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Organic amendments for reducing the plant uptake of cadmium from New Zealand soils

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Cameron Allan Hucker

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Abstract of a Dissertation submitted in partial fulfilment of the
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Organic amendments for reducing the plant uptake of cadmium from New Zealand soils

Abstract

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Cameron Allan Hucker

Cadmium (Cd) is a naturally occurring element in soils. It is a non-essential trace element that can have toxic effects on fauna at relatively low concentrations. Several studies have reported above background levels of the metal in New Zealand (NZ) agricultural soils . This is thought to be due to the repeated applications of phosphate fertiliser where Cd is a commonly found impurity. Cd is taken up by plants relatively easily and can accumulate there to potentially dangerous concentrations without any effects on the plant itself. This has resulted in the NZ government imposing a 1.8 mg/kg limit on Cd in soil after which P fertiliser applications have to cease. The addition of organic amendments into the soil has been shown to reduce the plant uptake of Cd. This study has been carried out to gain better understanding of which specific organic amendment has the greatest potential for reducing plant uptake of Cd.

The amendments used in the experiments were two types of peat, bio-solids from Kaikoura and Christchurch, coffee grounds, and municipal compost from Parkhouse Garden Supplies, Living Earth and Oderings. The study involved analyses of pH, conductivity, total organic carbon, water-soluble carbon (hot and cold water), elemental composition, cation exchange capacity (CEC) and the sorption potential for Cd of each amendment.

Results indicated that the two bio-solid samples had Cd concentrations that were too high for potential application to the soil as this would risk accumulation at rates of up to 10 times higher than the other amendments. The findings from the Cd sorption experiment indicate that Parkhouse (PH) compost had the greatest capacity to adsorb Cd, the Kd value was 11317. This result was significantly larger than all other amendments, with Living Earth (LE) showing the second highest value of 578. This suggests the potential ability of Living Earth compost to be used as an amendment for soils contaminated with Cd. The significant sorption of Cd by PH compost could be attributed to

the sulphur concentration of PH, as this was twice as high as any amendment (excluding bio solids). Parkhouse White (PHW) had the lowest S concentration but a similar CEC to PH, however the corresponding Kd was significantly lower (27). This suggests the addition of gypsum ($CaSO_4$) to municipal composts could cause the associated S groups to form complexes with Cd. Although, sulphides or thiol groups are more likely to form complexes with Cd, rather than the sulphate groups.

Overall, this study has indicated that the organic amendment with the greatest capacity to adsorb Cd is PH compost, with LE showing a reasonable capacity also. The next step would involve incorporating these composts into contaminated soils and to analyse the effect this has the plant uptake of Cd.

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Chapter 1

Introduction: Cadmium

Cadmium (Cd) is a naturally occurring heavy metal in soils. It is a non-essential trace element that can have toxic effects on biota at relatively low concentrations. In many countries Cd enters the soil as a result of a number of industrial and mechanical operations. Mining, smelting and the refinement of metals such as zinc, copper and lead can release Cd into the environment (International Cadmium Association, 2005). Cd in the transport industry is common, as it is used in metal plating's on vehicle parts and in tyres. Cd resulting from industrial production is found mostly in NiCd batteries, plating's, plastics and pigments. Burning of these products has the ability to release Cd into the environment, depositing on the soil surface (United States Department of Labour, 2016). Most Cd deposits in the soil come from atmospheric Cd that is a result of industry around the world. As New Zealand (NZ) does not have a large industry sector, atmospheric inputs make up only a small amount of soil Cd. NZ isolation also plays a part in the lack of atmospheric Cd deposits, being 3000km away from Australia (McDowell et al,. 2012). In New Zealand, the most significant source of Cd to soils has been the continued application of phosphate fertiliser (MAF, 2008). As there is no viable way to extract Cd from phosphate rock before fertiliser is applied to soil, it is likely that accumulation of Cd will continue into the immediate future (Cadmium Working Group, 2011).

Historically, the use of rock phosphate from the Pacific island of Nauru has resulted in high rates of Cd accumulation in NZ soils. The average concentration of Cd within Nauru rock phosphate was 450 mg Cd/kg P (MAF, 2008) . In 1995 it was imposed that rock phosphate sourced from Nauru would be phased out in favour of a source that had lower Cd concentrations, such as RPR from Morrocco. More recently Cd concentration within rock phosphate that is used on NZ soils was found to be 180 mg Cd/kg P (MAF, 2008). It was reported by Taylor et al. (2007) that NZ soils have a baseline average of 0.16mg/kg for Cd, found across all regions, and a national average of 0.35 mg/kg, with a range of 0 – 2.52 mg/kg. Taranaki, Waikato and Bay of Plenty were seen to have the highest concentration of Cd within their soils, as shown in Figure 1:1 below; the Cd concentrations that were highly related to horticultural land use were seen to have the highest average Cd concentrations. The lowest average concentration found in soils where unspecified dryland pastures dominated the land use. These findings were also published in Cadmium in New Zealand Agriculture (MAF, 2008).
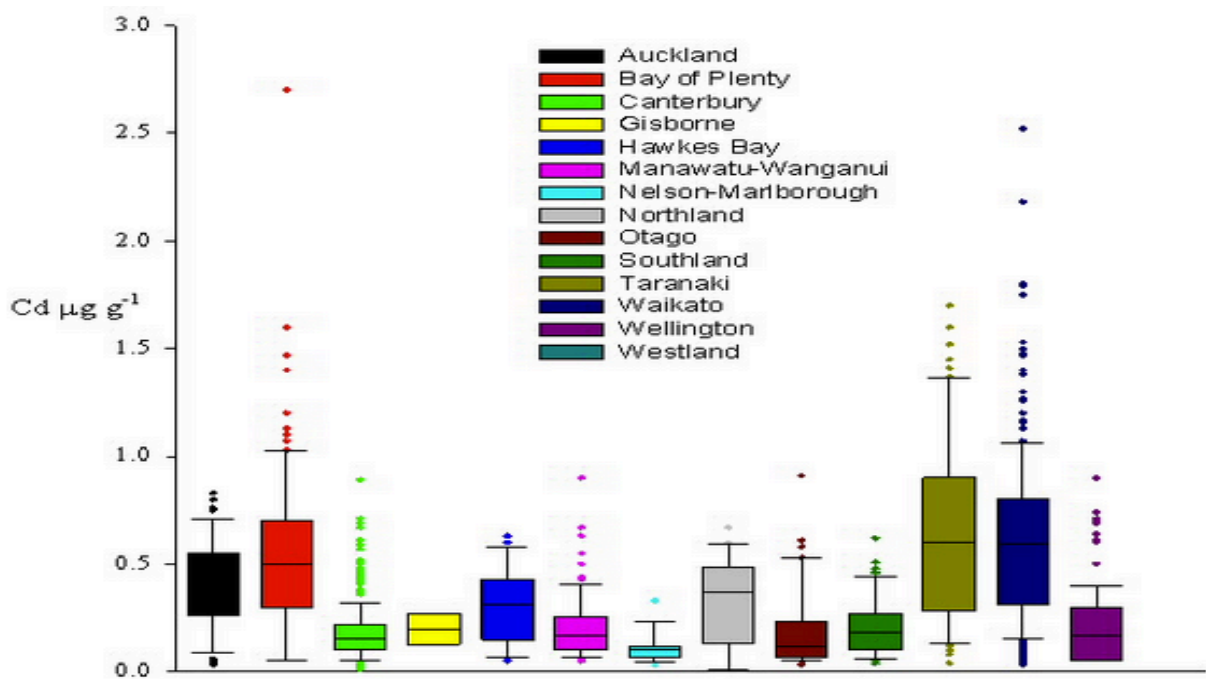
Figure 1:1 Cadmium levels in NZ topsoil, by region. (MAF, 2008)

In 2011 the Cadmium Working Group developed a management strategy for Cd in NZ soils. The objective of the strategy was to "To ensure that cadmium in rural production poses minimal risks to health, trade, land use flexibility and the environment over the next 100 years". To do this, a four-tiered system was put in place to manage fertiliser applications, with the goal of ensuring that Cd toxicity resulting from accumulation in soils would not eventuate. The Tiered Fertiliser Management System is as follows (Rys et al. 2011):

- Tier 1, there are no limits on the application of phosphate fertiliser other than a five yearly screening soil test for cadmium status. The trigger value to move to tier 2 = 0.6 mg Cd/kg soil.

- Tier 2, application rates are restricted to a set of products and application rates to manage accumulation, so that cadmium does not exceed acceptable threshold within the next 100 years. Landholders are required to test for cadmium every five years using approved programmes. The trigger value to move to tier 3 = 1.0 mg Cd/kg soil.

- Tier 3, application rates are further managed by use of a cadmium balance programme to ensure that cadmium does not exceed an acceptable threshold within 100 years. The trigger value to move to tier 4 = 1.4 mg Cd/kg soil.)

- Tier 4, above tier 4, no further accumulation of cadmium is allowed. The trigger value = 1.8 mg Cd/kg soil.

Cadmium in the soil poses a risk to humans and ecosystems, through bioaccumulation. Cd concentrations increase at every stage of the food chain. When present in the human body, Cd, exerts toxic effects on the kidneys, skeletal and respiratory systems, and it is classified as carcinogenic (Godt et al, 2006). Smoking can also cause Cd accumulation in the human body. Cd is often found in low concentrations in food and water. The FDA states that the maximum concentration of Cd in bottled water is 0.005 mg/L, while the World Health Organisation (WHO) states that the tolerable weekly intake for cadmium is 7 g kg/body weight/week. The Australian New Zealand Food Standard code (Food Standards Australia New Zealand, 2015) for Cd is as follows:

- Chocolate and Cocoa Products = 0.5 mg/kg
- Kidney of cattle, sheep and pig = 2.5 mg/kg
- Leafy vegetables = 0.1 mg/kg
- Meat of cattle, sheep and pig = 0.05 mg/kg
- Rice = 0.1 mg/kg
- Wheat = 0.1 mg/kg
- Molluscs = 2 mg/kg

Cd levels in New Zealand's food products currently do not pose a risk to human health, but there is a risk of some products exceeding food standards for Cd, typically offal and some vegetables (MAF, 2008). This creates the risk of NZ exceeding the Cd food standards of our many export markets, and as NZ is recognised globally as having a self proclaimed "Clean Green Image", that occurrence could subsequently damage that image. If Cd were to accumulate in our soils at high enough levels to exceed Cd food standards both domestic and export sales would be at risk of being rejected. As NZ is a nation heavily dependent on agricultural exports to source a large section of the economy, a scenario similar to this could negatively impact NZ's economy (MAF, 2008).

The solubility of Cd in soil and the subsequent uptake by plants is affected by a variety of soil chemical and physical factors, for example, organic matter, pH, oxides and other cations in the soil. These factors may result in the immobilisation of Cd or mobilising it, making it available for plant uptake (Black, 2010).

Chapter 2

Biogeochemistry of Cd in soils:

2.1 Cd in soil solution:

In soil Cd can be found in different forms and complexes. The speciation of Cd in soil is highly dependent on the soil makeup e.g. parent material, presence of organic matter, oxides, inorganic constituents, while it will also be affected by the pH value of the soil. In most soils, 99% of the Cd is associated with the soil solids and just a minor fraction occurs in soil solution (Simmler, 2012). Cd in soil solution is the primary focus of soil Cd chemistry since that it is the predominant source from which plants absorb Cd and other nutrients (Gray, 1998). In most soils the Cd free ion, Cd^{2+}, is the dominating soluble Cd species, or as soluble Cd complexes with inorganic ions such as chloride or sulphur (Scheffer et al. 2010). Once Cd is released into the soil solution either as a result of dissolution or due to additions of fertilisers, the Cd^{2+} is divided between the solution, mineral and organic phases of the soil (Gray, 1998). The concentration of this Cd^{2+} in solution is dependent on the chemical reactions it undergoes in the soil. These reactions include ion exchange, sorption/desorption processes and complexation (Gray, 1998).

2.2 Exchangeable Cd:

The exchangeable fraction of Cd consists of the metal being bound to colloidal or particulate material (John & Leventhal, 1995). Exchangeable Cd is found in equilibrium between soil solution and soil surfaces where it is either bound (immobilised) by adsorption processes, or soluble for plant uptake.   The immobilised form can also be found in soil solution as a result of reversible adsorption and can be easily mobilised, hence exchangeable, therefore being bioavailable for plant uptake. Sigel et al. (2013) indicated that quantity of exchangeable Cd decreases at higher pH because the metal can be adsorbed onto sites that are less accessible, and can only be displaced by acid extraction. Sigel et al. (2013) also found that exchangeable Cd fractions decrease considerably in some cases at lower pH. It has been found that CEC of the soil will also play a big part in determining how much exchangeable Cd there is in soil solution (Toshimitsu et al. 2015), as shown in Figure 2:1 below. This is because as CEC increases, more exchangable Cd will be found on binding sites on soil colloids and this will decrease the amount of exchangeable Cd in solution. Whereas, when the CEC of a soil is low, more exchangeable Cd will be found in the soil solution, as there is enough room on binding sites to be adsorbed onto soil colloids.
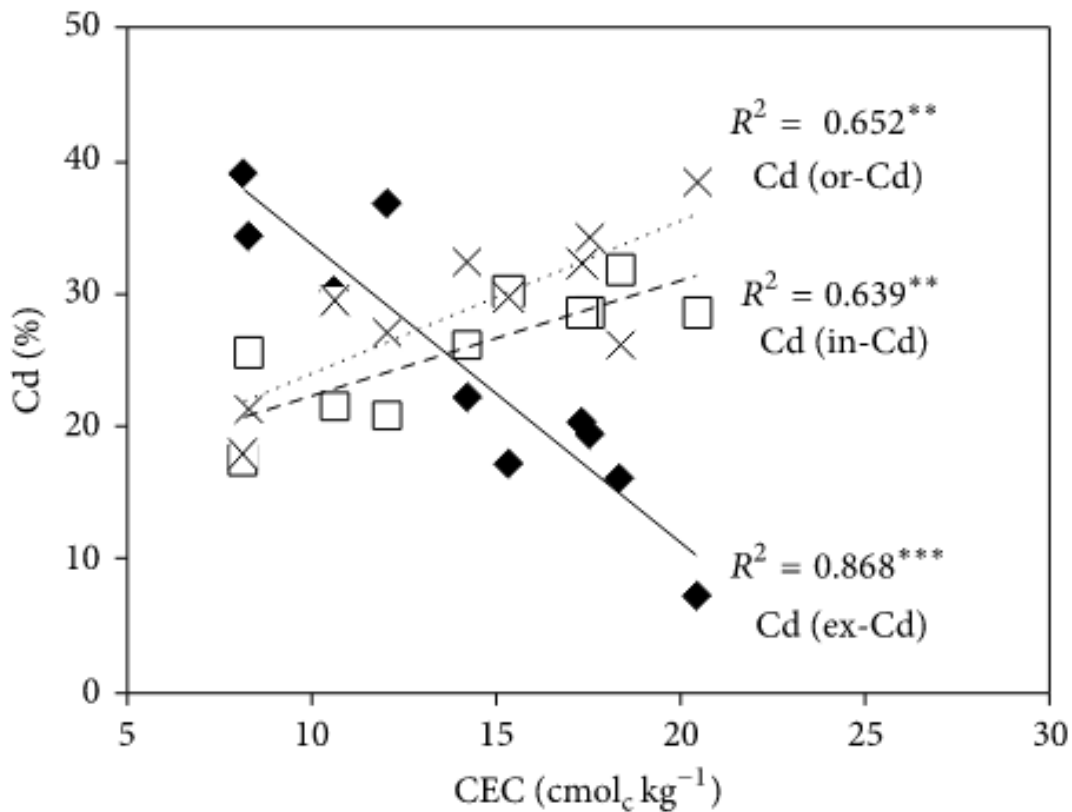
Figure 2:1 The effect of increasing CEC on Cd fractions within the soil. (Toshimitsu et al. 2015)

(*Cd % refers to the amount of Cd found in each variable; or-Cd = organic Cd; in-Cd = inorganic Cd; ex-Cd = exchangeable Cd*

2.3 Effect of Root Exudates:

Root exudates can solubilise Cd, making Cd available for plant uptake. Mench & Martin (1991) studied the ability of three different species' root exudates to solubilise Cd and other cations. It was found that root exudates of *Nicotiana* spp. enhanced the solubility of Cd. The range of Cd solubility by root exudates (*N. tabacum* L. *N. rustica* L. *Zea mays* L.) followed the same trend as Cd bioavailability when these plants were grown in soil, which could suggest that total concentration of Cd in soil has a big influence on how much Cd can be solubilised by root exudates. Mench & Martin (1991) concluded that an increase in Cd solubility in the rhizosphere of root zones due to root exudates is likely to be an important cause of the relatively high Cd accumulation in *Nicotiana* spp. Hirotaka et al. (2014) reported that roots influence microbial activities as well as Cd fractions in contaminated soils. They found that concentrations of exchangeable Cd increased near the roots as a result of an increase in pH values; inorganically fractions of bound Cd conversely decreased near the roots. They found that the rhizosphere had the highest concentrations of exchangeable Cd in the soil, but also had high amounts of bacterial and fungal metabolic activity. This suggests that the promoting effects of root exudates on microbial activity could cancel out the negative effects of Cd in the

rhizosphere of the soil. Sterckeman et al. (2005) found that while plants did not enhance Cd availability, the availability of previously immobile Cd in the rhizosphere had come about as a result of acidification through organic acid excretions by root exudates. However, the effects of root exudates may increase Cd availability through continuous acidification and organic acid excretions and increase root growth over time, potentially increasing Cd uptake from the soil (Sterckeman et al. 2005).

2.4 Soil chemical factors that affect Cd bioavailability:

The plant available fraction of Cd is sometimes termed as the "bioavailable fraction". Cd is taken up by plants from porewater. Factors that affect Cd in porewater will also affect it's bioavailability. These factors include: total Cd concentration, sorption, pH, soil composition, salinity, temperature, age and the effect of other elements (Black, 2010).

2.4.1 Total Cd Concentration

The total concentration of Cd in soil refers to the total amount of Cd found in fractions throughout the soil. These fractions range from the Cd in soil solution to exchangeable Cd found on clays and organic matter. The overall total concentration of Cd in soil plays a major role in determining the bioavailability of Cd and the resulting uptake by plants. The greater the abundance of Cd in the soil the less room there will be on soil binding sites that adsorb Cd, therefore a higher number of Cd ions will be present in soil solution, potentially available for plant uptake. Higher Cd concentration in soil will directly increase uptake by plants, therefore lower Cd concentration will result in a lower uptake by plants (Ministry for Primary Industries, 2007; Longhurst et al, 2004). Onyatta & Huang (1999) reported that Cd bioavailability in tropical soils was a function of the total Cd concentration. These findings indicated that total Cd concentration was higher in the topsoil, compared to the subsoil.

2.4.2 Sorption of Cd:

Cadmium sorption in soil occurs on binding sites that are found on clay minerals, organic matter, iron and manganese oxides and calcium carbonate deposits. These sorption sites may be highly specific for Cd and other trace metals, or they can be non-specific creating sites for a variety of cations to bind onto (Zanders, 1998). Cadmium adsorption processes can be seperated into two different groups, depending on how Cd binds to the corresponding sites (McBride, 1994). These groups are non-specific adsorption and specific adsorption

2.4.2.1 Cation Exchange Capacity:

The term cation exchange capacity (CEC) of a soil refers to its ability to replace cations on the soil exchange complex with other cations, effectively whether the soil can hold onto cations that are found in the soil (McLaren & Cameron, 1996). The exchange complexes are found on clay and organic matter particles which cations are attracted to as these sites are negatively charged. If the CEC of a soil is high this means

that there are more sites for Cd in solution to bind on to, taking it out of solution to become locked up in the solid soil phase. When the CEC is low the bioavailability of Cd will subsequently be high, as a result of less binding sites on the solid phase of soil, due to a higher total Cd concentration. Therefore Cd ions are more likely to be found in their soluble form in soil solution, potentially leading to plant uptake. Toshimitsu et al. (2015) reported that the proportion of exchangeable Cd in contaminated soil correlated with the overall CEC in the soil. They came to the conclusion that soil properties such as CEC will affect the proportions of Cd fractions in the soil and should be considered when studying Cd solubility in soil. Haghiri (1974) found that the effect of increasing soil CEC resulted in Cd uptake by oats being decreased. They concluded that the increased ability of the soil to adsorb Cd with increasing CEC resulted in a decrease in Cd availability as judged by the reduction in the Cd concentration of the soil extract.   These findings were similar to those of Miller et al. (1976), who studied the effect of CEC on the uptake of Cd by soybeans. The results indicated that Cd uptake at any given level of applied Cd was found to decrease with an increase in CEC.

2.4.2.2 Specific Adsorption:

Specific adsorption is the process where Cd ions are bound much more tightly onto the adsorbent surface. As a result, the Cd ions are less easily removed from this adsorbent surface. Specific adsorption of Cd ions creates the formation of inner-sphere complexes with the adsorbent surface, and as a result a specific chemical bond is formed within this complex of Cd (McLaughlin & Singh, 1999). Due to the effect of specific adsorption on Cd, we would expect to see Cd become less bioavailable as Cd is bound to adsorbent sites in the soil. Factors like pH and soil temperature are less likely to reverse this process as there are such strong bonds formed. Specific adsorption of Cd is more likely to occur at lower Cd concentrations, while at high Cd concentrations CEC is dominant (Tiller et al, 1984). If Cd is bound by specific adsorption onto a soil colloid it is less likely to have to compete with other macro-nutrient cations, as they will be found at higher concentrations, due to CEC. This is will lower Cd solubility in solution and reduce bioavailability.

2.4.3 pH:

The pH of a soil can effect an elements ability to move through the soil and influence whether it will be taken up by the plants that are growing in those particular soils (MAF, 2008). Most elements are bioavailable to plants at neutral pH, and also at slightly acidic and slightly alkaline pH in soils. H+ protons compete with Cd for binding sites on the soil colloids. At higher pH there are less protons present so more Cd is fixed, while as the pH decreases the abundance of protons in the soil increases, releasing Cd into solution. Although, in highly alkaline soils Cd can mobilised again due to the formation of monovalent hydroxyl species that do not occupy binding sites easily (Kabata-Pendias & Piotrowska, 1992; Simmler, 2012; Zander, 1998). Decreasing the pH of the soil will also decrease negative surface charge, reduce the stability of metal-ligand complexes and create conditions where occluding oxides can dissolve, allowing Cd

to mobilise into soil solution (Christensen & Haung, 1999). Peramaki (1992) reported that Cd can move through the soil more easily in slightly acid soils. These findings are backed up by Gray & McDowell (2015), where they established that between 5.5 – 6.5 pH Cd concentration in ryegrass decreased from the original application, whereas when the pH was between 4.5 – 5.5 Cd concentration was found to have increased. Simmler (2012) reported that in aerobic soils, solubility of Cd would increase when there is a subsequent decrease in pH. In addition it was found that under a pH of 6.5 a significant increase in Cd solubility occurred. Although, if the pH of the soil is low Cd has to compete with other acidic cations like aluminium and manganese to be in soil solution, meaning bioavailability of Cd may be lower in these soils (Reiser et al, 2014). In soils that have a pH higher than 7 or 8, hydroxide, phosphate and sulphate complexes may make up a significant amount of the total soluble Cd. This may also be the case in soils that have high concentrations of phosphates and sulphate present (Simmler, 2012). Precipitation of these soluble Cd complexes will mainly occur as a carbonate, phosphate or sulphide. Precipitation of carbonate and phosphate would usually take place in soils where the pH is above 7.5, while precipitation of sulphide will occur in anaerobic soils (Simmler, 2012; Scheffer et al, 2010). Egwu & Agbenin (2012) reported that at a higher pH, Cd adsorption was frequent, and at its maximum around a pH of 8, meaning Cd is less soluble in this pH range. Figure 2:2 below shows the effect of changing pH on the amonut of Cd found in solution, within three different soils. While figure 2:3 shows the speciation of Cd at differing pH.
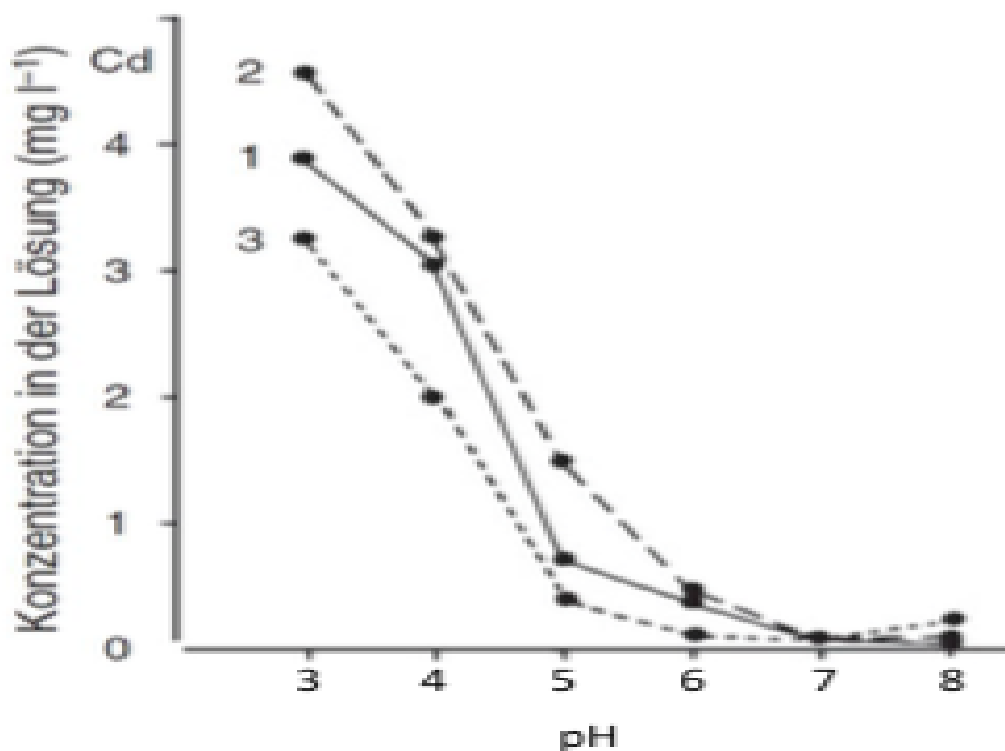
Figure 2:2 Dissolved Cd concentration in soil (*y-axis*)in three different soils, at different pH values. (Blume et al. 2010)
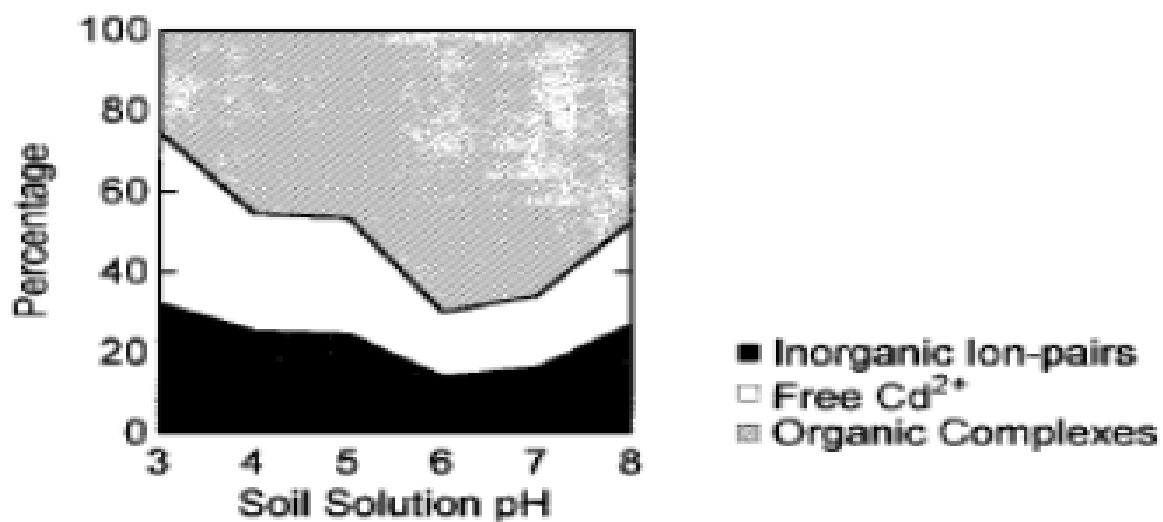
Figure 2:3 Occurrence of Cd in soil at differing soil pH values. (Sauve et al. 2000)

2.4.4 Soil Composition:

2.5.4.1 Soil Texture

Soil composition may also have an effect on the solubility and overall bioavailability of Cd. This obviously varies with different soil types and different areas in regions. Soils that are sand based have been found to contain higher concentrations of Cd within the soil solution due to the low CEC of these soils. Whereas soils that have high clay content have a larger surface area and a higher CEC, resulting from more non-specific and specific binding sites (McLaren & Cameron, 1996). This allows more Cd to be bound to soil of this composition, limiting solubility and uptake

2.4.4.2 Oxides:

In soils with high iron oxides content, Cd is more likely to be rendered unavailable, so it can not move through the soil freely (Reiser et al, 2014). The same negative correlation is seen with manganese oxides, as when there is more in the soil the less Cd is found in soil solution. This correlation is down to the oxides having highly adsorptive sites for Cd, due to a combination of high surface areas and pH-dependent surface charge characteristics. Chen et al. (2000) found that the application of Mn oxides decreased the Cd solubility in soil, and the subsequent uptake by plants. Yu et al. (2016) reported that amorphous Fe oxides were significantly and negatively correlated with Cd concentrations within two rice paddy fields in southern China. From these findings it was concluded that increasing the content of amorphous Fe oxides may have the potential to reduce the Cd fractions within soils that have similar composition to the two rice paddy fields.

2.4.4.3 Soil Organic Matter

Organic matter in soil has the ability to bind Cd. There are many different forms of organic matter that can be found in or applied to soil, which have various chemical properties creating different Cd immobilisation effects. Organic matter tends to possess high CEC properties due to the presence of humic substances within the OM (Haghiri, 1974). Cd also binds strongly to sulphur at certain pH values, and many organic matters have sulphur incorporated into them, in the form of thiol groups, creating more potential for Cd immobilisation (Zanders, 1998). Soil organic matter can reduce contaminant uptake into crops and leaching into groundwater through adsorption at the cost of long-term accumulation (Lehmann & Kleber, 2015). Huang et al. (2015) found that the addition of OM to a soil increased the adsorption of Cd in a red paddy environment, but when OM was removed from the soil Cd adsorption was decreased. He & Singh (1993) also studied the effect of OM on the concentration and adsorption of Cd. It was found that in a soil under a ryegrass crop at differing concentrations of Cd, the addition of OM reduced the Cd from the soil. Al Mamun et.al (2016) looked at the effect of a range of organic amendments applied to soil on Cd uptake by various vegetables. Sorption experiments were carried out and showed that Lignite and Compost had the greatest ability to adsorb Cd in solution, other amendments used included biosolids, sawdust, and charcoal. Subsequent field trials were run using the compost and lignite which showed that the compost reduced Cd concentrations in the vegetables by 60% in two test soils. The lignite decreased soil acidity, therefore was not as effective at lowering Cd concentrations, as immobilisation was counter-acted. Conversely, many studies have focused on whether dissolved organic matter complexes can become soluble and mobilise Cd again. Krishnamurti et al. (2004) reported on the bioavailability of organic Cd complexes to soil alga. These results showed that dissolved organic-Cd complexes are indeed bioavailabile to soil alga, resulting in toxicity problems associated with Cd. This data contradicts the long-held belief that dissolved organic-Cd complexes are not bioavailable to soil biota, even though they can increase mobility of Cd. It has also been found that above pH 7 Cd can be mobilised due to the formation of soluble organic complexes (Scheffer et al. 2010; Simmler, 2012).

2.4.5 Salinity

Bingham et al (1983) looked at how sodium chloride and calcium chloride affected the bioavailability of Cd in the soil with Swiss chard. Results showed that the overall percentage of Cd in solution increased once the chloride solutions had been added. This was also shown with the Cd present in the leaf of the plant. The additon of chloride also changed the distribution of Cd species in the soil and plant; Cd^{2+} species decreased and CdCl species become more prevalent. Recent studies also show the same effects of salinity on Cd bioavailability and accumulation. Zhang et.al (2016) found that when adding salts to the soil in which Carpobrotus rossii a native Australian plant was grown, it was seen that Cd accumulation in plant shoots nearly doubled, compared to plants that did not receive salts. Increased Cd accumulation occurred due to

the increased ionic strength in the soil, as a result of the salt additions and this subsequently increased the Cd mobility in the soil also.

2.4.6 Temperature:

Soil temperature is a important factor in trying to understand Cd bioavailability. Ge et al. (2016) have shown that raised soil temperature promoted Cd translocation from the root to shoot, and increased the Cd distribution in the shoot. The increased Cd translocation resulted in higher rice contamination, with the Cd concentration increasing from 0.27 to 0.65 mg/kg and 0.14 to 0.40 mg/kg, for Indica and Japonica rice respectively. A similar study was also carried out in 2016 by Cornu et al, where it was reported that Cd bioavailability decreased as the temperature was raised from 10 to 30 $^{\circ}$C, but the subsequent soil to plant transfer was seen to be promoted at higher temperatures. The decrease of Cd bioavailability seen in this study was attributed to the complexation of Cd in the pore water of the soil at the higher temperatures. The higher temperatures may have also enhanced the affinity of dissolved organic matter to bind Cd, resulting in decreased bioavailability. Hooda & Alloway (1993) indicated that uptake of Cd by ryegrass in soils amended by Cd salts and sludge application, was significantly higher in pots in the warmer (25°C) environment than those from the cooler (15°C) environment. Changing soil temperatures also may influence soil pH, either by decreasing it or increasing it. An decrease in pH due to changing soil temperature will potentially increase the solubility of Cd. Relative ability of temperature to influence bioavailibility may be determined by the makeup of the soil composition, regarding organic matter content, presence of oxides and pH.

2.4.7 Age:

It has been found by numerous authors that the age of a soil, or how long Cd spends in the soil will influence its solubility and potential bioavailability to plants (Gray et al, 1998; Tang et al, 2006). In soil, Cd will bind onto soil colloids as a result of sorption processes like CEC and specific adsorption. The effect of age is referred to as contact time. The longer the contact time of Cd in soil the more likely it is that these reversible bonds will become irreversible, decreasing the rate of desorption in the soil (Zanders, 1998). This suggests that the Cd ions bound onto soil surfaces could become fixed there, unable to return to the soil solution, decreasing the overall Cd solubility of the soil and bioavailability

2.4.8 Competing Cations:

The presence of other cations in soil solution can affect Cd bioavailability and adsorption in the soil. Recently, Baghenejad et al. (2016) looked at the competitive adsorptive between heavy metal cations, Pb, Cd, Zn and Cu. It was found that the sequence of metal adsorption was Pb > Cu > Zn > Cd. This was determined by considering K_d values of each cation. Therefore from these results we can see that Cd is adsorbed in lower amounts while in the presence of other heavy metals, suggesting that the risk of plant

uptake will be higher than that of other elements, as a result of Cd in soil solution. Calcium has also been seen to compete with Cd for adsorption sites on the soil surface. Escrig & Morell (1998) found that a tenfold increase in calcium concentration reduced the cadmium adsorption capacity approximately by one third, suggesting more Cd would be found in solution after the addition of calcium. Calcium will directly compete with Cd for binding sites in soils due to its higher concentration in soil. This competition will be at exchange sites as a result of calcium not forming inner-sphere complexes with soil constituents. Numerous authors have studied the effect of liming on Cd solubility and uptake, (Tan et al. 2011, Tsadilas et al. 2005, Tlustos et al. 2006). The findings from these studies indicate that the addition of lime to a contaminated soil will reduce the plant uptake of Cd, as a result of raising of the soil pH by 0.5 – 1 unit. Tan et al. (2011) reported that liming significantly reduced Cd uptake by most vegetables by 40%-70% mainly due to adsorption of soil Cd. Zinc is chemically similar to Cd, as well as being present in higher concentrations than other trace metals in temperate soils (Simmler, 2012). Therefore, it has the ability to compete with Cd for both adsorption sites in the soil and uptake through plant root cell membranes.

2.4.9 Effect of Sulphur:

The Lewis Acid/Base concept describes sulphides as hard bases, and Cd^{2+} as a soft acid, therefore these two elements should form specific complexes with each other in soil, rendering Cd unavailable for plant uptake (Pearson, 1968). Many studies have been carried out looking at the effect of S on Cd uptake by plants. Gao et al. (2008) reported that when Cd was present in soils at high concentrations the addition of S supressed the plant uptake of Cd. Although, the supply of S was seen to increase the supply of Cd to rice when the soil Cd concentration was low. This indicated that where higher concentrations of Cd are present, S additions are more likely to reduce plant uptake. Karlsson et al. (2007) reported that complexation with S groups might be the dominant binding mechanism of Cd in soils that have <5 mg Cd/g organic C. Martinez et al. (2002) used Sulphur – X-ray absorption near edge spectroscopy (XANES) analyses that showed a high percentage (35-45%) of the total S that exists in soil is found as sulphides and thiols, which are known to form complexes with Cd, therefore reducing solubility in soil. Organic matters are known to contain trace amounts of thiols (Ravichandran, 2004), therefore we would expect when present in the soil that Cd will be preferentially bound and form complexes with these thiols, reducing Cd solubility and uptake. Although, Cui et al. (2016) reported that the addition of elemental S increased the shoot concentrations of Cd, indicating that S resulted in Cd becoming more soluble in the soil. The reasoning behind this being that the elemental S acidified the soil making Cd more mobile.

2.4.10 Cultivar Type:

If Cd in soil is soluble, it can be taken up by plants and this will typically lead to Cd accumulation within the roots, shoots or leaves of that plant. However, the species of plant plays a big part in determining how much of that Cd is taken up and accumulated into the plant structure. Different crops will be affected

differently by high soil Cd levels, as a result of the ability of each crop to absorb Cd from the soil. Cd accumulation in plants is mostly found in the roots and leaves, from the effect of Cd translocation, which is the movement of Cd from roots to shoots. Gray et al. (1999) showed that when plants are grown in the same soil, Cd uptake and subsequent accumulation by different plant species has been shown to decrease in the order of leafy vegetables > root vegetables > grain crops > fruit. Zhou et al. (2016) also reported that the concentration of Cd decreased in the sequence as leafy vegetables > stalk/root vegetables > legume/melon vegetables. Cd uptake and accumulation by leafy vegetables was the highest, where that of melon vegetables was lowest. Suggesting that melon vegetables are the best option for growth in contaminated soil. The mechanism behind the ability of different plant species to mobilise Cd, and access different fractions of Cd in soils is still unclear (Gray, 1998). However it has been described that the differences seen in between plant species regarding the uptake and accumulation of Cd may be due to differences in the root exudates of each plant, which will influence the quantity of Cd extracted from the soil (Gray, 1998; Mench, 1998)
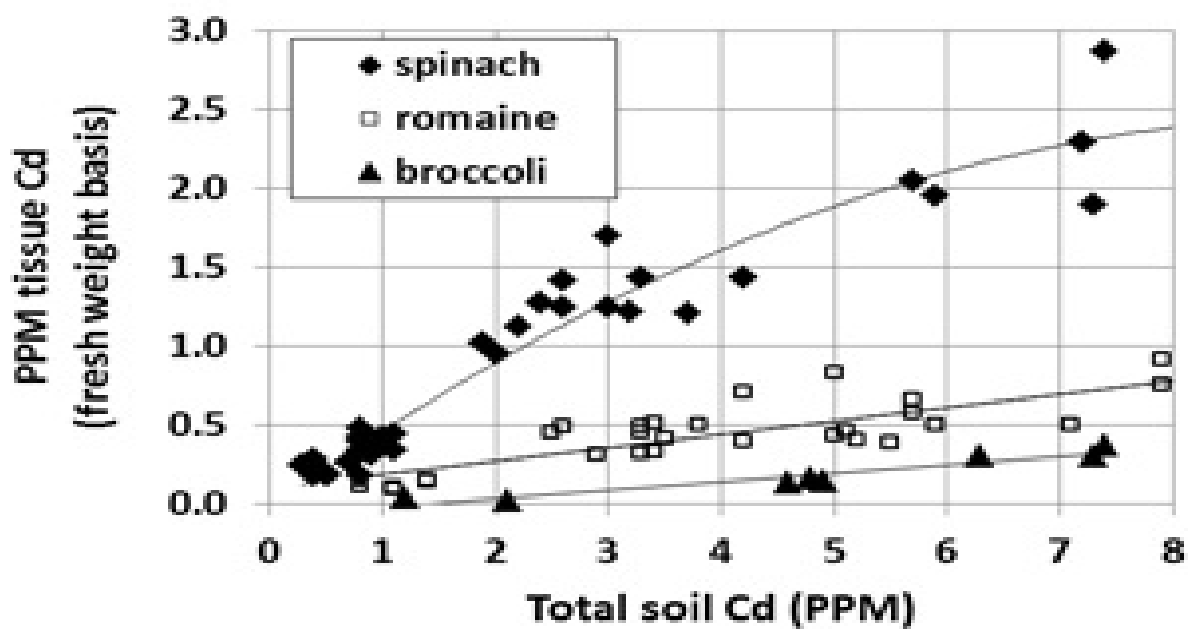
**Figure 2:4 Plant uptake of soluble Cd, shown in three different cultivars. (Smith & Hartz, 2016*)*

2.5 Management Options:

In previous years much of the focus was on hyperaccumulator plants, more so than that of manipulating soil chemical factors, as immobilisation techniques are seen to be more costly, and are often only appropriate for small areas (Martin & Bardos, 1996) (Pulford & Watson, 2002)**.** The potential ability of trees to act as suitable vegetative cover over contaminated land has been looked at in previous years (Pulford & Watson, 2002). This is due to their relative low cost, a sustainable and ecologically sound

solution to remediate heavy metal contaminated land (Dickinson, 2000). The phytoremediation ability of the Willow (*Salix. spp*) was analysed by Greger (1999) who reported that the Cd uptake capacity of 70 *Salix* genotypes could differ by as much as 43 times between clones trees with the highest and lowest values. The more successful clones had capacities nearly five times higher than the hyperaccumulators *T. caerulescens* and *Alyssum murale* due to high biomass production and transport of Cd to the shoot. Greger (1999) also reported that about 30% of the bioavailable Cd had been removed from the soil after the 90 day pot trial. It was found by Eriksson & Ledin (1999) that from the 8 soils where *Salix* were planted, exchangeable Cd levels were 30-40% lower than that of unplanted soils. However Felix (1997) reported that while *Salix* had the greatest metal accumulating ability of all plants tested, it would take 77 years to decontaminate the soil used in this study to acceptable Cd concentrations, outlining a possible limitation of phytoremediation, particularly if the land is needed to be remediated quickly.

Liming is one option that can be used to remediate contaminated soils, through the raising of pH (Tan et al. 2011; Tlustos et al. 2006; Tsadilas et al. 2005,). The findings from these studies all support the claim that the addition of lime to a contaminated soil will reduce the plant uptake of Cd. Suggesting that the subsequent raising of the soil pH by 0.5 – 1 unit will lower Cd uptake. Rahman et al. (2002) reported that the addition of lime to acidic soil was seen to significantly increase available P and B, while also increasing exchangeable Ca and Mg, raising the fertility status of the soil. However, the Ca that is added to the soil as a result of liming may induce competition for binding sites with Cd. This has the potential to increase Cd bioavailability as more Cd will be found in the soil solution Escrig & Morell, (1998).

The addition of organic matter to the soil is considered an environmentally friendly technique to remediate soils that are contaminated with Cd. Zhan et al. (2016) reported that the addition of organic matter in the form of humic substances both increased the uptake of Cd and plant biomass of *Anthryium Wardii*, a phytoaccumulator. These results indicate that the addition of humic substances could be a potential candidate for enhancing the phytostabilisation of *A.wardii* grown in Cd contaminated soils. Phytostabilization is controlling contaminants within the vadose zone through accumulation by roots or precipitation within the rhizosphere. This limits contamination in other areas by reducing migration via wind and water erosion, leaching, and soil dispersion (Bolan et al. 2011). Yousaf et al. (2016) looked at the affect of biochar and organic amendments on the bioavailability and transfer of Cd in the soil-plant system. It was found that the addition of press mud, farm manure, poultry manure and sewage sludge did not reduce Cd uptake by *Triticum aestivum L,* whereas the addition of biochar and organic composts subsequently resulted in decreased Cd uptake by *Triticum aestivum L.* These results indicate the potential of biochar and organic composts as remediators of Cd contaminated soils through in situ Cd immobilisation, while simultaneously improving soil chemical factors that will lead to increased plant growth. Other authors have also reported on the affect of organic matter additions to Cd contaminated soils (Gul et al. 2016;

Wang et al. 2015; Wang et al. 2012; Zhang et al. 2016;). All these studies indicate the potential of organic matters to remediate Cd contaminated soils through immobilisation and reduce plant uptake of Cd.

2.6 Aims:

Organic amendments are highly variable; they come from various different sources, with various different components, sourced at various different times of the year. We do not know how consistent their ability to bind Cd is. Most studies that refer to Cadmium mobility through the soil-plant system mention the potential of organic matter to immobilise Cd, subsequently reducing plant uptake. As it is, so far these studies have not looked at the Cd immobilising capacity of various organic amendements at once to specifically determine what amendment is the best suited to remediate Cd contaminated soils.
In this study the aim is to try and determine which organic amendment has the greatest capacity to adsorb Cadmium and reduce plant uptake, while at the same increasing the soils nutrient status, therefore increasing plant growth.

Chapter 3

Materials and Methods:

3.1 Background Information:

Various types of organic amendments from around the New Zealand were collected and were analysed for their chemical characteristics and Cd binding properties.

In total, twelve different organic amendments were investigated, including:

- Peat – both eutrophic and oligotrophic, the eutrophic peat has been sourced from close to Lincoln, while the oligotrophic peat was sourced from the Waikato region.

- Bio-solids – One sample from Christchurch, and another from Kaikoura.

- Coffee grounds from around Canterbury.

- Different composts supplied by two different garden suppliers, Oderings and Parkhouse Garden supplies, using different components (e.g. saw dust, pig manure, fish waste and sea-weed, and mushroom waste from the growing process). Living Earth compost (municipal compost) was retrieved from Living Earth Ltd. (Christchurch), from which a six month time series of samples were analysed to capture any seasonal variability in the composition of that compost. Gathered from Living Earth in Christchurch.

The samples were dried and sieved (<2mm) to reduce the variability between size fractions to make the results more comparable. Following this, the samples subject to the following analyses:

- pH and conductivity (in H_2O 1:10 w/w ratio) will provide information on the acid-binding capacity of the amendments, and how much solute they may release when applied to soils and how they can influence the soil pH.

- Total carbon (Loss on Ignition method) and total elemental content (digestion, followed by ICP-OES analysis) will give information on the chemical composition of each amendment.

- Cadmium binding measurements (batch sorption) will provide a measure of the capacity of the amendment to bind Cd and other trace elements and thereby affect their bioavailability for plant uptake.

- Cold and Hot Water Extractable Carbon analyses will give information on the likely stability of the organic amendment in the soil and tell us how likely the formation of potentially mobile organic ligands is.

- Specific UV Absorbance (SUVA) analysis of the Cold Water Extractable Fraction will give specific chemical information on the chemical composition of the dissolved fraction and its ability to bind cadmium.

- Cation Exchange Capacity

All samples were analysed in triplicates.

3.2 pH, Electrical Conductivity and Total Organic Matter and Organic Carbon

pH, electrical conductivity and organic carbon were measured according to the methods given by Blakemore et al (1987) and Rayment et al (2011) and are discussed briefly below.

pH

10g of each amendment was weighed out and deposited into individual 50 mL bottles. 25 mL of deionized water was added to each bottle containing amendments. The bottles were then shaken in the end-over-end shaker for 30mins. The samples were left overnight, to allow for stabilization. After overnight stabilization, samples pH was determined using the Mettler Toledo pH meter, calibrated with pH 4 and 7 standards.

Electrical Conductivity:

5 g of each amendment was weighed out and deposited into the appropriately labelled 50 mL centrifuge tube. 25 mL of deionized water was added to each centrifuge tube containing amendments. The samples were then placed into an end-over-end shaker, and shaken for 30mins. Following this the samples were centrifuged at 1500 rpm for 5mins, using the Kubota Centrifuge. The conductivity meter was calibrated using the 1413 μS/cm standard. Once calibrated, the conductivity of the samples was measured. From the electrical conductivity results the Total Soluble Salts were calculated:

- Total soluble salts (%, air-dry soil) = [$EC_{1:5}$ (μS/cm) x 0.35]

Total Organic Matter and Organic Carbon by Loss on Ignition:

Labelled porcelain crucibles were weighed, and this weight was recorded. 10 – 20 g of amendment was then weighed out and placed into a corresponding crucible. Samples were dried in a 105°C oven overnight. After being removed from the oven, and once cool enough to handle, the samples /crucible were reweighed on the same balance and oven dry-weight recorded. The samples were then placed in a muffle furnace, and combusted at 550°C for 4 hours. Samples were reweighed, to determine %total C content.

- LOI = (*Wt105 – Wt550 / Wt105) * 100.* SOC (%) = SOM(%) / 1.72?

3.3 Cold and Hot Water Extractable Carbon:

3g of amendment was weighed and put into a 50 mL centrifuge tubes. Followed by the addition of 30 mL of deionized water**.** Samples were then shaken for 30mins in the end-over-end shaker (cold water

extraction). The shaken samples were placed in the centrifuge and spun at 3000 rpm for 5mins. The supernatant from this extraction was filtered through 0.45 filters, and left to be analysed by the Total Carbon analyser. Further SUVA analysis was conducted using this supernatant. Another 30mL of deionized water was added to the left over sediments in the centrifuge tubes. The samples were then placed in an 80 degree water bath for 16 hours. (Hot water extraction). Samples were again centrifuged at 3000 rpm and the supernatant was filtered. This was followed by Total Carbon analysis. (Ghani et al. 2003)

3.4 Cadmium Sorption Experiment:

A Cd spiked $Ca(NO_3)$ solution was made up in order to obtain 0.5 mg/L of Cd in 0.05 M $Ca(NO_3)2$ solution. Amendments were weighed out into 5 g samples, along with replicate blanks, and put into a 50 mL centrifuge tube. 30 mL of spiked Cd solution was added to each tube and agitated using a vortex mixer. Samples were given time to settle, then the pH was taken. The target pH for this experiment was 5.5. If the pH was higher than this it was adjusted using 1M HNO_3, whereas when lower it was raised using 1M NaOH. Samples were then placed in the end-over-end shaker for 2 hours, followed by being centrifuged at 10,000 rpm for 10mins. The supernatant was filtered using Whatman #52 filter paper, keeping 20 mL. 2 mL of 10% HNO_3 was then added to acidify the samples. The ICP-OES was used to analyse the Cd content of the samples.

3.5 Specific UV Absorbance (SUVA):

Using UV/VIS spectrometer with a quartz cell (1.0 cm path length). The sample was allowed to warm to room temperature before measurement. SUVA254 values were determined by dividing the UV absorbance measured λ =254 nm by the DOC concentration and reported in the units of litre per milligram carbon per meter. Supernatant from the Cold Water Carbon extraction was used for this analysis. (Weishaar et al. 2003).

3.6 Elemental Composition:

Total elemental analyses were carried out using microwave digestion in 8 mL of AristarTM nitric acid (69%), diluted with milliQ water to a volume of 25 mL and filtered using Whatman no. 52 filter paper (pore size 2 mm). The concentrations of Cd together with other elements were determined using inductively coupled plasma optical emission spectrometry (ICP-OES) in soils (Kovacs et al. 2000).

3.7 Cation Exchange Capacity:

3.7.1 Reagent Preparation: 0.01 M AgTU+:

75 g of thiourea was placed into a labelled 5 L volumetric flask and approximately 1.5 L of deionised water was added. Stir bar was placed on magnetic stirrer. 8.494 g of silver nitrate was placed into a 5 L beaker

and approximately 2.5 L of deionised water was added. Stirred until dissolved completely. 2.5 L of silver nitrate was added to the thiourea solution using a funnel and while stirring. Stirrer bar was removed from solution and it was then made up to the volume with deionised water and transfered to a 5 L container. Bottle top dispenser was then fitted to deliver 35 mL.

3.7.2 Procedure:

A subsample of the air-dry amendments was weighed for moisture determination. 0.70 g of amendemnt was weighed into a falcon tube. Previous steps were replicated for analytical control soil. 35 mL of 0.01M AgTU+ solution was added. It was shaken for 16 hrs in the end-over-end shaker, followed by centrifugation at 3000 rpm for 10mins. Extractant was then filtered using Whatman 40 filters into a plastic vial. Samples and blanks were analysed cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Ag^+, Al^{3+} and Mn^{2+}) on the ICP-OES. The calculation of CEC AgTU is as follows:

CECAgTU (cmolc/kg) = $(1-[Ag^+])*50$

Where: $[Ag^+]$ = the Ag^+ from the ICP-OES expressed in molarity

50 = dilution factor

To convert to oven dry

CEC = CEC (cmolc/kg) x (100+ MC%)/100

3.8 Statistical Analysis

Once the data that was collated it was analysed using ANOVA with Fisher's Least- Significant-Difference (LSD) post-hoc test to compare means using Minitab 17 (Minitab Inc, State College, Pennsylvania, USA). The significance level was 0.05 (5%).

Chapter 4

Results:

4.1 Codes and Information:

Shown below in Table 4:1 is information relevant to the composition and source of the organic amendments used in the analysis. Five of the amendments are composts that have been sourced from various garden supply stores around Christchurch, and are composed of various materials including oceanic botanicals and wool slurry waste. There are two biosolid samples, one from Christchurch and one from Kaikoura, while the other three amendments are eutrophic and oligotrophic peat, and coffee grounds.

Table 4:1 General Information about Organic Amendments used in analysis.

Code:	Amendment:	Manufactured from:	Source:
EP	Eutrophic Peat	Naturally Occurring	Waikato
OP	Oliogtrophic Peat	Naturally Occurring	Canterbury
PHW	Parkhouse White	Seaweed, Fish Waste	Parkhouse Garden Supplies
KBS	Kaikoura Bio Solids	Sewage Sludge	Kaikoura Waste Water Treatment Plant
CFF	Coffee Grounds	Coffee Beans	Christchurch Cafes
OD	Oderings	Municipal Compost	Oderings Garden Centre
PHP	Parkhouse Premium	Municipal Compost	Parkhouse Garden Supplies
CBS	Christchurch Bio Solids	Sewage Sludge	Bromley Waste Water Treatment Plant
PH	Parkhouse	Pig Manure, Sawdust, Wool Slurry	Parkhouse Garden Supplies
LE	Living Earth	Municipal Compost	Living Earth, Christchurch

4.2 Amendment Elemental Data

The elemental composition of macro-nutrients and trace elements along with other soil properties for all amendments excluding LE samples are shown in Table 4:2 below. Of note is the pH of KBS and OP, with values of 3.68 and 3.26 respectively. As this is rather acidic, this would pose a problem regarding soil acidity if amendments were added to the soil. The cadmium content already present in the bio solids were found to be at high concentrations; CBS = 1.60mg/L, KBS = 3.55mg/L; potentially risking the soil of Cd accumulation if bio solids are to be applied. The subscript letters beside each value shows significant differences between means, resulting from the LSD test, of pH and conductivity. From this we can see that there are significant differences between all of the amendments for pH. While some significance between means is shown in the conductivity values.

Table 4:2 Properties and element concentrations of amendments used in experiments.

Properties:	Units:	EP:	OP:	CBS:	KBS:	PH	PHW:	PHP:	CFF:	OD:
pH:	-	7.13^{C}	3.26^{M}	6.49^{G}	3.68^{L}	6.92^{EF}	5.55^{I}	6.26^{H}	4.89^{K}	5.3^{J}
Cond:	uS/cm	307^{J}	296^{J}	6733^{CDE}	4340^{FG}	4060^{FG}	309^{J}	1408^{IJ}	2893^{GHI}	3096^{GH}
CEC:	me/100g	26.4	21.4	30.9	17.4	42	36.1	42.2	16.8	37.9
Ca:	mg/kg	8350	1486	30320	11200	27916	15848	15892	1140	10899
K:	mg/kg	2684	833	3354	3379	6020	3000	5019	4526	4843
P:	mg/kg	836	241	17760	5369	7378	836	2798	1158	2976
Mg:	mg/kg	2326	699	5842	4043	3965	9168	3008	1682	2931
Cd:	mg/kg	0.17	0.08	2	4	0.16	0.15	0.26	0.05	0.12
Zn:	mg/kg	0.78	0.18	16	20	9	1	2	0.21	6
S:	mg/kg	2538	2347	14867	10580	6856	837	3438	1496	3056
Pb:	mg/kg	13	2	61	135	6	11	10	0.21	8
Cu:	mg/kg	15	1.7	318	783	110	30	26	23	74

4.3 LE Elemental Data

The elemental composition of macro-nutrients and trace elements along with other soil properties for the LE compost samples are shown below in Table 4:3. Of note are the Pb concentrations within each LE sample. All of the samples have recorded concentrations that exceed 100 mg/kg, and range from 100 mg/kg – 224mg/kg. The issue associated with this is the potential of Pb accumulation in the soil after application of the compost. The CEC of these composts are the highest on average on all amendments studied suggesting that they have the greatest capacity to bind metals within the soil. The highest CEC was found in LE6 (47), and the lowest was found in LE3 (42.3)..

Table 4:3 Properties and element concentrations of amendments used in experiments. LSD significance test results on pH and conductivity values are shown in subscript letters

Properties:	Units	LE1:	LE2:	LE3:	LE4:	LE5:	LE6:	LE7:	LE8:	LE9:	LE10:	LE11:	LE12:
pH:	-	7.65^{A}	7.04^{CDE}	7.26^{CD}	7.11^{DEF}	7.01^{F}	6.9^{B}	7.37^{CD}	7.07^{CDE}	7.04^{CD}	7.08^{CD}	7.69^{A}	7.68^{A}
Cond:	uS/cm	2370^{HI}	7867^{BCD}	9295^{AB}	8097^{BC}	5105^{FG}	8823^{AB}	9690^{A}	7360^{CD}	6637DE	2213^{HI}	5393^{EF}	7633^{BCD}
CEC:	me/100g	44.8	43.1	42.3	44.1	44.1	47	45.8	45.4	45.5	45.6	46.3	45.7
Ca:	mg/kg	22406	30224	32500	35930	25838	30526	31463	28821	29407	25213	22938	36300
K:	mg/kg	5363	13629	13765	13701	11602	14219	14167	11782	12204	6051	11214	12147
P:	mg/kg	2786	5254	7063	6474	4690	5218	5648	5467	4945	3126	4545	6457
Mg:	mg/kg	4510	5753	5335	5661	5043	5390	5366	5740	5502	5108	5099	5425
Cd:	mg/kg	0.54	0.49	0.42	0.48	0.39	0.52	0.55	0.40	0.48	0.54	0.40	0.50
Zn:	mg/kg	294	337	333	362	312	363	331	319	347	308	290	335
S:	mg/kg	2360	3270	3224	3224	2839	3401	3264	3061	3181	2265	2793	3037
Pb:	mg/kg	100	147	192	166	137	145	186	151	224	150	117	166
Cu:	mg/kg	46	94	95	103	90	83	82	92	100	44	75	86

4.4 Adsorption Capacity of Amendment

From these adsorption results, the Kd of the amendments was calculated to determine which specific amendment had the greatest capacity to bind Cd from solution. It was found that PH indicated the greatest Cd binding capacity with a Kd value of 11317, the next highest was LE1 with 530, while the other amendments recorded Kd values of 100 or below. KBS had the lowest Kd of all amendments, which could be attributed to its acidic nature. Through statistical analysis (LSD) of this data, it was found that the PH mean is significantly different from the other amendment means. The PH Kd value suggests that addition to a Cd contaminated soils could result in the immobilisation of Cd, although it does contain the largest standard error of any amendment suggesting variation in data.
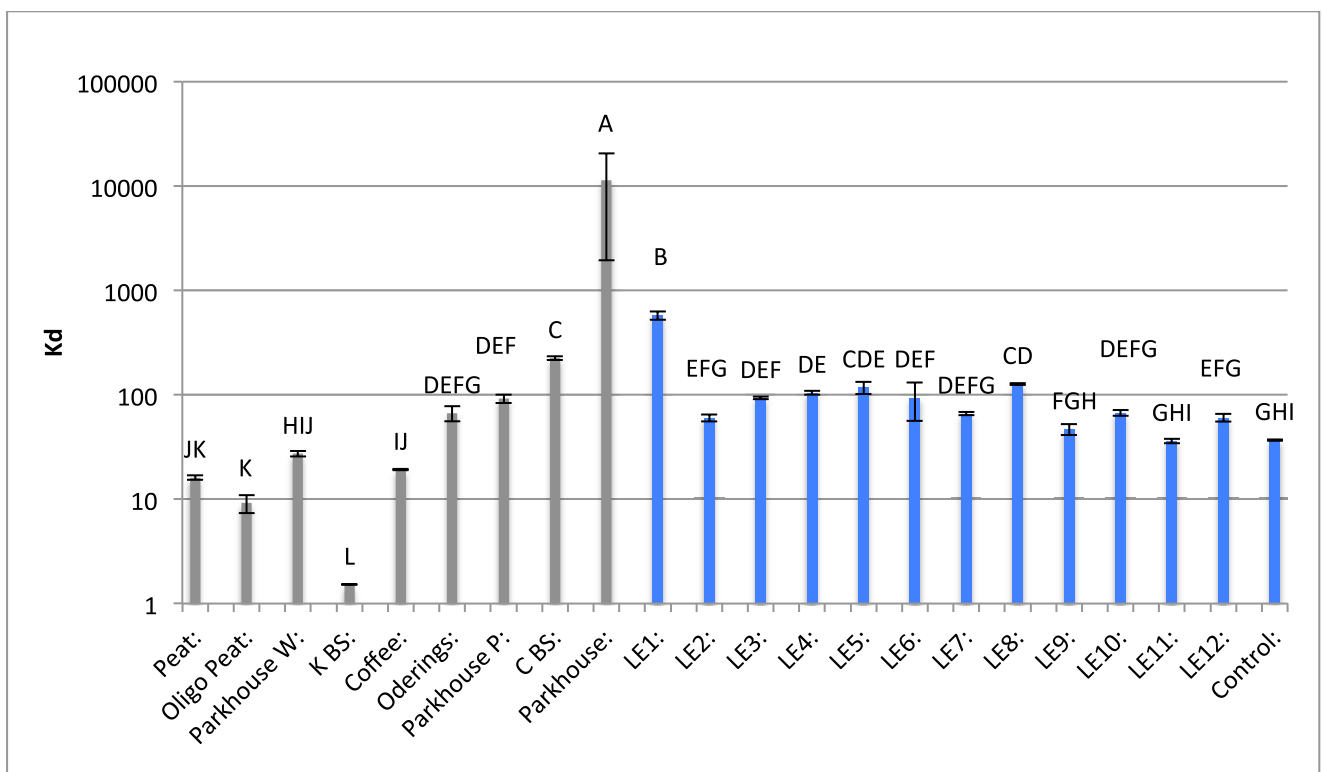
Figure 4:1 Kd of organic amendments at pH 5.5. LE compost samples are shown in blue. Error bars seen on graph indicate the standard error of the mean for each amendment. Letters in subscript represent One-way ANOVA LSD test.

4.5 Total Organic Carbon from LOI

CFF recorded the highest percentage of C of all amendments with a value of 57%; closely followed by OP with 55%. These two amendments show no significant difference from each other, symbolised by subscript A. CBS, LE and PHP show no significant difference. While EP and PHW were seen to have the lowest TOC percentages, with 17 and 18 respectively.
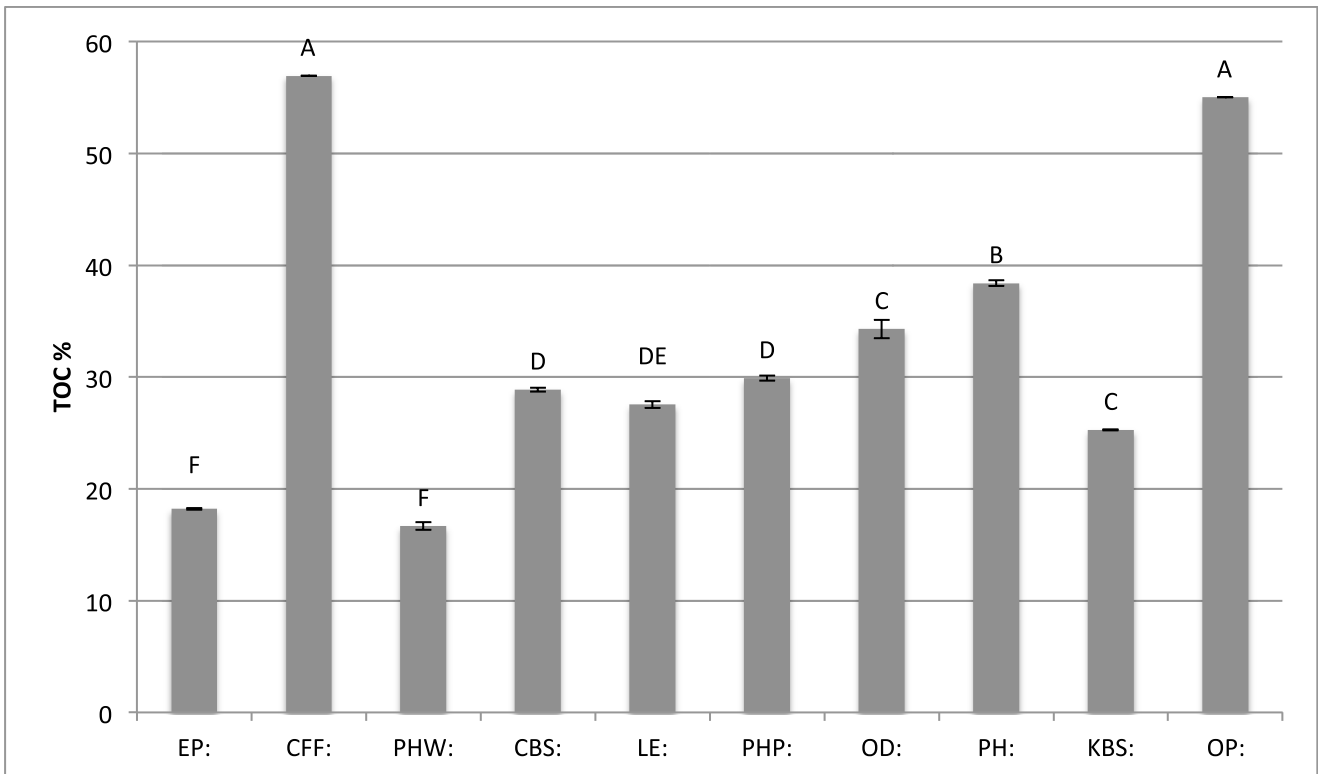
Figure 4:2 Total Organic Carbon from Loss on Ignition. Error bars represent standard error of the mean for each amendment. Letters in subscript represent One-way ANOVA LSD test.

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4.6 Hot Water extractable Carbon:

4.6.1 HWC as a % of TOC

The Hot Water extractable Carbon (HWC) as a percentage of TOC was analysed for all amendments excluding LE compost samples and the results can be seen in Figure 4:3 below. The highest HWC value was found in CBS with 3.90%, which is nearly twice as high as EP, which was seen to contain 2.16%. CFF was seen to have a value of 0.001, which was the lowest percentage of HWC in the experiment. The OC in the CBS is most soluble, the OC in the CFF is the least soluble.
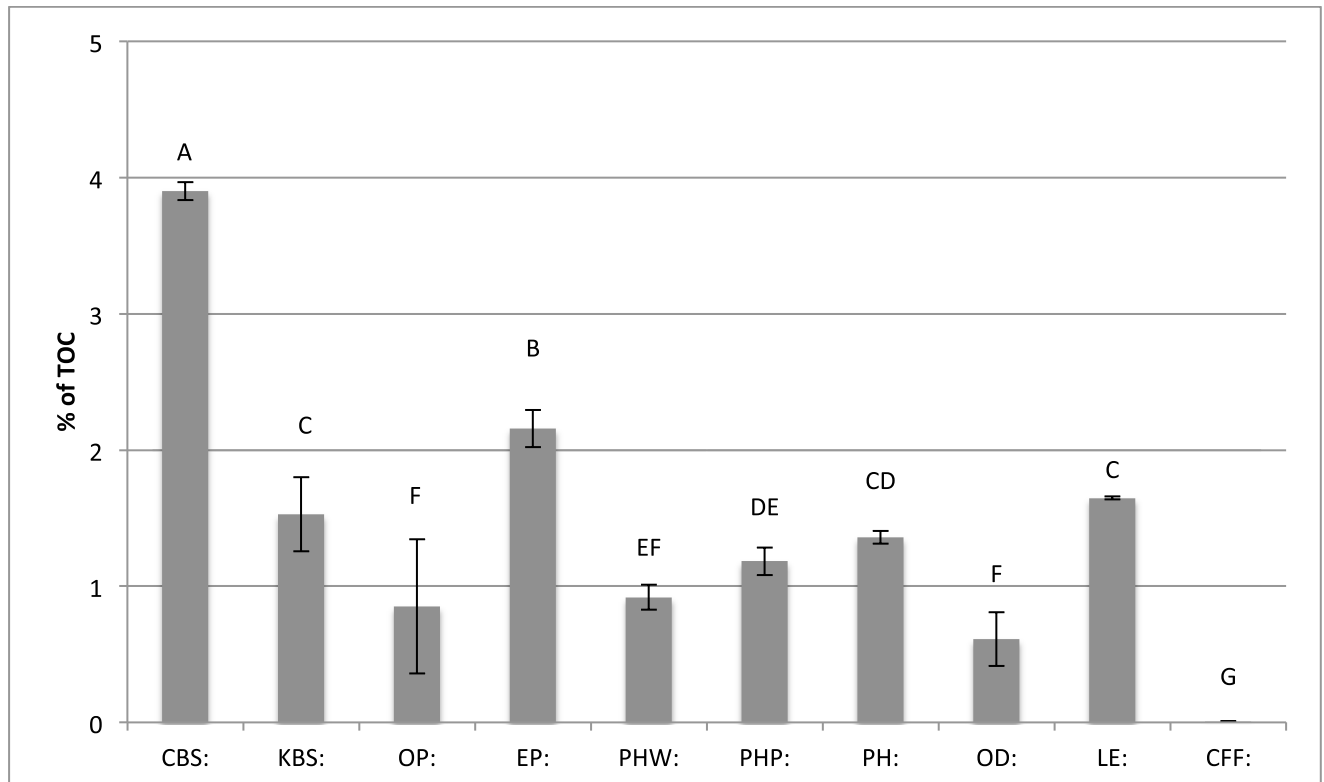
Figure 4:3 Hot water extractable Carbon expressed as a percentage of Total Organic Carbon. Error bars on graph signify the standard error of the mean for each amendment. Letters in subscript represent One-way ANOVA LSD test.

4.6.2 HWC by weight of amendment:

From figure 4:4 below we can see that CBS has the greatest proportion of HWC by weight of each amendment with 11265 μg C g^{-1}. The value from CBS is significantly different from the other amendments, as shown by the letters in subscript. The amendment with the next highest concentration of HWC was PH with 5219 μg C g^{-1}. This was a found to be similar to the values of OP and LE, 4690 μg C g^{-1} and 4538 μg C g^{-1} respectively. The lowest HWC value was found in CFF with 5 μg C g^{-1}, this was significantly different from the other amendment means.
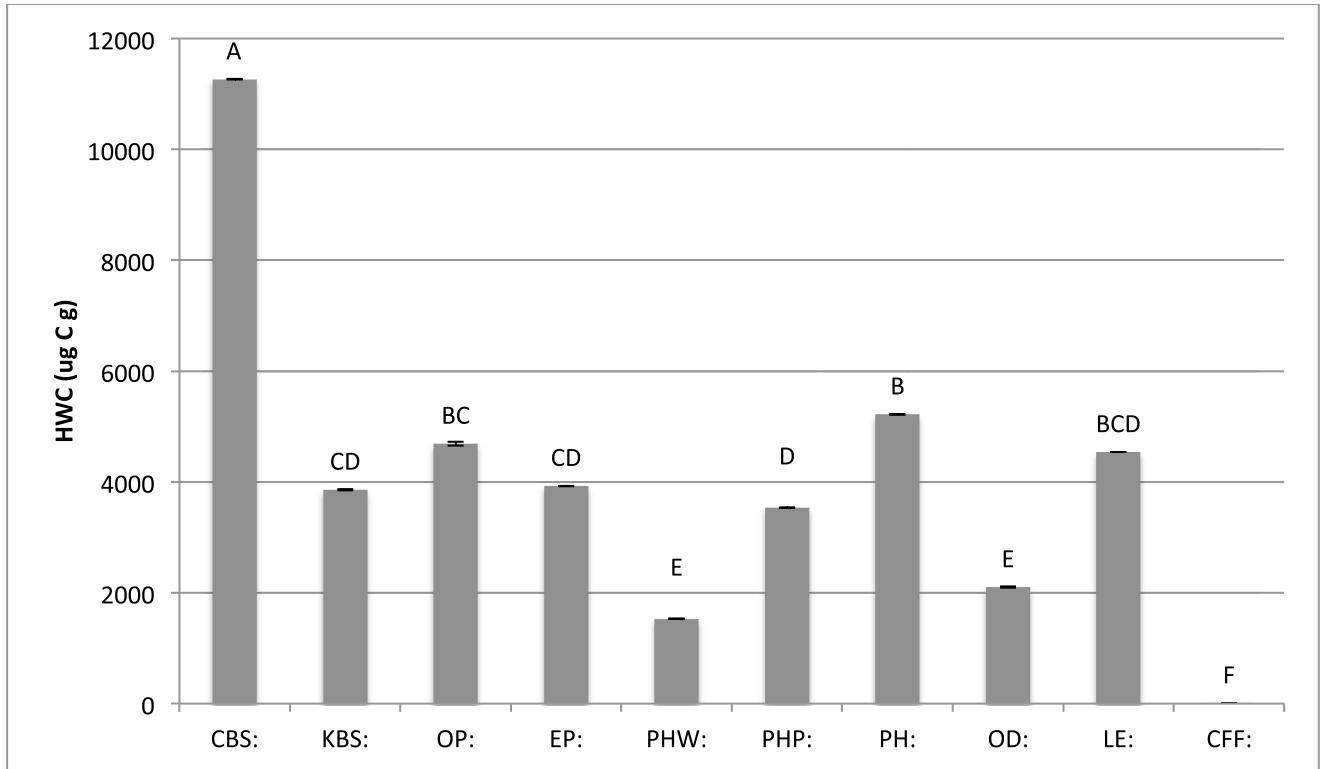
Figure 4:4 Hot Water extractable Carbon (microgram of C per gram of amendment). Letters in subscript represent One-way ANOVA LSD test.

Chapter 5

Discussion:

5.1   Elemental Composition Factors:

5.1.1 Cadmium concentration of amendments:

Current average Cd concentrations in New Zealand soils are 0.35 mg/kg, with a baseline level of 0.16 mg/kg, in a range of 0 – 2.52 mg/kg as reported by Taylor et al. (2007), MAF (2008). The tiered Cd management system (Rys et al. 2011) states that once a soil's Cd concentration reaches 1.8 mg/kg, no more accumulation of Cd is allowed. The elemental composition analysis of the potential organic amendments in this study indicates that all Cd concentrations, with the exception of the KBS, are all lower than the 1.8 mg/kg limit set in Rys et al. (2011) by at least 1.25 mg/kg (Table 4.1/4.2). Therefore, the risk of Cd accumulation in an agricultural soil through the additions of these particular amendments would likely be dependent on the application rate. By comparing the amount of Cd found in the amendments to that of Reactive Rock Phosphate used for fertiliser on NZ soils, we can see that it is substantially higher in RPR. New Zealand sources RPR from countries that include Togo and Morocco (MAF, 2008). Roberts (2014) reported that RPR from these countries have a Cd concentration of 58 mg/kg and 26 mg/kg respectively. These concentrations are substantially higher than that of the amendments in this study, indicating that amendment additions will result in lower levels of Cd accumulation in soil to that of RPR. CBS and KBS were the exception regarding Cd concentrations within the amendments. Both had levels that were greater than that of national average, at 1.60 mg/kg and 3.55 mg/kg respectively. There would be a greater degree of Cd accumulation if these amendments were applied to the soil, compared to the other amendments. It was reported by Simmler (2012) that in agricultural soils the addition of biosolids increased extractable Cd and increased plant uptake of Cd, outlining the potential risk of applying biosolids to soils. Biosolids typically are composed of municipal sludges that are sourced from domestic and trade wastes, along with contents of septic tanks. The incorporation of these wastes predominantly lead to the high levels of Cd found within the bio solids (New Zealand Water and Wastes Association, 2003). The US National Research Council (1996) reported that crops grown in soils that are amended with bio solids have elevated Cd concentrations, but no such toxicity issues from this source have been reported in humans or animals. Al Mamun et al. (2016) also used KBS as part of his study. The Cd concentration of that batch was recorded at 1.6mg/kg, indicating a difference of nearly 2mg/kg between the two batches. A difference such as this could be attributed to the composition of that particular influent flow that made up these biosolids.

5.1.2 Effect of Zinc on Cd concentrations:

Zinc concentrations found in the LE compost samples were in excess of 290 mg/kg. No other amendment contained such concentrations of Zn, but the corresponding concentrations for Cd recorded less than 0.60 mg/kg (see Table 4:2 and 4:3). Whereas, CBS and KBS had Zn concentrations of 16.03 and 19.60 mg/kg respectively, substantially lower than that of the LE composts. In turn the Cd concentrations were much higher, as shown in Tables 4:1 and 4:2. The LE composts are the only amendments that have a noticeable high Zn:Cd ratio, and as Zn is chemically similar to Cd, high concentrations of Zn in the soil will create competition for binding sites. This ratio may be the reason why Cd concentrations are lower than that of the bio solids, therefore indicating the potential ability of Zn to reduce Cd uptake as shown by Chaney et al. (2009); Kabata-Pendias et al. (2007). The fact that Zn is a plant micronutrient is also a benefit in its own right, and ideally this will increase plant growth in Zn deficient soils (Tsonev & Lidon, 2012).

5.1.3 Lead accumulation risk:

The LE composts recorded the highest Pb concentrations of all the amendments in this study, with an average concentration of 156.75 mg/kg (Table 4:3). The US EPA states that if soils contain Pb concentrations that are greater than 400 mg/kg, crops should not be planted in these soils (Agency for Toxic Substances and Disease Registry , 2010). As it is, LE composts do not exceed these Pb concentrations, but after the repeated application of the compost into soil, Pb is likely to accumulate (Siccama & Smith, 1978). If this compost were applied onto soil at a rate of 500 kg/ha/a (theorectical) the accumulation of Pb would be 78,375 mg/kg ha/a; increasing the Pb concentrations well above the 400 mg/kg EPA guideline. Accumulation of Pb in soil at high concentrations can lead to potential health risks due to the inhalation and ingestion of dust and soil. The reasoning behind the LE composts having high Pb concentrations cannot be directly proven, as the exact source of contents in the compost is not known. Although, the sources of Pb in the environment are rather well known therefore a relative idea can be formed from where the Pb has come from. In New Zealand Pb sources in composts and soils are primarily from paint and lead bullets (Woulfe, 2014). A decision regarding whether the positives are likely to outweigh the negatives would have to be made; Cd reduction vs Pb accumulation.

5.1.4 Addition of Nutrients:

5.1.4.1 Calcium, Potassium and Magnesium:

The addition of the compost amendments in particular will add large quantities of Ca to the soil. Once again LE compost was seen to have the greatest concentration of this element, >20,000 mg/kg (see Table 4:3), while OD had the lowest. The competition between Ca and Cd is centred around adsorption sites on soil colloids (Escrig & Morell, 1998). Typically, if both cations are present in the soil at high concentrations Ca will be adsorbed to soil colloids before Cd, or even replace Cd ions on the adsorptive surface. Bolan et al. (2003) showed that additions of Ca $(OH)_2$ to the soil subsequently resulted in the increase of Cd uptake

by mustard plants and this was attributed to the decrease of Cd adsorption resulting from Ca competition. Therefore, this suggests that the addition of Ca through compost amendments may result in increased plant uptake of Cd. Although, Al Mamum et al. (2016) reported that when LE compost of similar Ca concentrations was added to the soil plant uptake of Cd decreased. As Ca is a macronutrient in nature it is of great importance in the soil and plants. Plants require Ca at concentrations between 0.1 – 5% dry weight (Marschner, 1995).

Potassium and Magnesium concentrations can be seen in Table 4:2 and 4:3. From this we can see that the highest concentrations were found in LE and PH composts. K was more prevalent than Mg, as K was found in concentrations of more than 10000 mg/kg, whereas Mg in most cases was seen at concentrations of around 5000 mg/kg or less. Christensen et al. (1999) found that K and Mg are usually present in lower concentrations than Ca within the soil. This results in K and Mg creating less competition with Cd for adsorption sites. Therefore, it is likely that K and Mg will not increase the solubility and plant uptake of Cd. From our findings we would expect that this would be similar if composts were added to soils. Potassium plays a vital role in winter survival and hardiness of the grass plants, while Mg supports the photosynthesis process (Schwatrzkopf, 1972).

5.1.4.2 Phosphorus:

With the exception of CBS and KBS, LE and PH composts were seen to contain the greatest concentration of P, ranging from 2786 mg/kg to 7378.1 mg/kg (see Table 4:2/4:3). It has been found by Wang & Xie (2008) that increasing the concentration of P in soil can reduce Cd in solution due to an increase in pH, the result of adding KH_2PO_4. It was found that this correlates into a 59% - 86% reduction of Cd taken up by the plant grown in these soils. Dheri et al. (2007) also reported on the ability of P to reduce Cd concentration in the soil and the uptake of Cd by Spinach. This suggests that PH compost would theoretically have a greater effect on the reduction of Cd concentration in the soil as it has the greatest P concentration. Conversely, OP would be expected to have the smallest effect on Cd uptake, as it contained the lowest P concentration (241 mg/kg). As P is a vital macronutrient and the fact that pasture growth in NZ is most commonly limited by P (Simmler, 2012), it is essential that soil P levels are sufficient to ensure that production is maintained throughout the country.

5.1.5 Sulphur:

The sulphur content found in the amendments was lowest in PHW and the highest in PH. Sulphur like K and Mg was not found within the amendments in the same abundance as Ca. Nevertheless, due to its status as a macronutrient it is essential for plant growth. In NZ some areas have been found to be sulphate deficient (Curtis, n/a), which emphasises the importance of regular applications of S rich material. Therefore, applying amendments that have the dual purpose of having the capacity to reduce plant uptake of Cd and increase S concentrations in soil would be hugely beneficial. The addition of gypsum ($CaSO_4$) to

composts has been a common practice since the early 1920s, predominantly to reduce N loss via ammonia volatilisation (Tubail et al. 2013). This would indicate why the compost amendments in this study show relatively high concentrations of S compared that of OP and CFF.

5.1.6 Cation Exchange Capacity:

CFF has the lowest CEC with 16.8 me/100g and LE6 has the highest with 47 me/100g (Table 4:2 and 4:3). The CEC for LE and PH compost were similar to those measured by Al Mamun et al (2016). It was reported that the CEC for LE and PH composts were 45 me/100g and 47 me/100g, respectively. Haghiri (1974) and Miller et al. (1976) both reported that increasing the CEC of a soil would decrease the Cd solubility in soil and as a result subsequently reduce plant uptake of Cd at any given level. These findings would indicate that LE and PH composts should have a greater capacity to adsorb Cd than CFF would.

5.1.7 pH Effects:

The pH between amendments showed a large variation. The higher pH values were found among the LE composts. On the other end of the spectrum we found that the pH of OP and KBS were 3.26 and 3.55 respectively. Ideally, the pH of ameliorants for Cd contaminated soil should be as close to neutral as possible. This is due to the behaviour of Cd in soil at different pH values. Permaki (1992) and Gray & McDowell (2015) both reported that a decrease in pH was seen to increase Cd solubility and plant uptake. Therefore, suggesting that the application of OP and KBS to the soil as Cd amendments would create a risk of mobilising the Cd that is already locked up in the soil, due to the subsequent decrease in pH of the soil after addition. Whereas, the addition of the amendments that have relatively neutral pH (LE and PH composts) should not decrease the pH of a soil once applied, and as a result decrease Cd solubility.

5.2 Sorption of Cadmium:

5.2.1 Kd values:

The PH compost recorded a Kd of 11317 (see Figure 4:1), which was significantly higher than the other amendments. LE1 was seen to have the second greatest capacity for binding Cd, with a Kd of 578. These values showed substantial differences when compared to Al Mamum (2016), where LE and PH composts were also studied. He found that LE compost at pH 5.5 had a Kd value between 2000-3000; PH compost was seen to have a Kd of 3000-5000. The data does show a similar trend of PH having a greater capacity to bind Cd than that of LE. The differences in Kd between studies could be attributed to an analytical limitation. The relatively low concentration of Cd used in the spike solution (0.5 mg/L) meant that in many cases the dissolved Cd concentration was bordering on the ICP-OES detection limit. Therefore when it came to calculating the Kd values, a slight difference in sorption was made substantially larger, giving the Kd values that are shown in Figure 4:1. While the general relationship between different amendments is thought to be correct, the relative differences between the Kd values of different amendments may be

exaggerated. Al Mamum et al. (2016) used a concentration of 1.4 mg/L in their study, as well as higher concentrations of up to 24.5 mg/L. Cd concentrations in soil porewater are usually around 1000 times lower than those used by Al Mamun et al (2016). The Cd detection limits of most commonly used analytical instruments necessitates the use of higher concentrations than what would be encountered in most natural systems when measuring Kd. However, it should be recognized that the use of exceedingly high Cd concentrations is also problematic as it may give an misleading representation of a substance's sorption capacity. Differences in Kd could also be attributed to the composts being made at different times of the year, potentially resulting in the make-up of the compost being different. As Al Mamum's study was conducted throughout 2015, whereas this study began at the start of 2016. The lowest Kd values came from the KBS and OP, with 1.5 and 9 respectively. These results are likely to be due to the pH of these amendments, as they are rather acidic.

5.2.2 Parkhouse Compost:

The PH compost is made from pig manure, wool slurry and sawdust. The presence of pig manure within the compost may provide the reasoning behind why PH had such a large Kd value, as many authors have mentioned its potential as a soil amendment for heavy metals. Ping Li (2009) reported that the application of pig manure to a soil that was contaminated with Cd under rice, significantly reduced Cd in the roots by 9.7% – 49.9%, whereas the application of Zn fertiliser did not showed a significant decrease of Cd in roots. The application of pig manure also decreased the bioavailability of the Cd in the soil. This in turn reduced the uptake by the rice plants, ultimately resulting in the reduction of Cd in the roots and shoots of the rice plant. Sato et al. (2010) reported that Cd concentrations were 34% - 39% lower in soils that were treated with animal waste compost, including pig manure, than that of soils treated with chemical fertilisers. It was also said that the application of pig manure resulted in a large quantity of P to accumulate in the soil. Wang & Xie (2008) and Dheri et al. (2007) reported that increasing the P content reduced Cd bioavailability. Together, these results suggest that the addition of P to the soil from pig manure is the dominating factor that determines Cd bioavailability reduction. Phosphorus concentrations within the PH compost were recorded at 7378 mg/kg (see Table 4:1). This value was the highest of all amendment excluding biosolids. Therefore, this suggests that the P concentration in the PH may have had some influence on Cd sorption, which is shown in the Kd value.

5.2.2.1 Affect of Sulphur on Kd:

PH compost recorded the largest S concentration of all amendments with 6856 mg/kg (see Table 4:1), which was twice as much as any other amendment in this study. The addition of Gypsum ($CaSO_4$) to municipal composts is a common practice. We don't know whether gypsum has been added, but the high Ca concentrations suggests this is the case. SO_4 concentrations will increase due to the addition of gypsum, this could create a higher number of S-containing functional groups, potentially increasing the total S

concentration. This could suggest why the Kd of PH is so high. In comparison, PHW compost had an S concentration of 837 mg/kg, which was the lowest of all amendments. This may suggest why the corresponding Kd value for PHW was only 27, despite having a relatively similar CEC as PH compost. CFF recorded a lower CEC than PHW (16.8), but it's corresponding Kd value (19) does not suggest that the CEC is the dominant binding mechanism of Cd in this case. Instead, this could be attributed to the S concentration of CFF which was higher than PHW, 1496 mg/kg. Sulphur in SO_4^{2-} is in the oxidized, S(+6) form, rather than the reduced sulphide, S(-2) form, as found in thiol functional groups. This is unlikely to have contributed to the binding of Cd^{2+}. To establish whether S is indeed one of the dominant factors determining the Kd of PH and PHW compost, one could assess the compost's capacity to adsorb Hg. This is because Hg is a strong soft Lewis acid and S in a strong soft Lewis base (Ravichandran, 2004). Therefore adsorption capacity should be greater for Hg than that of Cd because Cd is only considered a relatively weak soft Lewis acid (Pearson, 1968). Further tests with other soft Lewis acids would be needed.

5.2.3 Water Soluble Carbon:

5.2.3.1 Hot Water Extractable Carbon:

Hot water extractable carbon (HWC) has been determined as a suitable soil quality indicator, due to being a component of the labile SOM pool, being closely related to soil microbial biomass and micro aggregation (Ghani et al. 2003). Ghani et al. (2003) reported that HWC was positively correlated with important soil quality parameters, such as: soil microbial biomass C, microbial nitrogen and mineralisable N. This suggests that soil amendments that have greater quantities of HWC are likely to positively influence soil quality in terms of soil fertility. The effect of land use on soil quality can also be described rather well by HWC being due to the positive relationships with soil C and N (Geraei et al. 2016; Xue et al. 2013). Ghani et al. (2003) found that untouched native soils have the highest HWC content with 4000 μg C/g^{-1}, whereas market garden soils were found to have the lowest concentration of HWC, with 850 μg C/g^{-1}. The results gathered here show that every amendment, except CFF, recorded a higher HWC concentration than that of the market garden soil found in Ghani et al. (2003). CBS recorded the highest concentration of 11265 μg C/g^{-1} (see Figure 4:4), indicating that an addition of this amendment to the corresponding market garden soil could raise the HWC concentration substantially. This would be at risk of Cd accumulation, due to the high Cd concentration within the amendment. Of note is that PH compost, which recorded the highest Kd, has the next highest HWC at 5219 μg C/g^{-1} (see Figure 4:4). The results suggest that all but three amendments would be suitable additions to a soil farmed under dairy pasture, as this would increase the HWC already present in the soil (3000 μg C/g^{-1}) (Ghani et al. 2003). Hot water extractable carbon is also a measure of how persistent the C is in the soil. Seremesic et al. (2013) reported soils with lower organic matter contents had low levels of HWC. Therefore, indicating that the persistent of organic matter in soil is dependent on the renewal of labile fractions. This suggests that regular additions of amendments with

high HWC will not only extend the ability to reduce plant uptake of Cd, but also will supplement organic matter levels.

5.3 Implications associated with amendments:

5.3.1 Cost:

The main issue with the additions of compost to the soil as an amendment for Cd is most likely to surround the cost. By using Al Mamum (2016) application rates for compost of 2.5% we can calculate the amount of amendment required per hectare and the corresponding price. Assuming the ploughing depth at 0.25m and the soil density at 1.3g/cm^3, we get 3250 tonnes of amendment. After incorporating the application rate into the equation, we can determine that we would need 81 tonnes per hectare of amendment. The tonnage retail cost of PH and LE composts from Parkhouse Garden Supplies and Living Earth Christchurch were $89 and $56, respectively. From this the cost of compost per hectare can be determined:

- Parkhouse Compost = $7,209/ha

- Living Earth Compost = $4,536/ha

The relative costs of the composts may influence the decisions made regarding what amendment to choose for Cd remediation. However, purchasing $1000 of PH compost equates to 11.2 tonnes, while purchasing $1000 of LE compost will provide the buyer with 6.7 tonnes more at 17.2 tonnes. Once we incorporate the relative sorption potential of these composts (Kd) into the equation, we see that for every $1000 spent on LE compost, the buyer will be benefitting from an effective total Kd of 10,346. However, if the same is said for PH compost, $1000 will provide the buyer with an effective total Kd of 126,750: 12 times more than that of the LE compost. This indicates that the Cd will most definitely be retained more effectively by the soil that has PH additions to it. The buyer can then decide on what is the best option for your soil. To obtain the same Kd as $1000 of PH compost, the buyer would need to spend $12,000, giving a total of 214 tonnes.

5.3.2 Feasibility:

Another issue that arises with the potential addition of soil amendments is whether there is going to be enough supply to meet demand. If any one of these amendments studied is found to reduce Cd uptake by plants significantly, it would be expected that the demand for that product would rise considerably, placing an increased pressure on producers of the product to meet these demands. This creates the potential issue of physically running out of the product. However, if a dramatic increase in demand for the compost products was to eventuate, one could assume that the manufacturers would upscale their production to meet this demand. The practice of manipulating soil chemical factors through addition of organic

amendments is seen to be rather expensive compared to other remediation methods such as the use of phytoaccumulator plants, although the time scales with Cd accumulation by these plants can be large (Felix, 1997). Organic matter additions to the soil are seen to be more effective on a small scale projects, and are not seen as feasible long term options for reducing Cd uptake (Martin & Bardos, 1996) (Pulford & Watson, 2002). The Tiered fertiliser management system for Cd described by Rys et al. (2011) states that soils with Cd concentrations of higher than 1.8 mg/kg are not allowed to receive anymore P fertiliser due to the risk of accumulation. Therefore, this could allow composts to be applied to these soils, reducing Cd accumulation and uptake, while adding the additional benefits of P, potentially turning the initial expense of the composts into profit over time.

Chapter 6

Conclusion:

The objective of this study was to determine which organic amendment has the greatest capacity to adsorb cadmium in soil and reduce plant uptake, while also providing other benefits to the soil in terms of nutrient additions.

From the resulting elemental analysis of the amendments, we have established that the biosolids (KBS and CBS) contained large concentrations of Cd. This may result in the potential of Cd accumulating in soils that these biosolids are applied to, although this will not be at levels that RPR will accumulate Cd. Nevertheless, this will then defeat the purpose of applying the amendments to the soil to reduce Cd uptake. Accumulation of Cd in soil has been seen to influence Cd bioavailability and subsequent plant uptake.

Results showed that Parkhouse (PH) compost had the greatest capacity to adsorb Cd, which was found to be significantly different from the other means. Such a capacity to adsorb Cd may be attributed to the binding potential of sulphur compounds within the compost, as PH contained an S concentration twice that of any other amendment, excluding biosolids. PH compost also contained the largest quantity of Phosphorus, which was the highest when again excluding the biosolids. This may play a small part in Cd adsorption, as it has been found that significant P applications to the soil have the potential to reduce plant uptake of Cd.

Living Earth (LE1) compost had the second highest capacity to adsorb Cd behind that of PH. This is a promising find due to the fact that LE compost is cheaper per tonne than PH compost. However, the resounding problem with LE compost was the Pb concentrations found within the compost. The application of this amendment to the soil will risk large quantities of Pb to accumulate over time, introducing another heavy metal contaminate sources into a soil that may already have high concentrations of Cd.

Overall, this study shows that PH compost has the greatest capacity to adsorb Cd from a solution. Therefore, this suggests that when applied to the soil in a practical situation we would expect to see a reduction in plant uptake of Cd. Also, in turn due to its high concentrations of macronutrients and high HWC content, I believe that this amendment will provide the needed nutrient benefits to the soil in question. Results also show the relative capacity of LE compost to adsorb Cd. Combined with the cheaper cost to incorporate into soil, this could be an option for soil remediation.   However, the source of the Pb in the LE composts may have to be determined so this can be eliminated from the compost recipe and ideally lower the risk of Pb accumulation in soils.

The limitation of this study was that we were not able to incorporate the organic amendments into soils and analyse the effect on Cd uptake by plants. It is therefore difficult to determine whether amendments with high Kd values would have reduced Cd uptake, and vice versa for low Kd values. This would be the next step in future research on this topic.

Appendix A

Elemental Composition (other elements):

Amendments:	Al	Cr	Fe	Mn	Na	Ni
Peat:	15888	17.9	14023	1012	158	10.694
Oligo Peat:	1364	1.2	<0.028	11	616	0.185
C BS:	15605	153.2	26756	385	795	31.388
K BS:	19008	41.9	18678	240	293	20.705
Parkhouse:	6666	10.2	6122	335	1222	4.585
Parkhouse W:	28189	33.7	27788	501	322	27.696
Parkhouse P:	12229	39.5	10798	312	733	5.613
Coffee:	4	0.0	<0.028	31	25	0.165
Oderings:	9840	23.9	9218	281	648	5.027
LE1:	10461	25.3	12784	310	910	7.474
LE2:	14232	44.1	14378	376	2236	9.093
LE3:	14632	39.5	14321	347	2338	9.601
LE4:	13873	43.4	15495	366	2275	9.236
LE5:	13522	45.2	13516	334	1870	8.292
LE6:	12566	34.5	16369	342	2269	10.194
LE7:	11955	33.7	13351	381	2332	8.961
LE8:	12452	32.6	13926	357	1834	11.491
LE9:	14419	52.1	14290	352	2226	9.049
LE10:	11846	26.5	13414	321	1095	7.491
LE11:	13573	35.4	14158	349	1828	8.422
LE12:	13235	40.2	15951	391	2177	9.178

Note: all resulted listed above are in mg/kg.

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