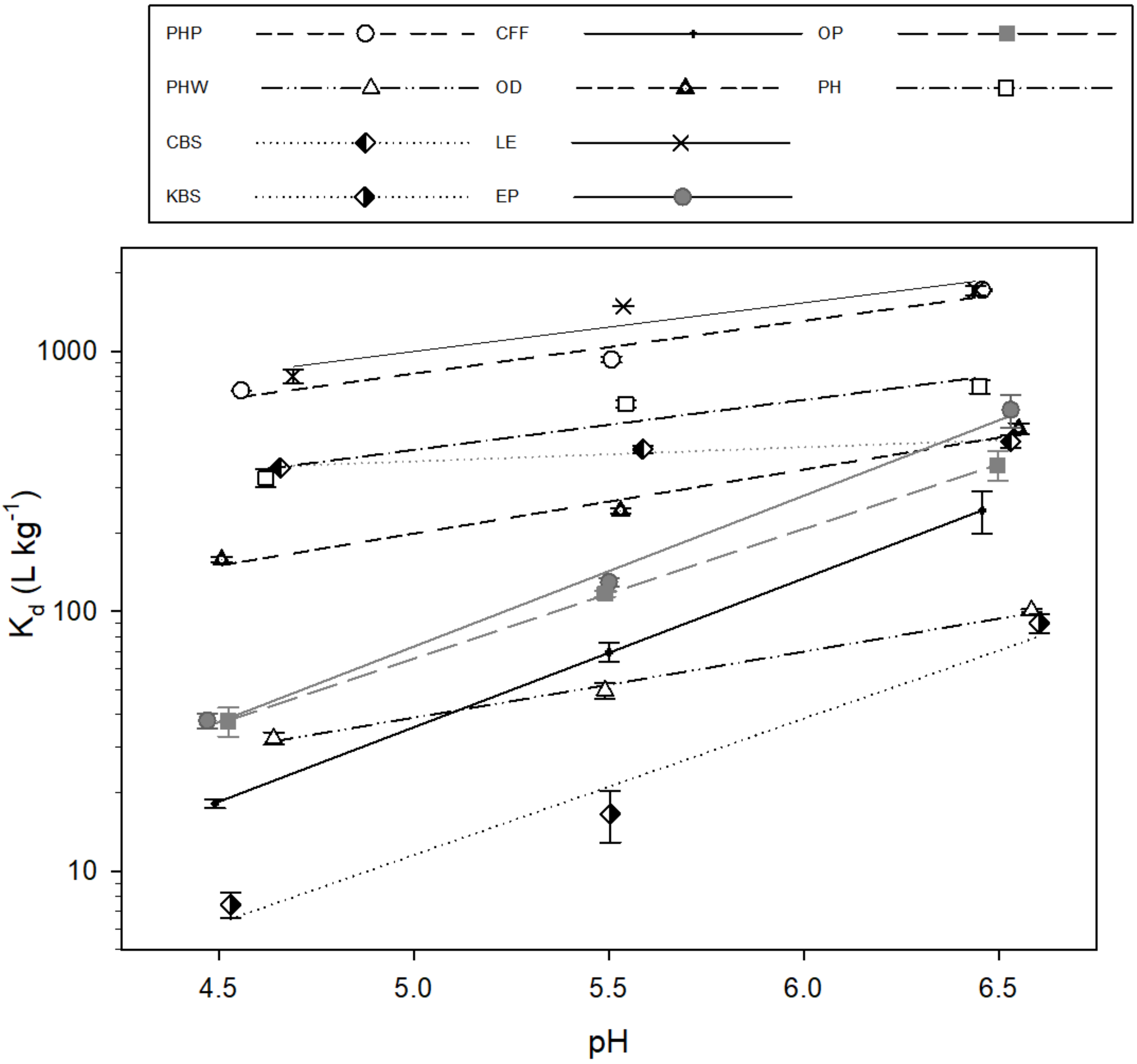


Figure 3.1: Sorption of Cd at three different pHs by the organic substrate considered. The error bar shows standard deviation (n=3).

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 ($p<0.05$) (Figure 3.2). Simmler et al. (2013) suggested that reduced organic sulphur containing functional groups (soft Lewis bases) in lignite enable it to bind Cd (a soft Lewis acid) effectively. Al Mamun et al. (2016) subsequently proposed that these functional groups may also be important in allowing composts to reduce the plant bioavailability of Cd, however they also observed that the bioavailability of Zn in the compost-amended soils may also be important. The stronger binding of Cd over Zn and Ni (intermediate Lewis acids) seen here provides further support for both these 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 (Figure 3.2, Table 3.2).

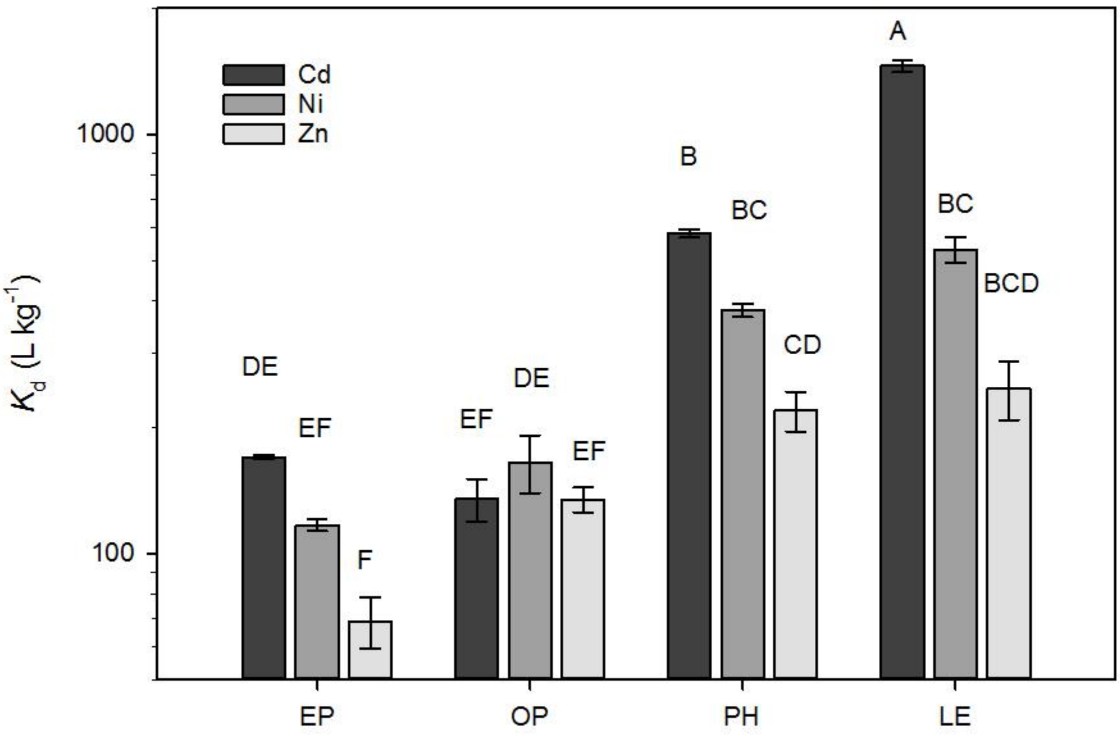


Figure 3.2: Average K_d of Cd, Ni and Zn at pH 5.5 in two types of peat (OP and EP) and two compost (PH and LE) The error bars show standard error of the mean, different letters indicate differences between the means ($p<0.05$, n=3, except $K_{d,Ni}$ for LE where n=2).

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 substrates. 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 an indicator of the labile fraction of the organic carbon in soils (von Lützow et al., 2007). Out of the substrates considered here, the HWEC fraction of CBS was over twice as high as the next highest (PH) (Table 3.1) 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 (~400 L kg^{-1} at pH 5.5, Figure 3.1) compared to most other substrates 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 M $Ca(NO_3)_2$ and the chemical characteristics of that DOM.

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

Geochemical modelling of the extracted solutions using WHAM suggested that over 99.4% of the total Cd, Ni and Zn was complexed by the DOM in all of the respective extracts (Table 3.2). This is considerably higher than seen in previous work when the WHAM model has been used to estimate trace metal speciation in soil extracts (Cornu et al., 2011; Ren et al., 2015b; Tipping et al., 2003). This is almost certainly due to the low metal:DOC ratios in the extracts, driven mainly by the large amount of DOM extracted from the organic substrates. 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 et al., 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 (Custos et al., 2014; Degryse et al., 2006) and organisms native to sediments (Amirbahman et al., 2013), and natural water (Buffle et al., 2009; Jansen et al., 2002; Shaked et al., 2012). These conditions are often identified when equilibrium-based methods fail to predict biological uptake (Zhao et al., 2016).

Table 3.2: 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 (L g-1 cm-1)
Cd	NTA	-	-	10.51	5.49	1.537 (±0.005)	5	2.38	99.6	nd
	EDTA	-	-	10.06	5.59	1.362 (±0.004)	5	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)	9.5	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	0.03	>99.9	nd
	EDTA	-	-	10.4	5.62	1.185 (±0.009)	5	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	0.29	99.5	nd
	EDTA	-	-	10.1	5.53	1.152 (±0.002)	5	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)

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 (Figure 3.3) (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 (Levy et al., 2012; Warnken et al., 2007). Cadmium was relatively labile in the OP extracts, however significantly less so in the EP and compost extracts, especially LE. This could indicate 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 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.

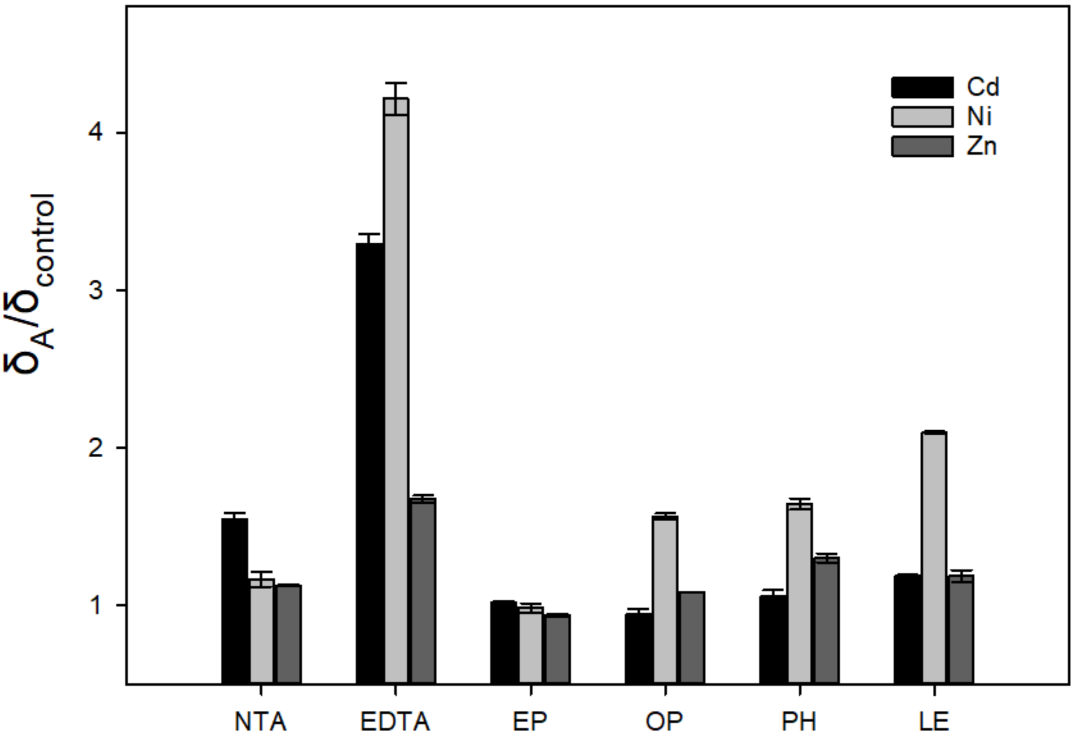


Figure 3.3: The relative kinetic limitation of Cd, Ni and Zn in the extracted spiked 0.05 M $Ca(NO_3)_2$ solutions from the four organic substrates and two model ligands, NTA and EDTA. The error bars show standard error (*n* = 3).

3.3.3 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 (Appendix B, Figure B.1) (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 (Baker et al., 2008; Luster et al., 1996; Ohno et al., 2008) and biodegradability (Hansen et al., 2016; Hudson et al., 2008).

The Peak T fluorophore indicates the proportion of bioavailable organic matter (Marschner et al., 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 (Figure 3.4b), 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 substrates 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 (Figure 3.4a) 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 3.2). Shafaei-Arvajeh 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.

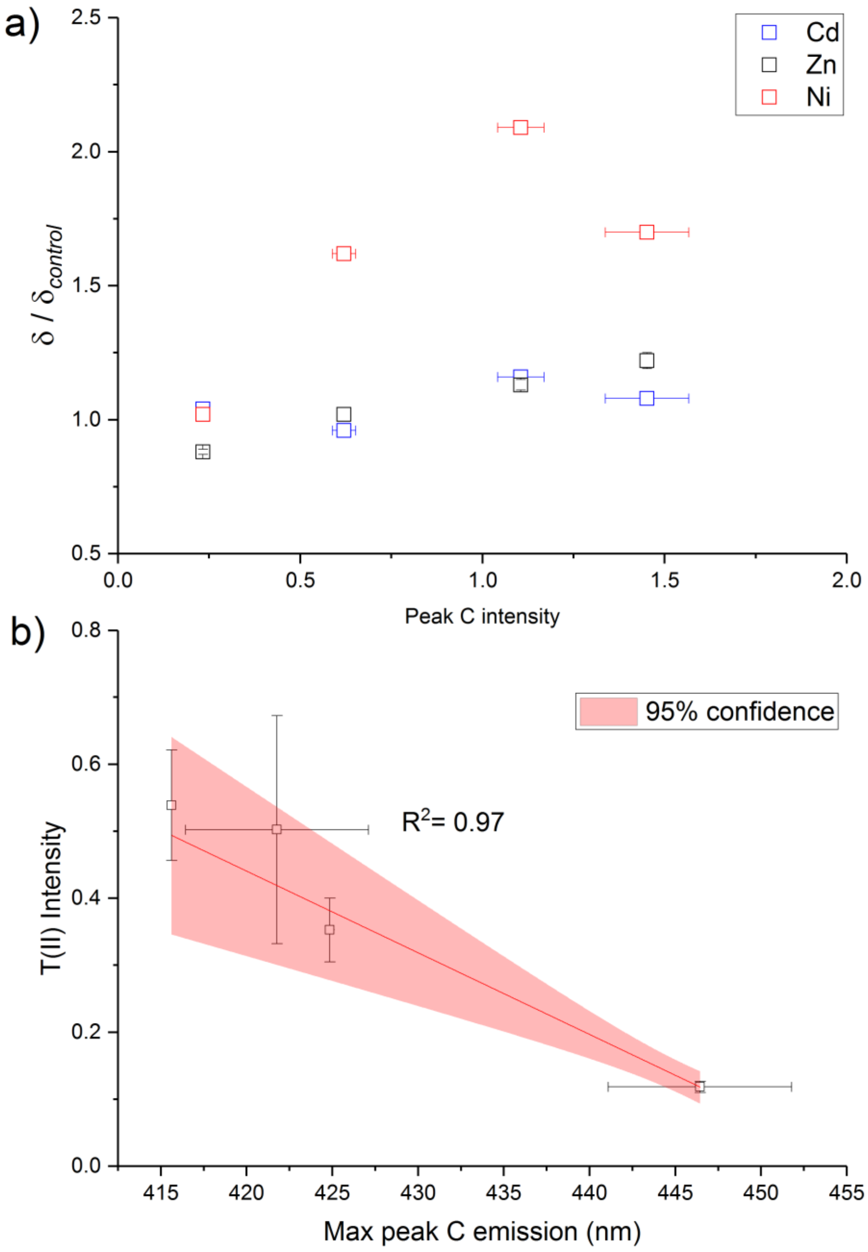


Figure 3.4: The relationship between the relative kinetic restriction of DOM-metal complexes ($\delta/\delta_{control}$) and DOM aromaticity (Peak C Raman-normalised intensity) (a); and (b) negative correlation between DOM amino-acid fluorescence (peak T2; inferred biodegradability) and DOM aromaticity (emission wavelength of maximum Peak C fluorescence intensity).

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 it enables the analysis of trace metal complexes under circumstances where extensive dilution of sample 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. Herein the metal:DOC ratios were normalized to be the same across the different metals-organic substrate combinations after the extraction solutions had equilibrated with the organic substrates considered. This was done 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 (Guthrie et al., 2003; Sekaly et al., 1999). 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 $Ca(NO_3)_2$ can provide a good estimate of plant bioavailable fraction of soil Cd (Black et al., 2011, 2012; Gray et al., 1999; 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 organic substrates 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.

3.4 Conclusions

Although various studies have reported the benefits of using composts for reducing Cd uptake by plants, the results here suggest that there may be an associated risk of Cd being transported from the location of the contamination. The risk of metal transport will probably be greater if compost was used to try managing Ni availability to plants, owing to its apparently greater affinity for DOM with a high aromaticity. While it should be recognized that this work only considered four types of organic substrate, 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 is likely to be an important factor.

Chapter 4

Soil cadmium mobilisation by organic matter amendments at different pHs

4.1 Introduction

Cadmium (Cd) accumulation in edible parts of plants can cause adverse health effects to humans and animals (Chen et al., 2018a; European Food Safety, 2012; Zang et al., 2019), with Cd accumulation in plants growing in contaminated soil well documented (Kabata-Pendias, 2007; Rizwan et al., 2017; Shahid et al., 2017). Plant uptake of Cd is governed by a combination of plant factors and soil Cd availability to plants. The latter can be reduced by various inorganic (e.g. lime and hydroxyapatite) and organic (e.g. compost, peat, and lignite) amendments (Al Mamun et al., 2016; Al Mamun et al., 2017; Bolan et al., 2014; Bolan et al., 2003b). In addition to enhancing soil properties (e.g. water holding capacity, cation exchange capacity) (Głąb et al., 2018) and providing essential plant nutrients (Al Mamun et al., 2017; Khan et al., 2007), amendments rich in organic matter (OM) are feasible and cost-effective in remediating soil to reduce available Cd (Al Mamun et al., 2016). The ability of OM amendments to retain Cd in soil depends on the properties of the amendment (Liu et al., 2019; Welikala et al., 2018) as well as the soil it is amended to (Al Mamun et al., 2016). However, chemical detail is lacking on how OM amendments affect the availability of Cd in soils for uptake by plant or transport to the surrounding environment (Bolan et al., 2014; Houben et al., 2013; Shuman, 1998). Hence knowing this may inform better application of OM amendments to prevent plant Cd uptake while avoiding soil Cd mobilisation.

Organic matter amendments may enhance the dissolved organic matter (DOM) concentration in the soil either by acting as a source of DOM or by promoting solubilisation of soil OM (Hernandez-Soriano et al., 2013; Kalbitz et al., 2000). Dissolved organic matter (DOM) is an important vector for transport of trace metals in the soil and surrounding environment (Amery et al., 2008; Welikala et al., 2018; Zhang et al., 2020). Solubility of OM and the mobility of DOM are affected by physical and chemical properties of soil (texture, pH, metal oxides) (Ghani et al., 2010; Gray et al., 2016; Kalbitz et al., 2000), characteristics of the amendment (maturity, organic components, pH) (Liu et al., 2019; Tapia et al., 2010), and climate variables (temperature and moisture) (Kalbitz et al., 2000). While the ability of various OM amendments to immobilise soil Cd is known, little is known on how these amendments may mobilise soil Cd via the supplied DOM as Cd-DOM complexes.

Mobilisation of soil Cd as Cd-DOM complexes to the surrounding soil environment is likely to controlled partly by the kinetics of Cd-DOM complex dissociation and the resistivity of DOM to biodegradation

(Liu et al., 2019; Welikala et al., 2018), which depends on the quality of the DOM. The quality (e.g. humification degree, aromaticity, resistance for biodegradation) of DOM released from OM amendments may depend on the parent OM's source, maturity and composition of various dissolved organic compounds (Guo et al., 2019; Huang et al., 2016).

Dissolved organic matter is a heterogeneous mixture organic molecules (e.g. humic-like, protein, lignin, polysaccharides), with various functional groups (e.g. carboxylic, phenolic, amino and reduced sulphur groups) that can show different affinities for complexing Cd (Bai et al., 2018; Karlsson et al., 2007; Kaschl et al., 2002a; Laborda et al., 2009). These organic molecules in DOM are often fractionated depending on their molecular weight, polarity (hydrophobic and hydrophilic), acidity (acidic, basic, and neutral) and humic or non-humic characteristics. Cadmium has been found associated with these fractions of DOM up to different extent of depending on the provenance of DOM (e.g. soil solution, surface and groundwater, compost extracts) (Bai et al., 2018; Kozyatnyk et al., 2016; Laborda et al., 2008; Ren et al., 2015b). In general, Cd has shown a strong affinity for high molecular weight (Mw) humic-like compounds (Bai et al., 2018; Kaschl et al., 2002a), which are numerous in colloidal DOM derived from aged OM (e.g. compost and peat) that are used as soil amendments (Laborda et al., 2008; Laborda et al., 2009). Further, the DOM emerging from aged OM are known to be less susceptible to biodegradation (Kalbitz et al., 2003), thus Cd associated with this DOM may persist in soil for a longer period. It follows that these substances may be important for Cd mobilisation in soil.

The study of dissociation kinetics for Cd-DOM complexes is difficult due to the heterogeneity of DOM. Much previous work focused on the complexation of Cd by various DOM fractions in soil, surface water or compost extracts in isolation (Bai et al., 2018; Kaschl et al., 2002b; Laborda et al., 2009; Ren et al., 2015b). Studies on the mobility and kinetic limitation of Cd released from soils amended with OM, however, are scarce.

Thus, this work aimed to investigate whether the type of OM amendment influences the extent of Cd mobilisation from distinct soils at different pHs, and the role of quality of DOM in determining this mobilisation. To fulfil the research objectives, short-term column leaching experiment was carried out with three different soils amended with compost and peat separately at three pHs ranging from 5.5 to 7.5.

4.2 Materials and methods

4.2.1 Sample collection and preparation

Soil from three New Zealand soil orders (as defined by (Hewitt, 2010)) with distinct properties were collected during January 2018 from New Zealand's South Island. 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), and the 'Waikari' soil is a Rhendzic Mellanic soil, collected from Waikari (42° 58′ 2″ S, 172° 38′ 22″ E). Soil from the respective top horizons (<0.25 m depth) was collected and the large stones and roots were removed manually. All soils were passed through a 2 mm nylon mesh. Subsamples of each soil were air-dried for characterisation. Cadmium was added as $Cd(NO_3)_2$ solution to increase the total Cd concentration by 2 mg Cd kg^{-1} (oven-dry basis). The soil moisture content of each soil was then 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 and the 0.05 M $Ca(NO_3)_2$ extractable Cd (see section 4.2.3 for method description) (Appendix C, Figure C.1).

Commercially produced compost and naturally formed peat were used as organic matter (OM) amendments. The compost was made from municipal green waste by Living Earth Ltd, Christchurch. The peat was sampled from a formation near Lincoln, New Zealand (43° 40′ 37″ S, 172° 26′ 52″ E). Both amendments were sieved through a 2 mm nylon mesh and air-dried. Subsets of each of the three Cd-spiked soils were treated with a combination of one of three organic matter treatments and three lime ($CaCO_3$, Sigma-Aldrich) rates. The OM treatment was either compost or peat applied at a rate of 2.5% (total organic carbon (TOC), wt/soil wt air-dried mass basis), while another subset of soil was left unamended as controls. Subsets of the three treated soils were then limed to achieve a final pH of 5.5, 6.5 or 7.5 (± 0.2 pH units). The moisture content in all soils was then adjusted to 60% of FC and incubated at 25 °C for 12 weeks.

4.2.2 Soil and organic matter amendments analysis

Soil pH (Mettler Toledo Seven Easy pH meter) was measured at a 1:2.5, soil: water ratio (1:5 for OM amendments) and conductivity (Mettler Toledo Five Easy) was measured at a 1:5 soil: water ratio (Blakemore, 1987). Total C and N were determined using an Elementar Vario MAX CN element analyser. Total organic carbon in the soil and amendments was analysed by pre-digesting inorganic carbon with 0.5-0.8 mL of 3% HCl prior to total C measurement. Samples were digested for pseudo-total element content analysis using CEM MARS XPRESS microwave (CEM Corporation, USA) as described in Kovács et al. (2000). Cation exchange capacity (CEC) of the soils and OM amendments was measured using the silver thiourea (AgTu) method as described by Blakemore (1987) (results are shown in Table 4.1).

4.2.3 0.05 M $Ca(NO_3)_2$ extractable cadmium

After six weeks of incubation following the OM and lime treatment (15 weeks after spiking), soil pHs had reached 5.7, 6.5 and 7.5 (±0.2) (Appendix C, Figure C.2). These soils were sampled and tested for

0.05 M $Ca(NO_3)_2$ extractable Cd using the method reported by Gray et al. (1999). Briefly, 5.00 g of soil was mixed with 30 mL of 0.05 M $Ca(NO_3)_2$ (Sigma-Aldrich) solution and equilibrated in an end-over-end shaker for two 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 ^{o}C prior to analysis for extracted trace metals and other elements.

Table 4.1: Chemical properties and element concentrations of soils and organic matter amendments.

	Craigieburn	Templeton	Waikari	Compost	Peat
clay/silt/sand%	10/50/40	4/22/74	7/36/57	nd	nd
pH (H_2O)	5.62	5.51	6.05	6.49	4.69
Conductivity (µS cm^{-1})	23.5(0.2)*	41.7(0.2)*	48.6(0.3)*	5347(24)*	560(12)*
CEC $_{AgTU^+}$ (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)	2,996(84)	1,635(27)
S (mg kg^{-1})	281(5)	225(3)	398(28)	2,579(11)	3,765(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})†	<0.001ŧ	<0.001ŧ	<0.001ŧ	0.5(0.003)	0.34(0.007)
Cd (mg kg^{-1}) Ŧ	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). ŧ below the detection limit. nd= not determined. † Pseudo-total Cd concentration in unspiked soil and organic amendment. Ŧ Total Cd concentration in Cd-spiked soil. CEC is the cation exchange capacity and BS is the base saturation.

4.2.4 Column leaching

After a further six weeks of incubation, soil pHs had stabilised at 5.4(±0.3), 6.3(±0.2) and 7.3(±0.1). These soils were packed into cylindrical PVC leaching columns to a height of 50 mm (internal Φ of 44 mm) and to a uniform bulk density of 1 g cm^{-3}. The bottom of each column was underlain 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 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 pore water volumes was collected at the bottom of the column. The leachates were collected into acid-cleaned containers in ice baths (<4 °C) to minimize microbial activity. Samples were filtered through 0.45 µm syringe filters (Phenex, cellulose acetate, Φ of 25 mm) and divided into subsamples within 12 h of the end of leachate collection. The filtered leachates were analysed for pH and conductivity, total dissolved elements, total organic (DOC), inorganic carbon (DIC) and dissolved anions. Cadmium in these samples will be forthwith referred to as 'mobilised Cd'. Filtered subsamples were also allocated for organic matter quality indices analysis, small volume diffusive gradient in thin-films (SV-DGT) analysis, and ultrafiltration (see below). Subsamples for dissolved element analysis were preserved by acidifying with high purity 1 M HNO_3 (pH < 2) (PrimarPlus-Trace Analysis grade, Fisher Scientific UK) and DIC samples were preserved with saturated mercuric chloride (0.02% V/V; $HgCl_2$, BDH, laboratory reagent). All the samples were stored at -20 ^{o}C for <4 weeks before analysis, except for samples allocated to the analysis of organic matter quality indices, these were stored at -80 ^{o}C for 2 months.

4.2.5 Ultrafiltration

The <5 kDa size fraction of Cd in the leachates of OM amended and unamended soils at pHs 5.4 and 6.3 were fractionated using a 200 mL polycarbonate stirred cell (Amicon® stirred cell, Merck Millipore) where, 50 mL of leachate was filtered through 5 kDa regenerated cellulose membrane (Φ of 63.5 mm, Merck Millipore). The pressure of N_2 (oxygen-free) was set at 250 kPa to get a continuous flow rate. The filtrate was then acidified to pH<2 with high purity 1M HNO_3 for subsequent Cd analysis.

4.2.6 Dissolved organic matter analyses

The DOC concentration in the leachates was measured using a TOC analyser (Vario TOC-cube, Elementar, Australia Pvt Ltd). UV-VIS spectrophotometry (UVmini, SHIMADZU) was used to elucidate certain qualitative characteristics of DOM: specific absorbance measured at 254 nm ($SUVA_{254}$) was used to estimate the aromaticity of the DOM (Weishaar et al., 2003), while the ratio of absorbance measured at 465 and 665 nm (E_4/E_6) was considered to reflect the degree of aromatic condensation of the substance in the DOM (Kleber et al., 2010). The ratio of the absorbance measured at 254 and 365 (A_{254}/A_{365}) 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 normalized using ultra-pure water Raman peak intensity (350 nm excitation, 398 nm emission) at the same analytical setting as the samples. Parallel factor analysis (PARAFAC) was carried out to distinguish the statistically independent fluorescence components within the EEM data set and their relative contribution to the total EEM of the sample (Fellman et al., 2010). PARAFAC analysis was carried out in MATLAB using N-way toolbox and DOMFlour toolbox for MATLAB (Stedmon et al., 2008). The two-component model was adopted based on the minimum residual sum of squares and maximum model core consistency. Common DOM quality indices (Fluorescence index, Humification index, and Biological index) were calculated for DOM leached using the EEMs (Gao et al., 2017; Parlanti et al., 2000; Wilson et al., 2009).

The fraction of humic acid (HA) in the leachate was determined using the method described by (Van Zomeren et al., 2007). Briefly, 30 mL of leachate was acidified to pH<1 with 6 M HCl (AnalaR NORMAPUR, BDH chemicals) and centrifuged at 2000 rpm for 10 min. The supernatant was carefully extracted and analysed for DOC, with the proportion of DOC as HA in the leachates being the difference in concentration between the initial non-acidified and the acidified leachate.

4.2.7 Kinetic limitation measurement

The kinetic limitation of Cd leached from the OM amended and unamended soils at pH 5.4 and 6.3 were evaluated using an adapted diffusive gradient in thin-films (DGT) method, small volume-DGT (SV-DGT). The operating principles and preparation of SV-DGT vials are described elsewhere (Welikala et al., 2018). Briefly, an approximately 2.2 mm thick 'binding layer' consisting of 1 g of cation binding resin (Chelex 100, 200-400 mesh, Bio-Rad), embedded in 1.5% agarose (Total Lab System, molecular grade) was cast in a bottom of pre acid cleaned 30 mL polycarbonate sample vial (Φ of 24 mm) by pipetting 1 mL of Chelex-agarose mixture. A *ca.* 3 mm thick agarose 'diffusive gel layer' was cast on top of the cation binding resin by pipetting 1.36 mL of agarose gel. The gels were then allowed to settle for 1 h and rinsed with high purity water by agitating side-to-side for 24 h, during which water was changed three times. The gels were conditioned and stored in 0.01 M $NaNO_3$ (trace metal free $NaNO_3$, Sigma-Aldrich) prior to deployment. The control solution was 0.077 µM Cd ($Cd(NO_3)_2.4H_2O$, BDH, AnalaR), where Cd is thought to exist as a fully labile species. The electrical conductivity of all samples was normalized to 2 mS cm^{-1} by adjusting with 0.1 M $NaNO_3$ (trace metal free $NaNO_3$, Sigma-Aldrich). The samples and control solutions (10.00 mL) were pipetted into respective SV-DGT vials and gently agitated side-to-side for 24 h. The solutions were then removed and acidified with 1 M HNO_3 for dissolved Cd analysis. The concentration of the solute remaining in the SV-DGT vial after 24 h can be expressed with equation 4.1.

$$C_{24h} = C_0 e^{\left[-\frac{D^{DL} \times A}{(\delta_{DBL} + \delta_{DL}) V_{SOL}} t\right]} \tag{4.1}$$

where, C_0 and C_{24h} are the experimentally determined concentrations of solute being tested before and after 24 h deployment, respectively. The other variables, A (cross-sectional area of the SV-DGT vial) and V_{sol} (volume of the test solution) are defined by the geometry of the deployment vessel, while D^{DL} is the diffusion coefficient of solute in the diffusive layer, and δ_{DL} and δ_{DBL} are lengths of the diffusive pathways through the diffusive layer and diffusive boundary layer, respectively. The diffusive flux of metal into the underlying resin layer is regulated by; (1) the length of the diffusive pathway in the vessel, that is, the combined thickness of material diffusion layer and the diffusive boundary layer and (2) the extent of which metal complexes dissociated during the deployment limits the flux of metal to the binding layer. The cumulative limitation from these factors is determined by solving equation 4.1 for the thickness of the apparent diffusion layer (δ_{ADL}) which is the sum of the δ_{DL} and δ_{DBL} for the solution being tested. The dissociation rates of Cd-DOM complexes in the test solution can be compared by calculating the ratio of $\delta_{ADL,T}$ to $\delta_{ADL,C}$ in the control sample, where only the diffusion is thought to limit the uptake of Cd by the binding layer (Welikala et al., 2018). Here, this ratio ($\delta_{ADL,T}$/ $\delta_{ADL,C}$) will be referred to as 'relative kinetic limitation' and serve as a semi-quantitative indicator of the extent to which Cd^{2+} ion may be released from Cd-DOM complexes in each test solution.

4.2.8 Cation and anion analysis

The concentration of Cd in 0.05 M $Ca(NO_3)_2$ extracts and elemental concentrations in acid digests were analysed using Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES; Varian 720 ES – USA). The leachates were analysed for cations (Ca, Mg, Na, K, Zn, Cu, Cd, Ni) and anions (Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) using ICP- Mass Spectrometry (ICP-MS, Agilent 7500cx, USA) and 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. Accuracy and precision of the analytical measurements were assessed by analysing standard reference materials (SRM) along with the samples. For the measurements done by ICP-MS, the SRM was 1643f, synthetic water from National Institute of standards and technology (NSIT). The concentrations in the SRM ranged between 91-100% of the expected values. For the anions SRM was WPB 1903-1, in which the concentrations were 98-106% of the expected values. All sample treatments and dilutions used high purity water (18.2 MΩ resistivity; Heal Force® SMART Series Ultra-pure water system, Model-PWUV), acid (HNO_3, PrimarPlus-Trace Analysis grade, Fisher Scientific UK) and reagents. All the equipment used to handle, contain, and/or analyse samples were thoroughly acid-washed before analysis. Blank extracts, filtrates, and solutions were analysed regularly to confirm low contamination levels.

4.2.9 Speciation modelling

The speciation of Cd in leachates collected from OM amended and unamended soils at pH 5.4 and 6.3 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 (FA) (Laborda et al., 2009; Ren et al., 2015b) and the measured HA concentration for each leachate was used for speciation modelling.

4.2.10 Statistical analysis

Data analysis and visualization were carried out using the R software (R core Team, 2018) and Minitab 18®(Mintab ® 18.1, Minitab, Inc.). Significant differences were tested by ANOVA with Tukey post-hoc at the 0.05 confidence level unless stated otherwise. Linear models were fitted to understand the statistical significance of the soil order, type of amendment 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 (*r*) at the 0.05 level of significance using Minitab 18®.

Note that, for simplicity, the pH of the soils are categorised to three groups as 5.6 (5.4-5.7), 6.4 (6.3-6.5) and 7.4 (7.3-7.5), corresponding to the median value of soil pH at the time they were extracted with $Ca(NO_3)_2$ and leached.

4.3 Results and discussion

4.3.1 Cadmium mobilisation from compost and peat amended soils at different pHs

In the unamended soils, at pH 5.6, 9.3, 12.2, and 7.5 µg kg^{-1} Cd was mobilised from Craigieburn, Templeton, and Waikari, respectively (Figure 4.1). Amending soil with compost significantly reduced the mobilisation of Cd by 17-70% in all three soils, while peat only reduced the mobilisation of Cd in Craigieburn and Templeton soils by 17% and 2% respectively (Figure 4.1). Note that, mobilised Cd here represents the initial concentration of Cd species in the soil solution and the Cd released from labile solid species into soil solution during leaching. Therefore, the trends shown by each OM and lime treated soil for Cd mobilisation reflects a combination of lability and mobility of Cd species supplied to soil solution.

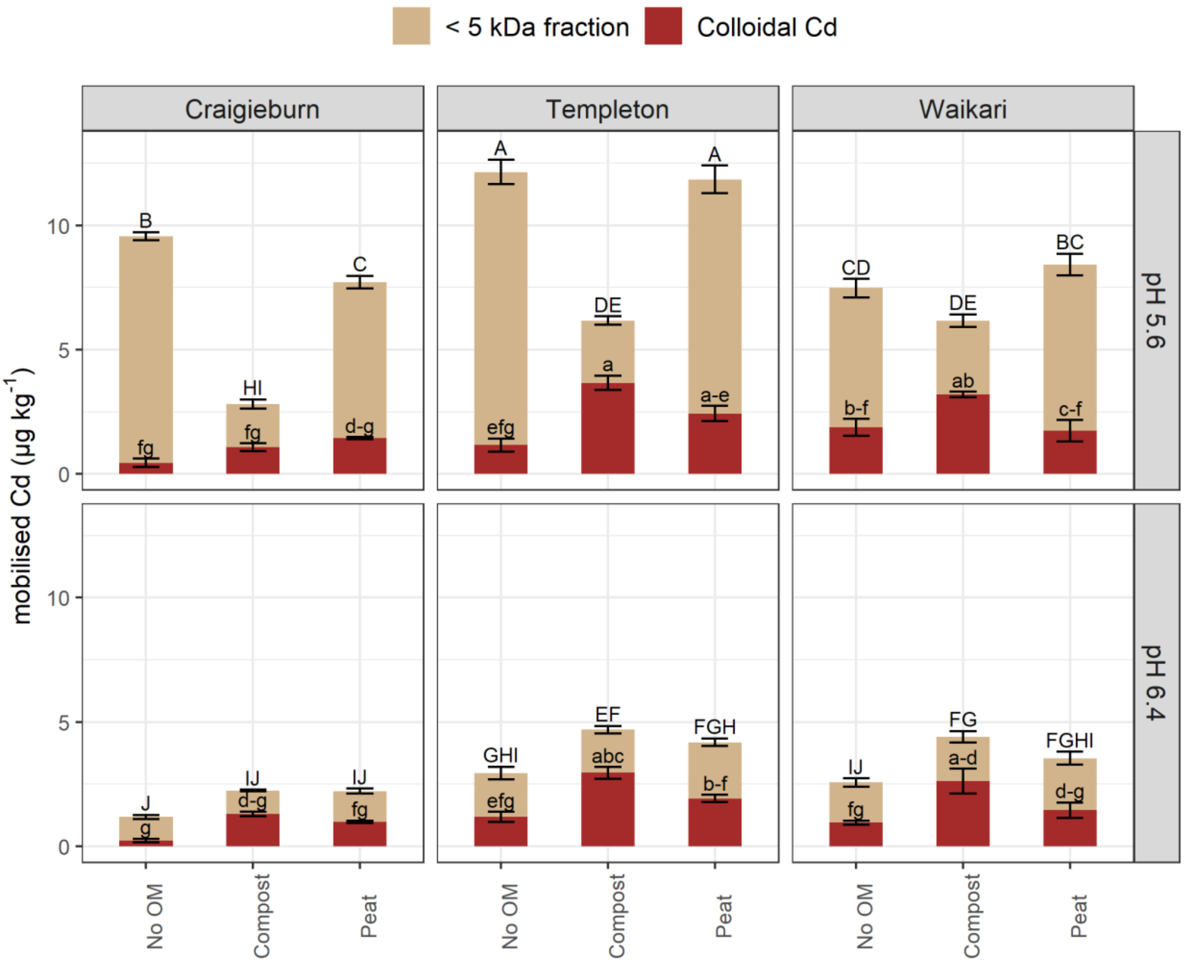


Figure 4.1: Cadmium mobilised during column experiments, expressed as the mass of Cd mobilised relative to the mass of soil. Error bars represent the standard error of the mean (n=3). The uppercase letters indicate the significant difference in the total dissolved Cd and lowercase letters indicates the significant differences for colloidal Cd only. The values sharing the same letter are not significantly different.

In the Craigieburn and Templeton soils, $Ca(NO_3)_2$ extract data (Figure 4.2) suggests an increased Cd binding capacity by both compost and peat at pH 5.6, which agrees with the reduced mobilisation. However, this relationship does not hold for the Waikari soil, where neither peat (*p*=0.69) nor compost (*p*=0.18) reduce Cd mobilisation despite the significant reduction in extractable Cd. At the lowest pH, both OM amendments were more effective in reducing $Ca(NO_3)_2$ extractable Cd (herein extractable Cd) than in reducing Cd mobilisation, the effect of compost was greater than that of peat. Compost reduced extractable Cd by 94% in both the Craigieburn and Templeton soils and by 87% in Waikari soil, whereas peat reduced the extractable Cd by 64%, 53% and 32% in Craigieburn, Templeton and Waikari soils, respectively. The $Ca(NO_3)_2$ extracts the Cd exchangeably bound to soil solid surface, which is most labile to release to soil solution, when soil solution Cd is depleted in a non-equilibrium system (Hooda, 2010). Other studies have shown that OM-rich amendments have the capability for binding Cd to the solid surface, thus reducing extractable Cd (Al Mamun et al., 2016; Al Mamun et al., 2017; Simmler et al., 2013), and so labile solid Cd pool. Overall, there was a significant positive correlation (*r*=0.61, *p*=1.06 X 10^{-6}) between the extractable and mobilised Cd. However, it was also noted that while Cd mobilisation was significantly positively correlated with the extractable Cd at low pH (*r*=0.74, *p*=8.6 X 10^{-6}) the relationship was weak at elevated pH (*r*=-0.32, *p*=0.105). This implies that despite the enhanced capability of soil solid surfaces to bind Cd at high pH, mobilisation of Cd is also plausible at elevated pHs. This was attributed to the OM dissolution at high pHs (Figure 4.3, see section 4.3.2 for detailed explanation).

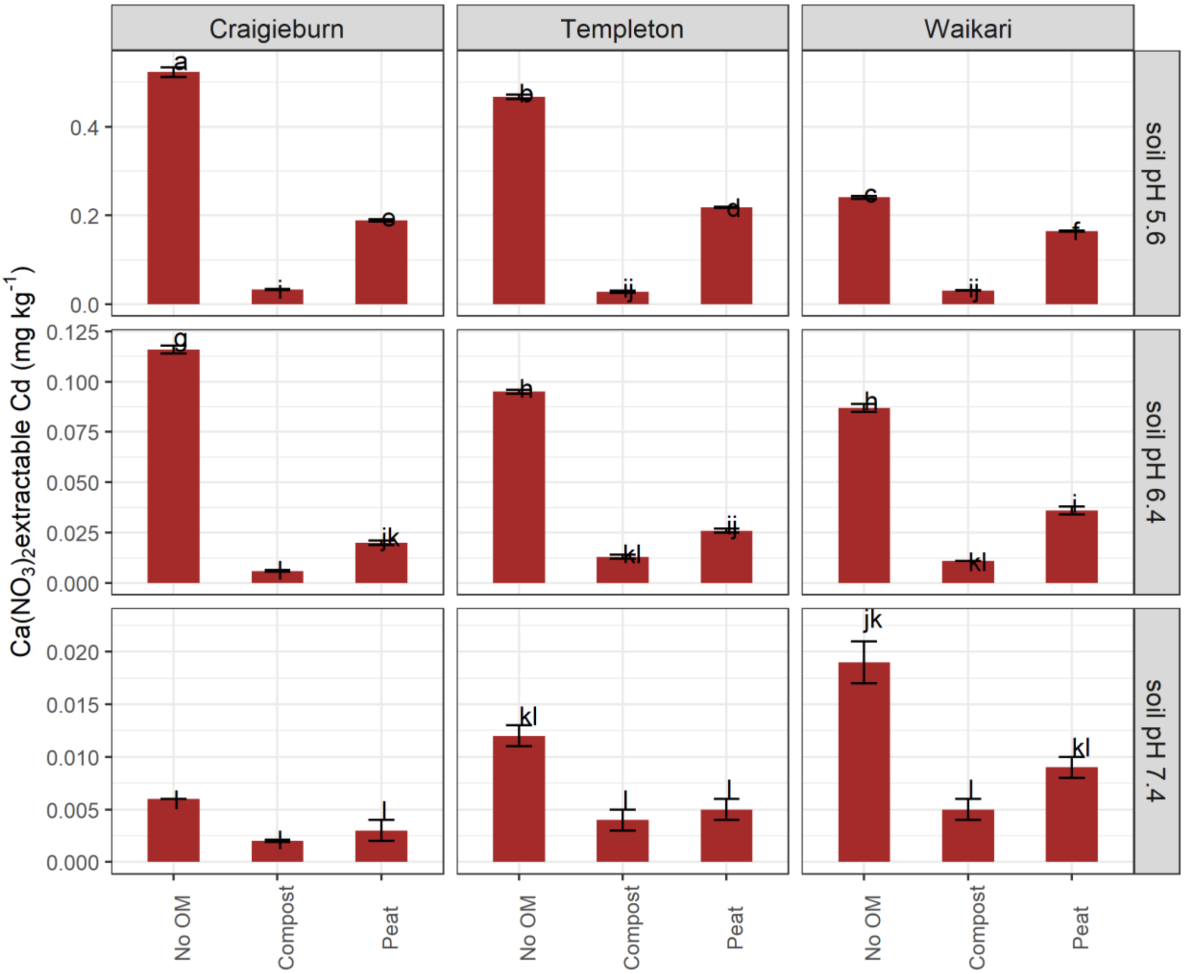


Figure 4.2: Soil Cd extracted with 0.05 M $Ca(NO_3)_2$. Error bars represent the standard error of the mean (n=3). The values that share the same letter are not significantly different (p>0.05). Note the differences in y-axis scales between soils. The values sharing the same letter are not significantly different.

The range of extractable Cd in compost treated soils at pH 6.4 (0.006-0.01 mg kg^{-1}) is similar to those reported by Al Mamun et al. (2017) from composts of varying provenance at pH between 6.0-6.4 (0.001-0.009 mg kg^{-1}), which reduced extractable soil Cd by 18% to 100%. Welikala et al. (2018) showed that peat might be less effective for retaining Cd, which is reflected here by its lower capacity for binding soil Cd than composts when applied as a soil amendment. They suggested that this is because of the lower CEC of peat than the composts, which also explains the lower extractable Cd observed for peat than compost shown here.

On average increasing pH of all soils from 5.6 to 6.4 reduced Cd mobilisation by 76%, 24% and 65% in OM unamended, compost and peat amended soils respectively, while the extractable Cd was reduced by 74%, 67% and 85% respectively in the same treatments. The reduced Cd mobility and extractability in soils with pH agrees with the previous research (Gray et al., 1999; Loganathan et al., 2012; McBride et al., 1997). Across all three soils with or without the OM amendment, 56% of the variation in Cd mobilisation was explained by soil pH ($p<2.2 \times 10^{-16}$). Al Mamun et al. (2016) and Welikala et al. (2018) also tested the ability of OM amendments to bind Cd across a range of pH and showed that binding increased across pH 4.5 to 6.5. The decrease in mobile and extractable Cd in OM amended soils corroborates with Al Mamun et al. (2016) and Welikala et al. (2018) and can be attributed to the Cd binding to dissociated acidic functional groups in solid OM (Essington, 2004; Evans et al., 2003). However, the extractable and mobilised Cd from OM amended soils did not decrease significantly between pH 6.4 and 7.4, while both were significantly reduced in OM unamended soils (see Figure C.3, Appendix C for total Cd mobilised at pH 7.4). In OM amended soils dissolution OM is possible at elevated pHs (Curtin et al., 2016) which is confirmed by the greater DOC mobilised with pH (Figure 4.3). Therefore, these OM amendments may not be effective at retaining Cd at elevated pH and agrees with Simmler et al. (2013) who found that lignite was less effective in reducing the extractable Cd at pH higher than 7.

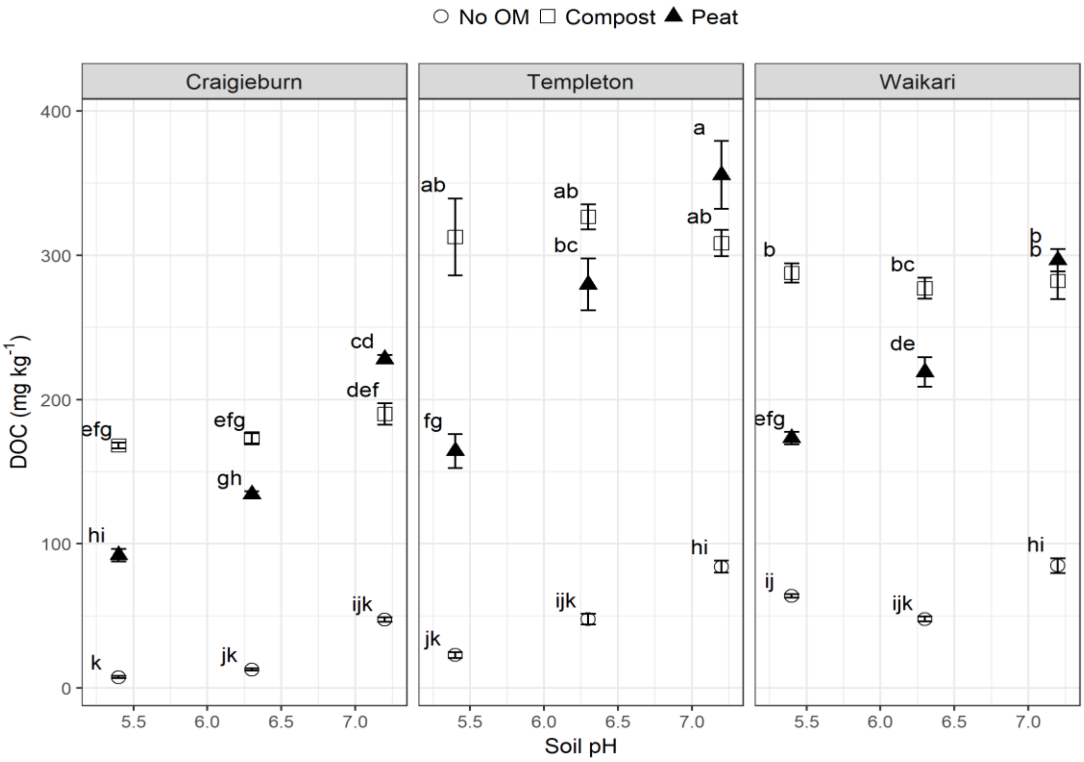


Figure 4.3: Dissolved organic carbon (DOC) mobilisation from OM amended and unamended soils at different pHs; expressed as the mass of DOC mobilised from the mass of soil or soil plus OM amendment (i.e. 76 g). Error bars represent the standard error of the mean (n=3). Values sharing the same letter are not significantly different (p>0.05). The values sharing the same letter are not significantly different.

Cadmium in OM amendments itself may be mobilised at elevated pH. There was a slightly higher amount of Cd mobilised from compost-amended soils at pH 6.4 than from the respective unamended soil across all soils. However, a comparison of extractable Cd from soils, OM amendments alone (Welikala et al., 2018) and soils treated with OM amendments showed that soil Cd is responsible for 99% and 100% of the extractable Cd from compost and peat amended soils respectively, across the pH 5.6-6.4. Therefore, mobilisation of OM-borne Cd was assumed to be not significant from the OM amendments used here (also, note that <5% of total Cd was added to soil from either amendment). Further, the Cu and Pb were enriched in both the compost and peat (Table 4.1) and may strongly bind to, and be mobilised with, DOM (Amery et al., 2007; Okkenhaug et al., 2018). The total Cu and Pb in the leachates were <1.5% and <0.2%, respectively, of the total of each metal added to the soil via OM amendment, thus justifying that OM-borne trace metals were not significantly mobilised at elevated pH in this study. Hence, the greater Cd mobilisation observed in OM amended soils at pH 6.4 suggests that the preferential binding of the soil Cd to the DOM (Naidu et al., 1998) in OM amended soils at elevated pHs (Figure 4.3).

The ANOVA analysis showed that soil order ($p<2.2 \times 10^{-16}$), type of the amendment ($p=3.95 \times 10^{-9}$) and the soil pH ($p<2.2 \times 10^{-16}$) had a statistically significant effect for the amount of Cd mobilised and the interactions between these three factors were also statistically significant (p=3.25$\times 10^{-6}$), implying the effect of OM amendment on Cd leaching was different for different soil order at different pHs tested here. This is consistent with the other studies (Khan et al., 2017; Mbarki et al., 2008). Notably, Cd mobilisation from the OM amended or unamended Templeton soil at pH 5.6 was significantly greater ($p\leq 6.3 \text{ X } 10^{-6}$) than that from the other two soils with the same treatment at the same pH; except for with compost amended Waikari soil (p=1.0) (Figure 4.1). Templeton soil has a more sandy texture than the other soils (Table 4.1), a feature that has been linked to high Cd leaching capacity (McLaughlin et al., 1996). Sandy soils have relatively less variable charge surface (OM and Fe, Mn, and Al-hydrous oxides), which displays greater Cd sorption capacity with greater pH (Gray et al., 2016; Gray et al., 2003a). The Craigieburn and Waikari soils had relatively higher amounts of Fe, Mn, and Al and TOC%, respectively than the Templeton soil (Table 4.1). This is reflected in the lower Cd mobility in the Templeton soil than in other two soils. Cation exchange capacities of the soils, which increased in the order of Craigieburn< Templeton< Waikari, negatively correlate with the extractable Cd from unamended soils at pHs 5.6 and 6.4 which decreased in the order of Craigieburn> Templeton> Waikari. Conversely, at pH 7.4, the greatest amount of Cd was extracted from the Waikari soil and the lowest from the Craigieburn soil. This may be because of the release of OM bound Cd due to dissolution of soil OM at elevated pH (Figure 4.3) (Andersson et al., 2001; Guggenberger et al., 1994): Waikari soil had the highest TOC% among the three soils (Table 4.1) and, consequently more Cd may have partitioned to organic species. However, despite the similar TOC% in the Craigieburn and Templeton soils, the lowest amount of mobilised Cd was observed in the OM amended Craigieburn soil. The Craigieburn soil is an allophanic soil, where allophane minerals are known to have strong sorption affinity for binding organic matter (Saggar et al., 1994; Yuan et al., 2000), and those organo-mineral complexes can enhance the metal sorption capacity (Arias et al., 2002; Latrille et al., 2003), thus explaining the lowest mobility of Cd resulted for Craigieburn soil across the pH range tested.

4.3.2 Mobile colloidal-cadmium and relation to quantity and quality of dissolved organic matter

Colloidal Cd highly correlated with mobilised DOC (r=0.77, p=1.74 X 10^{-11}) (Table 4.2) while Cd in <5kDa fractions did not (r=-0.12, p=0.40). The colloidal fraction may consist of high Mw humic acids as well as organo-minerals, which have shown a strong affinity for Cd binding (Chen et al., 2019; Kaschl et al., 2002a; Pokrovsky et al., 2005). In the Craigieburn, Templeton and Waikari soils that were not amended with OM, colloidal Cd was 5%, 9% and 25% of the dissolved Cd respectively at pH 5.6, and increased to 20%, 40% and 37% at pH 6.4. The lower amount of colloidal Cd mobilised from the Craigieburn soil at both pHs may be explained by the relatively small amount of mobilised DOC (Figure 4.3), and may due to the sorption of OM to allophane minerals as explained above. Sparling et al. (2016) and Ghani et al. (2010) have also reported that DOM leaching from Allophanic soils was less than other soil orders they studied. On average colloidal Cd was 50% and 20% of the dissolved Cd at pH 5.6 leached from compost and peat amended soils, respectively, and increased to 60% and 44% at pH 6.4 across all three soils. The positive relation between colloidal Cd and DOC also explains the higher proportion of colloidal Cd mobilised from the compost-amended soils than from the peat amended soils, where the amount of DOC mobilised was higher when compost was the amendment than peat at both pHs (Figure 4.3).

The amount of DOC mobilised here ranged from 0.4-8 mg DOC g^{-1} TOC which agrees with Vujinović et al. (2019) where they found about 1.5-5.5 mg DOC g^{-1} soil C mobilised from a laboratory leaching experiment with soils having comparable TOC amounts to the current study. It is noteworthy that, prior to leaching the soil with rainwater, the soil moisture was maintained at about 60-100% FC, meaning that soil columns used here were less likely to release additional DOM as influenced by the OM mineralisation resulting from a soil drying-rewetting event (Vujinović et al., 2019) other than the soluble DOM from each treatment. Therefore, Cd mobilised with colloidal DOM may be primarily due to dissolution of DOM.

The relatively greater amount of HA mobilised from OM amended soils than from the unamended soils (Table 4.2) agrees with previous studies, where the percentage of HA was greater in DOM from composts than in soils (Laborda et al., 2008; Laborda et al., 2009; Ren et al., 2015b). On average, across pH 5.6 and 6.4 the percentages of HA in the DOM mobilised from compost and peat amended soils were 20.5±5.2% and 24.1±5.7%, respectively, similar to compost extracts by Laborda et al. (2009). In OM unamended soils, HA percentages ranged between 0-31% across pH 5.6 and 6.4. The larger spread in HA percentage in these soils were because, DOM mobilised from unamended soils that had DOC concentration <10 mg L^{-1} resulted in large uncertainty in the percentage of HA, so, for those treatments, the concentration of HA was assumed to be zero. Overall, this indicates that more than 70% of the mobile DOM consisted of fulvic acid and/or non-humic substances released from either OM amended or unamended soils, which are also capable of complexing with Cd (Cornu et al., 2011; Kozyatnyk et al., 2016; Warnken et al., 2008).

Bai et al. (2018) showed that Cd has a higher affinity for binding by high Mw HA, which agrees with the correlation results where colloidal Cd had a positive correlation with the Mw of DOM (as determined by A_{254}/A_{365}, which inversely related to Mw of DOM) (Table 4.2). However, colloidal Cd had a significant negative correlation with the aromaticity of DOM ($SUVA_{254}$), suggesting that Cd binding ligands residing in non-aromatic structures in high Mw DOM may contribute to Cd binding. Welikala et al. (2018) also suggested Cd complexation to non-phenolic moieties in DOM while Chen et al. (2018b) proposed that reduced sulphide groups that reside in the non-aromatic structure of HA may play an important role in binding Cd.

The colloidal DOM may be formed through the polymerising or aggregating of small organic molecules, which can show more resistivity for biodegradation than the low Mw DOM (Kleber et al., 2010; Lehmann et al., 2015). Moreover, due to their higher Mw and stability, colloidal DOM, may not be labile for binding by soil solid mineral surfaces (Kleber et al., 2010), therefore, Cd associated with colloidal DOM may persist in the soil solution for longer time and have the potential to transport Cd in the surrounding environment.

In general, DOM from humified OM (e.g. peat) is likely to be more resistant for biodegradation than DOM from soil (Kalbitz et al., 2003). Likewise, the humification degree, of DOM mobilised from the compost and peat amended soils was greater than that from the unamended soils (Appendix C, Figure C.4). The OM produced from commercial composting can contains OM that is highly resistant for microbial degradation like recalcitrant OM in peat, whereas OM from the natural environment (soil) can be in various stages of decomposing (Guo et al., 2019; Kalbitz et al., 2000). Kalbitz et al. (2003) reported 8.6 and 2.3 years of half-life for stable DOM from humified OM (humified layer from *Spruce forest*) and agricultural soil, respectively, where the percentages of stable DOM were 94% and 75%, respectively, while half-life for labile DOM from both sources was <5 days. Thus, it can speculate that the DOM and hence the Cd associated with this DOM-released from compost or peat amended soils may persist in soils for long periods. However, further investigations on biodegradability of DOM from OM amended soils are recommended for estimating the longevity of Cd-DOM complexes in those soils.

The amount of colloidal Cd mobilised did not show a significant correlation with the soil pH (r=0.05, p=0.77), unlike the Cd in <5kDa fraction (r=-0.75, p=1.28 X 10^{-7}) (Table 4.2). With increasing pH, decreases in Cd in <5kDa fraction may be explained by the preferential sorption of free Cd^{2+} ions to the solid surface. Colloidal Cd remained unaffected by pH, likely since Cd would be specifically bound (inner-sphere complexation) to strong binding sites in these colloids. This is corroborated by the greater Cd mobilisation in OM amended soils than unamended soils at pH 6.4, where <5kDa Cd decreased with pH, while there was no significant change in the colloidal Cd (Figure 4.1). Furthermore, Figure 4.3 displayed that, for increasing pH, the OM in peat-amended soils was more susceptible to mobilising than the OM from compost-amended soil reflected by the relatively higher aromaticity (and thus the higher phenolic content) and low Mw of the DOM from peat-amended soils (Table 4.3).

Table 4.2: Spearman correlation matrix for the relationship among Cd mobilised, soil pH, kinetic limitation, and quantity and quality of DOM

	<5kDa Cd ($\mu g\ kg^{-1}$)	colloidal Cd ($\mu g\ kg^{-1}$)	soil pH	DOC ($mg\ kg^{-1}$)	C1/DOC	C2/DOC	$SUVA_{254}$	E_4/E_6	A_{254}/A_{366}
soil pH	-0.751***	0.053							
DOC ($mg\ kg^{-1}$)	-0.115	0.771***	0.434**						
C1/DOC	0.142	-0.413**	-0.455**	-0.468***					
C2/DOC	0.079	-0.448**	-0.382*	-0.43***	0.951***				
$SUVA_{254}$	0.166	-0.479***	-0.298.	-0.654***	0.922***	0.877***			
E_4/E_6	-0.522***	0.229	0.711***	0.61***	-0.366**	-0.271*	-0.398***		
A_{254}/A_{365}	0.069	-0.688***	0.157	-0.518***	0.178	0.246.	0.398***	-0.086	
kinetic limitation	-0.541***	-0.373*	0.502**	-0.006	-0.069	-0.03	-0.152	0.329*	0.122

p< 0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’. The C1/DOC and C2/DOC are the fluorescence intensities obtained for two fluorescence components (both resulted from humic-like compounds in DOM (Stedmon et al., 2005)) normalised to DOC concentration.

Table 4.3: WHAM VII speciation modelling results, and DOM quality indices via SUVA$_{254}$ and E$_4$/E$_6$. For, SUVA$_{254}$ and E$_4$/E$_6$, values are expressed as mean± standard error of the mean (n=3).

						WHAM speciation modelling results							
soil	amendment	soil pH group	leachate pH	Total [DOC] (mg C L^{-1})	[HA] (mg C L^{-1})	total dissolved Cd (µg L^{-1})	Cd bound by colloidal HA (%)	Cd bound by colloidal FA (%)	Cd bound by total DOM (%)	Cd^{2+}:DOC (M:M ×10^{-4})	SUVA$_{254}$ (L mg^{-1} m^{-1})	E$_4$/E$_6$	A$_{254}$/A$_{365}$
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

4.3.3 Kinetic limitation and speciation of cadmium in the leachates

The speciation modelling estimated that the total fraction of Cd bound by both HA and FA ranged between 4-21%, 30-62% and 32-77% in unamended, compost and peat amended soils respectively, across pH 5.6 to 6.4, with the fractions increasing with pH (Table 4.3). Therefore, at pH 6.4, mobilised Cd from each treated soil is expected to be more kinetically limited, since greater Cd-DOM complexes than at pH 5.4 (Welikala et al., 2018). The various Cd species percentages are in line with previous Cd speciation studies in soil solution (Cornu et al., 2011; Ren et al., 2015b). However, it is noteworthy that the variability in the fraction of Cd bound by DOM depends on the composition of HA and FA in DOM and the input variable (pH and concentration of other cations and anions) for the speciation model. The FA concentration was calculated assuming 25% DOM consisted of FA while measured concentration for HA was used. In general, for speciation modelling in WHAM VII, the active DOM involved in metal binding is considered as 65% of total DOM, which results in the active fraction of DOM (*F, F=active DOM/total DOC*) as 1.3 (Tipping et al., 2011). Various authors have emphasised the importance of actual *F* value for modelling the speciation of trace metal in soil solution and natural waters (Chen et al., 2018b; Djae et al., 2017; Groenenberg et al., 2010), which are both metal and DOM specific. Chen et al. (2018b) reported an optimum range of *F* values ranging from 0.3 to 1.1 for modelling Cd speciation in various DOM and agrees with range of *F* resulted in the current work by considering percentage of FA as 25 (i.e. 0.5-1.2). However, they also reported that assuming *F*=1.3 is also acceptable for predicting Cd speciation in various DOM. Speciation modelling in WHAM VII does not account for Cd binding by non-humic low Mw organic molecules (e.g. aliphatic amines, proteins and peptides), despite being known to bind Cd in soil solution and show considerably high stability constant for Cd complexation (Kaschl et al., 2002a; Kozyatnyk et al., 2016). Therefore, there can be other DOM-Cd complexes than Cd bound to humic like organic compounds, and these DOM-Cd complexes may also be kinetically limited, thus contributing to Cd transport.

Kinetic limitation measured by SV-DGT estimated that the dissolved Cd mobilised from OM amended and unamended soils at both pHs are relatively labile. Cadmium mobilised from compost-amended soils appeared to be more kinetically limited than that of Cd mobilised from peat amended soils at pH 5.6, vice versa at pH 6.4. The kinetic limitation of Cd in the peat amended and unamended soils increased with greater pH (from 5.6 to 6.4), while there was no significant change in the kinetic limitation of Cd mobilised from compost amended soils at the two pHs (Figure 4.4). This can be explained by the change in the metal: ligand ratio in solution with pH, where the metal: ligand ratio is an important factor in determining the lability of metal-ligand complexes (Guthrie et al., 2003). As the metal: ligand ratio increases, the strong metal-binding sites become increasingly saturated and remaining metal starts to bind to the weaker ligands, such as in various organic molecules in DOM, that can have a range of binding sites with different metal-binding strengths. The Cd: DOC molar ratio in the dissolved fraction mobilised from OM amended and unamended soils at pHs 5.6 and 6.4 declined with increasing pH (Table 4.3), while the reduction was less pronounced in compost amended soils. If hypothesised that the Cd mobilised at elevated pH was bound to stronger binding sites in DOM; the increased kinetic limitation for Cd in unamended and peat amended soils with pH supported this hypothesis (Figure 4.4). The kinetic limitations for Cd estimated for dissolved Cd from OM amended soils here are higher than the kinetic limitations for Cd observed by Welikala et al. (2018), which can be attributed to the 10^{-3}-10^{-6} lower Cd: DOC ratio used in this work.

It is important to note that during the SV-DGT experiment set-up, the conductivity of all leachates was brought up to about 2 mS cm^{-1} (similar to conductivity of leachates from compost amended soils at all pHs tested) in order to reduce the effect that differences in ionic strength may have on the dissociation rates of the Cd-OM complexes (Wang et al., 2016). Therefore, overestimation of kinetic limitation for Cd in leachates from OM unamended and peat-amended soils are plausible if DOM aggregated due to the increase in solution ionic strength (Cincotta et al., 2019; Mosley et al., 2019).

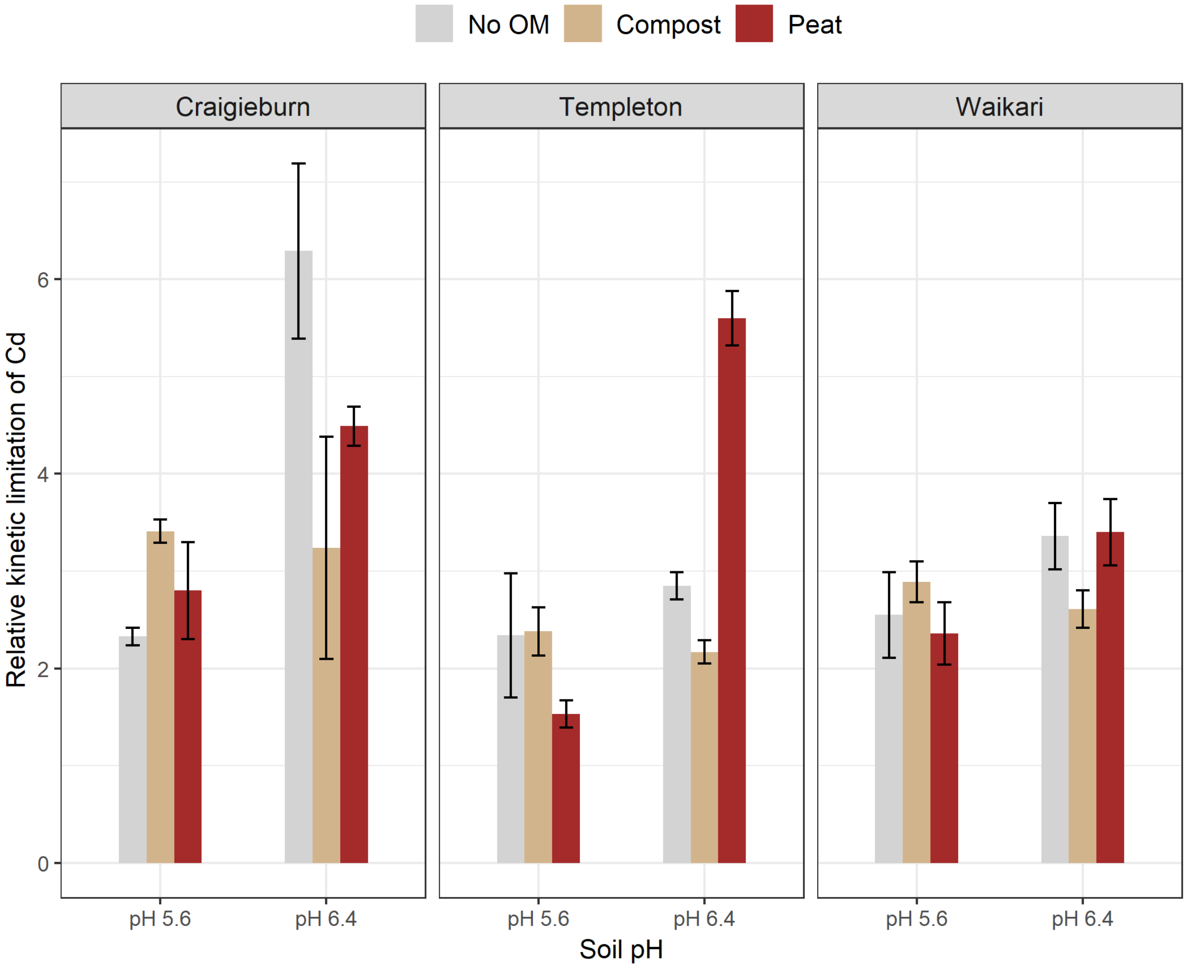


Figure 4.4: Relative kinetic limitation (arbitrary units) of Cd in OM unamended and amended soils at pH 5.6 and 6.4. Error bars represent the standard error of the mean (n=3).

4.4 Conclusions

The extent of Cd mobilisation from the OM amended soils depends on soil pH, characteristics of the soil (minerals and texture) and the amendment (CEC and pH). Soil pH was the dominant factor that, controlled both immobilisation and mobilisation of Cd in OM amended soils. Increasing soil pH by lime addition may reduce the overall Cd mobilising from the soils amended with OM by enhancing the sorption of free Cd^{2+} ions to the solid phase, but not the colloidal Cd. The colloidal Cd mobilised was highly correlated with DOM. Therefore, at elevated pH Cd associated with DOM colloids may be an important vector in determining the mobility of soil Cd. Compost amended soils released more colloidal Cd than the peat amended soils used in this work, which suggests that the provenance of the OM amendment may need to be considered to prevent the potential soil Cd mobilisation through OM amendments. The Cd released with colloidal DOM may persist in the soil for a longer period based on the quality of DOM (provenances and humification degree) and thus have the potential to transport the Cd in the surrounding environment.

Chapter 5

Mobilisation of stable Cd isotopes from soil by dissolved organic matter and chloride

5.1 Introduction

Cadmium (Cd) contamination of soil and water through anthropogenic activities is a global issue. Processing of non-ferrous materials, application of phosphate fertiliser and sewage sludge application are some of the most prevalent sources of soil Cd contamination (Kabata-Pendias, 2007; Smolders et al., 2013). Leaching of soil Cd added through fertilisers, sewage sludge, landfills, and wastewater application often the primary source for water Cd contamination for cases where the world health guidelines for drinking water have been exceeded (Kubier et al., 2019; World Health Organization, 2011).

Cadmium is generally poorly mobile in soil and tends to accumulate near the surface through sorption to soil solid phases, such as organic matter (OM) and, Al, Fe and Mn (oxyhydr)oxides (Salmanzadeh et al., 2016; Salmanzadeh et al., 2017b). This is problematic where plants readily take up Cd from soils (Kabata-Pendias, 2007; Rizwan et al., 2017; Shahid et al., 2017). The species of Cd in the soil solution (as free ions, complexed to organic and inorganic ligands, and associated with colloids) can be considered to be 'mobile species', which have the potential to transport Cd in the surrounding environment with water movement (Carrillo-González et al., 2006; Hooda, 2010). These mobile species of Cd can be considered as a potential threat to drinking water contamination and aquatic life toxicity (Kubier et al., 2019; Qu et al., 2013; Taylor et al., 2017).

Dissolved organic matter can enhance the solubility of Cd either by forming stable Cd-DOM complexes or preferentially adsorbing to soil surface over Cd (Antoniadis et al., 2002; Naidu et al., 1998). Chloride (Cl^-) also forms stable Cd-chloro complexes in soil solution (e.g. $CdCl^+$, $CdCl_2$) reducing Cd sorption (Loganathan et al., 2012). Therefore, chloride inputs have enhanced the mobility of Cd in soils under precipitation and irrigation (Gray et al., 2017; McDowell, 2019). Both DOM and Cl^- may influence the mobility of Cd in grazing lands (Carrick et al., 2014; Gray et al., 2017), where ruminant urine inputs can act as a source for both ligands: cow urine contains high Cl^- concentration (> 1 g mL^{-1}) and urine can solubilise soil organic matter by increasing soil pH (Haynes et al., 1993; Lambie et al., 2012a, 2012b; Miah et al., 2017). The potential influence of ruminant urine on Cd mobilisation is therefore important in intensively grazed lands. For example, in New Zealand, about 11 million hectares of land (40% of total land) is used for pastoral farming, which is mainly grazed by cattle and sheep (Statistics New Zealand, 2016), and up to 30% of these areas may be covered with urine patches annually (Moir et al., 2011). To date, there are two studies that considered the effect of cow urine on Cd mobility in stony soil, which is especially susceptible to leaching Cd (Kelliher et al., 2017). Since the extent of Cd mobility can differ between soils with varying characteristics (e.g. texture, Al/Fe/Mn oxides, soil organic matter and pH) (Gray et al., 2016; Gray et al., 2003a; McLaughlin et al., 1996), the influence of urine for Cd mobility may vary between different soils as well.

The analysis of stable isotopes in contaminated soils has been successful in identifying the fates of anthropogenic Cd in soil and soil-plant systems, which is permitted by the nine stable isotopes found in nature with varying natural abundances (Imseng et al., 2019; Salmanzadeh et al., 2017a; Wiggenhauser et al., 2019; Wiggenhauser et al., 2016). Isotope ratio tracing coupled with mixing models are effective in identifying the fate of anthropogenic Cd in contaminated soils (Salmanzadeh et al., 2017a; Wiggenhauser et al., 2019). This approach assumes that the sources of Cd are isotopically distinguishable, and so have distinct isotope ratios, meaning that the fractional contribution from each source (e.g. fertiliser, unfertilised soil) for a Cd pool (e.g. fertilised soil, plant) can be estimated (Salmanzadeh et al., 2017a; Wiggenhauser et al., 2019). Further, Cd isotope fractionation to lighter isotopes in the soil solid phase and fractionation to heavier isotopes in soil solution often occurs due to the difference in the bond lengths between Cd and its surrounding atoms in solid and solution phases (Imseng et al., 2018, 2019; Wiederhold, 2015). This allows evaluating the differences in Cd speciation in distinct soil environments, where Cd-ligand bond lengths are different in various soil and solution species like Cd bound to solid organic matter, associated with various mineral, Cd species in soil solution (Bochatay et al., 2000; Fulda et al., 2013; Karlsson et al., 2005; Ohtaki et al., 1981).

This work had two objectives: (1) determine the effects of DOM and Cl^- on Cd mobilisation in distinct soils with cow urine application and (2) explore the use of stable isotopes of Cd to study the transport of anthropogenic Cd in different soils. To achieve these objectives, a column leaching experiment was conducted to compare leaching potentials of spiked Cd isotopes in different soils. Further, influence of cow urine on Cd leaching was examined under two lime treatments, assuming that the soil's pH buffering capacity enhances at high pH, thereby influence of urine to increase the soil pH will be less effective.

5.2 Materials and methods

5.2.1 Soil sample collection and preparation

Soil representative of three New Zealand soil orders (as defined by (Hewitt, 2010)) was collected from different sites on New Zealand's North and South Islands. The soil collected from the Canterbury region (43° 30′ 22″ S, 172° 22′ 24″ E) is a Weathered Fluvial Recent soil ('Canterbury soil'), a Typic Orthic Allophanic soil was collected from the Taranaki region ('Taranaki soil') and a Peaty Orthic Gley soil was collected from the Waikato region (37^{o} 46′ 11″ S, 175^{o} 22′ 5″ E: 'Te Kowhai soil'). Plant roots and rocks were removed manually. The soils were then sieved through a 4 mm plastic sieve and air-dried. A subsample from each air-dried soil was sieved through a 2 mm nylon sieve for analysis of chemical and physical properties. Subsamples of the 4 mm sieved soils were mixed with appropriate amounts of lime ($CaCO_3$, ReagentPlus®, sigma-Aldrich) to adjust the soil pHs to either 5.5(±0.2) or 6.5(±0.2). Soil moisture contents of the lime-treated soils were increased to 40% of field capacity (FC) and incubated for 1 week at 20 °C.

Subsamples of each soil, at the different pHs, were spiked with ^{108}Cd and ^{116}Cd isotopes (Cambridge Isotope Laboratories, USA) and Cd at its natural abundance. Cadmium solution of 100 mg L^{-1} for ^{108}Cd and ^{116}Cd isotopes were prepared as described by Lee et al. (1998). Briefly, 10 mg of each metal was dissolved in 10 mL of 2% HNO_3 (PrimarPlus-Trace Analysis grade, Fisher Scientific UK), then diluted to 30 mL with high-purity water. The pH of the solution was adjusted to 7.0 with 1 M NaOH (Sigma-Aldrich) then, diluted to 100 mL with high-purity water. Cadmium solution of 100 mg L^{-1} where all the isotopes were assumed to present at their natural abundances (Rosman et al., 1998) was prepared from $Cd(NO_3)_2.4H_2O$ (BDH chemical). Each soil was spiked to 0.66 mg kg^{-1} of each enriched ^{108}Cd, ^{116}Cd and Cd at its natural abundance (i.e., total spike of 2 mg kg^{-1}). Soil moisture content of spiked and unspiked soils was then increased to 60% FC (maintained at 50-60% FC) and incubated at 20 °C for 5 months. The soils were mixed regularly to ensure aeration, and subsamples were analysed for pH and 0.05 M $Ca(NO_3)_2$-extractable Cd (see below) to monitor the equilibration between extractable and recalcitrant metal in the soils. After three months, soil pHs had stabilised at 5.4(±0.1) and 6.1(±0.1) and the amount of $Ca(NO_3)_2$ extractable Cd had plateaued (Appendix D, Figure D.1).

5.2.2 Column leaching

Soils were packed into cylindrical PVC columns to a height of 6 cm (internal diameter of 4.4 cm). The bottom 4 cm was packed with unspiked soil and the top 2 cm was packed with spiked soil at the same pH (herein these soil columns are referred as 'treatment column'), while the columns packed with only unspiked soils were used as the controls for each soil (herein 'control column'). The Canterbury, Taranaki and Te Kowhai soils were packed into 1.0, 0.75 and 0.85 g cm^{-3} bulk densities, respectively. These three soil orders were packed into different bulk densities, due to their distinct texture and drainage characteristics. Bottoms of the columns were underlain with a nylon mesh (mesh size= 20 µm) and a filter paper was lain on top of the soil to avoid the impact of the water droplet on the soil and to ensure uniform distribution of water or cow urine across the surface.

Cow urine was collected from Lincoln University dairy farm on the day before applying to the soil, and the N content was measured immediately using an Elementar Vario MAX CN (Elementar®, Germany) element analyser. The urine was also analysed for dissolved organic carbon (DOC) and chloride (Cl^-)

concentrations later (stored at -20 °C). To the treatment and control soil columns, 28 mL of urine was applied at once in at each pH (equivalent to 500 kg N ha^{-1}). Similarly, for another subset of treatment and control soil columns, equal volume of deionised water was applied instead of urine. The final soil moisture was increased to FC by adding deionised water and then left to equilibrate for 24 h. Each treatment was replicated three times. A subset of soil columns was allocated to measure the soil pH after 24 h of either urine or deionised water application and equilibrated at FC (Appendix D, Figure D.2).

Leaching was induced by synthetic rainwater (Zhao et al., 2007), applied at a rate of 0.2 mL min^{-1}. A pilot experiment carried out using 15 mg L^{-1} Br^- as the tracer, showed that Br^- breakthrough happened after 1-2 pore volume (Appendix D, Figure D.3) for all soils, therefore leachate volume equal to two pore volumes was collected. The leachates were collected in containers placed in ice baths (<4°C) minimize the microbial activity and then immediately filtered through 0.45 µm syringe filter (Phenex, cellulose acetate, Φ is 25 mm). Subsamples from leachates were allocated for the analyses : (1) pH, (2) electric conductivity, and (3) total dissolved elements including isotopes of Cd (acidified to pH<2 with 1 M HNO_3), (4) dissolved organic carbon (DOC), (5) dissolved inorganic carbon (DIC, preserved with saturated mercuric chloride (0.02% V/V; $HgCl_2$, BDH, laboratory reagent)), (6) dissolved anions, and (7) humic acid fraction. Summary of treatments and sample analysis is shown in Figure 5.1.

All sample dilutions used high-purity water (18.2 MΩ resistivity; Heal Force® SMART Series Ultra-pure water system, Model-PWUV) and acid (HNO_3, PrimarPlus-Trace Analysis grade, Fisher Scientific UK). All the equipment used to handle or contain samples were left in 10% HCl for 8 h, then 10% HNO_3 for 8 h after rinsing with high-purity water, followed by 8 h in high-purity water, and then thoroughly rinsed with high-purity water.

5.2.3 0.05 M $Ca(NO_3)_2$ extractable cadmium

The 0.05 M $Ca(NO_3)_2$ extractable Cd in the spiked soils at both pHs were measured using the method reported by(Gray et al., 1999). Briefly, 5.00 g of soil was mixed with 30 mL of 0.05 M $Ca(NO_3)_2$ (Sigma-Aldrich) solution and equilibrated in an end-over-end shaker for 2 h. The mixture was then centrifuged at 3000 rpm for 20 min followed by filtration (Whatman 52 filter paper). The filtrate was stored at -20 °C prior to analysis for extractable Cd isotopes and isotope ratios.

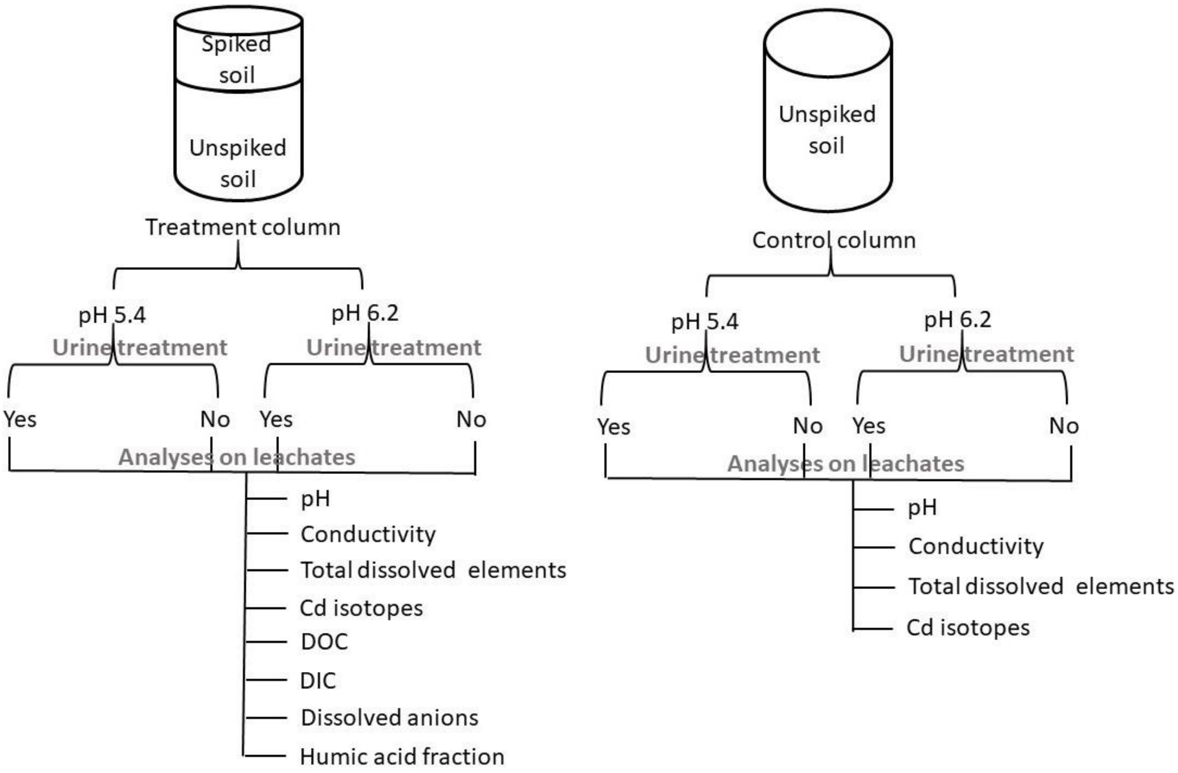


Figure 5.1: The treatments carried out on the treatment and control columns and the analyses on the respective leachates.

5.2.4 Soil and leachates chemical analysis

Physical and chemical properties of soils were analysed using standard methods. Soil particle size distribution was analysed by laser diffraction method with Mastersizer 2000 (Malvern Instruments Ltd, UK). For this analysis, the soils were pre-treated with 30% H_2O_2 to remove organic matter, which may interfere with the particle size measurements. Soil pH (Mettler Toledo Seven Easy pH meter) was measured in 1:2.5, soil: water ratio and conductivity (Mettler Toledo Five Easy) was measured at a 1:5, soil: water ratio (Blakemore, 1987). Total N was determined using an Elementar Vario MAX CN element analyser. The soil organic carbon (SOC) content was measured by loss on ignition (LOI) (Blakemore, 1987). Cation exchange capacities (CEC) of the soils were determined by the ammonium acetate (pH 7) method (I. C. Brown, 1943). The soil was acid digested using CEM MARS XPRESS microwave (Kovács et al., 2000) to determine the pseudo-total element contents (Na, K, Mg, Ca, Fe, Al, Mn, Zn, Cu, Ni) via Inductively Coupled Plasma- Mass Spectroscopy (ICP-MS, Agilent 7500cx). The concentrations of cations (Na, K, Mg, Ca, Zn, Cu, Ni) in the leachates was determined using ICP- Optical Emission Spectroscopy (ICP-OES, Cd was measured in both digests and leachates using ICP-MS – see section 5.2.4.1).Soil properties are presented in Table 5.1 The dissolved anions (Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, Br^-) was measured using a DIONEX (DIONEX, ICS-2100, Thermo Scientific, USA). Blank extracts, filtrates, and solutions were analysed regularly to confirm low contamination levels.

The concentrations of total dissolved organic (DOC) and inorganic carbon were measured using a TOC analyser (Vario TOC-cube, Elementar, Australia). UV-VIS spectrophotometry (UVmini, SHIMADZU) absorbance measurements were used to characterize the quality of leached dissolved organic matter (DOM). Specific absorbance measured at 254 nm ($SUVA_{254}$) was used to estimate the aromaticity of the DOM (Weishaar et al., 2003), while the ratio of absorbances measured at 465 and 665 nm (E_4/E_6) reflected the degree of aromatic condensation of the substance in the DOM (Kleber et al., 2010). The interference of nitrate concentration for the SUVA measurements was eliminated by diluting the samples with high nitrate concentrations to below 100 mg L^{-1} (Weishaar et al., 2003). The humic acid (HA) in the leachate was separated using the method described by Van Zomeren et al. (2007). Briefly, 30 mL of leachate was acidified to pH<1 with 6 M HCl (AnalaR NORMAPUR, BDH chemicals) and centrifuged at 2000 rpm for 10 min. The supernatant was then carefully extracted and analysed for DOC. The proportion of DOC from HA in total DOC was given by the difference in concentration between the initial non-acidified and acidified leachate.

5.2.4.1 Cadmium isotopes Analysis

The isotope ratios are generally measured by multicollector-ICP-Mass Spectroscopy (MS) (Rehkämper et al., 2004), and isotope ratios are reported relative to the isotope ratios in a standard material (Wiederhold, 2015). However, a triple-quadrupole (QQQ)-ICPMS (Agilent Technologies, Santa Clara, California, USA) controlled by MassHunter Workstation (version 4.5) was used here to measure the isotope concentrations and the ratios are reported as in per in the sample, which was possible because the isotopes used in the analysis here (^{108}Cd and ^{116}Cd) could be detected using the QQQ-ICPMS. This was confirmed throughout by repeat analyses of selected samples and internal standards.

The soil acid digests, leachates and $Ca(NO_3)_2$ extracts were analysed for Cd concentration (C_{Cd_NA}) based on the ^{111}Cd concentration (at its natural abundance of 12.8%) in the standard solutions assuming that ^{111}Cd and all other isotopes were present at their respective natural abundances (Rosman et al., 1998) in the standard solutions and the samples. However, C_{Cd_NA} does not account for the additional ^{108}Cd (C_{108Cd}) and ^{116}Cd (C_{116Cd}) concentration in the samples due to the spiking. Therefore, total ^{108}Cd and ^{116}Cd isotope concentrations in samples were measured with respect to calibration curve prepared for ^{108}Cd and ^{116}Cd isotopes based on their concentrations in the standard solutions, in which these isotopes present at their natural abundances. This method of calibration for each isotope was confirmed by repeated analysis of ^{108}Cd and ^{116}Cd isotopes with known concentrations. Then 'true' isotopic total Cd concentration (herein 'total Cd') in each sample is calculated using equation 5.1:

$$total\,Cd\,concentration(\mu g\,L^{-1}) = C_{Cd\_NA} - (C_{Cd\_NA} \times NA_{108Cd}) - (C_{Cd\_NA} \times NA_{116Cd}) + C_{108Cd} + C_{116Cd} \tag{5.1}$$

Where, NA_{108Cd} and NA_{116Cd} are the natural abundances of ^{108}Cd (0.89%) and ^{116}Cd (7.49%) isotopes, respectively.

The isotope ratio, $^{116/108}$Cd was measured in soil digests, leachates and $Ca(NO_3)_2$ extracts. Standards with known isotope ratios were analysed between each sample to correct for mass bias. All the mass bias and isotope ratios in samples were calculated using the MassHunter Workstation.

Table 5.1: Chemical and physical characteristics of soils

	Te Kowhai	Canterbury	Taranaki
Clay/silt/sand%	4/25/70	5/34/62	2/14/84
pH (H_2O)	5.5	5.3	4.9
N%	0.4	0.2	1.1
C:N ratio	9.2	12.7	9.7
SOC%	6.97(0.01)	3.68(0.04)	12.40 (0.05)
CEC (cmol kg^{-1})*	18	15	18
BS %†	56.5	47.2	35.9
Al (g kg^{-1})	40.8 (0.3)	32.1(0.6)	20.8(0.7)
Fe (g kg^{-1})	10.8(0.8)	20.5(0.5)	21.4(0.05)
Mn (g kg^{-1})	0.4 (8.2×10^{-4})	0.5 (0.01)	0.61(0.01)
Cd (mg kg^{-1}) Ŧ	0.6 (0.02)	0.04 (2.26×10^{-4})	0.64 (1.21×10^{-3})
Cd (mg kg^{-1}) ¥	2.62 (0.05)	2.14(0.04)	2.05(0.26)
^{108}Cd (mg kg^{-1})	0.56(0.01)	0.47(0.03)	0.44 (0.06)
^{112}Cd (mg kg^{-1})	0.40 (0.01)	0.27 (0.03)	0.33 (0.04)
^{116}Cd (mg kg^{-1})	0.59 (0.01)	0.69 (0.03)	0.41(0.07)

† BS is the base saturation. Ŧ Pseudo-total Cd concentration in unspiked soils based on the natural abundance of 111Cd. ¥ Total acid extractable Cd in spiked soils calculated based on equation 5.1. 108Cd,112Cd and 116Cd are the total acid extractable concentrations of each isotope in the spiked soils. Standard errors are given in the brackets (n=2).* Data from Analytical Research Laboratories (ARL), NZ.

5.2.5 Bayesian mixing model for source identification

A Bayesian mixing model described by Salmanzadeh et al. (2017a), was used to calculate the fractional contributions from the sources of Cd to the leachates from treatment soil columns. The model was defined based on $^{116/108}$Cd isotope ratios in leachates and sources. The two possible sources were the extractable pool of Cd in the spiked top-soil layer and unspiked bottom soil layer. The $^{116/108}$Cd ratios in the $Ca(NO_3)_2$ extracts of spiked and unspiked soils were used as the isotope ratios in these two sources.

5.2.6 Speciation modelling

Speciation of dissolved Cd in the leachates from the treatment columns was estimated using the Windermere Humic Aqueous Model (WHAM) VII (Tipping et al., 2011). 50% of DOM was assumed to consist of DOC (Cornu et al., 2011). For urine-treated soils only, 29% of DOC was soil-derived (Lambie et al., 2012a), which differs in character to urine-derived DOC (see below). Soil derived-DOM was assumed to consist of 25% fulvic acid (FA) (Laborda et al., 2009; Ren et al., 2015b) and the measured concentration of HA for each leachate was used for speciation modelling. Based on the model output, the percentage of each major Cd species (Cd^{2+} free ion, Cd-chloro complexes, Cd-DOM complexes) with respect to the total dissolved concentration of Cd was calculated.

5.2.7 Statistical analysis

Data analysis and visualisation were carried out using the R software (R core Team, 2018) and Minitab 18® (Mintab ® 18.1, Minitab, Inc.). Significant differences were tested by ANOVA with Tukey post-hoc at the 0.05 level of significance unless stated otherwise. The correlation between Cd mobilised and other parameters (e.g. soil pH, DOC and Cl^- mobilised) was determined using Spearman's rho *(r)* at the level of 0.05 level of significance.

5.3 Results and discussion

5.3.1 Cadmium mobilisation from the spiked soils

The Bayesian mixing model showed that 17-60% of the Cd mobilised from the soils that did not receive urine originated from the spiked soils in all three soils across both pHs (Figure 5.2). Given that only two pore volumes were collected in the leaching experiment, it is reasonable to assume that only dissolved and readily exchangeable Cd was likely to leach. The pilot experiment with Br^- tracer provided evidence for this where at least leachate volume equal to one pore volume was required flush the porewater in each soil in the column. Even though not all the extractable Cd may be susceptible to release during the leaching period, the study presented in Chapter 4 showed that the total Cd leached had a positive relation with $Ca(NO_3)_2$ extractable Cd (forthwith 'extractable Cd'). Therefore, the extractable Cd amounts can be used to help interpret the mobilisation of Cd from spiked and unspiked soils across both pHs (Ash et al., 2015). The extractable Cd from the spiked Taranaki and Te Kowhai soils was between 4- to 9-fold higher than the extractable Cd from the respective unspiked soil at the same pH (Figure D.4, Appendix D). In the Canterbury soil, the extractable Cd from the spiked soils was 236-fold and 323-fold greater than the extractable Cd from the unspiked soils at pH 5.4 and 6.2, respectively. Therefore, for all the soils, the total extractable Cd is greater in the spiked soil layer than the underlying unspiked soil layer, even though the mass of the unspiked soils was twice the mass of the spiked soil in the treatment columns. Accordingly, the contribution from the spiked soil to the total Cd leached is likely to have been greater than the contribution from the unspiked soil to the total Cd leached. If all the extractable Cd was to have leached from both spiked and unspiked soils, then 99% and 75% of total Cd leached from the Canterbury and Taranaki soils should have originated from the spiked soils, respectively, at both pHs. While in the Te Kowhai soil 79% and 67% of total Cd leached should have originated from the spiked soils at pH 5.4 and 6.2, respectively. However, after the mobilisation and leaching from the spiked soil, the Cd will have encountered the underlying unspiked soils. Given the higher soil Cd concentration and extractable Cd in the spiked soils (Figure D.4), the dissolved concentration in the leachate is likely to have been greater than the equilibrium concentration in the porewater of the underlying soil. The shift in the equilibrium in favour of sorption is therefore likely to have removed some of the leached Cd. This effect has been reported under field conditions where the concentrations of Cd seen in the top few centimetres are higher than in the underlying soils, despite long-term inputs (Gray et al., 2003a; Loganathan et al., 1997; Salmanzadeh et al., 2016). This provides a possible explanation for the relatively low contribution from spiked soils to the total Cd leached in the treatment columns than assumed by the extractable Cd, where the leaching of Cd from spiked soil is likely to have been restricted due to re-sorption of dissolved (mobile) Cd to the soil solid phases (immobile) in the underlying unspiked soil in three soils at both pHs.

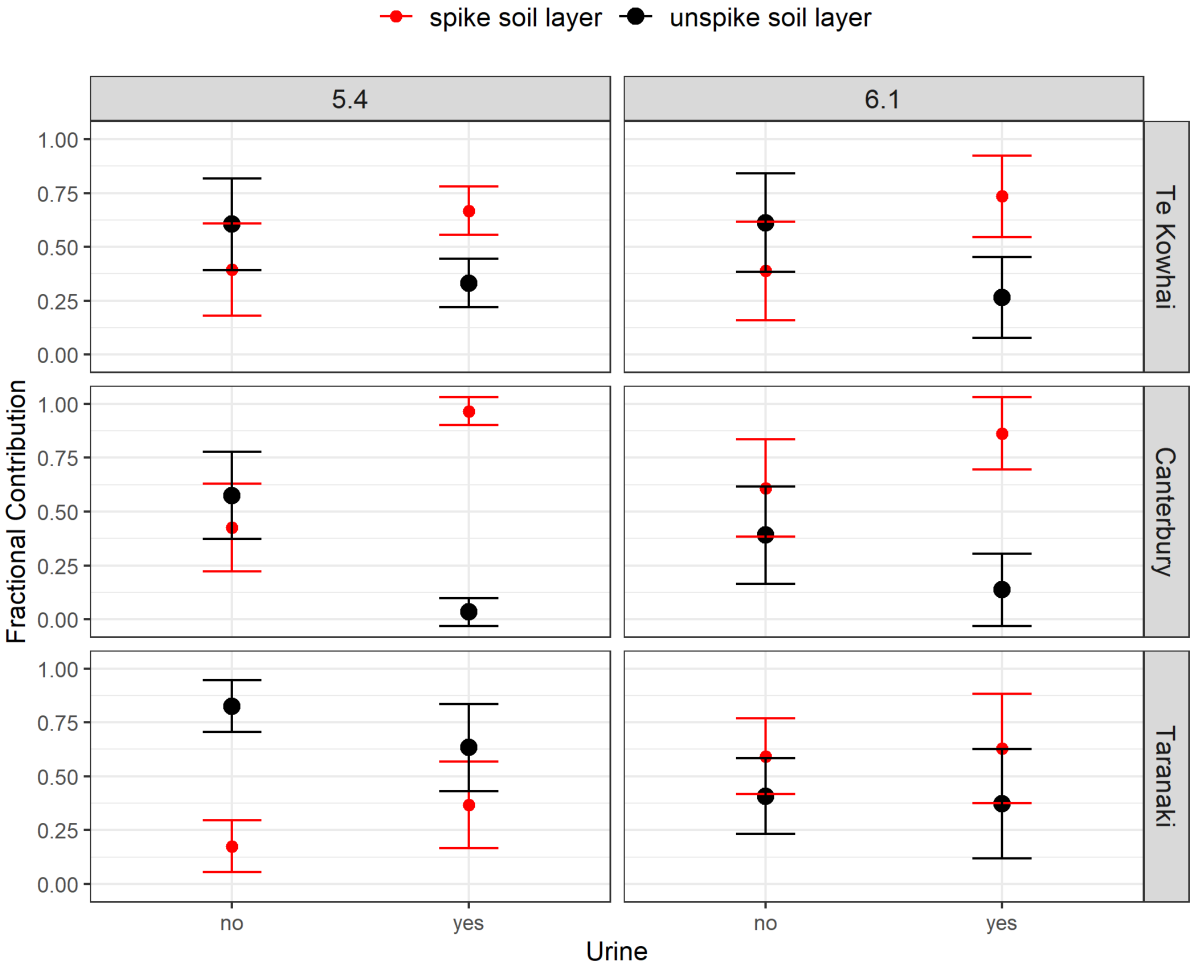


Figure 5.2: The fractional contribution of two different sources (labile solid pool from either spiked or unspiked soil layers) for $^{116/108}$Cd ratio in the leachates from the treatment columns. Error bars represent the standard deviation.

The fractional contribution of Cd from the spiked soil to the total Cd leached increased with increasing pH in the Taranaki and Canterbury soils, but not in the Te Kowhai soil that did not receive urine (Figure 5.2). This increased contribution from spiked soils is likely due to the reduction in re-sorption of dissolved Cd to the underlying unspiked soil at elevated pH, because, (1) with increasing pH, mobilisation of Cd as Cd-DOM complexes has increased due to increased DOM concentration (Table 5.3), which may not be labile to re-sorb as free Cd^{2+} ions, (2) available binding sites for Cd may be less due to sorption of DOM released (the effect of DOM on Cd mobilisation is discussed in detail later) (Antoniadis et al., 2002; Naidu et al., 1998).

The mixing model estimated that the urine application increased the fractional contribution from the spiked soil Cd to the total Cd leached in all three soils across both pHs, showing that urine inputs effectively increase the spiked Cd leaching (Figure 5.2). Similar to high pH soils, more DOM and Cd-DOM species leached from the urine treated soils compared to the soils that did not receive urine (Table 5.3) across three soils at both pHs. Therefore, re-sorption of dissolved Cd species from the spiked soil to the underlying unspiked soil is likely to have been lower in the urine treated soils and may be why the spiked soils contributed more to the total Cd leached than the soils at same pH that did not receive urine. Furthermore, the urine treatment increased the Cl^- concentration, where Cl^- is a major constituent of urine and therefore the percentage of Cd-chloro complexes in the leachates from the treatment columns (Table D.1, Table 5.3). These complexes reduce Cd sorption to soil phases and facilitate Cd mobility in soils (Bolan et al., 1999; Gray et al., 2017; McDowell, 2019). Therefore, Cd-chloro complexes also might have influenced the leaching of Cd from the spiked soils in all the urine treated soils at both pHs.

Accuracy of the mixing model output relies on minimum interference from processes that can cause isotope fractionation in the sample. These processes include: (1) redox reactions, (2) complexation with inorganic ligands and DOM, (3) sorption, (4) precipitation, (5) mineral dissolution (Imseng et al., 2019; Wasylenki et al., 2014; Wiederhold, 2015). If leaching of spiked Cd was restricted due to re-sorption, it can result in isotope fractionation in the soil solid phase and thereby it may indirectly affect isotope fractionation in the leachates at either pH. However, influence of isotope fractionation in the leachates due to re-sorption of Cd isotopes to the soil solid phase is not known for this study. Complexation reactions may affect the isotope fractionation in the leachates at high pH and in urine treated soils. At high pH (6.1), DOM concentration increased due to dissolution of OM, while urine increased the DOM and Cl^- concentration in the soils (Figure 5.4, Table D.1). These species are known to have a high affinity for Cd. Soil solutions can be enriched with lighter isotopes in the presence of DOM or Cl^- species than in the presence of free Cd^{2+} (Imseng et al., 2019; Wasylenki et al., 2014). Therefore, these ligands may influence the isotope fractionation in the leachates (see section 5.3.5 for further explanation). The impact of complexation on isotope fractionation appeared to be greater in the leachates from the urine treated soils, which in turns challenge the reliability of the mixing model output for those samples.

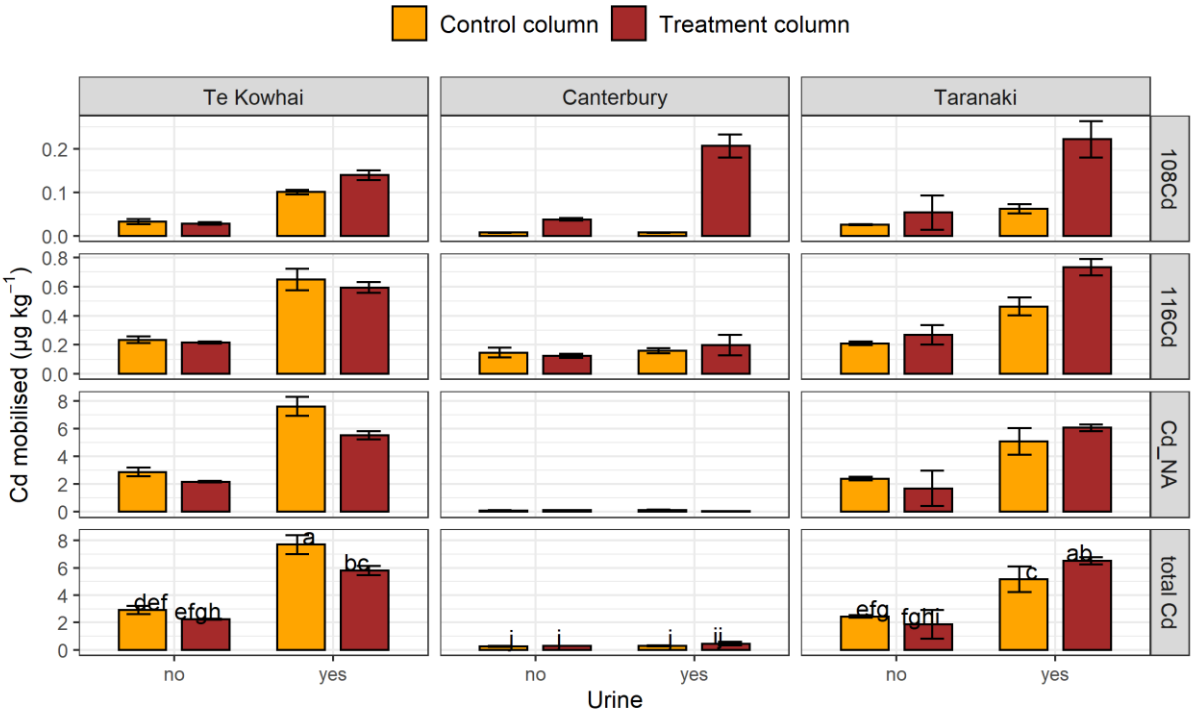
5.3.2 Mobilisation of individual and total cadmium isotopes from the soils

^{108}Cd isotope leached from most of the samples were greater from the treatment columns than from the control columns either with or without urine, indicating the mobilisation of spiked ^{108}Cd isotope (Figure 5.3). The standard deviation for replicate measurement of C_{Cd_NA} was greater than the average concentrations of ^{108}Cd and ^{116}Cd in many samples. This variability can mask the contribution of ^{108}Cd and ^{116}Cd isotopes from spiked soil layer for total Cd calculated for most of the leachates, hence there were few significant difference in the total amount of Cd mobilised between the control or treatment columns for all three soil types at each pH ($p>0.05$). The notable exceptions were for the urine-treated Te Kowhai ($p<1.0 \times 10^{-7}$) and Taranaki soils ($p<1.0 \times 10^{-7}$) at pH 5.4 (Figure 5.3).

Compared to treatments without urine, urine application significantly enhanced the total Cd mobilisation by 61% (p<1.0 X 10^{-7}) and 71% (p<1.0 X10^{-7}) in the Te Kowhai and Taranaki treatment soil columns at pH 5.4 and by 69% (p<1.0 X 10^{-7}) and 77% (p<1.0 X 10^{-7}) at pH 6.1, respectively (Figure 5.3). Urine application did not show a significant influence on Cd mobilisation from the Canterbury soil in the treatment columns at either pH. On average, total Cd mobilisation from the urine-treated Te Kowhai and Taranaki soils at pH 6.1 was ~43% less than that from urine treated soils at pH 5.4 in their treatment columns. The lower mobilisation of Cd from urine treated soils at pH 6.1 than pH 5.4 may be attributed to the reduced availability of labile soil Cd for mobilising at elevated pH, which may be due to increased Cd sorption to soil surface with greater pH (Loganathan et al., 2012). This is also supported by the ~55% lower Cd mobilisation from the treatment columns that did not receive urine at pH 6.1 than at pH 5.4 for both Te Kowhai and Taranaki soils.

The lowest total amount of Cd was mobilised from the Canterbury soil in all treatment and control columns at both pHs either with or without urine. This may be attributed to the difference in the texture of each soil, where soils having sandy texture have shown to leach more Cd than from clayey soils (McLaughlin et al., 1996); the Canterbury soil had low amount of sand content than the other two soils (Table 5.1).

(a) pH 5. 4



(b) pH 6. 1

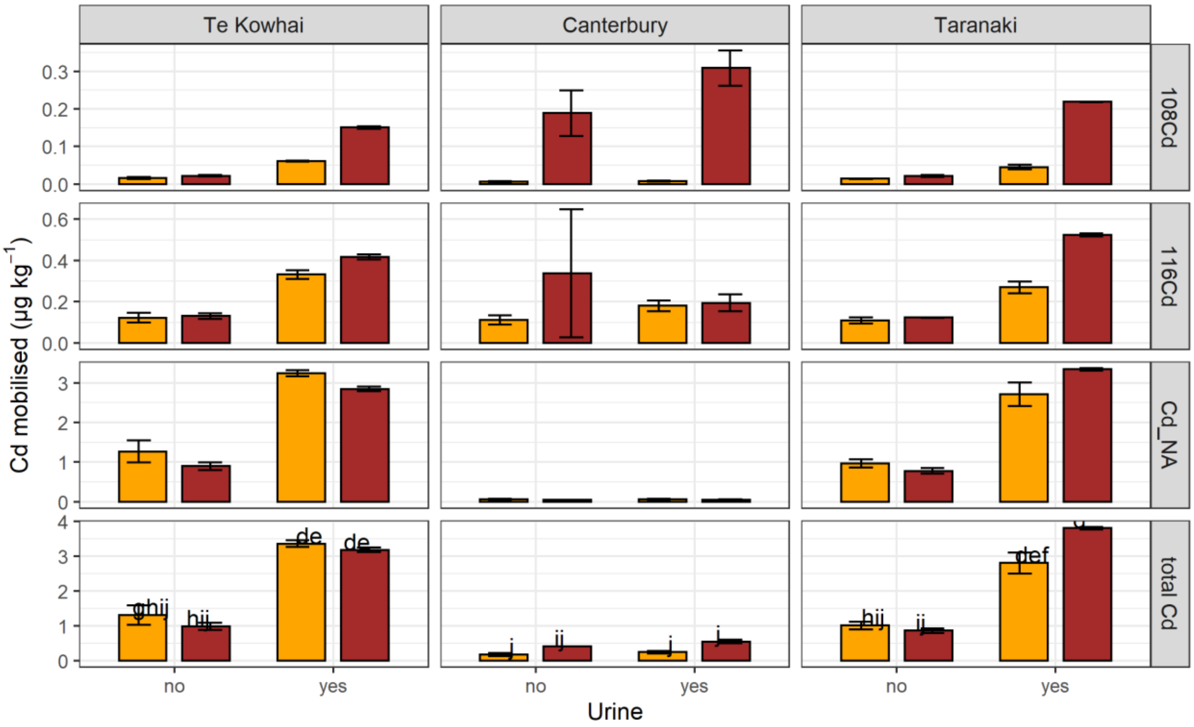


Figure 5.3: The isotopes and total Cd mobilised from soils at (a) pH 5.4 and (b) pH 6.1 with and without the urine application. 108Cd, 116Cd and Cd_NA represent the C_{108Cd}, C_{116Cd} and C_{Cd_NA} in the leachates, respectively, given as mass of Cd leached/mass of soil. The error bars represent the standard error of the mean (n=3). The values sharing the same letter are not significantly different (p>0.05). Note the differences in y-axis scales between soils.

5.3.3 Dissolved organic matter leaching and its influence for total cadmium mobilisation from the treatment columns

Dissolved organic matter leaching from the urine treated soils was greater than from the soils that did not receive urine at the same pH (Figure 5.4). This was attributed to the dissolution of soil organic matter due to the increase in soil pH with the urine application and leaching of urine-derived organic compounds (Carrick et al., 2014; Lambie et al., 2012b). The highest amount of DOC was leached from the urine-treated Canterbury soil at both pHs. Lambie et al. (2012a) collected the leachates (~two pore volumes) from undisturbed soil columns (diameter of 10 cm and depth of 5 cm) of Pumice soil 6 h after treating with either urine (500 kg N ha^{-1}) or water: they reported 1 g m^{-2} and 28 g m^{-2} of DOC leaching from water and urine treated columns respectively. This is in line with the DOC mobilised from urine treated and untreated Te Kowhai and Taranaki soils (Figure 5.4).

Even though both the Taranaki and the Te Kowhai soil contained a large amount of SOC% (Table 5.1), the DOC mobilised from both were less than that from Canterbury soil. The Taranaki soil is an Allophanic soil, in which DOM leaching is generally low due to adsorption to allophane minerals (Ghani et al., 2010; Parfitt, 1990), which explains the relatively low DOM mobilised from that soil. In addition, Lambie et al. (2012b), found that adsorption of urine carbon to soil was insignificant, which showed no relation to soil depth or clay content but a weak positive correlation to soil carbon content. This may be a possible reason for the greatest DOM mobilisation from the urine treated Canterbury soil, because this soil had the lowest SOC% among three soils (Table 5.1).

The DOM leached from urine treated soils may consist of both urine- and soil-derived organic components. In a laboratory scale column experiment, Lambie et al. (2012a) found that 71% of C in urine treated soil leachate was urine-derived C. In the current study, most of the DOC leached from urine treated soils appeared to be derived from fulvic acid (FA) and/or low molecular weight (Mw) organic compounds derived from either soil or urine (Figure 5.4). The amount of urine-derived organic compounds mobilised in this study can be estimated by the quality of mobilised DOM. The urine contains low Mw organic compounds like amino acids (Bristow et al., 1992; Selbie et al., 2015) while soil derived organic compounds generally have higher Mw. The E_4/E_6 and $SUVA_{254}$ results support this argument: generally, the E_4/E_6 ratio was higher for DOM from urine treated soils than from soils without urine while vice versa for $SUVA_{254}$ (Table 5.3). The E_4/E_6 ratio for leachates collected from urine treated soil was more closely related to E_4/E_6 found for low Mw FA (9.18-19.0) than for high Mw HA (5.95-6.94) (Wang et al., 2019b). However, the $SUVA_{254}$ in these leachates was less than what has been reported for FA (Wang et al., 2019b) and for DOM from soil leachates (Vujinović et al., 2019), which may be due to the urine-derived low Mw organic components that are more aliphatic in nature (Selbie et al., 2015). Therefore, it is likely that urine-derived DOM is dominant in the DOM leached from urine treated soils.

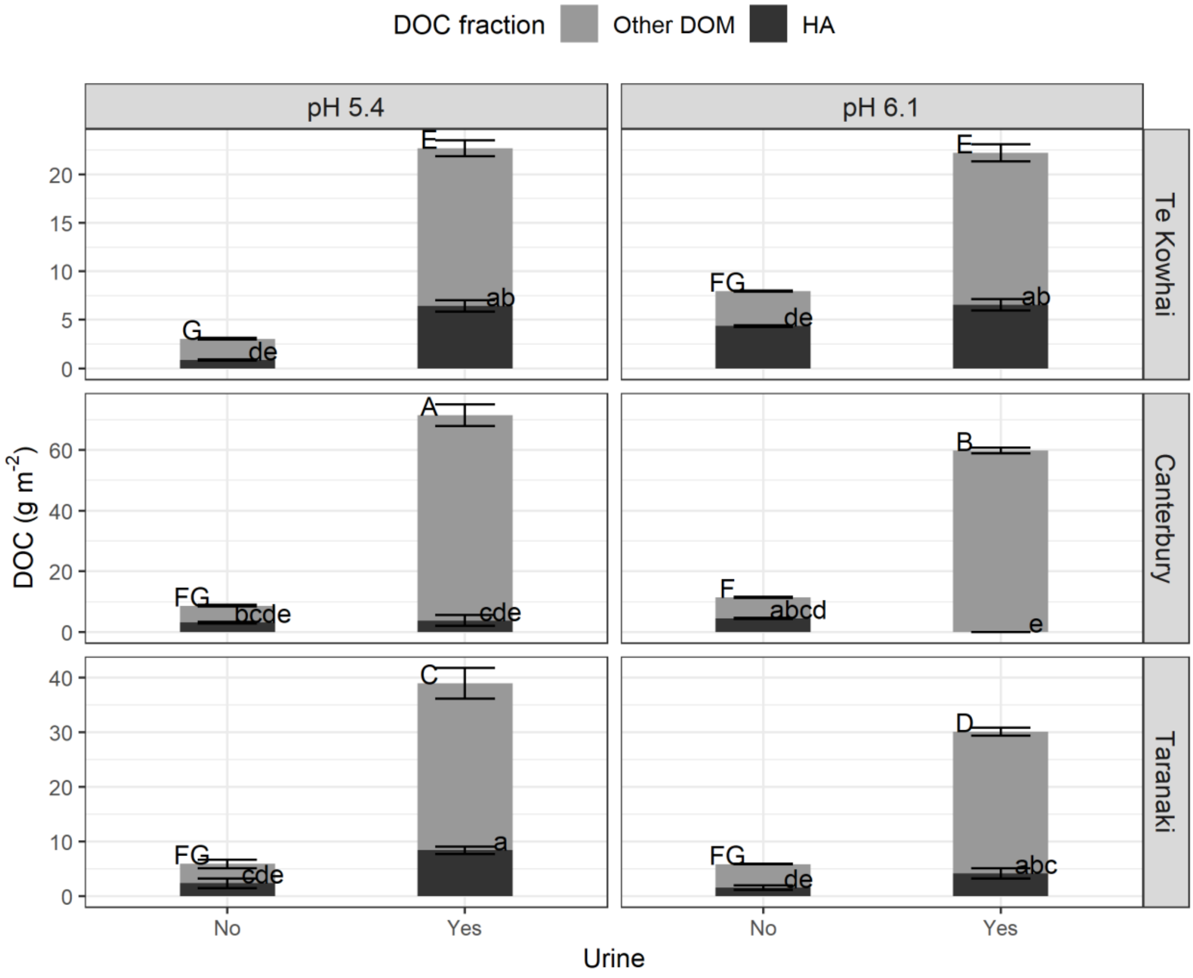


Figure 5.4: The amount of DOC from humic-like acid and other urine- and soil-derived dissolved organic compounds of the total DOC mobilised from the treatment soil columns. The error bars represent the standard error of the mean (n=3). The uppercase letters indicate the significant difference in the total DOC leached and the lowercase letters indicate the significant differences in the DOC from HA only. The values sharing the same letter are not significantly different (p>0.05). Note the differences in y-axis scales between soils.

There was a significant positive correlation between the amount of total Cd and HA mobilised (r=0.73, p=7.2 X 10^{-7}), while the other organic compounds did not show any significant correlation to the amount of Cd mobilised (Table 5.2). Dissolve organic matter is known for its impact on increasing the mobility of trace metals in soil (Amery et al., 2008; Zhang et al., 2020). Urine-derived low Mw DOM such as amino acids and organic acids are also found in soil solution and have shown affinity for binding Cd (Kaschl et al., 2002a; Kozyatnyk et al., 2016). However, compared to soil derived high Mw DOM, these low Mw organic compounds have been shown to be less important in binding Cd (Groenenberg et al., 2010; Ren et al., 2015b), which may apply here as well. Therefore, urine-derived DOM is unlikely to influence Cd mobilisation, while solubilised OM from the soil may enhance the Cd mobility through the formation of Cd-DOM complexes that are more mobile than inorganic Cd. The lack of significant difference in Cd mobilised from Canterbury soil with and without the urine application also can be explained by the lack of HA mobilisation (*p*=1.0). Further, this correlation suggests that the influence of urine for solubilising soil organic matter may be more pronounced in soils with high organic matter content. Given the affinity of soil organic matter for retaining Cd in soil (Al Mamun et al., 2016; Gray et al., 2016; Hamid et al., 2019), any inputs that enhance the solubility of that organic matter may mobilise Cd in soils with high organic matter content. It should be noted that the humic substances (HA and FA) are unlikely to occur in natural conditions, given that these substances are extracted with highly concentrated acids and bases and also the concept of 'humification' is currently under debate (Kleber et al., 2010; Lehmann et al., 2015). However, details provided by operationally defined humic substances promotes understanding of the interaction between Cd and colloidal DOM, because humic substances may serve as representative of aggregated and polymeric organic components in DOM (Kleber et al., 2010).

Table 5.2: The correlation between the total amount of Cd mobilised and soil pH, quality/quantity of DOM, and Cl^- mobilised

	Soil pH*	HA-DOC ($mg\ kg^{-1}$)	DOC-from other than HA ($mg\ kg^{-1}$)	Cl^- ($mg\ kg^{-1}$)	$SUVA_{254}$ ($L\ mg^{-1}\ m^{-1}$)	E_4/E_5
Total Cd mobilised ($\mu g\ kg^{-1}$)						
correlation coefficient	0.48	0.73	0.2	0.31	-0.31	0.27
p value	0.003	7.2×10^{-7}	0.25	0.07	0.07	0.12

*Soil pH after equilibration with either water or urine before leaching the soil with rainwater

5.3.4 Speciation of cadmium in the leachates from the treatment columns: influence of dissolved organic matter and chloride with urine application

Other than the influence by the DOM, Cd in the urine treated soils may also be mobilised through formation of Cd-chloro species due to Cl^- ions present in the urine (Gray et al., 2017; McDowell, 2019). The urine applied here had 1.3 g L^{-1} Cl^- content; thereby the Cl^- concentration in the leachate was increased by 3- to 49- fold across the three soils compared to soil without urine. In a field lysimetric study with cow urine application, Gray et al. (2017) reported a significant positive correlation between leached Cd and Cl^-, therefore they claimed that the greater Cd leaching with the urine application is may be due to the formation and leaching of Cd-chloro complexes. However, they did not model the speciation of Cd in the leachates, so the actual incorporation of Cd with Cl^- ligands is not known. In the current study, while there was only a slight positive correlation between mobilised Cd and Cl^- (r=0.31, *p*=0.07; Table 5.2), the Cd complexed to Cl^- (as $CdCl^+$ and $CdCl_2$) increased from 1% to 10% of the total mobilised Cd in the urine applied Te Kowhai and Taranaki soils across both pHs (Table 5.3) in the treatment columns. In the Canterbury soil leachates, only a 1.5% increase in the concentration of total Cd-chloro complexes was shown for urine treated soil at pH 6.1, compared to the soil without urine at the same pH. However, the percentage of total Cd-chloro complexes ranged from 5-8% of the total Cd in all the leachates from this soil.

Even though the highest average Cl^- concentration of 406 mg L^{-1} was found in the leachates of the urine treated Canterbury soil at both pHs, the leachates of the Canterbury soil that did not received urine also contained 112 mg L^{-1} of Cl^- (Appendix D, Table D.1). Therefore, the Cl^- concentration in soil leachates with the urine application was only increased by 3.5-fold in the Canterbury soil, while there was a 22- and 45- fold increase for the Taranaki and Te Kowhai soils, respectively, at both pHs. This might be a reason for why the Cd-chloro complexes in the leachates from the Canterbury soil did not markedly increased with the urine treatment as they increased in the Taranaki and Te Kowhai soils. In addition, the Te Kowhai and Taranaki soils had a higher sandy content than the Canterbury soil, a soil characteristic that often relates to greater leaching of anions like nitrate (Di et al., 2002; Ghorbani et al., 2019; Lehmann et al., 2003). Therefore, similarly greater Cl^- leaching can be expected in sandy soils than in clayey soils. Hence, the influence of Cl^- ligands in urine to bind Cd in leachates may be more pronounced in the Te Kowhai and Taranaki soils than in the Canterbury soil with the urine application.

Consistent with previous studies, the WHAM VII model showed that the majority of mobilised Cd (more than 67%), exists as Cd^{2+} (aquo complexes) at the lower pH in the soils which did not receive urine, except for the Canterbury soil (Cornu et al., 2011; Ren et al., 2015a). In the leachates of the Canterbury soils without urine, the Cd: DOC molar ratio is approximately 100 times less compared to the ratio in the leachates from other soils that did not receive urine, therefore, there may be more organic ligands available from DOM for binding Cd, which can result in a low amount of Cd^{2+} species. In the leachates of urine treated soils, the percentages of Cd^{2+} ions were reduced due to complexation by both DOM and Cl^- ligands compared to respective soil without urine at the same pH across three soils. The total percentages of Cd^{2+} ions, Cd-chloro complexes, and Cd-DOM complexes were >98% of the total mobilised Cd and therefore implies that those species are responsible for transporting Cd.

The results of this study contradict the findings by Gray et al. (2017), who reported that Cd leaching with urine application is governed by the mobilisation of Cd-chloro complexes where they did not observed significant change in DOC concentration in their leachates. While in the current study, Cd leaching as Cd-chloro species appeared to be masked by Cd-DOM complex formation (Table 5.3). As Gray et al. (2017) suggested and compared to current study, reasons for consistent DOC leaching from their soil can be, (1) soil pH was sufficiently buffered to not to release significantly higher amounts of DOM after urine application, (2) due to low soil carbon content. Therefore, influence of Cd-chloro species towards Cd mobilisation with urine application was prominent in their study.

Table 5.3: Results from the speciation modelling and the results for quality analysis of DOM.

soil	pH	Urine Treatment	(Cd^{2+}/ total mobilised Cd) %	(total Cl complexes / total mobilised Cd) %	Cd % bound to colloidal HA	Cd % bound to colloidal FA	Cd % bound to total dissolved humic substances	$SUVA_{254}$ ($L\ mg^{-1}\ m^{-1}$)	E_4/E_6
Te Kowhai	5.4	No	83	0.7	5	9	14	3.29	18.0
Te Kowhai	5.4	Yes	26	10.7	27	34	62	2.46	15.9
Te Kowhai	6.1	No	41	0.4	37	20	57	3.41	20.0
Te Kowhai	6.1	Yes	23	9.1	30	36	66	2.9	15.8
Canterbury	5.4	No	40	7.9	22	30	52	3.87	11.8
Canterbury	5.4	Yes	10	6.7	12	71	83	1.38	17.2
Canterbury	6.1	No	25	5.2	31	39	70	3.66	15.8
Canterbury	6.1	Yes	11	6.7	0	82	82	1.67	15.4
Taranaki	5.4	No	67	1.0	14	17	30	2.47	30.0
Taranaki	5.4	Yes	25	9.1	24	40	64	2.13	20.6
Taranaki	6.1	No	66	1.2	11	20	31	3.61	35.7
Taranaki	6.1	Yes	28	10.5	16	43	59	2.61	21.1

5.3.5 Soil solution speciation of cadmium: insights gained from isotope fractionation

The isotope fractionation in the solution phase (leachates) may provide useful information on speciation of Cd in soil with respect to different treatments (pH and urine). The $^{116/108}$Cd ratio in the leachates at pH 6.1 was lower than the isotope ratio at the pH 5.4 in three soils which did not receive urine (Figure 5.5). This isotope ratio was lower in the leachates from urine treated soils, relative to the leachates from the respective soil at same pH without urine, except for the Canterbury soil at pH 6.2.

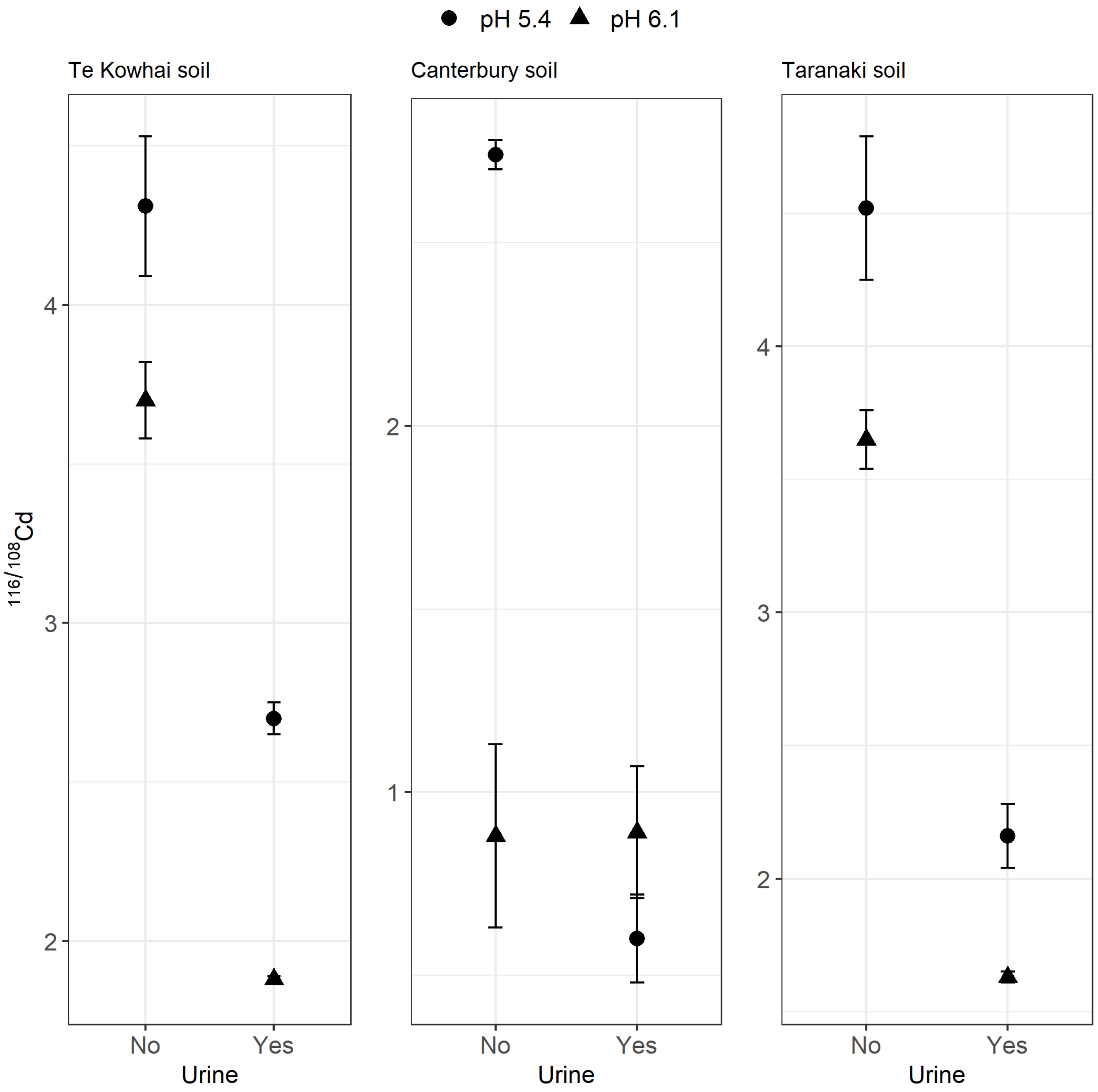


Figure 5.5: The $^{116/108}$Cd ratio in the leachates from the treatment columns. The error bars represent the standard error of the mean (N=3). Note the differences in y-axis scales between soils.

Isotope fractionation in solid and solution phases is generally attributed to the bond lengths of Cd isotopes with their surrounding atoms: heavier isotopes form bonds with lower zero-point energies than lighter isotopes of the same element, therefore bonds formed by heavier isotopes are stronger resulting in shorter bond lengths (Imseng et al., 2019; Wiederhold, 2015). Cadmium in soil solution mainly exists as an aquo-complex, where Cd forms coordination bonds with neighbouring oxygen atoms. Bond lengths of Cd-O in aqueous solution and in Cd-DOM complexes range between 2.24 and 2.30 Å (Karlsson et al., 2005; Ohtaki et al., 1981), while the bond lengths of Cd-O and Cd with other atoms are slightly longer in soil solid phase, for example, Cd bound by goethite has Cd-O bond lengths of 2.30-2.33 Å (Bochatay et al., 2000). The Cd-S bond lengths found in Cd-soil organic matter complexes and CdS (Cadmium sulfide) are around 2.5 Å (Fulda et al., 2013; Karlsson et al., 2005). Therefore, heavier Cd isotopes are likely to be more abundant in the soil solution where the majority of Cd exists as free Cd^{2+} ions (aquo-complexes) while lighter isotopes are enriched in the soil solid phases. This has explained the often-observed Cd fractionation to heavier isotopes in soil solution (Imseng et al., 2018, 2019; Wasylenki et al., 2014) and therefore can be applied to understand the isotope fraction in the leachates with pH and urine treatments.

The change in $^{116/108}Cd$ ratio in leachates with either lime or urine treatment was reflected by the speciation of Cd in the leachates (Table 5.3), where the leachates was enriched with the lighter Cd isotope with decreasing percentage of free Cd^{2+} ions and, therefore, with increasing Cd bound by total dissolved humic substances (Cd-HS; HS-humic substances) and Cd-chloro complexes. This observation can be explained by two theoretical phenomena. Hill et al. (2009) found that chloro-complexes of Fe^{3+} were enriched with lighter Fe isotopes than in aquo-complexes of Fe. Employing the same principle, Wasylenki et al. (2014) suggested that the abundance of chloro complexes of Cd may result in larger Cd isotope fractionation between solution and sorbed phases with Mn-hydroxide than with Cd-*aquo* complexes. Therefore, the first phenomenon that may cause Cd fractionation to lighter isotopes in leachates, especially from urine treated soils is, Cd-chloro complexes may be enriched with lighter isotopes than in Cd-aquo complexes. The second phenomenon that might have caused isotope fractionation is the preferential association of lighter isotopes with the DOM. The bond lengths measured by extended X-ray absorption fine structure spectroscopy (EXAFS) has revealed that the bond lengths of Cd-S in Cd-DOM complexes and Cd-O in organic acids are longer than the Cd-O bond lengths in Cd-aquo complexes (Isaure et al., 2015; Karlsson et al., 2005; Ohtaki et al., 1981). Therefore, in accordance with shorter bonds formation with heavier isotopes, DOM may be enriched with lighter isotopes. The latter phenomenon may be more pronounced in either lime or urine treatment than the influence of Cl^- on isotope fractionation since both treatments increased the Cd-DOM complexes in the leachates to a greater extent than the Cd-chloro complexes.

Cadmium mobility under urine application in shallow columns reflects the potential for Cd leaching towards the subsoil, where the extent of mobility is likely to be determined by the lability of the Cd species to be bound by the soil solid phases. Further, the extent of Cd mobility with DOM complexes may depend on the biodegradability of the DOM. Here, more than 70% of the Cd mobilised from the urine treated soils were found to be associated with soil HS indicating Cd complexation with high Mw DOM, which are relatively resistant to microbial degradation. However, the application of urine may enhance the biodegradability of DOM via the 'positive priming effect', which is the additional or acceleration of decomposition of soil organic matter due to the addition of easily decomposable organic substrate (Kuzyakov et al., 2000; Lambie et al., 2012a, 2013). Therefore, under these conditions, biodegradation of Cd-DOM complexes can release Cd^{2+} ions to the soil solution, which may then adsorb to soil solid phases. This may reduce the topsoil accumulation of Cd in grazed lands (McDowell, 2019). However, leaching of these Cd-DOM complexes to groundwater or other water sources may pollute the drinking water, while biodegradation of those complexes in water bodies may enhance the Cd availability for uptake by aquatic biota.

5.4 Conclusions

The mixing model showed that the contribution of spiked Cd to the total Cd leached was relatively low, which may be attributed to the re-sorption dissolved Cd to the solid phases in the underlying unspiked soil layer. Further testing of soil layers with sequential extractions before and after the leaching may provide useful information in this regard. Mixing models should be carefully applied for source identification under TM leaching, where re-sorption of TMs and changes in dissolved ligands can influence the accuracy of model outputs. Isotope fractionation in solution phases is a useful tool for investigating the speciation of Cd with changes in the solution ligands (DOM and Cl^-), where high Mw DOM and Cl^- ligands may cause Cd isotope fractionation towards lighter isotopes in the soil solution. The work here sought to provide the initial test to understand the potential transport of Cd from contaminated topsoil to subsoil and/or groundwater using isotope tracing.

This work showed that Cd is mainly mobile in soils as Cd^{2+} ion, Cd-DOM, and Cd-chloro complexes, while the percentages of these species differed between soils and with pH and Cd: DOM ratio. The influence of DOM for mobilising Cd was more pronounced than Cl^- in these soils, where Cd-DOM was higher than Cd-chloro complexes. Humic acid-like dissolved organic components played a major role in mobilising Cd in these soils and highlights the potential importance of colloidal DOM as an important species contributing to transport of Cd in soil. The mobilisation of Cd-DOM with cow urine application is likely to be important for Cd leaching in grazed lands. Further understanding is needed to estimate the extent of the mobility of Cd-DOM complexes with cow urine under field conditions investigating the biodegradability of DOM in those complexes.

Chapter 6

3D DIFS-DGT induced metal flux model to identify labile solid pools of isotopes of Cd in soils

6.1 Introduction

Cadmium (Cd) is a toxic metal to biota, which exists in the terrestrial environment at trace levels (Adriano, 2001; Smolders et al., 2013). Fate of soil Cd is a great concern; because Cd that is accumulated in soil can take up by plants, and then enter to animal and human body via food chain, while leaching of soil Cd is a potential threat to drinking water standards and aquatic life toxicity (Kubier et al., 2019; Six et al., 2014; Smolders et al., 2013; Taylor et al., 2017).

In soil, most of Cd is bound to the soil matrix with typically <0.05% present in soil solution (Hooda, 2010). In the solid phase Cd may be associated with structural components, precipitated as carbonates and sulphides, sorbed to organic matter and clay minerals surfaces, while in solution phase it may present as free ion, organic and inorganic complexes and associated with organic and inorganic colloids (Hooda, 2010; Sauve et al., 2000). Free Cd ion is the most reactive species of Cd. Other species may be categorised in to 'labile' to 'non-labile' pools depending on its potential to replenish free ions to the soil solution, when free ion concentration it is depleted by processes like plant uptake or leaching (Degryse et al., 2009).

In most studies, the labile pool of trace metals is expressed by its partitioning between solid and solution phases (i.e. by distribution coefficient). This is frequently determined by sequential or single extractions methods, where the labile pool is operationally defined by the nature of the chemical reagent used for extraction, the volume of extractant with which the soil equilibrates (i.e. soil: extractant ratio) and the duration of the extraction also likely to be important (Degryse et al., 2009). Sequential extractions use harsh acids and bases to determine the different metal pools in soil (e.g. exchangeably bound, organically bound, and residual). These extractions are unlikely to mimic natural soil conditions with the presence of biota, and so may not be suitable for evaluating the potential lability of trace metals. Single extraction methods such as isotope exchange and, extraction with dilute salt or with chelating ligand generally provide a better measure of the soil labile Cd pool (Gray et al., 2003b; Young et al., 2000). However, these extractions also operate with high soil to solution ratio and the soil mixtures are mechanically disturbed from hour to days. For past two decades, the diffusive gradient in thin films (DGT) and DGT-induced flux in soils and sediments (DIFS) have been used to estimate the labile pool of various trace metals in soils, which works under a minimum disturbance of soil and at soil moisture closer to its field capacity (Ernstberger et al., 2002; Lehto et al., 2008; Lehto, 2016), and thus more likely represents natural soil conditions.

Stable isotope ratio is an important tool for studying the fate of trace metals in the environment (Oelze et al., 2014; Okkenhaug et al., 2018; Strobel et al., 2001). As there are nine stable isotopes of Cd with varying natural abundance (^{106}Cd (1.3%), ^{108}Cd(0.9%), ^{110}Cd (12.5%), ^{111}Cd (12.8%), ^{112}Cd (24.1%), ^{113}Cd (12.2%), ^{114}Cd (28.7%), ^{116}Cd (7.5%) (Rosman et al., 1998)) in the environment, Cd isotope ratios have been increasingly used to study the fate of anthropogenic Cd in soil (Imseng et al., 2018, 2019; Salmanzadeh et al., 2017a; Wiggenhauser et al., 2016). It has provided details on the source of contamination, redistribution in soil layers and distribution in various parts of plants.

Cadmium isotopes have been reported to be fractionated to lighter isotopes in soil solid phases and to heavier isotopes in the solution phase (Imseng et al., 2018, 2019; Wasylenki et al., 2014). Therefore, heavier isotopes may be predominantly leached to groundwater from topsoil (Imseng et al., 2018).

The extent of trace metal leaching (or mobility) in soil is largely controlled by the sorption-desorption of soil Cd and these processes may also influence the Cd isotope fractionation (Gray et al., 2003a; Gray et al., 1999; Loganathan et al., 2012; Wiederhold, 2015). Recent study reported that the sorbed Cd is isotopically lighter than desorbed Cd (Imseng et al., 2019). This suggests that heavier Cd isotopes bound to solid phases may be more labile than the lighter isotopes. To date, there have not been any study that have evaluated the size of labile pools and dissociation kinetics of different isotopes of Cd in soils. This information may provide insights to isotope fractionation during desorption from soil labile pools to solution, which is important to study the fate of Cd in soils via isotope ratio tracing.

This study sought to investigate if the labile pool of different Cd isotopes varies between soils and isotopes. The specific objectives were to: (1) evaluate the distribution coefficients for three Cd isotopes (^{108}Cd, ^{112}Cd, and ^{116}Cd) in three soils using the DIFS model for the first time and (2) study the difference between labile pool measured by DIFS and salt extractions for each isotope.

6.1.1 Principles of DGT and DIFS

The DGT device contains a metal-binding resin overlaid with a diffusive gel and a protective filter membrane. When a DGT device is deployed in soil, free metal ions at the soil-diffusive layer boundary start to diffuse through the diffusive gel, which are then readily and strongly bound by the resin, thus the free metal ion concentration at the resin-gel boundary is effectively zero. Soon after deployment (~1 h) a linear concentration gradient between the soil-diffusive layer interface and the resin-diffusive gel interface develops, resulting in a constant diffusive flux of metal ions to the DGT device. The metal flux (*F(t)*) to the binding resin can be expressed by Fick's law of diffusion, which is expressed by equation 6.1.

$$F(t) = \frac{\varphi_d \times D_d \times C(t)}{\Delta g} \tag{6.1}$$

where φ_d is the porosity of the diffusive gel, D_d is the diffusion coefficient for the metal in the diffusion gel, Δg is the thickness of the diffusive layer and *C(t)* is the metal concentration in the solution.

The mass accumulated in the resin per unit area at a certain time (*M*) can be calculated by integrating the *F(t)* with time. Once *M* has been measured, equation 6.1 can be adapted to estimate the average metal concentration at the soil-diffusion layer interface over the deployment period. This is expressed as C_{DGT} and can be calculated using equation 6.2.

$$C_{DGT} = \frac{M \times \Delta g}{\varphi_d \times D_d \times t} \tag{6.2}$$

where, *t* is the deployment time.

M can be determined experimentally by equation 6.3 where $C_{e,}$ is the concentration of the metal in the elute after elution of the binding resin with 1 M HNO_3 for Cd, V_{HNO3} and V_{gel} are the volume of the acid and the resin gel respectively, and f_e is the elution factor and A_E is the effective exposure area of the DGT probe.

$$M = \frac{C_e \times (V_{HNO_3} + V_{gel})}{f_e \times A_E} \tag{6.3}$$

When a DGT probe is deployed in soil, the dissolved metal ion concentration at the probe interface is depleted and induces metal ion dissociation of labile metal-ligand complexes in the solution and desorption from labile soil solid phases. Therefore, the mass accumulation in the resin during the deployment is governed by: (1) concentration of free metal ions, (2) dissociation from labile complexes and (3) desorption from solid phases.

The comparison of DGT labile concentration with the soil solution concentration (C^{soln}) by calculating the ratio *R* (equation 6.4) reflects the extent of metal depletion in the soil medium induced by DGT over a given time (*t*),

$$R(t) = \frac{C_{DGT}(t)}{C^{soln}} \tag{6.4}$$

The time dependence of *R* is determined by two key parameters, (1) K_{dl}, the distribution coefficient based on labile solid pool components that can exchange with the solution phase and, (2) $T_{c,}$ response time, the time taken by the DGT labile solid pool and solution concentration to reach to 63% of their equilibrium values if the solution concentration depleted to zero (Honeyman et al., 1988). Both K_{dl} and T_c are determined by the sorption-desorption rate of labile Cd species in soil solid and solution phases. Therefore, K_{dl} and T_c are expressed by sorption and desorption rate constants, k_1 and k_{-1} respectively (equations 6.5 and 6.6).

$$K_{dl} = \frac{C^{ls}}{C^{soln}} = \frac{k_1}{P_c \times k_{-1}} \tag{6.5}$$

$$T_c = \frac{1}{k_1 + k_{-1}} \tag{6.6}$$

where, C^{ls} (g kg^{-1} of soil) is the metal concentration in the DGT labile solid phase and P_c is the particle concentration, expressed as mass of particles in a given volume of soil (g cm^{-3}).

6.2 Materials and Methods

6.2.1 DGT gel preparation and probe assembly

A detailed description of gel preparation and assembly of the most commonly used 'standard' DGT probes employed here is given elsewhere (Zhang et al., 1995). Briefly, the diffusive gel was prepared by polymerizing a gel solution containing 15% acrylamide (Acrylamide Solution, Fisher BioReagents) and 0.3% DGT cross-linker (DGT Research Ltd, Lancaster, UK) by adding ammonium persulphate (APS; Sigma-Aldrich) and TEMED (tetramethylethylenediamine; Sigma-Aldrich) and left for 1 h at 45 °C for settling. The binding resin was prepared by mixing Chelex-100 (200-400 mesh, Bio-Rad) with the gel solution and polymerizing similarly with APS and TEMED and settling for 45 minutes at 45 °C. The gels were hydrated for 24 h in high-pure water (18.2 MΩ resistivity; Barnstead^{TM} GenPure^{TM} Pro Water Purification System, Thermo Scientific) during which the water was changed 3-4 times. The thicknesses of the hydrated diffusive and resin gels were 0.08 and 0.04 cm, respectively. The DGT plastic holder designed for soil deployment were supplied by DGT Research Limited, Lancaster, UK. In the DGT holder, the diffusive gel was placed on top of the binding resin and overlain by a protective filter membrane (thickness of 0.013 cm), in which the metals have similar diffusion characteristics as in the diffusive gel (Davison et al., 2016). Therefore, the total thickness of the material diffusion layer, δ^{MDL} is 0.093 cm.

6.2.2 Soil locations, characterisation and cadmium spiking

Three soils were collected from distinct soil orders from New Zealand (as defined by Hewitt (2010)). The soil collected from Canterbury region (43° 30′ 22″ S, 172° 22′ 24″ E) was a Weathered Fluvial Recent soil ('Canterbury soil'); a Typic Orthic Allophanic soil was collected from Taranaki ('Taranaki soil') and a Peaty Orthic Gley soil was collected from Waikato region (37° 46′ 11″ S, 175° 22′ 5″ E; 'Te

Kowhai soil'). After manually removing plant materials and rocks, soils were sieved through a 4 mm plastic sieve. Subsamples of soil were air-dried and sieved through a 2 mm nylon sieve for analysis of following physical and chemical properties.

Soil characterisation: Soil particle size distribution was analysed by laser diffraction method using Mastersizer 2000 (Malvern Instruments Ltd, UK); the soils were pre-treated with 30% H_2O_2 to remove organic matter, which may interfere with the particle size measurements. Soil pH was measured in a 1:2.5 ratio, soil: solution mixture using a pH meter (Mettler Toledo Seven Easy pH meter) (Blakemore, 1987). Total soil N was determined using Vario MAX CN element analyser (Elementar, Germany). Soil organic carbon (SOC) content was measured by loss on ignition (LOI) (Blakemore, 1987). Cation exchange capacity (CEC) of the soils were determined by the ammonium acetate (pH 7) method (Brown, 1943). The soil was acid digested using CEM MARS XPRESS microwave (Kovács et al., 2000) to determine the pseudo-total Cd, and other elements (eg. Al, Fe) in ICP-Mass Spectroscopy (ICP-MS, Agilent 7500cx). Soil properties are shown in Table 6.1.

Spiking with Cd isotopes: Each soil was spiked with ^{108}Cd, ^{116}Cd (Cambridge Isotope Laboratories, USA) isotopes and with Cd at its natural abundance ($Cd(NO_3)_2.4H_2O$,BDH chemical: ^{108}Cd: 0.9%, ^{112}Cd: 24.2% and ^{116}Cd: 7.5%). Cadmium solutions of 100 mg L^{-1} for ^{108}Cd and ^{116}Cd isotopes were prepared as described by Lee et al. (1998). Briefly, 10 mg of each isotope was dissolved in 10 mL of 2% HNO_3 (PrimarPlus-Trace Analysis grade), then diluted to 30 mL with high-purity water. The pH of the solution was adjusted to 7 with 1 M NaOH (Sigma-Aldrich) and diluted to 100 mL with high-purity water. Cadmium solution of 100 mg L^{-1} where all the Cd isotopes assumed to present at their natural abundance (Rosman et al., 1998) was prepared from $Cd(NO_3)_2.4H_2O$ (BDH chemical). Each soil was spiked to 0.66 mg kg^{-1} with ^{108}Cd, ^{116}Cd isotopes and Cd at its natural abundance (i.e total spike of ~2 mg kg^{-1}). These soils were then left to equilibrate for 5 months at 20 °C after spiking with lime ($CaCO_3$, Sigma-Aldrich), during which the moisture was maintained at 50-60% of field capacity (FC). The pH of all soils stabilised at 6.1±0.1 and the $Ca(NO_3)_2$ extractable Cd plateaued after 3 months (Appendix E, Figure E.1). The Cd spiked soils were air-dried, and then acid digested to measure the total concentrations of ^{108}Cd, ^{112}Cd and ^{116}Cd isotopes in ICP-MS (Agilent Technologies, Santa Clara, California, USA.)

6.2.3 Soil slurry preparation and DGT deployment

The time series deployment of DGT probes followed the basic principles first employed by Ernstberger et al. (2002), with a key modification to allow entry of air to a greater volume of soil and thus reduce the possibility of anoxic conditions occurring. The soils were prepared for DGT deployment by creating a slurry from 500 g of each Cd spiked soil and bringing to 100-120% of the FC, with deionised water, and allowing it to equilibrate for 24 h before the deployment. The slurry was placed on top of the DGT device up to exactly 1.2 cm height and contained within a pre-acid cleaned plastic sleeve wrapped around the circumference of the probe cap, thus providing a well-defined geometry for the soil (Figure 6.1). DGT probe-soil set-ups were prepared for the deployment times between 4 h to 20 days, where the maximum deployment times for the Canterbury, Te Kowhai, and Taranaki soils were 480, 384 and 192 h, respectively. These deployment times were selected according to times used by Ernstberger et al. (2005), who deployed DGT probes for 480 h in soils with ~5% of SOC. The deployment times were reduced by 20% and 40% to account for the higher SOC content in Te Kowhai and Taranaki soils respectively, to reduce the chance of anoxia occurring in the soil. The weights of the DGT probe-soil assembly with and without the soil were recorded to calculate the average particle concentration and the porosity of each soil. The DGT probe-soil assembly was covered with a plastic bag, which contained a few drops of deionised water and incubated at 20 °C throughout the deployment period. The bags were opened and refreshed with air regularly and the moisture level of the soil slurry was maintained at 90-100% of the initial moisture content. At the end of the deployment period, the DGT probe was retrieved and adhering soil was gently washed off using a jet of deionised water. The probe was then disassembled, and the resin gel was eluted with 1 mL of 1 M HNO_3 (PrimarPlus-Trace Analysis grade, Fisher Scientific, UK) for 24 h. After, the binding resin was removed, and the eluent was diluted with 1% HNO_3 and analysed for ^{108}Cd, ^{112}Cd and ^{116}Cd isotopes via ICP-MS.

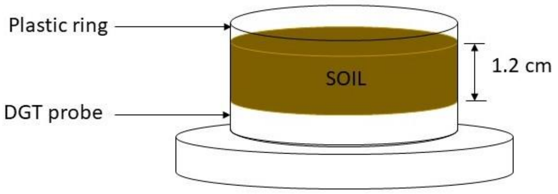


Figure 6.1: The DGT-soil deployment experimental assembly

The mass accumulated in the resin was calculated by substituting experimentally determined Cd concentration in the equation 6.3 for each time step. The V_{HNO3}, V_{gel}, A_E and f_e were 1 mL, 0.2 mL, 3.08 cm^2 and 0.84 (Garmo et al., 2003), respectively. This mass was used to calculate the DGT labile concentration (C_{DGT}) using the equations 6.2, where Δg, φ_d, D_d was 0.093 cm, 0.95 and 6.26×10^{-6} cm^2 s^{-1}, respectively. Then R was calculated for each time step using the C_{DGT} and the porewater concentration measured as described in section 6.1.1.

6.2.4 Soil porewater

Subsamples of soil slurry were packed to 50 mL pre-acid cleaned plastic containers, in triplicates. Acid-cleaned Rhizon samplers (Rhizon Research Products, The Netherlands) were inserted horizontally to the soil to collect the soil porewater to measure the concentration of each isotope in soil porewater (C^{soln}). The Rhizon samplers collected approximately 2-3 mL of the soil porewater over 12 h, which was then diluted with 1% HNO_3 and analysed for Cd isotopes (^{108}Cd, ^{112}Cd and ^{116}Cd) concentrations by ICP-MS (Table 6.1).

6.2.5 Soil-nitrate concentration

After retrieval of each DGT probe, the soil was extracted with KCl to determine the soil nitrate (NO_3^-) concentration (Blakemore, 1987) to ensure that the soil had not become anoxic during the deployment period (Scholz, 2016). Briefly, 4.00 g of wet soil was equilibrated with 40 mL of 2 M KCl (Reagent grade, Scharlau) for 1 h in an end-over-end shaker. Then the soil mixture was centrifuged for 10 minutes at 2000 rpm, and the supernatant was filtered through Whatman 42 filter paper and analysed for NO_3^- concentration by photometry using SMARTCHEM 200 (AMS Alliance, France). Another subsample of soil was oven-dried to determine the moisture content to express NO_3^- concentrations on an oven-dried basis; nitrate concentration was stable throughout the deployment period (Appendix E, Figure E.2).

6.2.6 0.05 M $Ca(NO_3)_2$ extractable cadmium

Exchangeable each Cd isotope was measured by extracting soil samples with 0.05 M $Ca(NO_3)_2$, as described by Gray et al. (1999). Briefly, 5.00 g of air-dried soil was mixed with 30 mL of 0.05 M $Ca(NO_3)_2$ (Sigma-Aldrich) then homogenised in an end-over-end shaker for 2 h. The soil solution mixture was centrifuged at 2000 rpm for 20 min and filtered through Whatman 42 filter paper. The solutions were frozen at -20 °C until analysed for Cd isotopes (^{108}Cd, ^{112}Cd and ^{116}Cd) in ICP-MS. The extractions were performed in three replicates. By dividing the $Ca(NO_3)_2$ extractable Cd concentration of each isotope (µg kg^{-1}) (Table 6.1) by Cd concentration of the respective isotope in the soil porewater (µg L^{-1}), distribution coefficient (K_{d_EX} (g cm^{-3})) for exchangeable Cd (Ernstberger et al., 2002) was calculated for each isotope.

6.2.7 Measuring cadmium isotope concentrations

Cadmium isotope (^{108}Cd, ^{112}Cd and ^{116}Cd) concentrations were measured using triple-quadrupole (QQQ)-ICP-MS (Agilent Technologies, Santa Clara, California, USA) controlled by MassHunter Workstation (version 4.5). Calibration curve for each isotope was prepared with respect to concentration of each isotope in a series of standard solutions, in which all Cd isotopes assumed to present at their natural abundance (Rosman et al., 1998). Accuracy of the calibration in the isotope analyses was confirmed by repeated analysis of ^{108}Cd and ^{116}Cd isotope solutions with known concentrations.

Table 6.1: Physicochemical properties of soils and concentration of each isotope in porewater and 0.05 M $Ca(NO_3)_2$ soil extracts.

	Te Kowhai	Canterbury	Taranaki
Clay/silt/sand%	4/25/70	5/34/62	2/14/84
pH (H_2O)†	5.5	5.3	4.9
CEC (cmol kg^{-1})*	18	15	18
Soil organic carbon (SOC)%	6.97(0.01)	3.68(0.04)	12.40 (0.05)
Al (g kg^{-1})	40.8 (0.3)	32.1(0.6)	20.8(0.7)
Fe (g kg^{-1})	10.8(0.8)	20.5(0.5)	21.4(0.05)
Mn (g kg^{-1})	0.4 (8.2×10^{-4})	0.5 (0.01)	0.61(0.01)
^{108}Cd (mg kg^{-1})ŧ	0.56(0.01)	0.47(0.03)	0.44 (0.06)
^{112}Cd (mg kg^{-1})ŧ	0.40 (0.01)	0.27 (0.03)	0.33 (0.04)
^{116}Cd (mg kg^{-1})ŧ	0.59 (0.01)	0.69 (0.03)	0.41(0.07)
Porewater concentration (µg L^{-1})			
^{108}Cd	1.57(0.03)	2.73 (0.03)	1.39(0.06)
^{112}Cd	1.11 (0.004)	1.35(0.03)	1.08(0.04)
^{116}Cd	1.95 (0.1)	3.31(0.06)	1.72(0.07)
Concentration in $Ca(NO_3)_2$ extracts (µg kg^{-1})			
^{108}Cd	21.3(3.0)	10.1(0.7)	38.7(7.3)
^{112}Cd	16.6(2.9)	6.2(0.4)	17.5(3.3)
^{116}Cd	30.7(2.7)	12.0(0.8)	44.7(7.8)

†pH of the unlimed soils. ŧ Total acid extractable concentrations of each isotope in the spiked soils Standard error of the mean is given in the brackets (n=2, except n=3 for acid extractable isotope concentrations in soil and concentration in $Ca(NO_3)_2$extracts).
* Data from Analytical Research Laboratories (ARL), NZ.

6.2.8 Statistical analysis

Data analysis and visualisation were carried out using R (R core Team, 2018) and Minitab 18®(Mintab ® 18.1, Minitab, Inc.). Differences for K_d values were tested by ANOVA with Tukey post-hoc at the 0.05 significance level.

6.2.9 DIFS model concept and inputs

In this work K_{dl} and T_c for different Cd isotopes were determined numerically by modelling the Cd accumulation in the binding resin employing the same model concepts used for 1D and 2D-DIFS modelling software (Harper et al., 1998) but via the COMSOL multiphysics® (v.5.1; Comsol Inc., Stockholm, Sweden) finite modelling framework. The model concepts and formulations used for this work are briefly explained here; a detailed explanation of underlying principles and assumptions for DIFS modelling in the soil are documented elsewhere (Harper et al., 1998; Sochaczewski et al., 2007).

The model consists of two compartments, the dissolved phase and sorbed phase, and two subdomains, diffusive gel and the soil (Lehto, 2016). The model domain for the 3D model was built up as a 2D-axisymmetric model, following the previously applied method of providing 3D representation but with reduced demands on computer power (Menezes-Blackburn et al., 2019; Santner et al., 2015). The approach here relies on the 2D model domain having infinite planes of symmetry, which can be achieved by establishing the origin at the centre of the binding resin-diffusive gel interface of the DGT probe-soil deployment system.

The model assumes, (1) there is no interaction of the metal with the diffusion layer, (2) a stationary binding phase, (3) metal binding to the resin is effectively irreversible during the deployment (defined by low metal-resin complex dissociation rate constant) and the metal bound by the resin is stationary and (4) transport of metal on soil colloidal is negligible. The metal transport in the diffusive gel and the soil solution is solely by diffusion, which is described by Fick's law of diffusion that includes a metal and temperature-specific diffusion coefficient. The reactions determining the metal binding by the resin are given below (Figure 6.2). The mobile species is likely to have included the free metal ions, as well as the metal-ligand complexes (organic and/or inorganic) in the soil solution. For simplicity, it was assumed that the metal associated with these complexes was fully labile within the deployment period.

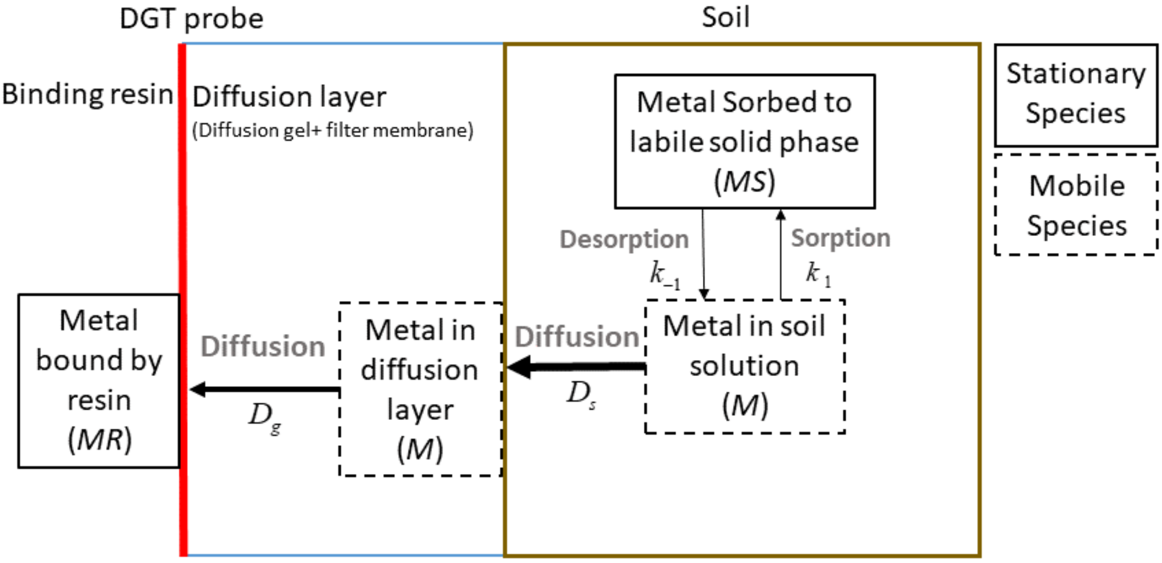


Figure 6.2: Components and process in DIFS model. D_g, D_s are diffusion coefficients of metal in the diffusive gel and soil, respectively. k_1 and k_{-1} are the sorption and desorption rate constants, respectively.

Concentration (*C*) of metal species in solution and solid phases are derived from the below equation 6.7, which is determined by the diffusion of metal in solution and any reaction (R_E) taking place in the solid or solution phase of interest. The D_{s_m} is the diffusion coefficient of the species *s*, in the medium *m*.

$$\frac{\partial C}{\partial t} = \nabla\left(D_{s\_m}\nabla C\right) + R_E \tag{6.7}$$

The metal species can exist as mobile solution species (*M*), metal sorbed to soil solid phase (*MS*) and metal bound to resin (*MR*) in the model domain. The below equations describe the kinetics and transport of the metal species in the diffusive gel (equation 6.8), soil solution (equation 6.9) and in the soil solid phase (equation 6.10) derived from equation 6.7, D_g and D_s are the diffusion coefficients of the metal in the diffusive gel and soil, respectively.

$$\frac{\partial M}{\partial t} = \nabla\left(D_g \nabla M\right) \tag{6.8}$$

$$\frac{\partial M}{\partial t} = \nabla\left(D_s \nabla M\right) + k_{-1} P_c MS + k_1 M \tag{6.9}$$

$$\frac{\partial MS}{\partial t} = \frac{k_1 M}{P_c} + k_{-1} MS \tag{6.10}$$

The metal concentration in the binding resin-diffusive gel interface is defined by constant zero concentration boundary condition, which sustains the diffusive flux of metal to the binding resin. Thus, the model simulates the metal accumulation in the binding resin by integrating the metal flux to the resin over the deployment period. For various combinations of K_{dl} and T_c, the metal accumulated in resin per unit area of the resin, was calculated using the COMSOL Multiphysics software. Once this is known, the C_{DGT} (equation 6.2) and R (equation 6.4) were calculated manually for those combinations of K_{dl} and T_c. An error index (*E,* equation 6.11) was used to determine the best fit between modelled R values from different combination of K_{dl} and T_c and the for experimentally determined *R* (Lehto et al., 2008).

$$E = 100 \times \sqrt{\sum_{i=1}^{N}\left(R_e\left(t_i\right) - R_m\left(t_i\right)\right)^2} \tag{6.11}$$

where, $R_e(t_i)$ and $R_m(t_i)$ are experimentally and model derived *R*, at time t_i respectively. Combination of K_{dl} and T_c that gives lowest E value is the best fit to explain the experimental *R*. Often, range of K_{dl} and T_c gives equally low *E* values (Lehto et al., 2008; Menezes-Blackburn et al., 2019), therefore, *E* was calculated for ranges of K_{dl} and T_c for each isotope in each soil. These E values were mapped against ranges of K_{dl} and T_c tested to find the ranges of K_{dl} and T_c, which can explain the experimental R.

In this study to avoid soil reaching an anoxic condition during long deployment period, the soil sink was constrained to small volume by the experimental design, hence the accurate definition of domain dimensions was also necessary to understand the kinetics involved in this specific DGT-soil domain, which can be easily done in model development by COMSOL multiphysics. Moreover, while other studies used a generally accepted particle density of 2.65 g cm^{-3} for all soil-even though it can vary (2.4-2.9 g cm^{-3}) depending on soil minerals composition and the organic matter content (McBride et al., 2012; Skopp, 2000), current study measured the particle density (ρ_p) for each soil using pycnometer method (Flint et al., 2018), thus porosities and particle concentrations are calculated precisely for each soil. The input parameters for the DIFS model are listed in Table E.1 and E.2 in Appendix E.

Here, for C_{DGT} calculations and DIFS modelling assumed that ^{108}Cd and ^{116}Cd had similar diffusion properties as ^{112}Cd. The diffusion coefficient (D) for divalent ions in water has shown an inverse power-law mass dependence ($D \propto m^{-\beta}$) with $0.00<\beta<0.01$ (Bourg et al., 2010). According to this concept, the difference in diffusion coefficients for ^{108}Cd and ^{116}Cd isotopes compared to ^{112}Cd were <0.05%, therefore equal diffusion coefficient for all three isotopes in water was assumed. This has also been confirmed experimentally for DGT devices in solutions (Mahdiyeh Salmanzadeh, Personal Communication, 10th Feb. 2020). Hence, any difference in the mass accumulated in the binding resin over the deployment period, and therefore the R-values of each isotope should be attributed to the resupply kinetics of each isotope from the labile solid pool rather than their transport properties.

6.3 Results and discussion

6.3.1 K_{dl}, T_c, k_{-1} and K_{d_EX} variation between different isotopes

The K_{dl} for ^{112}Cd isotope was generally below those for ^{108}Cd for all soils, but the K_{dl} ranges for these two isotopes overlap slightly in the Taranaki soil. The K_{dl} determined for the ^{116}Cd isotope in the soils were generally less well defined. In the Te Kowhai and Canterbury soils, K_{dl} for ^{116}Cd is lower than ^{108}Cd but higher than for ^{112}Cd. In the Taranaki soil K_{dl} for ^{116}Cd is higher than for the ^{112}Cd, but effectively similar to ^{108}Cd isotopes. This may be because of the low sensitivity to isotope partitioning effects due to the small size of the labile solid pool (K_{dl}<8 cm^3 g^{-1}) in that soil. The slightly lower K_{dl} for ^{112}Cd than for the other two isotopes in three soils possibly due to the differences in the contact time of each isotope with the soil. Soil extractions with dilute salts have shown that, extractable Cd reduced with the increasing contact time between soil and the spiked Cd (Gray et al., 1998). Gray et al. (1998) suggested this was because of the redistribution of metal ions to the non-labile pools and/or solid-state diffusion of metal ions to mineral lattice structures with increasing contact time. Given that ^{112}Cd is the most naturally abundant Cd isotope, ^{112}Cd should have been at a greater abundance in theses soils than the other two isotopes before spiking. Hence most of ^{112}Cd may be strongly associated with the soil solid phases, more so than the other two isotopes which are relatively freshly applied.

The response time, T_c and the desorption rate constant, k_{-1} for different isotopes reflect desorption kinetics of each isotope (Harper et al., 1998). For all three soils, T_c was higher for ^{112}Cd isotope than for ^{108}Cd and ^{116}Cd isotope. In the Te Kowhai and Taranaki soils, the ranges of T_c for ^{108}Cd and ^{116}Cd isotopes were similar, while in the Canterbury soil T_c for ^{116}Cd was lower than for ^{108}Cd. In three soils, k_{-1} for three isotope had similar k_{-1} ranges, however the spread of range was larger for ^{116}Cd than the other two isotopes. Overall higher T_c for ^{112}Cd than the other two isotopes can also possibly due to the different contact time of each isotope with the soils. McLaren et al. (1998) studied the Cd desorption kinetics from soil clay fractions with respect to contact time, by employing different sorption periods. They found that the time taken for Cd solution concentration to reach half of its initial concentration after desorption (half-life) became longer with increasing sorption time, which they attributed to movement of Cd to slow desorption sites with increasing contact time. As suggested above most of ^{112}Cd may be strongly sorbed on to soil solid phases than ^{108}Cd and ^{116}Cd isotopes, because of its longer contact time. Therefore, in agreement with McLaren et al. (1998) this may result in slow desorption of ^{112}Cd to the soil solution than the other two isotopes. However, there may be fast desorbing ^{112}Cd isotopes as well, because some ^{112}Cd was freshly added to the soils with the Cd spike solution where all Cd isotopes were assumed to be at their natural abundances. Therefore, further investigation is recommended with less naturally abundant isotopes to investigate whether the contact times of different isotopes affect their labile pools and desorption kinetics to avoid interference from native Cd isotopes in soils. Overall, the K_{dl}, T_c and k_{-1} for all three Cd isotopes agree with previously found results for Cd in soils using one- and two-dimensional DIFS models (measured at their natural abundances) (Ernstberger et al., 2002; Ernstberger et al., 2005; Lehto et al., 2008).

The 0.05 M $Ca(NO_3)_2$ extract-derived K_{d_EX}, for ^{112}Cd was slightly lower than for ^{108}Cd and ^{116}Cd isotopes in all three soils but they were not significantly different ($p>0.05$) (Table 6.2). The slightly lower K_{d_ex} for ^{112}Cd than for the other two isotopes can also be related to the difference in the contact time of each isotope with soil as explained for K_{dl}.

Table 6.2: DIFS Modelled parameters (K_{dl}, T_c , k_1, k_{-1}) and error function *E* and K_{d_EX} for the isotopes of Cd.

	^{108}Cd	^{112}Cd	^{116}Cd
Te Kowhai			
K_{d_EX} $Ca(NO_3)_2$ exchangeable (cm^3 g^{-1})	13.5±1.9AB	15.0±2.6AB	15.7±1.4A
K_{dl} (cm^3 g^{-1})	115-215	90-110	95-160
T_c (s)	960-1140	1860-2140	980-1160
E	≤14.5	≤11	≤15
k_{-1} (X 10^{-6} s^{-1})	2.41-5.33	2.50-3.51	3.18-6.32
k_1 (X 10^{-4} s^{-1})	8.73-10.75	4.65-5.34	8.57-10.17
Canterbury			
K_{d_EX} $Ca(NO_3)_2$ exchangeable (cm^3 g^{-1})	14.2±2.7AB	13.0±2.5 AB	13.5±2.4AB
K_{dl} (cm^3 g^{-1})	55-70	25-50	40-48
T_c (s)	3000-3070	4450-5550	2000-3100
E	≤11.5	≤10	≤11.5
k_{-1} (X 10^{-6} s^{-1})	1.56-2.04	1.21-3.00	2.25-4.19
k_1 (X 10^{-4} s^{-1})	3.24-3.32	1.78-2.23	3.20-4.96
Taranaki			
K_{d_EX} $Ca(NO_3)_2$ exchangeable (cm^3 g^{-1})	7.3±0.5AB	5.7±0.3B	7.0±0.4AB
K_{dl} (cm^3 g^{-1})	3-7.4	1.7-3.5	2.6-7.6
T_c (s)	9000-16000	15000-35000	8000-19500
E	≤9.0	≤7.5	≤10.5
k_{-1} (X 10^{-6} s^{-1})	4.87-19.16	4.33-17.92	3.90-24.22
k_1 (X 10^{-4} s^{-1})	0.52-1.02	0.21-0.57	0.41-1.16

The K_d values sharing the same letters are not significantly different ($p<0.05$, n=3). The standard error of the mean is given in the brackets (n=3).

6.3.2 Labile pool of cadmium measured by DGT vs $Ca(NO_3)_2$ extracts

The K_{dl} values for each Cd isotope in the Taranaki soil were in best agreement with ifs K_{d_EX} values, while for the Canterbury soil both values were considerably closer, but higher K_{d_EX} than K_{dl} (Table 6.2). However, for the Te Kowhai soil there was a large difference between those values. The higher K_{dl} than K_{d_EX} is consistent with Ernstberger et al. (2002), who also observed higher K_{dl} for Cd, Cu, Ni and Zn than K_d determined by 0.1 M $Ca(NO_3)_2$ extractions. It is noteworthy that the equilibrium time allowed by Ernstberger et al. (2002) was 5 days for $Ca(NO_3)_2$ extraction, while in current study soils were only equilibrated with 0.05 M $Ca(NO_3)_2$ for 2 h. It was also reported that K_{dl} for Cd is closely related to K_d

determined by isotope exchange experiments (Ernstberger et al., 2002; Ernstberger et al., 2005), where isotope exchangeable trace metals are often used to identify the labile metal fraction in soils (Degryse et al., 2009; Young et al., 2000). For the Taranaki soil, the K_{dl} and K_{d_EX} are much more closely related, suggesting that the same labile pool of Cd is measured by both DGT and $Ca(NO_3)_2$ extractions, likely just the exchangeably bound Cd. The higher K_{dl} than K_{d_EX} for the Te Kowhai and Canterbury soils imply that DGT labile Cd pool is larger than the labile pool measured by $Ca(NO_3)_2$ extracts in those soils. The $Ca(NO_3)_2$ extraction measures the equilibrium partitioning of metal between the soils and solution, while DGT measures this partitioning based on kinetics of metal sorption-desorption between soil and solution and transport properties of metal in a dynamic non-equilibrium system. Thus, the DGT-labile Cd solid pool is a better estimate of the labile soil Cd pool, which has potential to replenish the Cd to soil solution when Cd in soil solution is removed by biota and/or via leaching.

6.3.3 Labile pools of cadmium in different soils

Sorption-desorption kinetics and size of the labile pool of Cd in soil may vary between soils depending on available soil solid phase surface (e.g. organic matter, clay minerals, and metal oxides) for binding Cd. The highest K_{dl} was observed for the Te Kowhai soil and the lowest for the Taranaki soil (Table 6.2). A similar trend was shown for the K_{d_EX} between soils, but the K_{d_EX} between the Taranaki and other two soils were only significantly different (p=0.5-0.03) (Table 6.2). Ernstberger et al. (2005) tested the partitioning of Cd in five distinct soils by extracting soils with 0.1 M $Ca(NO_3)_2$ for 5 days and then calculated a K_d using the ratio between total extractable and porewater concentration. They also measured K_{dl} using DGT-DIFS for Cd like here, except that they used the one-dimensional version of the model available at the time and only measured Cd at its natural abundance. They reported that the soil with highest SOC content (5.81%) had higher K_{dl} (1800 mL g^{-1}) and K_d (2750 mL g^{-1}) compared to soils with SOC content below 1.5% (K_{dl}: less than 50 mL g^{-1}, $K_{d,}$: less than 100 mL g^{-1}). Conversely, in the current study, the Taranaki soil, which had the highest amount of SOC (12.2% Table 6.1), had lower K_d and K_{dl_EX} for three isotopes than the other two soils. The low K_{dl} and K_{d_EX} for Cd isotopes in the Taranaki soil despite its high SOC content may be due to its sandy texture (84%), since both K_{dl} and K_{d_EX} tend to scale with clay content (Ernstberger et al., 2005). Further, this is an allophanic soil, where the allophane minerals have a high affinity for binding Cd (Bolan et al., 2013), so bound Cd may not be labile to desorb during the DGT deployment time. The K_{dl} for the isotopes in the Canterbury soil is in agreement with K_{dl} measured by Ernstberger et al. (2005) for Cd in a sandy brown soil, where both soils belong to same texture group (sandy loam) and had similar soil pH (6.1-6.2).

In agreement with Ernstberger et al. (2005), the longest response time and highest desorption rate constant were obtained for the soil with the smallest labile pools for three isotopes (Taranaki soil, low K_{dl}). High T_c obtained for the Taranaki soil may be because of the strong Cd binding to allophane minerals and/or OM in that soil resulting in slow Cd desorption, which is also supported by low K_{dl} and K_{d_EX}. The k_{-1} for Cd isotopes in three soils ranged from 2.4 X 10^{-5} to 1.21 X 10^{-6} s^{-1} for all samples are in agreement with k_{-1} measured in marine particle (3.5 X 10^{-5} to 1.2 X 10^{-5} s^{-1}) and in soils (1.6 X 10^{-5} to 1.35 X 10^{-4} s^{-1}) (Ernstberger et al., 2005; Nyffeler et al., 1984).

6.3.4 3D-DIFS model for estimating the optimum K_{dl} and T_c to fit the experimental *R*-values

Sochaczewski et al. (2007) suggested that a 3D-DIFS model would provide a better representation of soil DGT deployment than models working in one and two dimensions. They suggested that was because a 3D-DIFS would include lateral diffusion of solute from the soil matrix, which affects the calculation of metal flux from the soil to the binding resin. Lateral diffusion of solute in the diffusion layer is also likely to be important (Santner et al., 2015). The modelling here also considered a constrained soil volume, which further necessitated the bespoke modelling approach employed. First demonstrated by Lehto et al. (2008), and subsequently Menezes-Blackburn et al. (2019) by a range of K_{dl} and T_c fitted well with the experimental *R*-values giving equally low *E*-values (Figure 6.3). For a better comparison of model vs experimental R values, some points that clearly deviated from the data trend were excluded (Figure 6.4, red colour data points). The best fits (lowest *E*) for experimental *R* for the three isotopes were obtained for the Taranaki soil while the worst was for the Te Kowhai soil. In the Te Kowhai soil, the data points after 48 h did not fit to the model unlike the in the other two soils (Figure 6.4), which may be the reason for the large variation in K_{dl} in that soil, where usually the data points between 50-300 h estimate the K_{dl} (Lehto et al., 2008). Lehto et al. (2006b) reported that for small labile solid phase (K_{dl} =10 cm^3 g^{-1}), the T_c has little effect on the accumulation of solute by DGT, and thus on *R*. Therefore, for all the soils considered here, the error caused by the spread in T_c is expected to be small, especially for the Taranaki soil, in which the labile pool was relatively small (K_{dl}= 1-8 cm^3 g^{-1}).

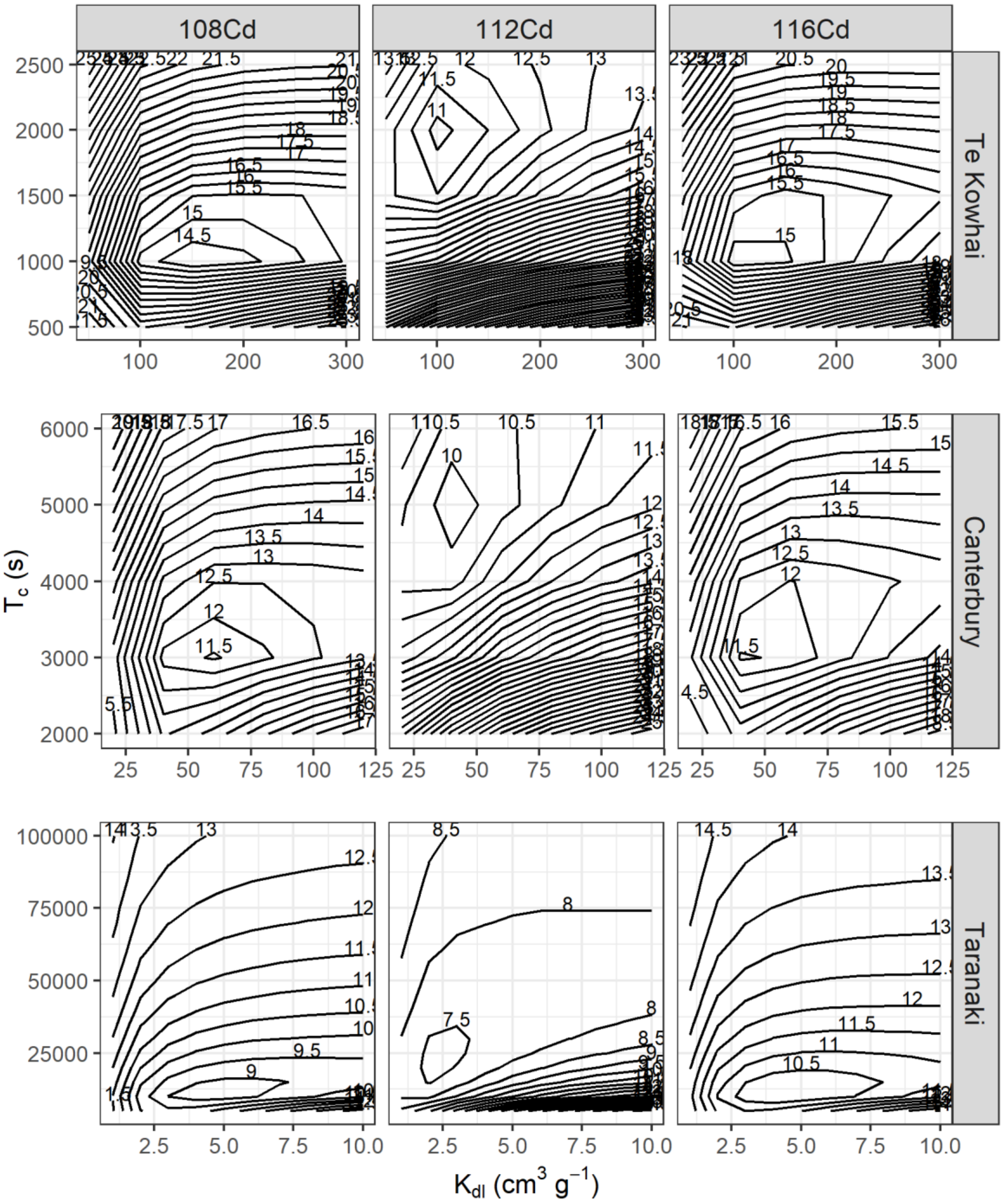


Figure 6.3: Maps of error function (*E*) near its minimum, showing range of K_{dl} and T_c values that fit to the experimental *R* for three isotopes of Cd. Note the differences in x and y-axes scales between soils.

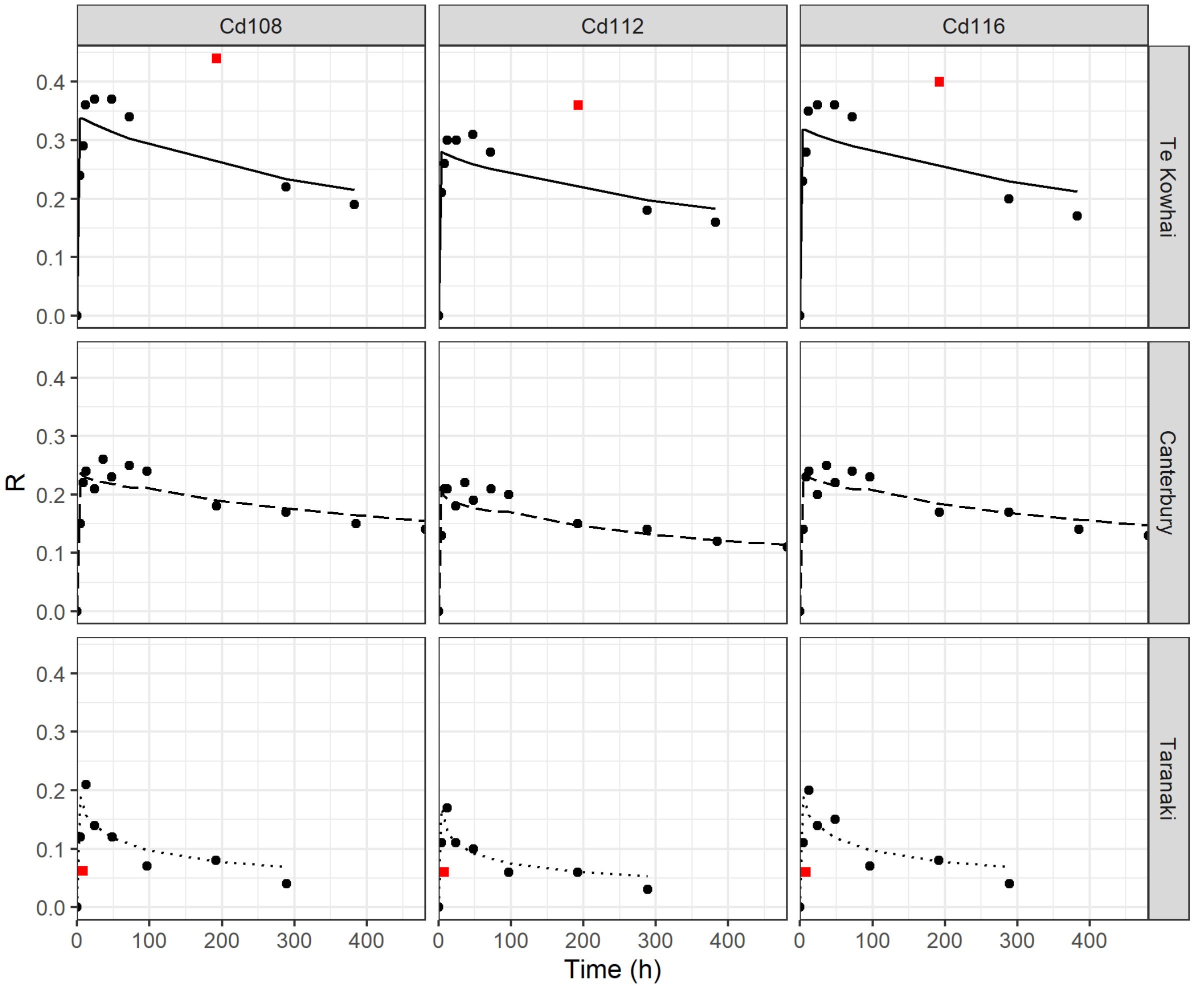


Figure 6.4: The experimental *R*-values (points) and model fit (lines). The red data points were not considered in the model, due to their deviation from the trend.

The DIFS model assumes only one labile solid pool, while under natural soil conditions there can be numerous pools, in which k_1 and k_{-1} may vary depending on the properties of soil phase surfaces and their affinities for Cd sorption. This has been shown by Lehto et al. (2012). The fit of the DIFS model used here was unable to fit precisely the *R*-values to the data points less than 50 h in the Te Kowhai soil (Figure 6.4), where there can be fast desorption of Cd from a unique solid phase pools and, which would not be reflected by a single pair of K_{dl} and T_c values. Here the multiple-pool model may describe the behaviour of Cd isotopes better. Moreover, the slow diffusion and dissociation of partly-labile Cd-DOM complexes during the deployment may also contribute to the supply of Cd to the DGT, which would in turn affect the trend of the R results over time; however, the exact effect of this should be explored in greater detail with an advanced model that consider both solution phase and solid phase speciation with kinetics. This was not possible here due to the high computational demands of implementing such a model in three dimensions.

6.4 Conclusions

The sizes of the DGT labile solid pool and the desorption kinetics of ^{108}Cd and ^{116}Cd isotopes were similar in each soil. The DGT labile pool of ^{112}Cd was smaller than the labile pools of ^{108}Cd and ^{116}Cd in the same soil, which might have been influenced by the contact time of different isotopes. Further testing is required to understand the effect of contact time of Cd with soils for the DGT labile solid pool and desorption kinetics of different Cd isotopes. The size of labile pool and resupply kinetics for the same isotope were distinct in each soil, thus various soil properties (e.g. texture, minerals) are likely to be important in determining the lability and desorption kinetics Cd isotopes in different soils. The role of allophanic minerals in soils in fixing the Cd in solid phase should be explored further. While soil salt extractions provide equilibrium partitioning of Cd between soil and solution, the labile pool measured by 3D-DIFS model may provide a better estimate for the labile pool of Cd in a dynamic soil system.

Chapter 7

General discussion, conclusions, and future work

7.1 General discussion

The overall aim of this thesis was to investigate the potential mobility of Cd in soils and how this is influenced by the factors that may affect the speciation of Cd in agricultural soils. To address this, the specific focus was to explore the potential mobility of Cd in soils as affected by organic matter (OM) amendments, dissolved ligands, and soil pH and whether soil type affected a further influence.

Soil organic matter contains many functional groups that are capable of binding Cd and other trace metals, making the bound Cd less mobile in the surrounding environment (Essington, 2004). Various OM-rich amendments (composts, peat, biosolids and spent coffee grounds) have the potential to add to this ability, as shown in Chapter 3 and other studies involving similar amendments (Al Mamun et al., 2016; Simmler et al., 2013; Ulmanu et al., 2003). The amendments used in this work were derived from different parent materials, therefore the relative distribution of various organic compounds (e.g. polysaccharides, amino acids, proteins, and lignin) and thus the functional groups (e.g. carboxylic, phenolic, amine, reduced sulfur) were likely to be diverse. These functional groups can serve as metal binding ligands and have different affinities for Cd and other trace metals: Cd can show higher affinity to be bound by the reduced sulfur ligands, while Ni and Zn have strong affinity for carboxylic and phenolic groups (Essington, 2004; Karlsson et al., 2005). This was reflected by the binding of Cd, Ni, and Zn by two composts and peats, where the extent to which the metal was bound decreased in the order Cd> Ni> Zn, implying ligands in solid surface of these amendments have higher affinity for Cd over Ni and Zn.

The variable charge sites in these OM amendments played an important role in Cd sorption, where the sorption increased with increasing pH. Hence, managing soil pH is a critical factor in how effective these amendments are for retaining soil Cd. This has been reported by other workers who used OM amendments to reduce bioavailability of soil Cd. Al Mamun et al. (2017) reported higher rates of lignite application was less effective in reducing bioavailability of Cd than lower application rates, which they attributed to the reduction in soil pH with higher lignite rates.

According to the different capacities of OM amendments to sorb Cd, a commercial compost and natural peat, which showed high (K_d=1488 L kg^{-1}) and moderate (K_d= 129 L kg^{-1}) Cd binding capacities at pH 5.5, respectively were selected to amend soil to test their ability to immobilise Cd in soils at three different pHs in Chapter 4. Compost retained more Cd than peat in each soil, providing further evidence to suggest that the provenance and, hence, the composition of the amendment is important for the extent of Cd immobilisation. The Cd retention by compost and peat was tested at pHs ranging from 5.6 to 7.4, which brackets the optimum soil pH required for growing most plants, fruits, and vegetables. Increasing the soil pH in soil-OM amendment mixtures from 5.6 to 6.4 significantly increased the amount of Cd retained in the solid phase, while Cd retention did not change significantly when increasing pH from 6.4 to 7.4. Managing soil pH appears to be crucial for optimising Cd immobilisation with OM amendments and, may be increasingly less effective for this purpose due to dissolution of OM when pH increases from 6.5 in similar soils to those studied here.

Column leaching experiments (Chapter 4) revealed how OM amendments can influence the potential mobility of soil Cd. The leachates collected there represented the initial concentration of Cd in soil pore water and the Cd released from labile solid phase species into soil solution during leaching. The results from column leaching experiment with compost and peat amended soils showed that the Cd mobilisation at pH *ca.* 5.5, was reduced by compost but not by peat. Ligands in OM can form relatively inert inner-sphere complexes with Cd, therefore it is expected that the resupply of free Cd ions to the solution in OM amended soils are lower than from non-amended soils (Karlsson et al., 2005; Loganathan et al., 2012). The amount of Cd mobilised from each OM amended soil was reflected by its associated exchangeable Cd pool as determined by 0.05 M $Ca(NO_3)_2$ extraction (r=0.61, p=1.06 X 10^{-6}), suggesting that higher the exchangeable Cd, larger the labile Cd solid pool, therefore more susceptible for leaching. It was also noted that, regardless of the high capability of soil solid phases to bind Cd, mobilisation was also plausible at elevated pH (around pH 6.4), where correlation between mobilised and extractable Cd deteriorated (r=-0.32, p=0.105). This was attributed to the dissolution of OM at elevated pHs and the associated increase in the amount of mobile Cd-DOM complexes. Al Mamun et al. (2016) showed that composts are a feasible cost-effective soil amendment for reducing the bioavailability of soil Cd, while the current study found composts also reduce the mobility of Cd at relatively low pH (*ca*. 5.5). The compost used here and by Al Mamun et al. (2016) was produced from municipal green waste (kitchen waste and garden waste). The ANOVA analysis revealed that the amount of Cd mobilised from OM amended soils depends on the type of the OM (p=3.95 X 10^{-9}), and the extent of this mobilisation is controlled by the interactions between type of OM, type of soil and pH (p=3.25 X 10^{-6}). Therefore, the extent of Cd mobilisation by other composted materials (e.g. sawdust, pig manure, fish waste, and mushroom waste) may vary depending on their provenance as they showed different capacities for binding Cd in Chapter 3. The pHs of the OM amendments tested in Chapter 3 varied between acidic to slightly higher than neutral pH, therefore OM amendments also have potential to influence the mobility of soil Cd by altering the soil pH which they are amended to (Al Mamun et al., 2016), especially in soil with low pH buffering capacity thus low CEC (McLaren, 1996).

Dissolved OM mobilising more from OM amended soils than from unamended soils in Chapter 4 emphasises a greater concern of potential mobility of Cd in the surrounding environment as Cd-DOM complexes in OM rich and/or OM amended soils. Two separate column leaching experiments, one conducted with OM amended soils (Chapter 4) and one focused on cow urine treated soils (Chapter 5), showed that humic-like molecules in DOM may play a major role in mobilising soil Cd. The OM added to the soil can act as a source for DOM, while cow urine can solubilise soil OM by increasing microbial breakdown of the soil OM ('positive priming') and increasing soil pH (Kuzyakov et al., 2000; Lambie et al., 2012b, 2013). The DOM can promote the mobility of Cd by competitive binding of soil Cd to make stable dissolved Cd complexes and/or by competing with Cd for binding sites in the solid phase (Antoniadis et al., 2002). Even though existence of these humic-like molecules in the natural environment is uncertain (Lehmann et al., 2015), these molecules have a high molecular weight (Mw) and, therefore can be considered to represent aggregated or polymerised organic components present in DOM (as colloidal DOM) (Kleber et al., 2010).

Approximately 50% of Cd mobilised from OM amended soils existed in the dissolved colloidal fraction and was correlated well with mobilised DOM (r=0.77, p=1.74 X 10^{-11}). Either high Mw DOM or colloidal organo-mineral complexes or both may bind Cd in this fraction (Bai et al., 2018; Pokrovsky et al., 2005). The strength of Cd-ligand association is typically greater in high Mw DOM than in low Mw DOM complexes (Kaschl et al., 2002a). Therefore, Cd associated with this colloidal fraction can be considered to be a vector for transporting Cd in soil. Because, one can hypothesise that Cd-DOM complexes with strong Cd-ligand association are less labile to resupply free ions to soil solution and thus may have greater potential for transporting Cd in the soil environment compared those complexes with weaker Cd-ligand association that can release Cd as free ions to be sorbed by soil solid phases. This phenomenon has also been suggested for Cu mobility in soil, which has even more affinity for DOM (Amery et al., 2010; Strobel et al., 2001). High stability constants for Cd-ligand association in high Mw DOM (HA) has been attributed to affinity of Cd for soft donor ligands (N- and S- containing groups) than hard donor ligands (phenolic and carboxylic) (Kaschl et al., 2002a; Laborda et al., 2008): the former is more pronounced in high Mw DOM while the latter is common in low Mw DOM (Bai et al., 2018; Essington, 2004). The significant negative correlation found between Cd and DOM aromaticity but positive correlation between Cd and humic acid in solution throughout this study showed for Cd may be preferentially bound by the ligands in non-aromatic structures in high Mw DOM. Chen et al. (2018b) also reported negative correlation between aromaticity of DOM and the affinity of active faction of DOM for Cd, in DOM collected from natural water. They suggest this may be due to Cd binding to the reduced sulfur containing groups residing in non-aromatic structures of DOM. Therefore, it is probable that Cd associated with high Mw DOM here also strongly bound by the soft donor ligands in non-aromatic structures of the DOM, which also support why aromaticity of DOM from OM amendments was not a determinant factor for kinetic limitation of Cd-DOM found in Chapters 3 and 4.

The adapted DGT method (SV-DGT) used in this work can be used as a reliable tool for comparing the kinetics of trace metal-ligand dissociation between solutions and, thus the lability of those complexes. Conventional DGT probes are used successfully to determine the kinetics of metal-ligand complexes in natural waters (Davison, 2016; Zhang et al., 2000), however, the requirement of a large volume (usually 2-5 L) of solution has limited the use of DGT for soil extracts. Therefore, the SV-DGT method first used by Amery et al. (2010) and further developed in this work can be used to provide information on complex lability where conventional DGTs cannot be applied. In Chapter 3, kinetic limitation measured at pH 5.5 in $Ca(NO_3)_2$ extracts showed that Cd release from compost-derived Cd-DOM complex was more kinetically limited than Cd release from the peat-derived complexes. Similarly, in Chapter 4, Cd leached from compost amended soils were more kinetically limited than Cd released from peat amended soil at pH 5.6. Together, both results suggested that at low pH (around 5.5) Cd-DOM mobilised from compost-amended soils may persist in soil solution for a longer time than Cd-DOM released from peat-amended soils. This was attributed to the strong Cd binding sites in compost due to the relatively lower Cd to dissolved organic carbon (Cd: DOC) molar ratio compared to peat. It also emphasises that the dissociation of Cd from binding ligands in compost-derived DOM may be lower than its dissociation from binding ligands in peat-derived DOM. The SV-DGT method can be further modified (e.g. by using different diffusive layer thicknesses) to calculate the dissociation rate constants for trace metal-ligand complexes (Scally et al., 2003; Warnken et al., 2007); however, this was not done here for financial and time constraints.

In addition to the resistance of colloidal Cd-DOM in resupplying free ions to solution, colloidal Cd-DOM can be resistant to microbial biodegradation, due to their aggregated structure (Kleber et al., 2010). Relatedly, the humification index for the DOM released from the compost and peat amended soil was higher than for DOM from the soil itself: mechanically composted OM may consist of organic components that are resistant to microbial degradation and naturally degraded peat contains more recalcitrant OM than the OM in soils (Guo et al., 2019; Kalbitz et al., 2003).

Even though the Cd released in urine treated soils also appeared to be mobilised with high Mw (humic-like) DOM, the existence of urine-derived organic compounds in this DOM may have enhanced the biodegradation of soil-derived DOM through the positive priming effect (Kuzyakov et al., 2000; Lambie et al., 2013). Therefore, the extent of Cd mobilisation via Cd-DOM complexes under urine patches needs further investigation. This could be studied by size-fractioning (via ultrafiltration) the leachates to separate the colloidal DOM fraction and then evaluating their biodegradability.

Urine can also increase Cd mobility by forming stable Cd-chloro complexes in soil solution. It increased the mobilisation of Cd-chloro complexes from 1% to 10% from soil received cow urine, however, Cl^- concentration only had a slight positive correlation with mobilised Cd, which may be masked by the higher affinity of Cd for the DOM. Mobility of Cd-chloro complexes arises to be a greater issue in coarse soils than in finer soils. Soil solution analysis has found that free Cd^{2+} ions, Cd-DOM and Cd-chloro complexes are the main solution Cd species (Cornu et al., 2011; Ren et al., 2015b; Sauve et al., 2000) and this study shows that these species can be responsible for mobilising Cd in soil. The relative effects of these species are likely to depend on soil pH, OM content, DOM and chloride concentration.

As indicated by the isotope tracing study (Chapter 5), poor mobility of Cd in soils may be related to the redistribution of dissolved species to the soil phases via sorption. However, presence of DOM and stable dissolved Cd species (Cd-DOM and Cd-chloro complexes) may reduce this re-sorption facilitating Cd transport to the subsoil and hence influence eventual Cd leaching to groundwater.

Cadmium mobility was lower in soils with high OM content and/or allophane minerals than in soils without allophane minerals and/or had low OM content, which agrees with previous work that reported low Cd leaching in similar soils (Gray et al., 2016; Gray et al., 2003a). This may be attributed to the inner-sphere complexes formed by OM or allophane minerals with Cd (Loganathan et al., 2012). The size of the labile Cd pool estimated by the DIFS model (Chapter 6) provided further evidence for this, where the labile pool was smaller in allophane-rich soil than in the soils without the mineral. Furthermore, allophane minerals have a high affinity for binding OM, and this was reflected by the lower DOM mobilisation seen in the Allophanic soils. With this effect, even though the Allophanic soils (Craigieburn and Taranaki) had a relatively high OM content, less Cd-DOM species mobilised from those soils. So, leaching of Cd-DOM complexes is less likely to be an issue in allophanic soils. This could be further investigated with synthetic allophane and Cd-DOM complexes as tested for other minerals like goethite using quartz sand columns (Chen et al., 2019; Ohashi et al., 2002).

In agreement with work by McLaughlin et al. (1996) , the Cd mobilisation was higher in sandy soils than from clayey soils (Chapters 4 and 5). As determined by DIFS model in Chapter 6 and by (Ernstberger et al., 2005), labile solid pool of Cd was smaller in coarser soils than in the finer soils. Therefore, the extent of resupply of Cd to the soil solution from labile solid phases may be limited in coarser soils if Cd is continuously leached for a prolonged time.

Greater Cd leaching in urine treated soils emphasises the potential for Cd transport to water bodies from grazed lands that are frequently irrigated or receive high rainfall. This can be an issue in intensively farmed areas in New Zealand, like the Waikato and Taranaki regions, where pasture lands in these regions also report some of the greatest soil Cd concentrations (~0.7 mg kg^{-1}) (Stafford et al., 2014; Taylor et al., 2017; Taylor et al., 2007). In the current experiment, urine was applied once and then after 24 h, leaching was induced, representing a likely worst-case scenario, where soils should reach peak pH due to hydrolysis of ammonia in urine (Owens et al., 2016). In Chapter 4 and 5, mobilised Cd-DOM complexes had a positive correlation with pH because OM solubility was greater at high pHs.

Therefore, mobilisation of Cd-DOM complexes under urine patch could be less pronounced if those soils were irrigated after soil pH decreased nearly to its natural pH. Owens et al. (2016) showed that water-extractable carbon in urine treated and periodically irrigated pasture soil was greatest five days after urine application before it gradually decreased over six days to initial extractable carbon concentrations. One can hypothesise that the leaching of Cd-DOM species under urine patches may not be prominent if those soils are irrigated much later after urine application. Therefore, implying that the Cd leached as Cd-DOM complexes under urine patches could be reduced by managing irrigation timing, but further investigation is required to evaluate Cd mobilisation with urine application under field conditions. Out of the soils analysed, the potential for Cd leaching with urine treatment was higher in soils with higher OM content. This suggest another potential issue for land used for grazing animals: because soils with high OM content generally retain more Cd (Gray et al., 2016) in soil due to its Cd binding affinity, therefore the risks for Cd leaching with urine application may be pronounced in those soils.

7.2 Conclusions

This research has shown for the first time that the amount of Cd transported from soil can be strongly dependent on the type of the OM used to amend. The extent to which this happens is modulated by interaction between the type of OM, soil type and its pH. These factors should be important considerations when OM are used to immobilise the soil Cd and for any subsequent management, including grazing irrigation and pH adjustment. Mobilisation of colloidal-Cd increased with OM amendments where Cd may bound to mobile high Mw DOM emerged from the amendments. While increasing pH from 5.6 to 6.4 can significantly reduce the Cd in <5 kDa dissolved fraction, mobility of colloidal-Cd species was less likely to be affected by changes in pH.

In high Mw DOM (therefore in colloidal DOM), Cd may be bound by the ligands in the non-aromatic structures. As a result, aromaticity of DOM is not a determinant factor for lability of Cd in the Cd-DOM complexes. Lability of the Cd-DOM complexes depend on the source of the DOM, pH, and Cd:DOC ratio. Dissolved OM emerged from OM amended soils may persist in soil solution for longer time than the DOM from soil itself. Therefore, unless this DOM is (bio)degraded, the colloidal Cd-DOM species in these OM amended soils can be considered to be an important vector for Cd transport in soil and the surrounding environment.

Free Cd^{2+}, Cd-DOM and Cd-chloro species are mainly responsible for transporting Cd in soils, where the relative contribution from these species depends on properties of soil, pH, OM content, DOM and Cl^- concentrations. On the other hand, the extent of Cd resupply to soil solution is determined by the size of the labile solid pool of Cd, which is smaller in soils with greater OM content and/or allophane minerals and at elevated soil pH. Further, the extent of Cd mobility in soil used here appeared to be partly controlled by soil texture, where coarser soils tended towards greater Cd mobility.

The work here sought to provide the initial test to understand the potential transport of Cd from contaminated topsoil to subsoil and/or groundwater using isotope tracing. Isotope ratio analysis coupled with mixing models can be used for Cd source identification in soil solution or groundwater. Resupply kinetics of different Cd isotopes from labile soil solid pool appeared not to confound the Cd isotope fractionation in soil solution in these. However, presence of DOM and Cl^- species, which can skew Cd isotope ratios in soil solution towards the lighter isotopes, should be considered for obtaining reliable output from mixing models.

7.3 Suggestions for future work

Key recommendations for further research:-

- In natural conditions, DOM mobilisation in soils may not be as high as shown in these laboratory studies, where a greater proportion of DOM is likely to be rapidly mineralised and/or sorbed to soil solid phase. Field studies should be carried out to estimate Cd mobilisation in OM amended soils closer to natural conditions.

- The practical implication from the urine application study is that in grazed lands, timing of irrigation may need to be considered to avoid the potential leaching of Cd to deeper soil layers and water bodies. Therefore, laboratory and field experiments should be performed to investigate the potential leaching of Cd under urine patches, with different irrigation frequencies.

- In this study, the employed DIFS model did not consider the resupply of Cd from Cd-DOM complexes, which can play an important role when Cd resupply for DGT is mainly diffusion-controlled depending on the strength of Cd-ligand association in those complexes. Hence, one can implement the Cd-DOM complexes as another component in the DIFS model matrix to consider the role of dissociation kinetics of those complexes for resupplying Cd as used by Lehto et al. (2012). Furthermore, the use of DGT probes with double binding resins combination with the DIFS model can be employed to investigate the dissociation kinetics of various Cd-DOM complexes (Shafaei-Arvajeh et al., 2013) in soils, with possible complementary information gained from SV-DGT measurements.

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Appendix A

Underline theory of kinetic limitation estimated by Small-Volume DGT method

In the laboratory scale, to conduct a DGT experiment usually about 5 L of solution is required to satisfy the assumptions of DGT principles. However, when dealing with soils, collecting such a volume of soil solution is difficult. Therefore, an adapted a DGT method, which was first used by Amery et al. (2010) was used to estimate the kinetic limitation of trace metals in a small volume of solution, forthwith SV-DGT. A description of the preparation of SV-DGT device is given in chapters 3 and 4, while the underline theory is explained below.

The SV-DGT device consisted with, Chelex-100 resin (binding layer) embedded in 1.5% agarose hydrogel matrix cast into a 30 mL sample vial, which is then overlain with 1.5% agarose diffusive gel (diffusive layer). When a solution containing trace metals, existing mainly as their free ion species, is deployed in SV-DGT device, the metal ions progressively diffuse through the diffusive layer, where they are rapidly bound by the chelating resin. Within approximately 60 minutes, a linear concentration gradient is developed within the diffusion layer. The diffusive flux progressively depletes the free metal ion concentration in the solution. The diffusive flux (J ,mol cm^{-2} s^{-1}) of the metal ions from the solution can be expressed according to the Fick's first law of diffusion, where the flux, is defined by the diffusion coefficient for the solute in the given medium (D), concentration gradient of the solute (dc/dx) where c and x are the concentration and distance along the concentration gradient, respectively. At steady state the flux in and out each layer is constant and equal to the adjoining layers as given below, where D^{DBL} and D^{DL} are diffusion coefficient of solute and δ_{DBL}, δ_{DL} are thicknesses of the diffusive boundary layer and diffusive layer, respectively. C_{SOL}, C_{DL} and C_R are the concentrations of solute in solution, diffusive layer and binding resin, respectively (equation A.1).

$$J = \frac{D^{DBL}}{\delta_{DBL}}\left(C_{SOL} - C_{DL}\right) = \frac{D^{DL}}{\delta_{DL}}\left(C_{DL} - C_R\right) \tag{A.1}$$

C_R can be set to zero when solutes rapidly bind to the resin, then C_{SOL} is the sum of concentration difference between diffusive boundary later and diffusive layer, given by:

$$C_{SOL} = J\left(\frac{\delta_{DBL}}{D^{DBL}} + \frac{\delta_{DL}}{D^{DL}}\right) \tag{A.2}$$

If the rate of diffusion of solute in the diffusive layer and the surrounding solution is assumed to be the same, then $D^{DBL}= D^{DL}$ and concentration of the solute in solution at a given time *t* above equation can be rearranged as shown in equation A.2,

$$J(t) = C(t)\left(\frac{D^{DL}}{\delta_{DBL} + \delta_{DL}}\right) \tag{A.3}$$

In conventional DGT solution deployments, it is assumed that the concentration of solute in the solution does not change significantly. However, in SV-DGT this assumption cannot be used because of the relatively low volume of solution used (10 mL). If an assumption is made that the flux of trace metal is directly proportional to the concentration at the edge of the DBL, then the flux, *J* (mass per unit area per unit time) can be expressed as follows,

$$J = \frac{C_t}{A \times t} V_{SOL} \tag{A.4}$$

Where, C_t concentration of solute in the solution at time *t*, *A*, cross-sectional area of the SV-DGT device, V_{SOL} volume of the solution.

Then by combining the above equations A.3 and A.4 the change of solution concentration of a solute can be modelled as follows,

$$\frac{C_t \times V_{SOL}}{A \times t} = C(t)\left\{\frac{D^{DL}}{\delta^{DBL} + \delta^{DL}}\right\} \tag{A.5}$$

The equation A.5 is rearranged to,

$$\frac{C_t}{t} = C(t)\left\{\frac{D^{DL} \times A}{\left(\delta^{DBL} + \delta^{DL}\right)V_{SOL}}\right\} \tag{A.6}$$

Rate of change of solution concentration with time can be written as,

$$\frac{-\Delta C^{SOL}}{t} = kC(t)$$, where constant $$k = \frac{D^{DL} \times A}{\left(\delta^{DBL} + \delta^{DL}\right)V_{SOL}}$$

Then, by integrating the above equation (A.6) with time 0 to t, the concentration of solute at time *t* (C_t) is given by;

$$C_t = C_0 EXP\left\{\frac{-D^{DL} \times A \times t}{\left(\delta^{DBL} + \delta^{DL}\right)V_{SOL}}\right\} \tag{A.7}$$

C_0 is the concentration of solute at time=0. Given the highly confined nature and slightly concave nature of the diffusive gel, determination of δ_{DBL}+δ_{DL} is challenging. However, when C_t and C_0 are known the equation can be solved for δ_{DBL}+δ_{DL}. Henceforth the sum of δ_{DBL} and δ_{DL} is known as *apparent diffusion layer* (ADL, δ_A), which is the average diffusive path length between the bulk solution and the resin layer interface during the solution deployment in the SV-DGT device. Moreover, ADL is an operationally defined parameter that integrates the differences in the rates of diffusion between DBL and diffusion layers.

Appendix B

Supplementary Information for Chapter 3

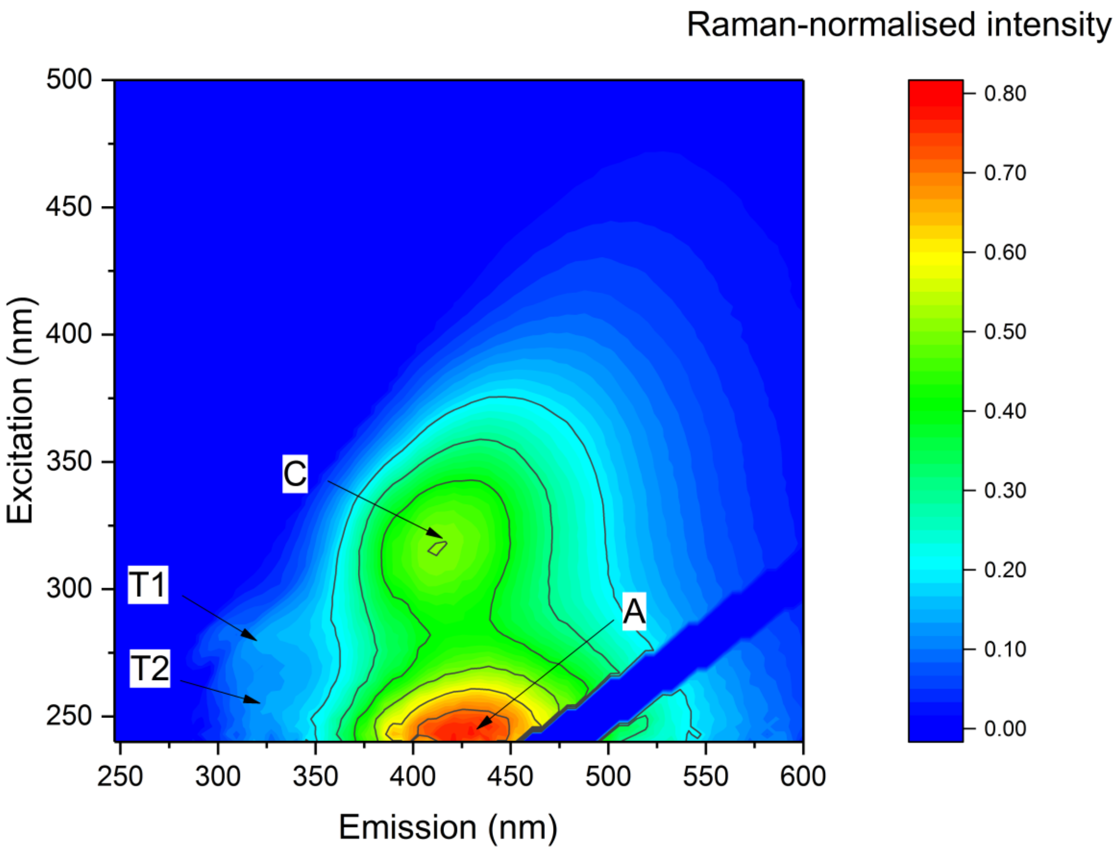

Figure B.1: Peak identification of 3D EEM output. Peaks A and C are humic-like, T1 and T2 are tryptophan and tyrosine-like peaks, respectively.

Appendix C

Supplementary Information for Chapter 4

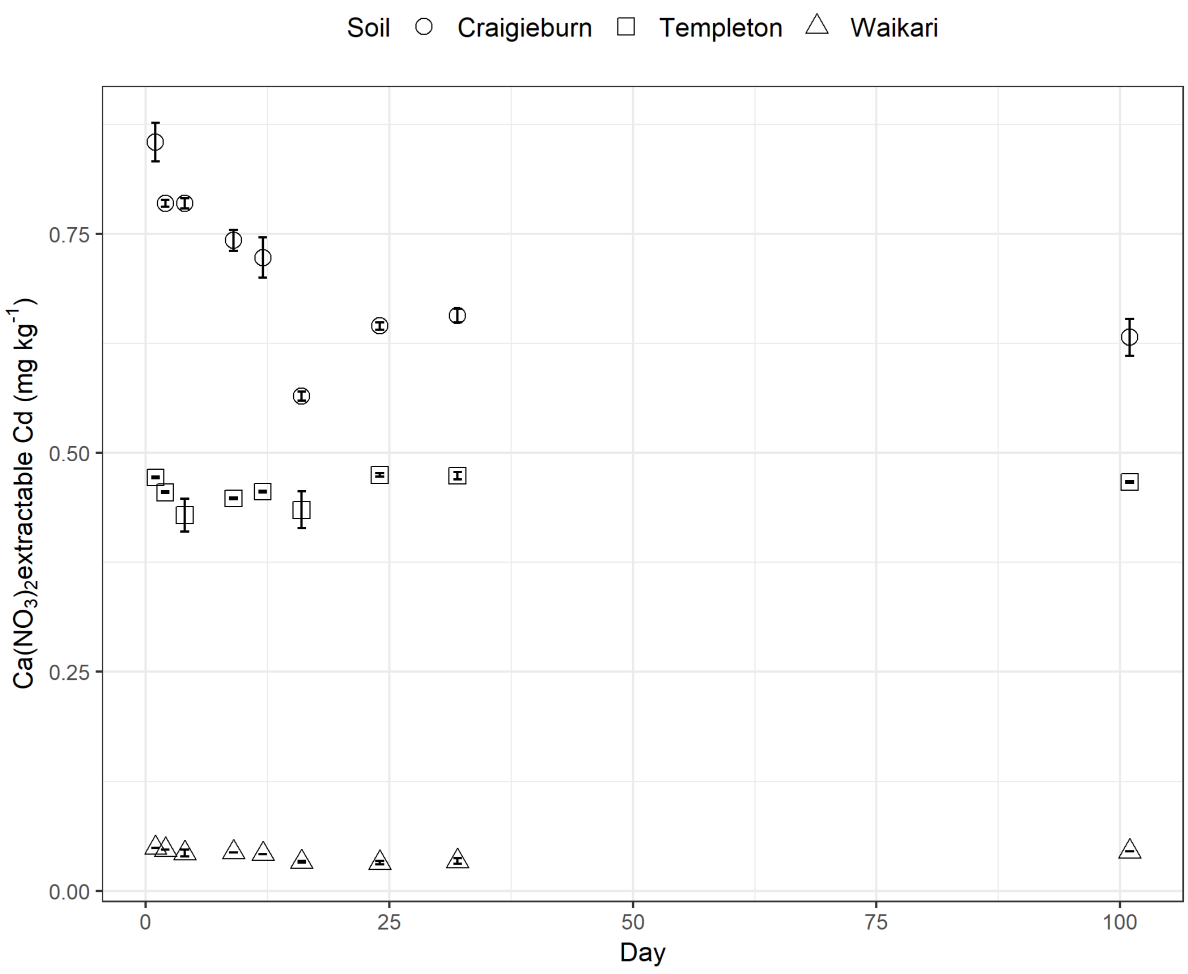

Figure C.1: The change in $Ca(NO_3)_2$ extractable Cd in spiked soils. The error bars represent the standard error of the mean (n=3).

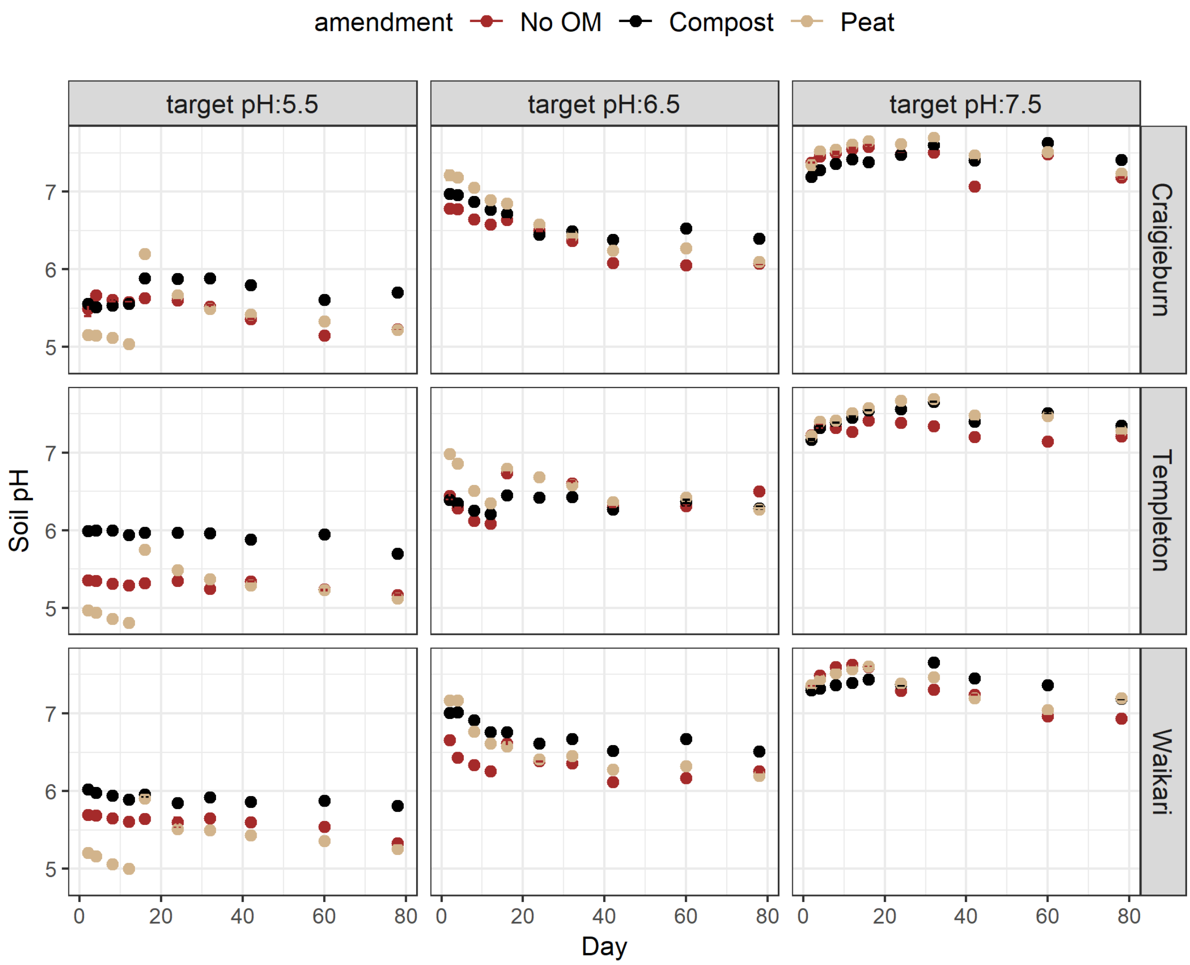

Figure C.2: The change in soil pH of OM unamended and amended soils after liming with different lime rates to bring up to three targeted pHs.

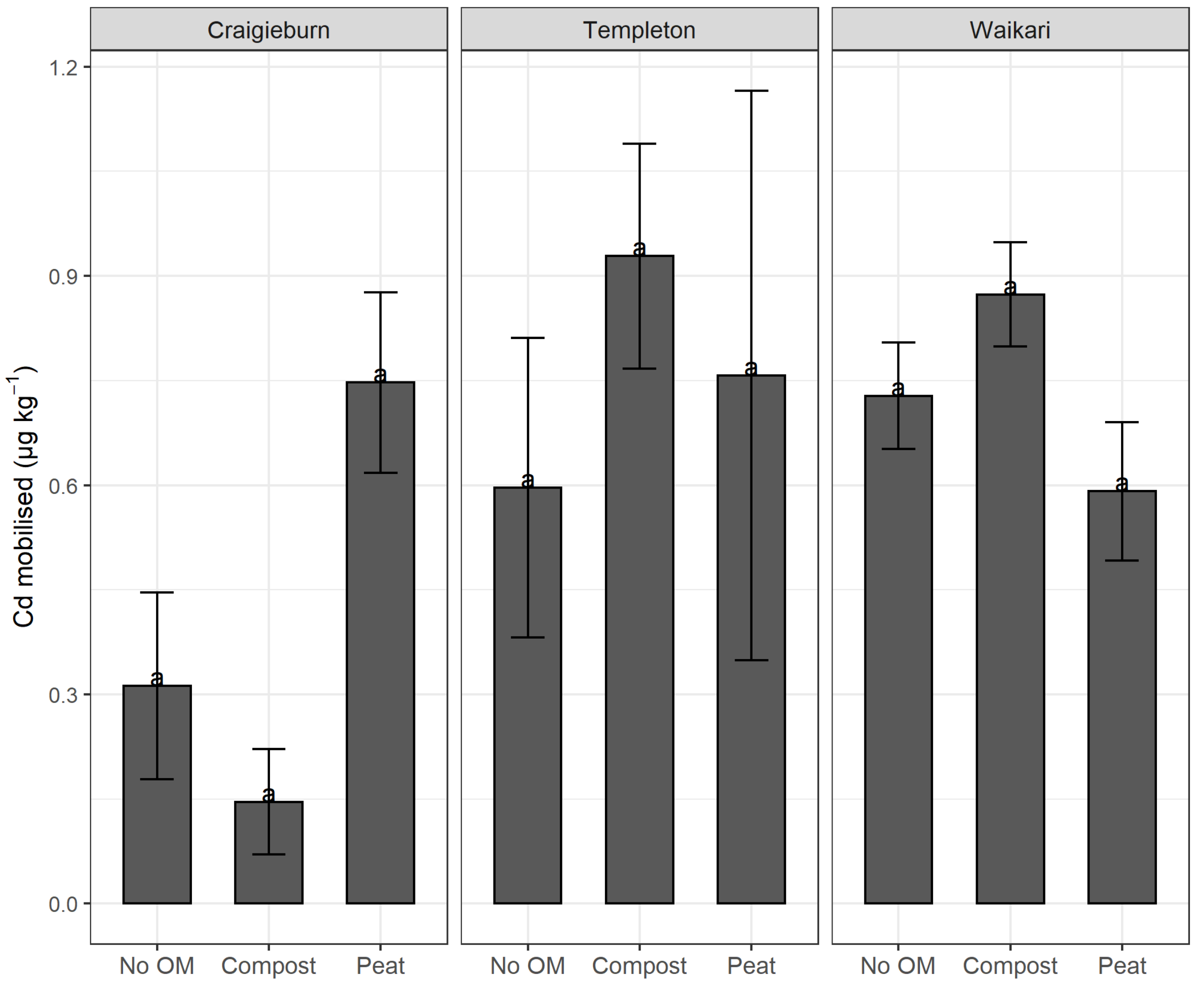

Figure C.3: Cadmium mobilised from soils at pH 7.4 (Cd leached is measured using the ICP-OES). The error bars represent the standard error of the mean (n=3). Values sharing same letter are not significantly different (*p*>0.05).

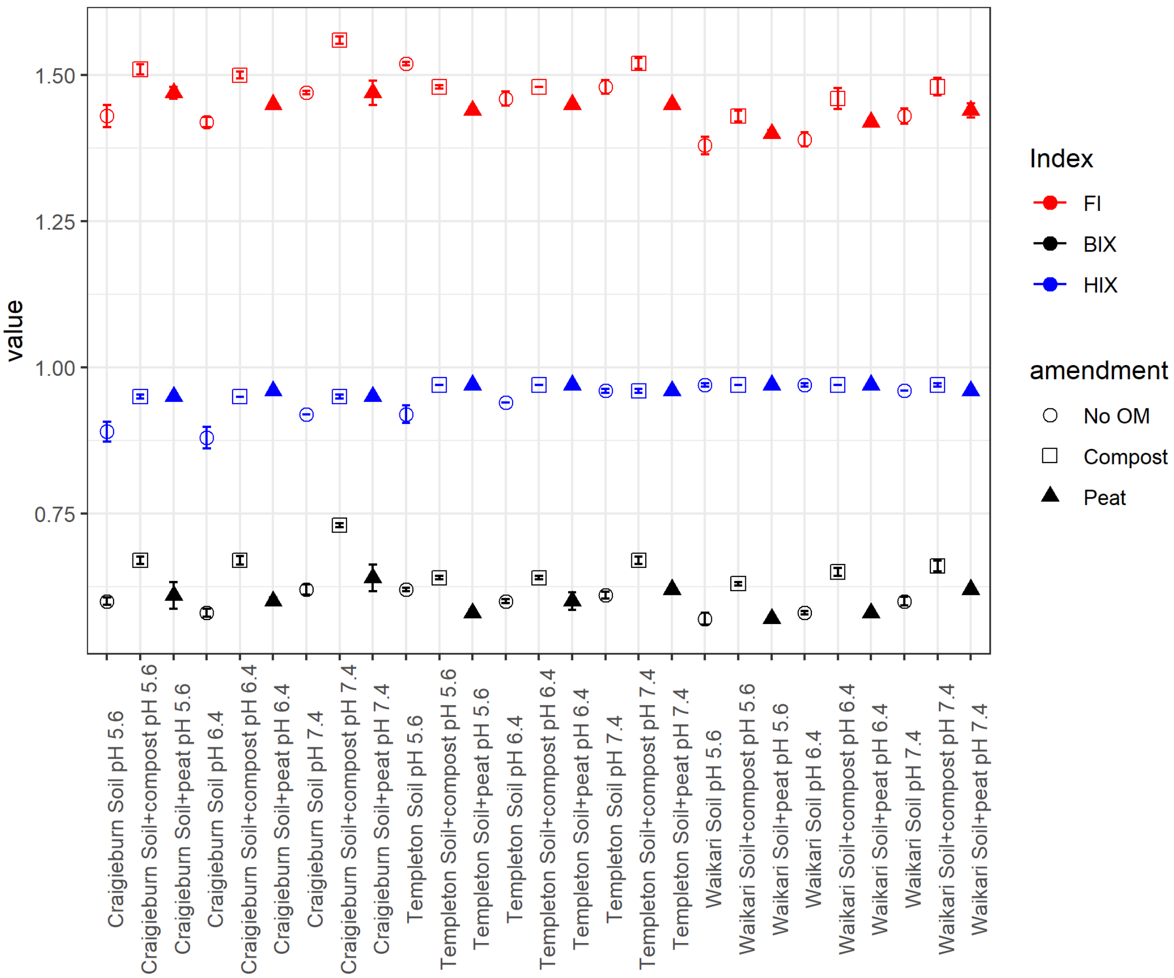

Figure C.4: Fluorescence indices. FI is the Fluorescence Index, BIX is the Biological Index, HIX is the Humification Index. The error bars represent the standard error of the mean (n=3).

Appendix D

Supplementary Information for chapter 5

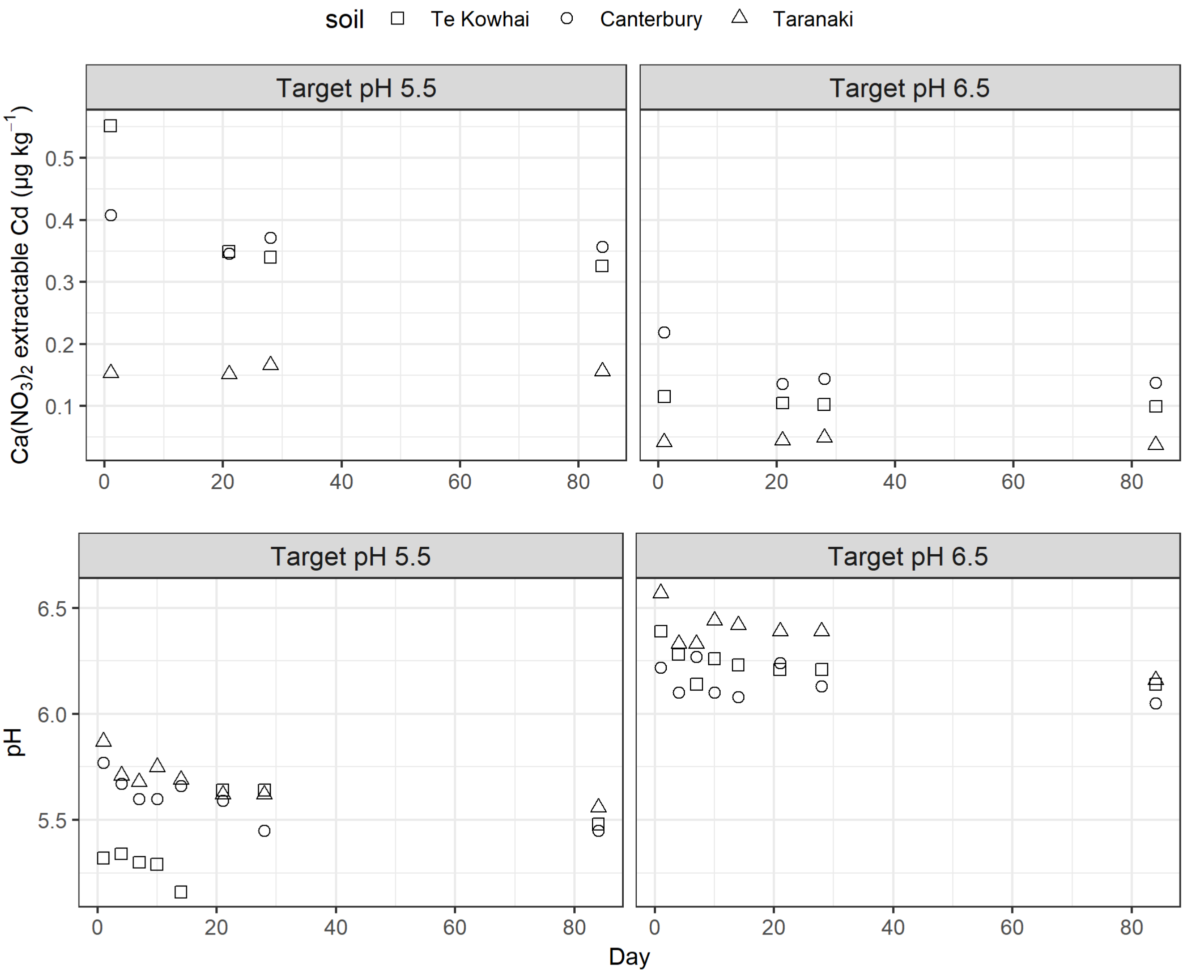

Figure D.1: Monitoring the change in total $Ca(NO_3)_2$ extractable Cd and the pH change after spiking with Cd and lime application over around 3 months.

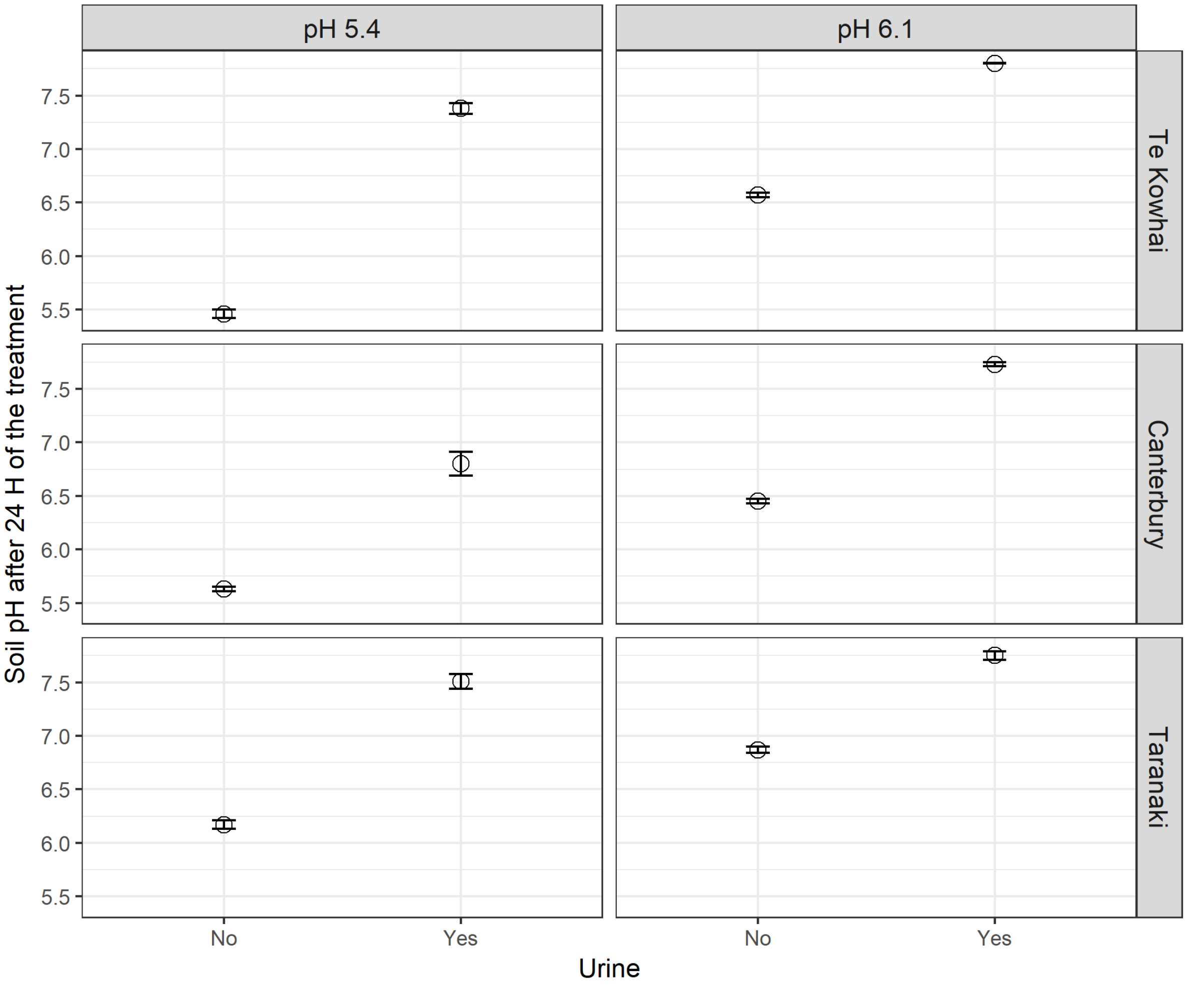

Figure D.2: The change in pH of soils after 24 h of the urine or water application that were prepared to leach with synthetic rainwater. The error bars represent the standard error of the mean (n=2).

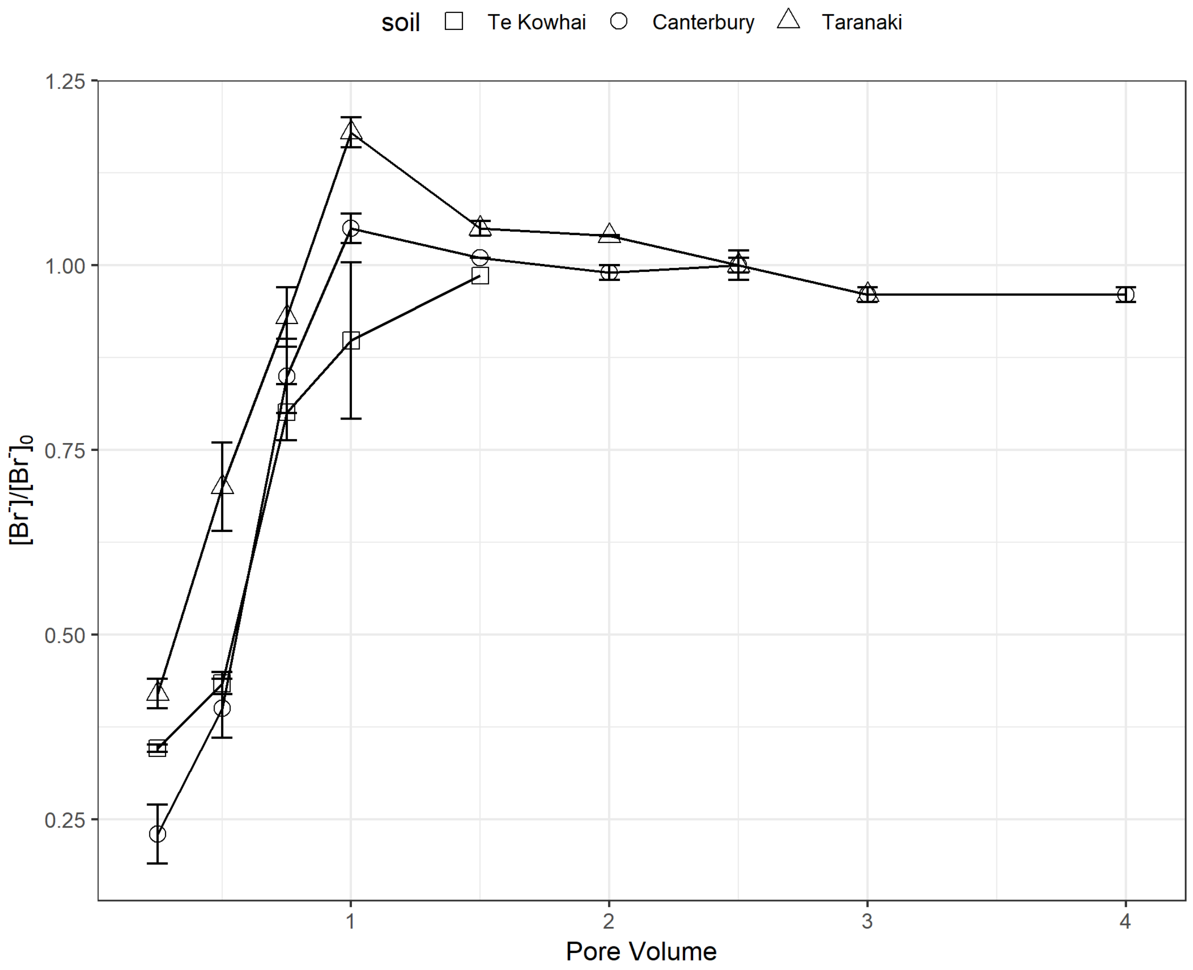

Figure D.3: The breakthrough for the bromide applied with synthetic rainwater for the three soils. The error bars represent the standard error of the mean (n=3).

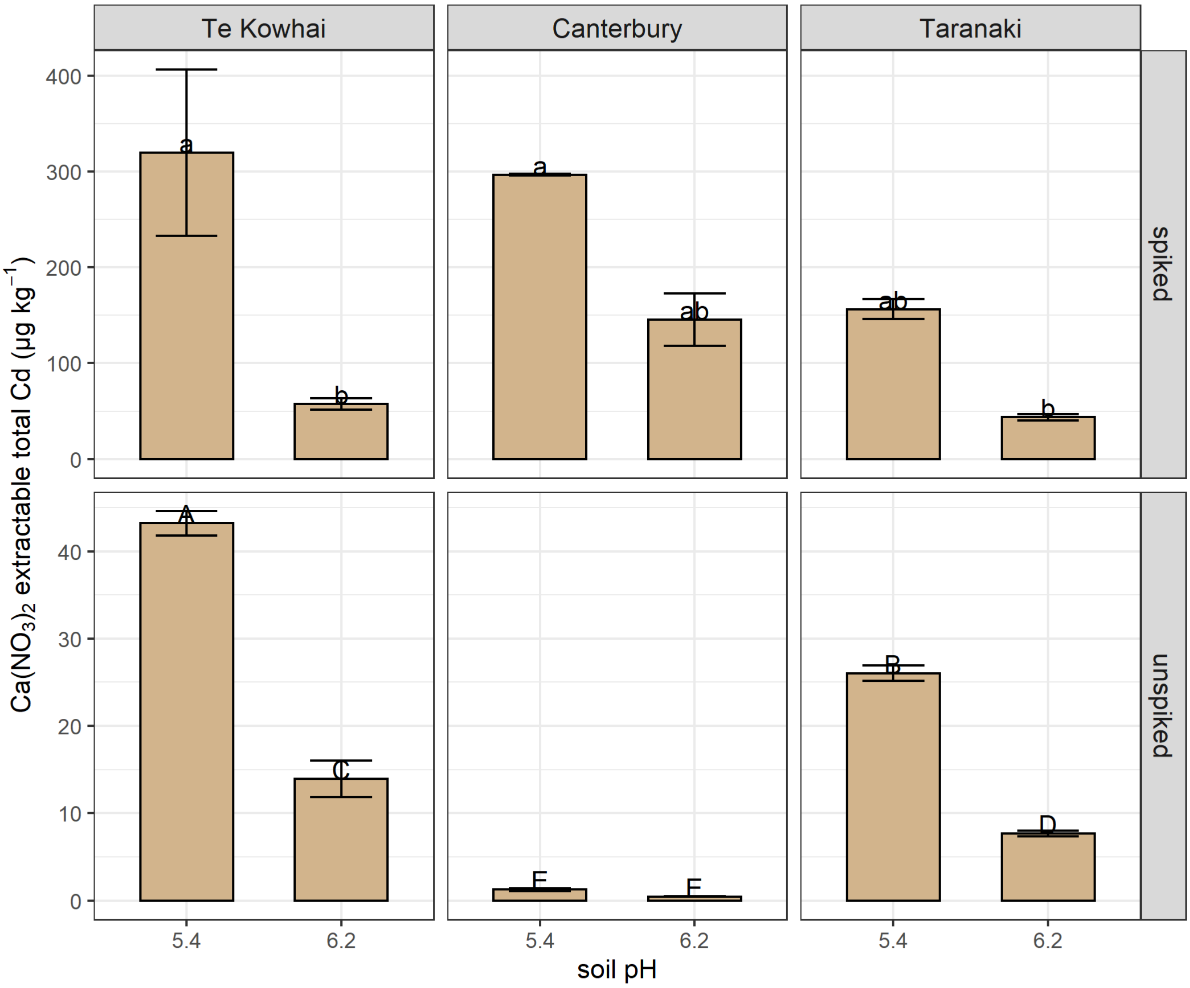

Figure D.4: Total amounts of Cd extracted with 0.05 M $Ca(NO_3)_2$ from spiked and unspiked soils at each pH. The error bars represent the the standard error of the mean (n=3, except n=2 for the unspiked Canterbury soil at pH 6.2). The uppercase and lowercase letters indicate the significant differences between unspiked and spiked soils, respectively. The values sharing same letters are not significantly different (*p*>0.05). Note the difference in y-axis scales between spiked and unspiked soils.

Table D.1: The chloride concentration in the leachates from treatment columns.

Soil	pH	Urine	Cl^- (mg L^{-1})
Te Kowhai	5.4	No	5.6
Te Kowhai	5.4	Yes	277.8
Te Kowhai	6.1	No	7.1
Te Kowhai	6.1	Yes	277.5
Canterbury	5.4	No	106.4
Canterbury	5.4	Yes	413.5
Canterbury	6.1	No	118.3
Canterbury	6.1	Yes	397.6
Taranaki	5.4	No	10.8
Taranaki	5.4	Yes	263.6
Taranaki	6.1	No	13.8
Taranaki	6.1	Yes	275.8

Appendix E

Supplementary Information for Chapter 6

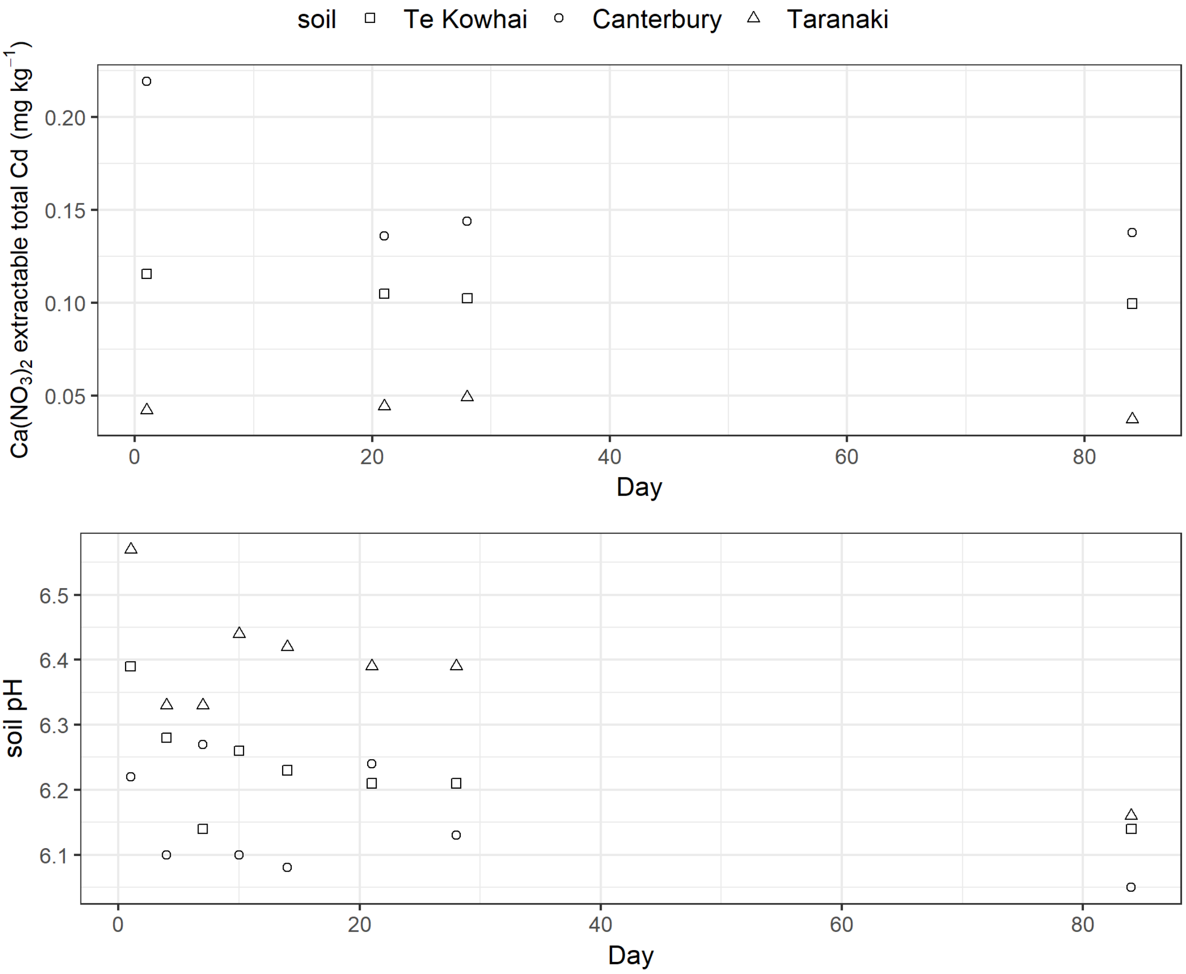

Figure E.1: $Ca(NO_3)_2$ extractable Cd and the soil pH during the first three months of the soil aging process after spiking with Cd isotopes and lime.

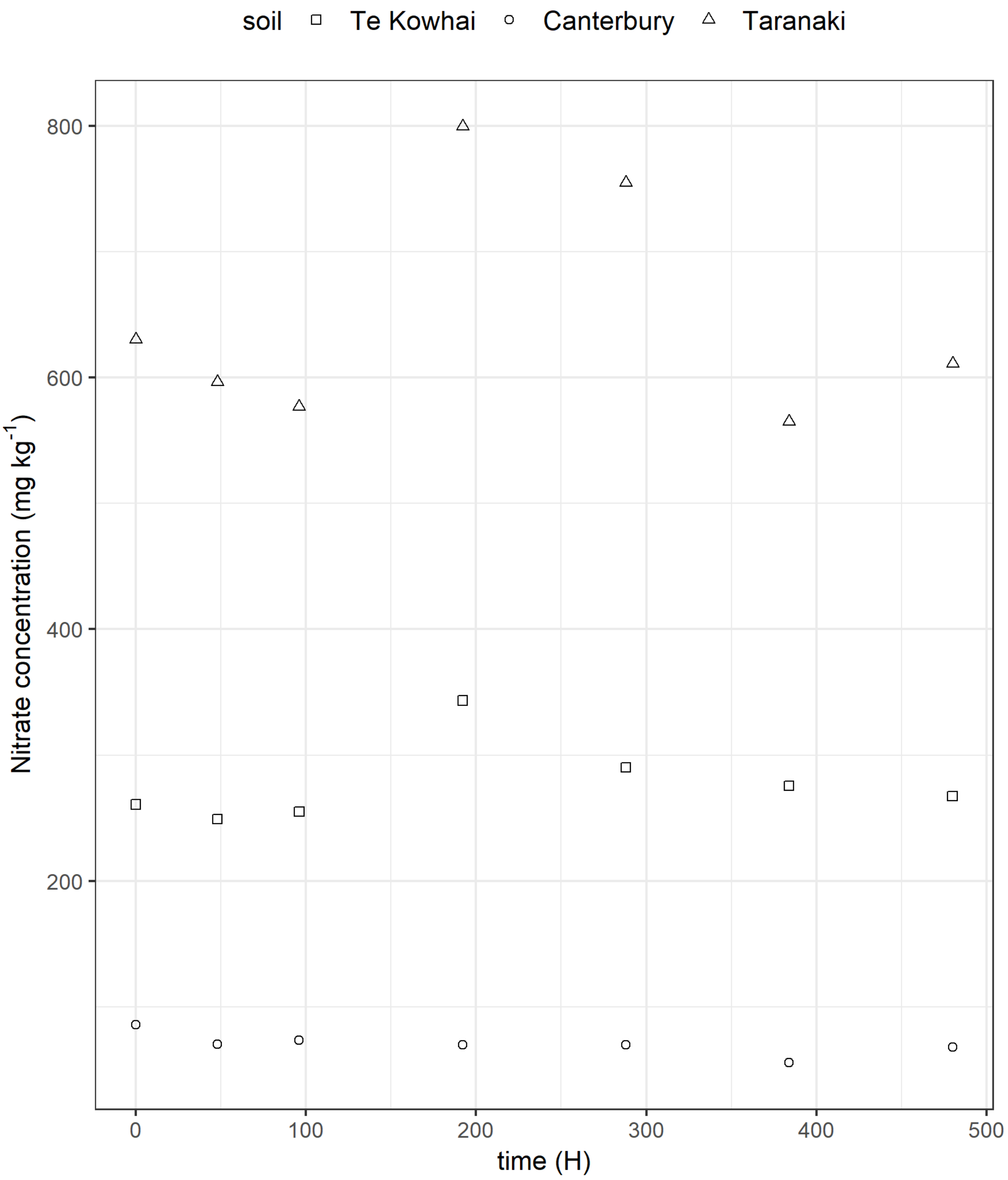

Figure E.2: Nitrate concentration in the soils after retrieval of the DGT probe.

Table E.1: Input variable and definitions used in the model simulation-1

Variable	Unit	Value/formula	Description
C_0	µg L^{-1}	Table E2	Initial soil solution concentration
C_S	mg g^{-1}	K_{dl} / C_0	Initial sorbed concentration
ρ_p	g cm^{-3}	Table E2	Particle density
P_c	g cm^{-3}	Table E2	Particle concentration
ϕ_s		$\rho_p /(P_c + \rho_p)$	Porosity of soil
ϕ_g		0.95	Porosity of diffusion layer
Δg	cm	0.093	Diffusion layer thickness
D_0	cm^2 s^{-1}	6.26 *10-6	Diffusion coefficient in water at 20 °C
D_g	cm^2 s^{-1}	6.26 *10-6	Diffusion coefficient in diffusion layer at 20 °C
D_s	cm^2 s^{-1}	$D_0/(1-2\log(\phi_s))$	Diffusion coefficient in soil at 20 °C
k_1	s^{-1}	$K_{dl}\times P_c/(Tc+(K_{dl}\times P_c\times T_c))$	Sorption rate constant
k_{-1}	s^{-1}	$1/(T_c+(K_{dl}\times P_c\times T_c))$	Desorption rate constant
K_{dl}	cm^3 g^{-1}	model variable	DGT labile metal distribution coefficient
T_c	s^{-1}	model variable	Response time

Table E.2: Input variable and definitions used in the model simulation-2

	Te Kowhai	Canterbury	Taranaki
P_c (g cm^{-3})	1.69	2.96	1.6
ρ_p (g cm^{-3})	2.29	2.56	2.35