Lincoln University Digital Dissertation

Temporal variations in arsenic and copper and lead concentration in Christchurch municipal compost and their accumulation in Canterbury soils

---

A Dissertation

submitted in partial fulfilment

of the requirements for the Degree of

Bachelor of Agricultural Science (Hons)

at

Lincoln University

by

Arnoldus De Jager

Lincoln University

2017

Abstract of a Dissertation submitted in partial fulfilment of the requirements for the Degree of BAgSci. (Hons).

Temporal variations in arsenic, copper and lead concentrations in Christchurch municipal compost and their accumulation in Canterbury soils

by

Arnoldus De Jager

Arsenic (As) is a naturally occuring element in soils. It is a non essential trace metal that can have toxic effects in both plants and animal at relatively low concentrations. Anthropogenic sources of As have included its use in insecticides, herbicides and defoliants in the past while today its commonly used in agricultural production include mining and smelting of non-ferrous metals from runoff or mine tailing waste or smelter emissions. It is widely used as a feed additive for poultry and swine, and the resulting manures can contain elevated As concentrations. Minor sources of As are also derived from phosphate fertilisers, and fossil fuel combustion.

This study was completed to investigate the potential sources of the seasonal elevated concentrations of As in Christchurch municipal compost and to investigate potential issues arising from the application of the compost product to agricultural soils in terms of trace metal accumulation.

Results indicated a significant trend in As where concentrations were at a minimum during winter while also having significant positive correlations with both chromium (Cr) and copper (Cu). Additionally, As had a significant negative correlation with average Christchurch temperatures, which all suggested CCA treated timber could be a possible source of the variation due to the burning of the treated timber and subsequent addition of the ashes to the green waste bins.

An accumulation model was also formulated to attempt to quantify the accumulation of As, Cu, and lead (Pb) within agricultural soil to.

Keywords: Municipal solid waste, MSW, chromated copper arsenate, CCA, treated timber, Lead.

Acknowledgements

Table of Contents

List of Tables

List of Figures

Chapter 1

Introduction: Municipal compost

Waste management policy in New Zealand cities as well as in other countries around the world is increasingly looking to composting as a potential way of minimising the amounts of waste going into landfill. This is becoming a more serious problem with the exponentially expanding global population producing more and more waste every year.

Municipal compost is a potential long-term solution as it diverts some of the material from the landfill. This is achieved by separating out and subsequently composting the organic fraction of municipal solid waste (MSW), which can then be reused as a soil conditioner and fertiliser. The organic fraction commonly consists of household food waste as well as garden green waste and makes up about 65% of the total MSW (Kaldjian, 1988). Hence, the separation and composting of this waste is considered a relatively cost-effective way of reducing a substantial amount of waste going into landfills while also producing a saleable product thathas benefits for arable production in terms of nutrient supply and enhanced soil properties (Epstein, Chaney, Henry, & Logan, 1992; Eriksen, Coale, & Bollero, 1999; Wolkowski, 2003). The main issue with the use of municipal compost is the presence and potentially high concentrations of trace metals and other micronutrients which can accumulate within soils and potentially pose threats to agricultural productivity and human health.

Arsenic is a non-essential trace metal in both plants and animals. It has been used in the past as insecticides, herbicides and defoliants in agricultural production. This includes inorganic salts and various organic compounds of both arsenite (As[III]) and arsenate (As[V]) (Peterson, Benson, & Zieve, 1981). Arsenic is naturally found in some sedimentary rock and in geothermally active areas (Peterson et al., 1981). Anthropogenic sources of As include mining and smelting of non-ferrous metals from runoff or mine tailing waste or smelter emissions. It is also widely used as a feed additive for poultry and swine, and the resulting manures can contain elevated As concentrations. Minor sources of As are also derived from phosphate fertilisers, fossil fuel combustion (including land disposal of fly ash and from municipal sewage sludges (O'Neill, 1990; Peterson et al., 1981).

Chapter 2

Sources and management of trace metals in municipal compost:

2.1 Municipal compost background:

2.1.1 Potential benefits and issues:

Potential benefits as well as potential issues arising from the application of municipal compost is directly affected by overall compost quality. Compost quality in turn is highly dependent on sources of variation within the compost such as composting facility design, composting procedure, compost maturity and feedstock source and the proportions used (Hargreaves, Adl, & Warman, 2008).

Effects on soil physical properties:

Municipal compost is a good source of organic matter (OM) with a low bulk density. Surveys of municipal compost found on average 20% of total compost carbon (C) was organic C, 8% was carbonate C, and 71% was residual C. Additionally most of the humic substances in the compost was humic acid with a humic acid to fulvic acid ratio of 3.55. Humic acid is more stable than fulvic acid and has been associated with an improved soil buffering capacity (He, Logan, & Traina, 1995). The increased OM also resulted in an improved soil water holding capacity and overall soil structure (Hernando, Lobo, & Polo, 1989). Additionally when applying the compost consistently the soil C:N ratio also increases (Crecchio, Curci, Pizzigallo, Ricciuti, & Ruggiero, 2004; Garcıa-Gil, Ceppi, Velasco, Polo, & Senesi, 2004; Montemurro, Maiorana, Convertini, & Ferri, 2006; Perucci, 1990). The application of a compost with a good C:N ratio (25-30:1) could therefore result in a soil C:N ratio that is better suited to the needs of soil microbes which would result in less losses of N out of the system (less surplus N) and better overall productivity (McLaren & Cameron, 1996). Application rates of 30 and 60 t/ha of municipal compost increased aggregate stability of soil which also improved overall soil structure (Hernando et al., 1989). Additionally, the process of composting has benefits of killing all or most pathogens and reducing the prevalence of bad odours within the MSW feedstock while the final product also has benefits in reducing the rate of germination of weeds when applied to agricultural soils (Jakobsen, 1995).

Effects on soil microbiological properties:

Soil microbiological properties are most sensitive to changes in the soil environment (Pankhurst, Doube, & Gupta, 1997). Increases in soil biomass N, C, S and P have been observed immediately following the application of MSW compost and up to 1-5 months after application (Perucci, 1990). Soil basal respiration rate (used to monitor microbial activity) was also seen to increase in MSW

amended soils and would last up to eight years after application (Pascual, García, & Hernandez, 1999). Additionally, the application of MSW compost showed significant increases in enzyme activity within the soil (Perucci, 1990). Therefore, the amendment of soils with municipal compost can improve soil microbiology and enzymatic activity.

Effects on soil chemical properties:

Application of municipal compost has been observed to increase soil pH and which is considered an advantage (Mkhabela & Warman, 2005). The increase is usually proportional to application rate and is believed to be due to the mineralisation of carbon and resulting production of OH⁻ ions by ligand exchange as well as the introduction of basic cations from within the compost (Mkhabela & Warman, 2005). An alkaline pH is considered advantageous because micronutrients and metal cations are commonly more available for plant uptake under acidic conditions (Brady & Weil, 1996). Therefore, trace metal availability could potentially be managed by controlling compost pH.

A potential issue is the resulting increase in surrounding soil electrical conductivity (EC) following the application of municipal compost. Excess salts and sodium (Na) concentration in soil can have negative effects on soil structure and plant growth. Soil EC is commonly used as an indicator of soil salinity and salt content as it relates to the amount of dissolved solutes within the soil (Brady & Weil, 1996). The EC in municipal compost was found to be higher than that of agricultural soils in a US soil survey with EC levels of 3.69-7.49dS/m and 0-4 dS/m respectively (Brady & Weil, 1996). A study found that municipal compost applied at rates of 40-120 t/ha proportionately increased the soil EC (Iglesias-Jimenez & Alvarez, 1993; Walter, Martínez, & Cuevas, 2006). It is suspected that the EC content in municipal compost is mostly associated with feedstock used and the compost facility procedure (Hicklenton, Rodd, & Warman, 2001).

Although municipal compost applies a wide range of soil nutrients (N, P, K, S), it is believed to be a poor source of plant available nitrogen (N). Phosphorus (P) and potassium (K) were found to be supplied at equivalent rates to mineral fertiliser (deHaan, 1981; Eriksen et al., 1999; Iglesias-Jimenez & Alvarez, 1993), whereas only about 10-21% of total N in municipal compost is made plant available in the first year of application (deHaan, 1981; Eriksen et al., 1999; Iglesias-Jimenez & Alvarez, 1993). For this reason, some reports have claimed municipal compost to be a poor source of available N and less effective in the first year in supplying N when compared to mineral fertiliser and concluded they require application rates over 200 t/ha to effectively supply N to the soil plant system (Iglesias-Jimenez & Alvarez, 1993). This high application rate often leads to the main problem of over-supply of micronutrients and trace metals to agricultural soil. Additionally, it has been that at application rates over 200 t/ha some downward movement of phosphorus (P) was observed in the soil profile (M. Zhang, Heaney, Henriquez, Solberg, & Bittner, 2006).

Additionally, MSW may contain elevated concentrations of persistent organic toxins from materials within the feedstock such as pesticides, oils, solvents, and the ink on paper products (Epstein, 1996). The most prevalent organic toxins have been found to be phthalate esters such as dioxin/furans and polychlorinated biphenyls (PCB) which were found at higher concentrations in mechanically separated vs source separated MSW (Logan, Henry, Schnoor, Overcash, & McAvoy, 1999).

2.2 Common trace metals in municipal compost:

Compost source material is believed to be the main factor that determines which trace metals are present in the compost and at what concentrations (He, Traina, & Logan, 1992). MSW compost will commonly have As, cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn) present at detectable levels with the highest levels usually seen in Zn and Pb (Zennaro, Cristofori, Formigoni, Frignani, & Pavoni, 2005). However, these concentrations can vary largely, especially when factors such as feedstock, source separation vs mechanical sorting are considered, as well as any differences in composting procedure.

Trace metals occur ubiquitously in the environment as they originate from within the earth's crust and as such can occur in soils simply as a result of the weathering process. Additionally, there are other anthropogenic sources which have come about due to urbanisation and industrialisation though, namely agricultural sources, industrial sources, domestic effluent, and atmospheric sources.

2.2.1 Arsenic chemistry, bioavailability and phyto-availability:

Arsenic commonly occurs in soil as arsenite (As[III], mostly in flooded soils), arsenate (As[V], most common species in aerobic soils) as well as in methylated forms (much lower concentrations) such as mono-methyl arsonic acid (MMA) and di-methyl arsonic acid (DMA). High application rates of As to soils can lead to As phytotoxicity in crops (Steevens, Walsh, & Keeney, 1972). This is not as likely though because As has a very similar chemistry to P and plant uptake is achieved by the same pathway meaning P competitively inhibits As uptake (transporters have a higher affinity for P than As) (Meharg, Naylor, & Macnair, 1994). Both ions are also strongly sorbed onto clay and iron oxide/hydroxide surfaces in soil (Asher & Reay, 1979; Meharg et al., 1994; O'Neill, 1990; Ullrich-Eberius, Sanz, & Novacky, 1989). Thus, arsenate concentration in soil solution is commonly quite low. Unlike P, As translocation to the plant shoot is relatively low meaning the roots are the main area where any As phytotoxicity damage occurs meaning aerial plant parts are commonly relatively low in As (<2 mg/kg), and crop damage or failure is expected before it becomes a human health hazard (O'Neill, 1990; Peterson et al., 1981). In animals, arsenate and arsenite are toxic, however organic As compounds (such as arsenobetaine) are much less

toxic (Mertz & Underwood, 1986). This is believed to be because they are not metabolised and are rapidly excreted.

2.2.2 Copper chemisty, bioavailability and phyto-availability:

Copper is an essential nutrient in both plants and animals. It commonly occurs at 2-25 μg/g in plants with Cu deficiency observed at between 2-5 μg/g and toxicity at levels above 25-40 μg/g (Hemphill, 1972). Cu has a very low bioavailability, meaning toxicity in both ruminants and humans occur infrequently (Epstein et al., 1992). When municipal composts and even sewage sludges with normal concentrations of Cu have been applied to land, even at high application rates, no Cu phytotoxicity was observed. Only when Cu content exceeded 2000 mg/kg and was applied to highly acidic soils did some plants show Cu phytotoxicity (Marks, Williams, & Chumbley, 1980; Webber, Soon, Bates, & Haq, 1981) This is believed to be due to its ability to form complexes with organic compounds which reduce its bioavailability (Hernando et al., 1989). Furthermore, it is believed only a small fraction of total Cu is leachable (Tisdell & Breslin, 1995).

2.2.3 Lead chemistry, bioavailability, phyto-availability:

Lead is a non-essential nutrient for both plants and animals. However, phytotoxicity is only likely in highly contaminated soils; because Pb is strongly adsorbed by soils. Additionally, plants grown in fertile (high/adequate phosphorus content) soils don't tend to accumulate Pb as transport is inhibited by phosphorus (P) (Epstein et al., 1992). Therefore, it was found that the potential risk of Pb in municipal compost to animals and humans was more from direct ingestion of Pb from such things as Pb based paints than the accumulation within plants. Adsorption of different forms of Pb is complex but the bioavailability of Pb within soils, municipal compost and sewage sludges has low bioavailability within monogastric animals and ruminants unless present at very high concentrations (Chaney, Mielke, & Sterrett, 1989). Additionally, only a small amount of Pb within municipal compost is believed to be leachable (Tisdell & Breslin, 1995).

2.2.4 Other non-essential trace metals:

Cadmium is not essential for plant growth and animals and can lead to toxicity within animals. Phytotoxicity has mostly been observed in acidic soils but has been found to be non-toxic to plants under natural conditions (Gough, 1979). Zinc commonly occurs at 70-200 times higher concentrations in Cd enriched soils, therefore Zn would become phytotoxic long before Cd toxicity was seen (Epstein et al., 1992).

Mercury is a non-essential nutrient for both plants and animals, and toxicity is possible. However, Epstein et al. (1992) found no evidence of excessive accumulation of Hg in both food crops or the liver of livestock grazing municipal compost amended pastures.

2.2.5 Essential trace metals:

Nickel is essential for plants and animals; however, deficiency is seldom seen. Nickel phytotoxicity occurs in most plant species at levels of exceeding 25-50 µg/g in leaves. However, toxicity occurs at lower levels in plants than animals so can be managed. Epstein et al. (1992) found MSW composts were usually low in Ni unless co-composted with high Ni sewage sludges.

Zinc is essential for plants and animals. Many plants show signs of deficiency at levels below 15-20 µg/g, while toxicity is seen at over 400mg/kg. Marks et al. (1980) found phytotoxicity to only occurred at high concentrations of Zn in sewage sludges when applied to very acidic soils (pH<5.5). Zn tolerance and requirements within animals are much more complex as it is affected by several nutrients and elements. As with Ni, toxicity is seen in plants before harmful concentrations in animal tissues are reached (Epstein et al., 1992)

Chromium is a non-essential nutrient to plants but essential to animals. Chromium is found within the soils Cr^{3+} and Cr^{6+} where Cr^{6+} is believed to be more bioavailable soluble and thus more bioavailable than its counter-part. Chromium toxicity is believed to be around 5-100mg/g dependent on speciation and accumulation (Oliveira, 2012).

2.3 Sources of trace metals in municipal compost:

2.3.1 Plant residues:

The most common source (not necessarily the highest concentrations but the most widely occurring) of trace metals in municipal compost would be from the residues left behind in waste plant tissue such as leaf and root material after the plants have accumulated any background and elevated trace metal concentrations from the soil. Any removed and disposed plant material that may contain these trace metals would then be added to the municipal compost.

2.3.2 Industrial residues:

Industrial sources of trace metals in municipal compost could include mining, and refinement processes (mine spoil and tailings, transport of ore, smelting and metal finishing and recycling of metals). Mining is known to emit Al, As, Cd, Hg, Mn, Pb, U, and V depending on the type of mining (Nagajyoti, Lee, & Sreekanth, 2010). Coal mines are sources of As, Cd, Fe which can enrich the soils surrounding the mine directly or indirectly while soil contamination can also occur from the

erosion and water runoff of mine waste. High temperature processing of metals such as castings and smelting can release metals in vapor and particulate forms. This can lead to the potential release of As, Cd, Cu, Pb, Sn, and Zn which combine with water to form aerosols in the atmosphere. They are then either dispersed by wind (dry dispersion) or precipitated in rainfall (wet dispersion) causing contamination of water as well as soil (Nagajyoti et al., 2010). Other industrial sources could include the processing of plastics, textiles, microelectronics, and paper processing (Nagajyoti et al., 2010).

2.3.3 Animal residues:

Farmed animals such as poultry and pigs are often fed certain feeds with additives to aid in production. Some of these additives are high in certain trace metals and could therefore potentially find their way either into the meat or simply into the environment through the animal manure. Trace metals such as As, Cu, Cd, and Zn were found in animal manures. Arsenic was believed to come from compounds added to pig and poultry feeds to improve weight gain, feed efficiency and pigmentation in poultry. Copper was believed to be from the use of footbaths in the dairy industry and as growth promoters in both pigs and poultry. The Cd levels were not considered to be due to direct additions of Cd, but that it was present as an impurity in mineral supplements such as Zn sulphate and Zn oxide. The Zn levels were found to mainly be attributed to its use as a medicine for scouring in pigs, and for multiple uses in poultry (growth, feather and skeletal development, and reproduction) (F. Zhang, Li, Yang, & Li, 2012).

2.3.4 CCA treated timber waste:

The most common and widely used form of treated timber globally is CCA (chromated copper arsenate) treated timber. In New Zealand and in general all around the world CCA treated timber is manufactured to meet a specific ratio of [Cr]:[Cu]:[As]. This is usually referred to as type C or type 1 and is also defined in NZS3640:2003 as seen in the Table 2.1 below, while the different hazard class woods also require certain retention levels of trace metals in them (table 2.2) (T. Smith, Personal communication, May 16, 2017).

The CCA mixture is applied to oven dried timber according to the class of timber which is dependent on its end use as seen in Table 2.3.

Table 2.1 specification for the ratio as percentages of total treatment solution as set out by NZS3640:2003.

Copper (%)	Chromium (%)	Arsenic (%)
23 - 25	38 - 45	30 - 37

(Standards_New_Zealand, 2003)

Table 2.2 Minimum concentration of CCA mixture in different classes of timber

H3.2	H4	H5	H6*
0.37%	0.72%	0.95%	0.4%

Expressed as percentages on wt/wt.
* Concentration based solely on Cu content
H3.2, H4, and H5 based on sum of all element contents together.
(Standards_New_Zealand, 2003)

Table 2.3 Common timber use by hazard class rating

Timber hazard class rating	Description
H1	The treatment level for low hazard situations where timber is not exposed to the weather. Its major use is for framing timber and interior linings. This is split into two categories.
H1.1	Timber used in situations protected from the weather, dry in service and where resistance to borer only is required.
H1.2	Timber used in situations protected from the weather but where there is a risk of moisture exposure conducive to decay.
H2	This level is similar to H1 but includes an insecticidal treatment to protect against termite attack for use in Australia.
H3	For moderate decay situations where timber is exposed to the weather but is not in contact with the ground. This is also split into two categories.
H3.1	Timber used outdoors above ground, exposed to the weather – generally in non-structural applications; i.e. fascia boards, weatherboards.
H3.2	Timber used outdoors above ground, exposed to weather or protected from the weather but with a risk of water entrapment; i.e. decking, fencing and pergolas.
H4	Used in high decay areas such as ground contact or fresh water. Generally used for fence posts and landscaping timbers.
H5	Used for severe decay hazard risks such as ground contact where conditions of severe or continuous wetting may occur. End uses for this hazard class are house piles and poles, retaining walls, crib walling and horticultural supports.
H6	This hazard class is for marine use. Wharf piles and fenders, marine and jetty components regularly immersed in seawater or estuarine ground.

(NZTPC, 2004)

CCA treated timber could potentially be a significant source of As, Cr and Cu in municipal compost. This could occur by dumping and composting of intact waste wood or as ash following burning of the treated timber. CCA treated timber has historically been believed to be the main source of As in municipal compost (Epstein et al., 1992). The trace metals could potentially leach out of the waste wood over time and enter the compost as leachate or as ash when residential home owners burn

treated wood for heating and discard the ashes with their garden waste. In New Zealand timber is only treated at hazard rating H3.2 and above therefore if the assumption is made that most residents would have H3.2 and H4 timber in higher supply than other grades of treated timber (H5 and H6 more specialised end uses – Table 2.3). This would mean the likely concentration of CCA present before burning would be between 0.37 and 0.72% m/m which translates to about 2.4 kg CCA oxides/m^3 and 4.7 kg CCA oxides/m^3 respectively. Therefore, 30-37% which can be averaged to 34% and would result in between 0.82 kg and 1.60 kg of As retained in the timber.

A study observing the combustion of CCA treated timber found that at high and low burning temperatures a substantial amount of As was volatilised and in general unstable within the resultant ash but when burnt between 500 and 600°C between about 65 and 88% of total As was accounted for within the ash respectively. If its assumed most household fireplaces burn at about 550°C then about 75% of total feed As would be found within the ash (Rogers, Stewart, Petrie, & Haynes, 2007). Therefore, for every m^3 of timber burnt, between 0.62 kg and 1.20 kg of As could be expected to be found within the ash. Rogers et al. (2007) also found the concentrations of Cu and Cr to be relatively stable within the ash with no volatilisation observed in Cu, and very little volatilisation observed in Cr. If the 23-24% for Cu was averaged to 24% and the 38-45% for Cr to 42% then the same sample would have between 0.58 to 1.13 kg Cu, and between 1.01 and 1.97 kg Cr. Compost quality is dependent on length of maturation and composting procedure. Many studies have found reduced chemical extractability and water solubility when composting trace metals. Studies have found that metal availability decreased with the period of composting and compost maturation time (Leita & De Nobili, 1991). Additionally, immature MSW compost tended to have a lower pH prior to the thermophilic stage, which in some cases resulted in some metals having higher water-extractable concentrations (Brady & Weil, 1996). Therefore, composts that have matured are believed to have lower leaching potentials of trace metals than immature counterparts and even raw un-composted MSW (Leita & De Nobili, 1991). It is believed that the decrease in metal availability with increasing compost maturity can be explained by the formation of stable metal-humus complexes during the composting process (Garcia, Moreno, Hernandez, Costa, & Polo, 1995).

2.4   Management / mitigation of elevated trace metal concentrations:

2.4.1 Compost maturity:

Compost quality is dependent on degree of maturation and composting procedure. Studies have found reduced chemical extractability and water solubility of trace metals within MSW that have been composted. The studies also found that metal availability decreased with increasing period of composting and compost maturation time (Leita & De Nobili, 1991). Additionally, immature MSW compost tended to have a lower pH prior to the thermophilic stage, which in some cases resulted in

some metals having higher water-extractable concentrations (Brady & Weil, 1996). Therefore, composts that have matured are believed to have lower leaching potentials of trace metals than immature counterparts and even raw un-composted MSW (Leita & De Nobili, 1991). It is believed that the decrease in metal availability with increasing compost maturity can be explained by the formation of stable metal-humus complexes during the composting process (Garcia et al., 1995).

2.4.2 Source separation:

Source separation is a method of waste collection where the organic component is separated from the other non-organic components at the source before collection and processing. In terms of MSW there are a lot of possible sources of heavy metals within the home, such as household dust, batteries, disposable household materials (such as bottle tops), within plastics, paints and inks, body-care products, medicines and household pesticides (Bardos, 2004). As a result, when these materials are separated from the compostable organic component at the source, there is less chance of contamination of heavy metals later in the composting process, and composts produced from this source separated waste is generally reported to contain smaller amounts of heavy metals compared to mechanically-sorted products (on average reduced by a factor of 2-10) (Amlinger, Pollak, & Favoino, 2004; Epstein et al., 1992; Sharma, Canditelli, Fortuna, & Cornacchia, 1997). This is the method already in place in New Zealand where household waste is separated into organic garden waste, recyclable waste and waste to landfill. As a result, source separation of compostable material is widely accepted as the most effective approach to minimise metal concentrations in MSW compost (Amlinger et al., 2004; Bardos, 2004; Richard & Woodbury, 1992).

2.4.3 Dilution of metal concentration with a bulking agent:

Co-composting of MSW with bulking agents such as sawdust has been researched to observe their effects on compost quality. It is believed that the application of sawdust (provided it has a lower concentration of heavy metals than in the MSW) could have a dilution effect on the overall heavy metal concentration within the final product. Yousefi, Younesi, and Ghasempoury (2013) completed a study with MSW co-composted with sawdust at 0, 16, 32 and 70% sawdust (per dry weight) and found significant decreases in heavy metal concentrations in all heavy metals observed after seven weeks of composting (Table 2.4). Additionally, they found increasing the percentage of sawdust increased the C/N ratio, but decreased the EC value (therefore lower salinity with higher sawdust application) and the pH (although they were still within optimum pH ranges) (Figure 2.1).

Increasing the percentage of sawdust in the mixtures would increase the initial starting C/N ratios and essentially the final C/N ratios once composting was completed (seen in results). Microbes only digest C and N at certain ratios and any extra material will usually not be digested (McLaren &

Cameron, 1996). Therefore, higher than ideal C:N ratios as seen in the treatments with higher %
sawdust would lead to slower C breakdown. The C:N ratio of 25-30 is believed to be ideal for
composts (Tchobanoglous & Kreith, 2002). Therefore, a sawdust application % would need to be
applied that resulted in an initial and final C:N ratio 'range' (C:N ratio decreased during composting)
that was in the ideal region of 25-30 to reach optimum microbial breakdown.

Table 2.4 Heavy metal concentrations of MSW co-composted with sawdust at different % (0, 16, 32, 70) of applied sawdust

	Metal concentrations mg/kg				
	Sawdust	MSW0	MSW16	MSW32	MSW70
Fe	0.01 ± 0.00	0.78 ± 0.01^a	0.523 ± 0.1^{abc}	0.35 ± 0.02^b	0.164 ± 0.02^c
Cu	1.4 ± 0.26	53.71 ± 7.82^a	40.46 ± 5.13^b	41.5 ± 7^b	17.6 ± 1.08^c
Zn	19.66 ± 2.1	138.74 ± 20.16^a	106.175 ± 8.28^b	110.44 ± 4.02^b	71.54 ± 8.84^c
Mn	23.46 ± 1.65	173.98 ± 1.38^a	143.075 ± 13.47^b	132.23 ± 6.93^b	96.575 ± 8.6^c
Ni	0.6 ± 0.13	37.41 ± 10.07^a	26.91 ± 3.22^{ab}	23.74 ± 6.10^{bc}	11.92 ± 3.18^c
Cr	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	n.d.	31.33 ± 6.28^a	27.83 ± 3.37^a	24.41 ± 3.54^a	11.33 ± 1.42^b
Cd	n.d.	n.d.	n.d.	n.d.	n.d.
Hg	0.037 ± 0.00	0.34 ± 0.03^a	0.25 ± 0.016^b	0.23 ± 0.04^{bc}	0.19 ± 0.01^c

Values are mean ± standard deviation (n=3). Means in each column with different superscript letters are significantly different (p<0.05). (Yousefi et al., 2013).
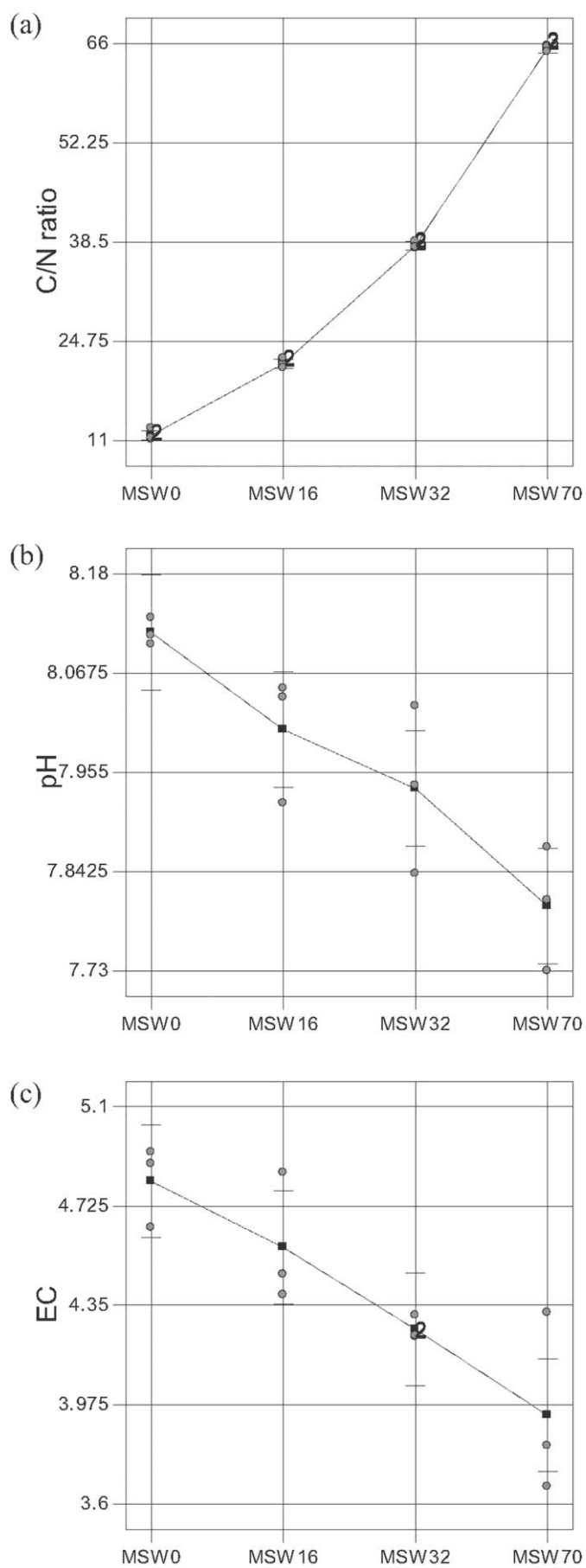
Figure 2.1 The effect of sawdust application % (0,16, 32, 70) to MSW on (a) C/N ratio, (b) pH, and (c) EC after 7 weeks of co-composting process (Yousefi et al., 2013).

2.5 Aims:

The study was completed at Lincoln university with data used that was collected at Living Earth Ltd. in Christchurch, New Zealand. They have been recording consistent seasonal spikes in Arsenic (As) concentrations over winter in their commercially available kerbside organics (KSO) compost. The hypothesis is that the elevated As concentrations were due to the burning of chromated copper arsenate (CCA) treated timber as a residential heating fuel over the winter months and the subsequent addition of the ashes to the residential green waste bins which are emptied by Living Earth Ltd.

The aims of this honours research were to ascertain whether any patterns could be found that would disprove the initial hypothesis and to investigate potential issues arising from the application of the compost product to agricultural soils in terms of trace metal accumulation and subsequent human health, environmental or productivity issues.

Chapter 3

Materials & Methods:

3.1 Background information:

Living Earth Christchurch produce two main green waste composts for use by businesses, industry and the public. Their KSO compost is produced from a variety of materials and used predominantly in the agricultural sector, while Canterbury compost is more controlled feedstock material and therefore available for sale to the public. This study focussed specifically on the inputs and trace metal concentrations of the KSO compost.

KSO compost is made up of a variety of waste materials. This includes waste from the residential kerbside collected bins, yard waste from the eco-drop (figure 3.3b), food waste from commercial businesses such as restaurants (Figure 3.1d), source separated wood waste from Fulton Hogan Ltd. and Maugers Contracting Ltd., river weed collected from the Avon and Heathcote rivers (Figure 3.3c) and woodchip from various arborist companies (Figure 3.1a). The ratios of material used within the compost stayed relatively constant with minor differences occurring in the early spring where they commonly receive a larger amount of green grass clippings in the kerb-side bin collection and as a result they add more tailings to bulk up the compost and decrease the bulk density allowing for better airflow through and rate of degradation of the compost.

The waste material is combined with a loading tractor (Figure 3.2a) and processed through a shredder (Figure 3.2b) before being loaded and sealed within enclosed concrete bunkers for further composting (figure 3.2c,d). During the composting process the waste material can reach temperatures as high as 80°C. The developing compost is left within these tunnels to degrade for 14 days (slightly shorter periods during later spring/early summer) before being taken out and arranged outside in small windrows on the asphalt (commonly about the amount of material coming from two tunnels) to aid in final maturation before being combined into larger three-meter high windrows (two smaller windrows brought together). The compost is finally put through sorter one final time to separate the coarse material (Figure 3.3a) (tailings - incorporated back into the system to further compost and degrade) from the finer composted material (Figure 3.3d). The windrows are turned all through the process to aid in air flow.

Figure 3.1 waste material ready to be incorporated into compost, a) sawdust; b) partly sorted material that has been brought back in for further composting (tailings); c) unsorted greenwaste d) food waste.

(a)

(b)

(c)

(d)

Figure 3.2 a) Loading of material into shredder; b) Shredder mixes and mechanically breaks down the coarser material; c) the composting tunnels; d) the loading tractor loading waste material into the tunnels

(a)

(b)

<center>(c)   (d)</center>

Figure 3.3 Final stage of maturing outside on the asphalt, a) tailings that have been separated from mature compost; b) green material with grass clippings from ecodrop; c) riverweed; d) final mature composts ready for use.

3.2   Trace metal sample collection:

Trace metal Samples were collected by Living Earth staff from the windrows at Living Earth, Christchurch, New Zealand (43°32'17.384"S 172°42'30.225"E). Sampling was completed as part of standard operating procedure for compliance of KSO compost with the threshold standards set by AsureQuality and NZ standard NZS4454 (Table 4.2). Samples were collected weekly from windrows a week after leaving the concrete tunnels and being combined. 10 100ml grab samples per tunnel (i.e. if sampling from three windrows / 3 tunnels, a total of 30 grab samples would be taken) were taken and combined, mixed and hand-screened through a 20mm sieve. 700mls of the subsamples were sent away for analysis while the rest stored in sealed bags for any later retesting.

This resulted in 52 to 53 subsamples per year (corresponding to the number of weeks in a year) sent for analysis. Sampling continued from the start of 2010 to the current date, however only data from 2013 to 2016 was used in this study.

3.3   Christchurch climate data:

Average temperature data was collected from the Christchurch Aero station (station No: 4843, 43°29'34.8"S 172°32'13.2"E) with data retrieved from the National climate database (NIWA, n.d.) for the time between the start of 2013 and the end of 2016 to supplement the trace metal concentration data.

3.4   Sample analysis:

The samples were analysed by Hill Laboratories in Hamilton. They are a New Zealand accredited laboratory by IANZ (International accreditation New Zealand) and meet requirements set by NZS/ISO/IEC 17025:2005 (Standards_New_Zealand, 2005b).

Samples were dried and the <2mm fractions analysed with Nitric/Hydrochloric acid digestion and Inductively coupled plasma mass spectrometry (ICP-MS) to quantify the concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn. Phosphate buffer extraction followed by colorimetry was used to quantify the concentration of the Cr^{6+}. The weekly Trace metal concentrations are not included in the results, however averaged trace metal concentrations with additional measures of central tendency are shown in Table 4.1 including values from the previously mentioned New Zealand compost trace metal thresholds in Table 4.2.

3.5 Statistical analysis:

3.5.1 Data normality:

The raw data (temperature data and trace metal concentrations) were analysed for normality and transformed accordingly to ensure the data was normally distributed. This resulted in all the concentrations for Cr, Cr^{6+}, Cu, Hg, Pb, and Ni being log transformed.

3.5.2 Pearson linear correlations:

The dataset was split into the four observed years and Pearson linear correlations completed for all trace metals and average temperature for the whole dataset (Table 4.3) and each separate year where necessary. These analyses were completed on Microsoft Excel 2016 using the analysis tool pack add in software. The level of significance was 0.05 and relevant r values at the yearly and overall levels are shown in Table 4.4.

3.5.3 Weeks to season conversion and assumptions:

Assumptions were made regarding what weeks within each year the seasons fit into. Each season was averaged to about 11-week lengths with a week period in between each season to account for the differences between seasons. The seasons were set to follow closely what is considered the change of season in New Zealand with the seasons starting on the first days of the respective months. The start of March – end of May is considered autumn, start of June – end of August is considered winter, start of September – end of November is considered Spring and the start of December to the end of February the following year is considered summer. This translated to a start of Autumn set from week 10 to week 21, winter from week 23 to week 34, spring from week 36 to week 47, and summer from week 49 to week 8 the following year.

3.5.4 ANOVA

ANOVAS were completed for each trace metal to ascertain how much of the variation in concentration was due to differences in season. The season sorted data was averaged for each year giving 16 values (4 values for each season). One-way ANOVAs were completed treating years as

blocking and the seasons as treatment factors, and results for summer and winter are shown in Figure 4.3. These Analyses were completed using GenStat *for Windows* 18th edition (V S N Interna tiona l, H em el Hem ps tead, U K . Web pa ge : G en S tat.co.uk).

3.6   Trace metal accumulation model:

3.6.1   Model Assumptions and values used:

Certain assumptions needed to be made to model trace metal accumulation in soil. It was assumed that the compost was incorporated into the top 10 cm of soil at time of sowing crops. It was also assumed that following application of the compost the trace metals accumulated only in the top 10 cm and that any losses out of the soil system such as from leaching, volatilisation and other losses were negligible. The range of ~1.13 – 1.4 t/m^3 was used for the soil bulk density in the calculations as this covers what the bulk density is within the top 10 cm of common Canterbury soil types (Table 5.3).

Background trace metal concentrations from Christchurch soils were used as starting points for the accumulation (Table 5.2) and application rates of 25, 50, and 100 t/ha (fresh weight – in dry weight terms this translates to 13, 26 and 51 t/ha respectively) were used to simulate normal application rates by farmers (Horrocks, Curtin, Tregurtha, & Meenken, 2016). In terms of application frequency, it was assumed application was completed pre sowing in either Autumn or Spring (results included for both scenarios) every three years as was practised in a study by Horrocks, Tregurtha, and Meenken (2015).

Table 3.1 The background concentrations of selected trace metals in Christchurch urban and rural gardens

Land use	Background trace metal concentrations (mg/kg)		
	As	Cu	Pb
Rural	0.9-36.9	2.1-27.3	3.63-44.4

(Ashrafzadeh et al., 2017) as reported by Environment Canterbury in 2007

Table 3.2 Bulk density of common Canterbury soils

Soil type	bulk density (t/m^3)	Source
Templeton silt loam	~1.3 – 1.4	(Harrison, Cameron, & McLaren, 1994)
Shallow stony Lismore silt loam	~1.06 – 1.2	(Francis & Knight, 1993)
Timaru silt loam	~1.13 – 1.38	(Houlbrooke, Paton, Littlejohn, & Morton, 2011)
Wakanui silt loam	~1.17 – 1.31	(Francis & Knight, 1993)

3.6.2 Accumulation calculation:

The accumulation model includes factors such as the background trace metal concentration in soil, trace metal concentration in the compost, the application rate of compost, the soil bulk density (Table 3.2), and the volume of soil in the top 10 cm in a Ha area.

Firstly, the volume of soil in a hectare (10'000 sqm) are had to be worked out as seen below:

100 m *100 m * 0.10 m = 1000m^3 (volume of soil per ha, v)

The equation to work out the accumulation in soil after one application of compost can be described by equation 1:

$$c_{soil} + [(c_{compost} * rate) / (\rho * v)] \quad\quad\quad\quad\quad\quad (Equation1)$$

Where $c_{baseline}$ is the background concentration of the trace metal in the soil before application of the trace metal, $c_{compost}$ is the concentration of the trace metal in the compost, ρ is the bulk density of the soil, rate is the application rate of the compost, and v is the volume of soil.

The accumulation was simmulated for the first three applications under different environmental conditions (soil density, background concentration, trace metal concentration) and then it was calculated how many applications would lead to the respective trace metal reaching their compost threshold level (as shown in Table 4.2).

Chapter 4

Results:

4.1 Trace metal concentrations:

Table 4.1 shows the average As concentration as well as the upper quartile value was above the 20mg/kg thresholds set by both AsureQuality and standard NZS4454. On further inspection of the dataset, it was found that 40.2% of the time during the four-year period between the years 2013 and 2016 the As concentrations were above the 20 mg/kg thresholds (Figure 4.1). Average Cu concentrations weren't higher than their thresholds (Table 4.2), however they did increase past the AsureQuality threshold 17% of the period of sampling. All other trace metals had average concentrations below their respective thresholds and only increased in concentration above their thresholds between 0 - 4.6% of the time (Table 4.1).

Table 4.1 Average trace metal concentrations in KSO compost for the years 2013, 2014, 2015, and 2016 including standard deviation (SD), lower Quartile (25th%) and upper quartile (75th%).

	Mean/geomean (mg/kg)	S.D.	L.Q.	U.Q.
Arsenic	20.10	6.57	15	25
Cadmium	0.50	0.13	0.4	0.6
Chromium*	27.56	20.68 – 36.73	23	31
Chromium 6*	0.45	0.35 – 0.57	0.4	0.4
Copper*	51.38	38.23 – 69.05	44	57
Mercury*	0.09	0.06 – 0.13	0.07	0.1
Lead*	113.81	90.58 – 143	98.25	130
Nickel*	9.80	6.91 – 13.89	7.8	12
Zinc	250.73	64.73	230	260

* geometric mean

Table 4.2 Relevant trace metal concentration thresholds for organically certified compost in New Zealand

	Standards for limits in compost (mg/kg)	
	AsureQuality[1]	NZS4454[2]
Arsenic	20	20
Cadmium	0.7	3
Chromium	70	600
Chromium 6	1	no limit
Copper	60	300
Mercury	0.4	2
Lead	200	250
Nickel	25	60
Zinc	300	600

[1](AsureQuality, 2016) [2](Standards_New_Zealand, 2005a)
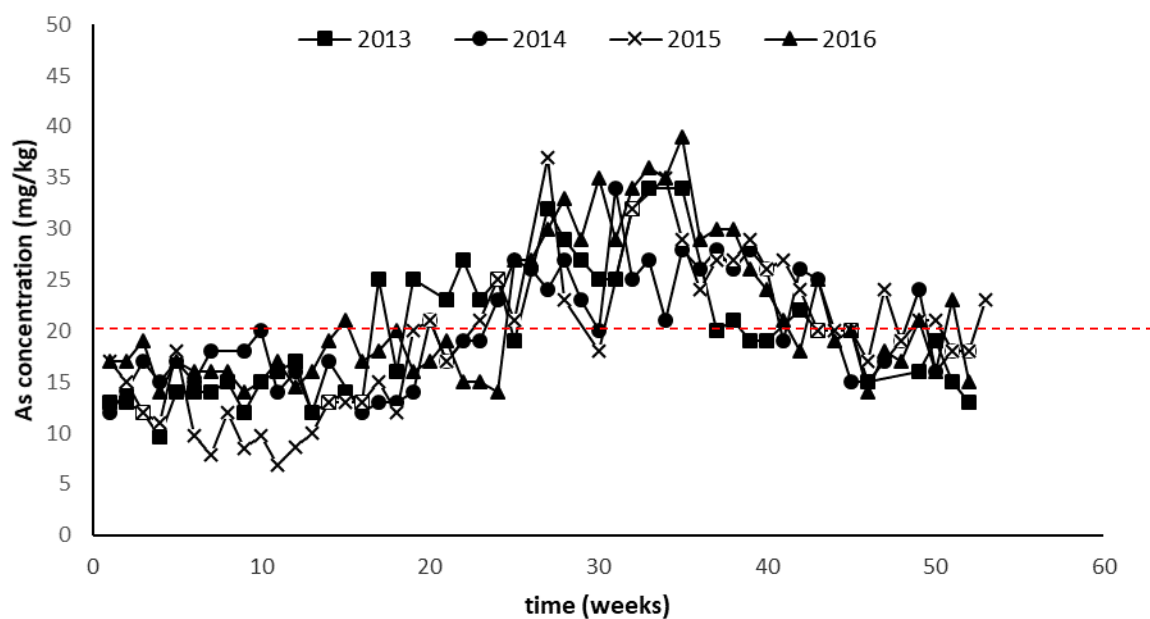
Figure 4.1 Arsenic concentrations within KSO compost in the years 2013, 2014, 2015, and 2016, against the 20 mg/kg threshold (as set by AsureQuality and NZS4454 - red dashed line)

4.2 Correlations:

Table 4.3 Summary of correlations between trace metal concentrations within KSO compost for the years 2013, 2014, 2015 and 2016. Expressed as r.

	temp	Arsenic	Cadmium	Chromium	Chromium 6	Copper	Mercury	Lead	Nickel	Zinc
temp	1.000									
Arsenic	-0.662	1.000								
Cadmium	-0.185	0.042	1.000							
Chromium*	-0.180	0.234	0.339	1.000						
Chromium 6*	0.258	-0.237	-0.088	-0.075	1.000					
Copper*	-0.261	0.292	0.138	0.122	-0.021	1.000				
Mercury*	0.176	0.007	-0.545	-0.353	0.020	-0.113	1.000			
Lead*	-0.315	0.476	0.110	0.215	-0.055	0.120	-0.125	1.000		
Nickel*	0.033	-0.023	0.293	0.754	0.050	0.062	-0.327	0.061	1.000	
Zinc	-0.039	0.102	0.110	0.296	0.047	0.137	-0.073	0.176	0.264	1.000

* trace metals that were log transformed for normality, highlighted boxes are significant correlations (see Table 4.4) with relevance to variation in As concentration.

Table 4.4, Critical r values for significance of Pearson correlations of KSO compost trace metal concentrations when degrees of freedom (d.f.) is at 51 (n = 53) for per year correlations, (refer to Appendix a for correlation tables), and 192 (n = 194) for total data set (Table 4.3)

(d.f.)	Probability (P)		
	<0.05	<0.01	<0.001
51	0.271	0.351	0.440
192	0.141	0.185	0.235

4.2.1 Arsenic:

In terms of the overall dataset, As concentrations had a strong negative correlation with average temperature (r = -0.66, d.f.=192, P<0.001) (Figure 4.2, Table 4.3). When this was observed at the per year level (Appendix A) from 2013 to 2016 for confirmation, the r value averaged at r=-0.66 and never went below r=0.592 (2014). This still resulted in a highly significant correlation (d.f.=51, p<0.001) (Figure 4.4).

Arsenic Also correlated highly significantly with the log of trivalent (Figure 4.3) and hexavalent Cr (r=0.23, d.f.=192, p<0.01; r=-0.24, d.f.=192, p<0.001), however the correlation was positive with trivalent Cr and negative with hexavalent Cr. On further inspection, when comparing trivalent Cr at yearly basis an average of r=0.290 was obtained (p<0.05, d.f.=51), however the correlation for 2014 was negative (r=-0.058). At the yearly basis hexavalent Cr was only significant in 2014 (r=-0.343, p<0.05) and 2016 (r=-0.272, p<0.05).

Arsenic had a highly significant correlation with the log of Cu (r=0.29, d.f.=192, p<0.001) (Figure 4.4). When compared at the per year level, it resulted in an average of r=0.348 (d.f.=51, p<0.05) with the lowest r value being 0.165.

Arsenic also had a significant correlation with the log of Pb (r=0.48, d.f.=192, p<0.001) (Figure 4.5). when this was observed at the yearly level, an average r value of r=0.477 (d.f.=0.51, p<0.001) and never went below r=0.351 (p<0.01).
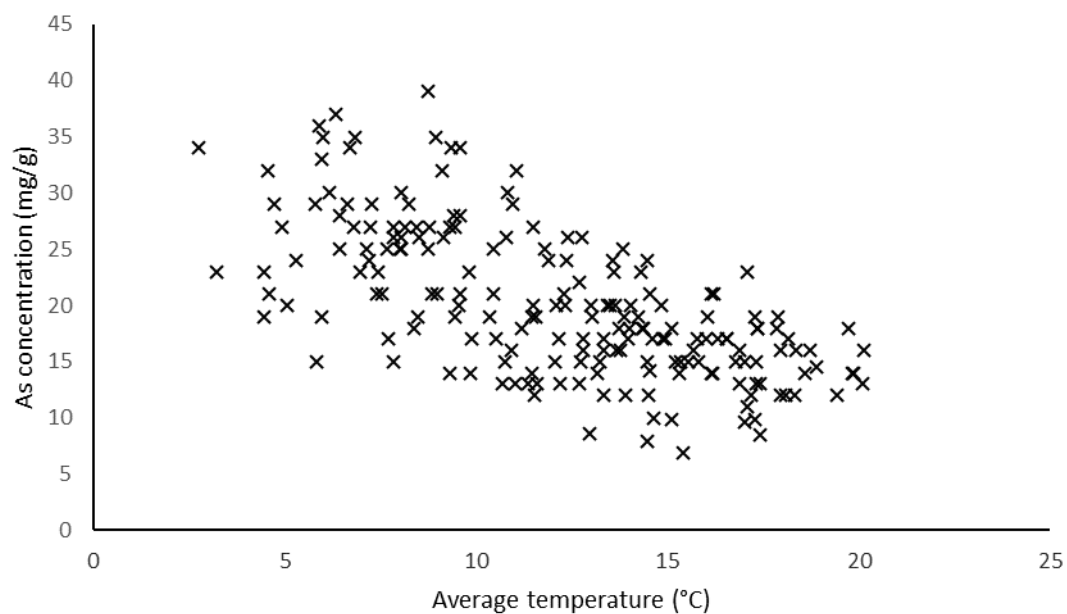
Figure 4.2 Correlation plot between average temperature and As concentrations in KSO compost between 2013 and 2016
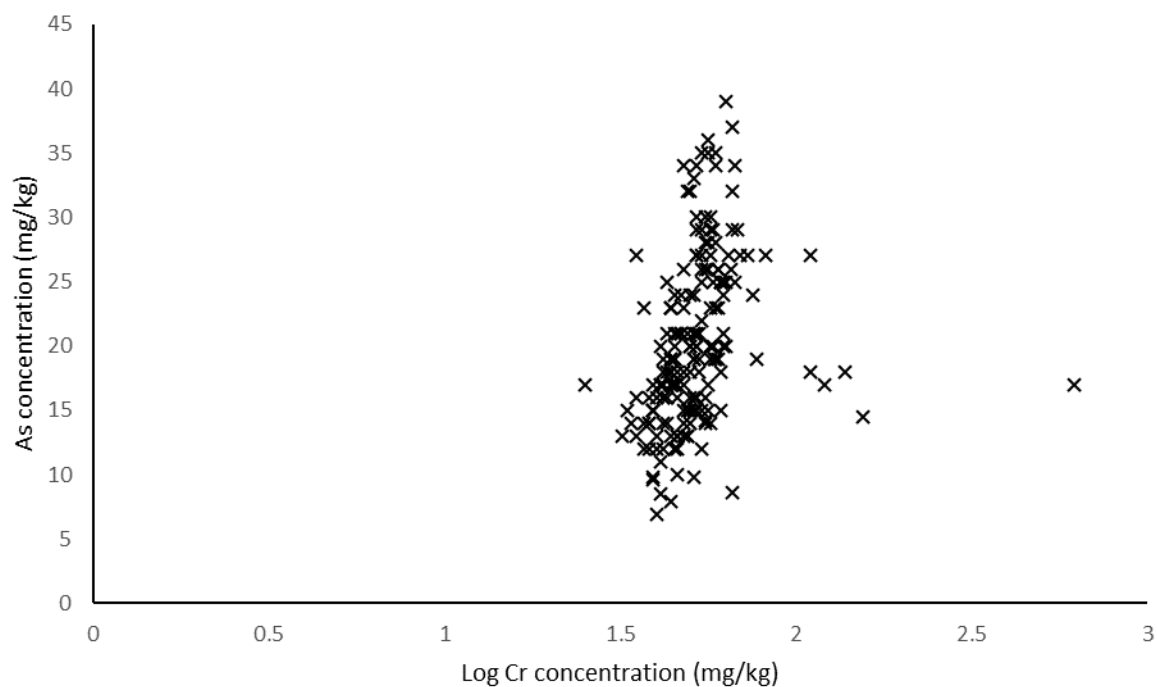
Figure 4.3 Correlation between As concentration and Log Cr (trivalent) concentration in KSO compost for all years between 2013 and 2016
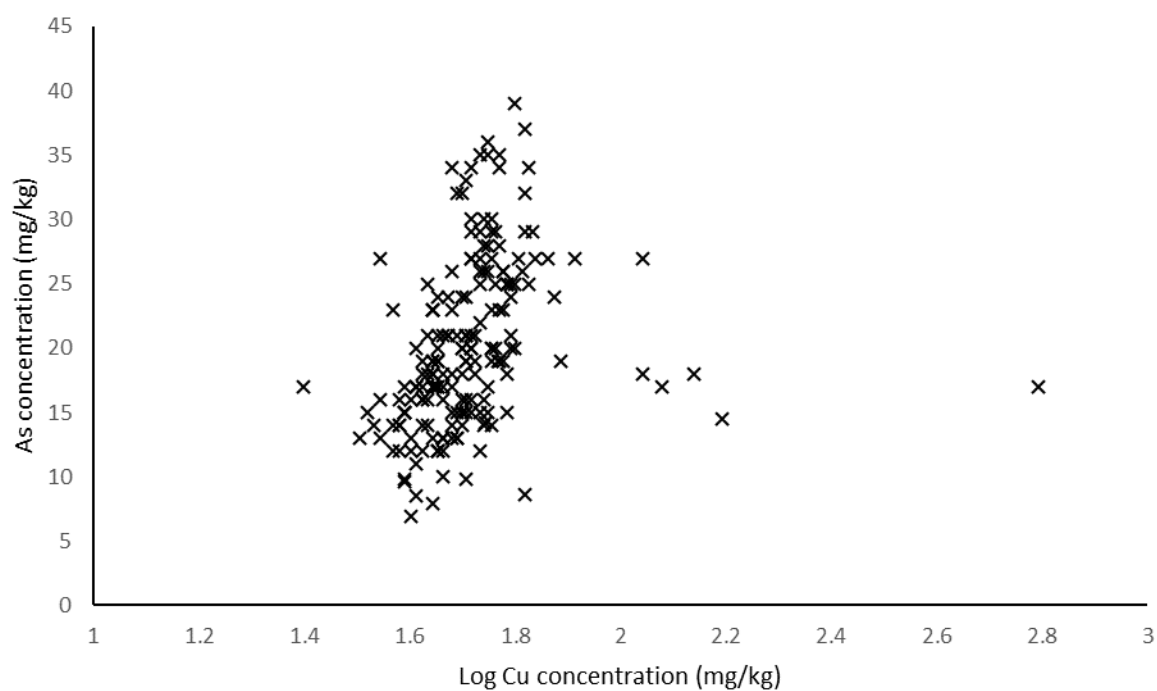
Figure 4.4 Correlation between As concentration and Log Cu concentration in KSO compost for all years between 2013 and 201
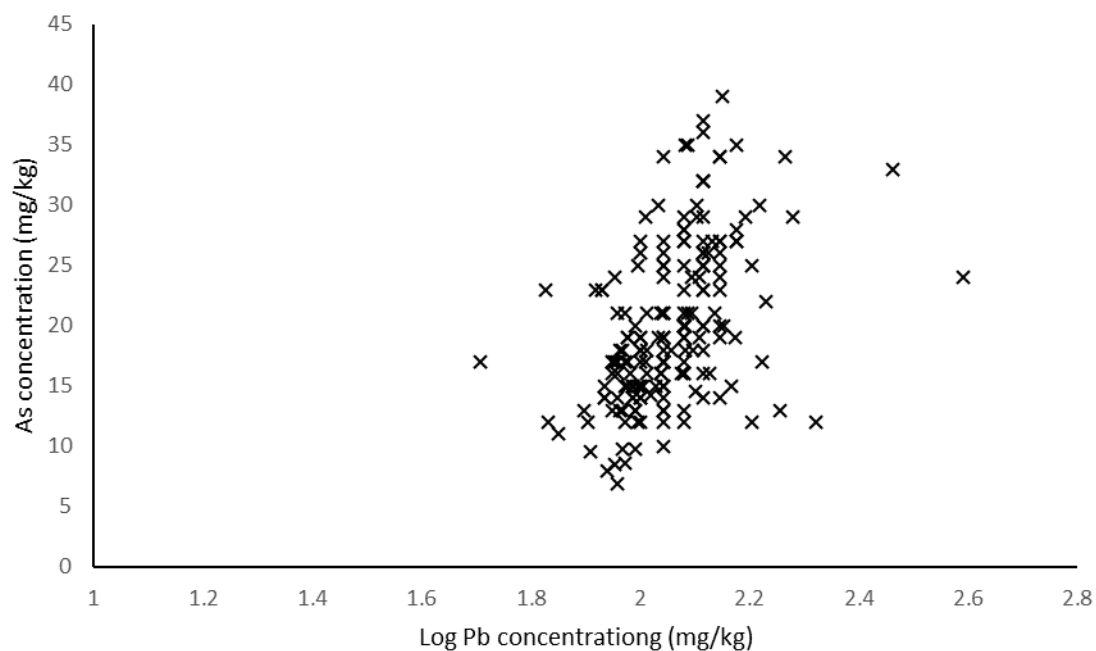
Figure 4.5 Correlation between As concentration and Log Pb concentration in KSO compost for all years between 2013 and 2016

4.3 ANOVA: Seasonality of As concentrations

The ANOVA completed for As showed the differences in concentration between summer and winter seasons were significant (F = 37.32, p<0.001) (Figure 4.3). The As concentrations increased from 2013 to 2016 when comparing within season variation (Figure 4.2), however the differences weren't significant except for the winter peak concentrations in 2014 which were significantly lower than the winter peak concentrations in 2016 and the summer minimum concentrations in both 2013 and 2014 which were significantly lower than the concentrations obtained in the summer of 2015. Additionally, Figure 4.1, 4.6 and 4.7 showed the repetitive nature of the As concentration over the trial period. The ANOVAs completed for the other trace metals yielded no significant results therefore were omitted from the report.
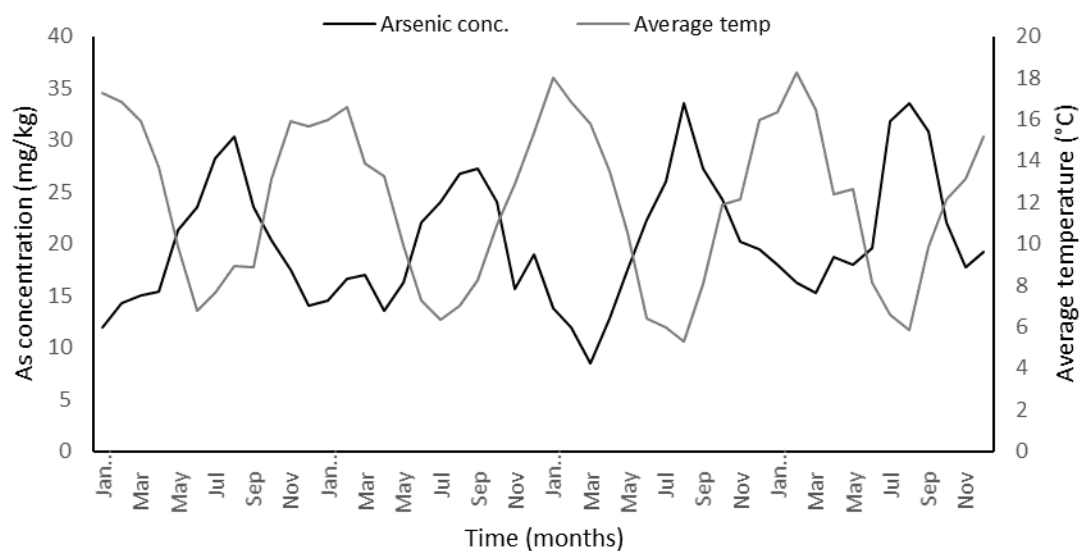
Figure 4.6 Arsenic concentration within KSO compost against average temperature for the years 2013, 2014, 2015, and 2016.
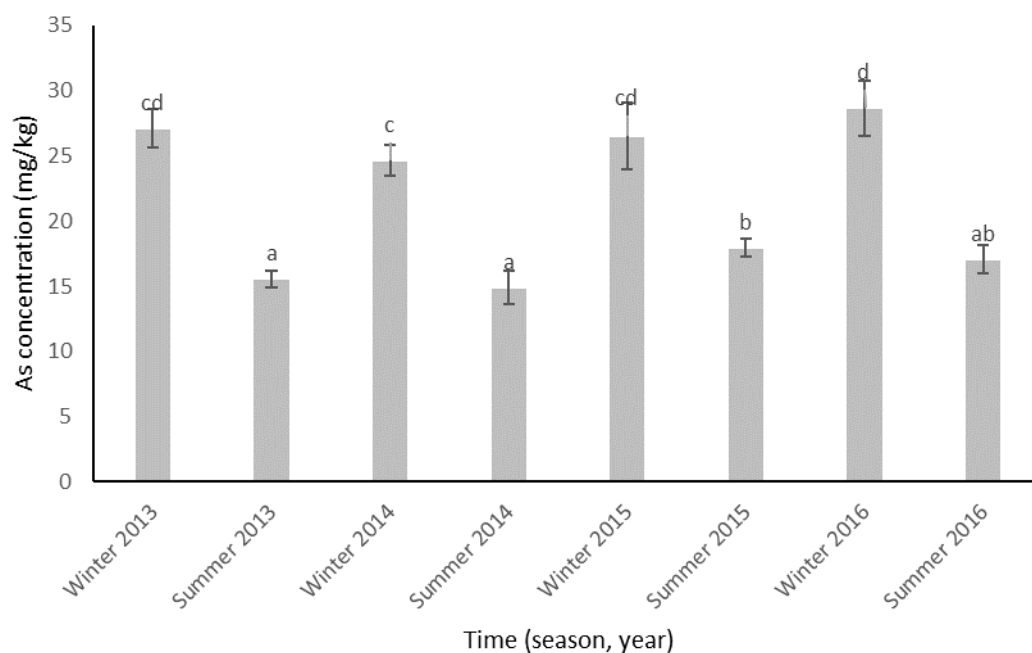
Figure 4.7 Comparison of winter and summer As concentrations in KSO compost for the years 2013, 2014, 2015, and 2016. a, b, c, and d denote significant differences and seasons with the same letters aren't significantly different. Error bars relate to the standard error (SE) of each season.

4.4 Trace metal accumulation:

As seen in Table 4.5, 4.6, 4.7 and 4.8 the model predicted maximum accumulation when the soil bulk density was at a minimum (ρ = 1.13), trace metal concentration in compost([t.m.], $c_{compost}$) was at a maximum, and application rate was a maximum. The background soil trace metal concentrations (c_{soil}) did not influence the rate of accumulation however as seen in Table 4.6 and 4.8, it did affect the starting point of accumulation and therefore affected how quickly the soil accumulation reached the threshold limits.

4.4.1 Autumn compost application:

Arsenic accumulation:

Autumn As levels of between 13.28 – 17.46 mg/kg were used for As concentrations within the compost as these were the minimum (2015) and maximum (2016) average concentrations in compost found for autumn in this study. Arsenic accumulation rates according to the model would be between 0.12 - 0.20, 0.25 – 0.40 and 0.48 – 0.79 mg/kg/application for compost application rates of 13, 26 and 51 t DM/ha respectively. This would result in an average As concentration within the soil after three applications of compost of between 1.27 and 39.26 mg/kg (Table 4.5).

The model predicted extremes of between 0 – 155 applications of compost applied before the AsureQuality 20mg/kg threshold was breached.

Copper accumulation:

Compost Cu levels of between 42.73 – 102.27 mg/kg were used in the model as these were the maximum (2014) and minimum (2013) average concentrations in KSO compost for autumn obtained from the dataset. The Cu accumulation rates would be between 0.4 – 1.18, 0.79 – 2.35, 1.56 – 4.62 mg/kg/application for compost applied at 13, 26, and 51 t DM/ha respectively. This resulted in an average soil Cu concentration after three compost applications of between 3.29 and 41.15 mg/kg (Table 4.5).

The model predicted extremes of between 8 - 146 applications before the soil concentration exceeded the 60 mg/kg threshold set by AsureQuality and between 60 – 751 applications before the NZS4454 300 mg/kg threshold was breached (Table 4.6).

Lead accumulation:

Compost Pb levels of between 95.083 – 117.636 mg/kg were used in the model as this was the range between minimum (2015) and maximum (2014) average concentrations in the KSO compost for autumn in this study. The Pb accumulation rates would be between 0.88 – 1.35, 1.77 – 2.71, 3.46 – 5.31 mg/kg/application for compost applied at 13, 26, and 51 t DM/ha respectively. This could result

in an average soil Pb concentration of between 6.28 and 60.33 mg/kg after three compost applications (Table 4.5).

The model predicted extremes of between 31 – 143 applications needed to breach the AsureQuality 200 mg/kg threshold and between 39 – 280 applications before the soil Pb concentration exceeded the 250 mg/kg threshold set by NZS4454 (Table 4.6).

Table 4.5 Accumulation of As, Cu, and Pb in soil after 1, 2, and 3 applications in soils with bulk densities of between 1.13 and 1.4 t/m³ and minimum and maximum background trace metal concentrations when applying composts in autumn with a lower and upper maximum trace metal (t.m.) concentration.

ΔSoil		[t.m.]	App rate	Application 1				Application 2				Application 3			
1.13	1.4			1.13		1.4		1.13		1.4		1.13		1.4	
				min	max	min	max	min	max	min	max	min	max	min	max
		As														
0.15	0.12	13.275 (min)	13	1.05	37.05	1.02	37.02	1.21	37.21	1.15	37.15	1.36	37.36	1.27	37.27
0.31	0.25		26	1.21	37.21	1.15	37.15	1.51	37.51	1.39	37.39	1.82	37.82	1.64	37.64
0.60	0.48		51	1.50	37.50	1.38	37.38	2.10	38.10	1.87	37.87	2.70	38.70	2.35	38.35
0.20	0.16	17.458 (max)	13	1.10	37.10	1.06	37.06	1.30	37.30	1.22	37.22	1.50	37.50	1.39	37.39
0.40	0.32		26	1.30	37.30	1.22	37.22	1.70	37.70	1.55	37.55	2.11	38.11	1.87	37.87
0.79	0.64		51	1.69	37.69	1.54	37.54	2.48	38.48	2.17	38.17	3.26	39.26	2.81	38.81
		Cu														
0.49	0.40	42.727 (min)	13	2.59	27.79	2.50	27.70	3.08	28.28	2.89	28.09	3.57	28.77	3.29	28.49
0.98	0.79		26	3.08	28.28	2.89	28.09	4.07	29.27	3.69	28.89	5.05	30.25	4.48	29.68
1.93	1.56		51	4.03	29.23	3.66	28.86	5.96	31.16	5.21	30.41	7.89	33.09	6.77	31.97
1.18	0.95	102.273 (max)	13	3.28	28.48	3.05	28.25	4.45	29.65	4.00	29.20	5.63	30.83	4.95	30.15
2.35	1.90		26	4.45	29.65	4.00	29.20	6.81	32.01	5.90	31.10	9.16	34.36	7.80	33.00
4.62	3.73		51	6.72	31.92	5.83	31.03	11.33	36.53	9.55	34.75	15.95	41.15	13.28	38.48
		Pb														
1.09	0.88	95.083 (min)	13	4.72	45.49	4.51	45.28	5.82	46.59	5.40	46.17	6.91	47.68	6.28	47.05
2.19	1.77		26	5.82	46.59	5.40	46.17	8.01	48.78	7.16	47.93	10.19	50.96	8.93	49.70
4.29	3.46		51	7.92	48.69	7.09	47.86	12.21	52.98	10.56	51.33	16.50	57.27	14.02	54.79
1.35	1.09	117.636 (max)	13	4.98	45.75	4.72	45.49	6.34	47.11	5.81	46.58	7.69	48.46	6.91	47.68
2.71	2.18		26	6.34	47.11	5.81	46.58	9.04	49.81	8.00	48.77	11.75	52.52	10.18	50.95
5.31	4.29		51	8.94	49.71	7.92	48.69	14.25	55.02	12.20	52.97	19.56	60.33	16.49	57.26

Soil background metal concentrations: As min/max = 0.9 – 36.9 mg/kg; Cu min/max = 2.1 – 27.3 mg/kg; Pb min/max = 3.63 – 44.4 mg/kg. Δ soil denotes the amount the soil trace metal concentration increases by with each application in soils with bulk densities of 1.13 and 1.4 t/m³.

Table 4.6 Number of compost applications needed for As, Cu, and Pb to exceed their AsureQuality and NZS4454 concentration thresholds in the soil when comparing soils with bulk densities of between 1.13 and 1.4 t/m³ and minimum and maximum background trace metal concentrations and when applying composts in autumn with a lower and upper maximum of trace metal content.

[t.m.]		Threshold AsureQuality				Threshold NZS4454			
	rate	1.13		1.4		1.13		1.4	
		min	max	min	max	min	max	min	max
As									
13.28	13.00	131	0	155	0				
	26.00	66	0	78	0				
	51.00	34	0	40	0				
17.46	13.00	100	0	118	0				
	26.00	37	0	59	0				
	51.00	26	0	31	0				
Cu									
42.73	13.00	118	67	146	83	607	555	751	688
	26.00	59	34	73	42	304	278	376	344
	51.00	31	17	38	22	155	142	192	176
102.27	13.00	50	28	61	35	254	232	314	288
	26.00	25	14	31	18	127	116	157	144
	51.00	13	8	16	9	65	60	80	74
Pb									
95.08	13.00	180	143	223	177	226	188	280	233
	26.00	90	72	112	89	113	94	140	117
	51.00	46	37	57	45	58	48	72	60
117.64	13.00	146	115	180	143	183	152	226	189
	26.00	73	58	90	72	92	76	113	95
	51.00	37	30	46	37	47	39	60	48

Soil background metal concentrations: As min/max = 0.9 – 36.9 mg/kg; Cu min/max = 2.1 – 27.3 mg/kg; Pb min/max = 3.63 – 44.4 mg/kg.

4.4.2 Spring compost applications:

Arsenic accumulation:

Spring As levels of between 19.500 – 23.750 mg/kg were used for As concentrations within the compost as these were the minimum (2013) and maximum (2015) average concentrations in compost found for autumn in this study. Arsenic accumulation rates according to the model would be between 0.2 -0.27, 0.4 – 0.55, 0.7 – 1.07 mg/kg/application for compost application rates of 13, 26

and 51 t DM/ha respectively. This would result in an average As concentration within the soil after three applications of compost of between 1.44 – 39.50 mg/kg (Table 4.7).

The model predicted extremes of between 0 – 87 applications of compost applied before the AsureQuality 20mg/kg threshold was breached. (Table 4.8).

Copper accumulation:

Compost Cu levels of between 52.417 – 56.00mg/kg were used in the model as these were the maximum (2016) and minimum (2014) average concentrations in KSO compost for autumn obtained from the dataset. The Cu accumulation rates would be between 0.50 – 0.64, 1.00 – 1.29, 1.9 – 2.53 mg/kg/application for compost applied at 13, 26, and 51 t DM/ha respectively. This could result in an average soil Cu concentration after three compost applications of between 3.56 and 34.88 mg/kg (Table 4.7).

The model predicted extremes of between 13 - 97 applications before the soil concentration exceeded the 60 mg/kg threshold set by AsureQuality and between 108 - 495 applications before the NZS4454 300 mg/kg threshold was breached (Table 4.8).

Lead accumulation:

Compost Pb levels of between 114.750 – 151.000 mg/kg were used in the model as this was the range between minimum (2013) and maximum (2015) average concentrations in the KSO compost for autumn in this study. The Pb accumulation rates would be between 1.1 – 1.74, 2.1 – 3.49, 4.2 – 6.84 mg/kg/application for compost applied at 13, 26, and 51 t DM/ha respectively. This could result in an average soil Pb concentration of between 6.83 and 64.91 mg/kg after three compost applications (Table 4.7).

The model predicted extremes of between 23 – 150 applications needed to breach the AsureQuality 200 mg/kg threshold and between 31 – 188 applications before the soil Pb concentration exceeded the 250 mg/kg threshold set by NZS4454 (Table 4.8).

Table 4.7 Accumulation of As, Cu, and Pb in soil after 1, 2, and 3 applications in soils with bulk densities of between 1.13 and 1.4 t/m3 and minimum and maximum background trace metal concentrations when applying composts in spring with a lower and upper maximum trace metal (t.m.) concentration.

Δ Soil 1.13	1.4	[t.m.]	App. rate	Application 1 1.13 min	max	1.4 min	max	Application 2 1.13 min	max	1.4 min	max	Application 3 1.13 min	max	1.4 min	max
		As													
0.22	0.2	19.500 (min)	13	1.12	37.12	1.08	37.08	1.35	37.35	1.26	37.26	1.57	37.57	1.44	37.44
0.45	0.4		26	1.35	37.35	1.26	37.26	1.80	37.80	1.62	37.62	2.25	38.25	1.99	37.99
0.88	0.7		51	1.78	37.78	1.61	37.61	2.66	38.66	2.32	38.32	3.54	39.54	3.03	39.03
0.27	0.2	23.750 (max)	13	1.17	37.17	1.12	37.12	1.45	37.45	1.34	37.34	1.72	37.72	1.56	37.56
0.55	0.4		26	1.45	37.45	1.34	37.34	1.99	37.99	1.78	37.78	2.54	38.54	2.22	38.22
1.07	0.9		51	1.97	37.97	1.77	37.77	3.04	39.04	2.63	38.63	4.12	40.12	3.50	39.50
		Cu													
0.6	0.5	52.417 (min)	13	2.70	27.90	2.59	27.79	3.31	28.51	3.07	28.27	3.91	29.11	3.56	28.76
1.21	1		26	3.31	28.51	3.07	28.27	4.51	29.71	4.05	29.25	5.72	30.92	5.02	30.22
2.37	1.9		51	4.47	29.67	4.01	29.21	6.83	32.03	5.92	31.12	9.20	34.40	7.83	33.03
0.64	0.5	56.000 (max)	13	2.74	27.94	2.62	27.82	3.39	28.59	3.14	28.34	4.03	29.23	3.66	28.86
1.29	1		26	3.39	28.59	3.14	28.34	4.68	29.88	4.18	29.38	5.97	31.17	5.22	30.42
2.53	2		51	4.63	29.83	4.14	29.34	7.15	32.35	6.18	31.38	9.68	34.88	8.22	33.42
		Pb													
1.32	1.1	114.750 (min)	13	4.95	45.72	4.70	45.47	6.27	47.04	5.76	46.53	7.59	48.36	6.83	47.60
2.64	2.1		26	6.27	47.04	5.76	46.53	8.91	49.68	7.89	48.66	11.55	52.32	10.02	50.79
5.18	4.2		51	8.81	49.58	7.81	48.58	13.99	54.76	11.99	52.76	19.17	59.94	16.17	56.94
1.74	1.4	151.500 (max)	13	5.37	46.14	5.04	45.81	7.12	47.89	6.44	47.21	8.86	49.63	7.85	48.62
3.49	2.8		26	7.12	47.89	6.44	47.21	10.60	51.37	9.26	50.03	14.09	54.86	12.07	52.84
6.84	5.5		51	10.47	51.24	9.15	49.92	17.31	58.08	14.67	55.44	24.14	64.91	20.19	60.96

Soil background metal concentrations: As min/max = 0.9 – 36.9 mg/kg; Cu min/max = 2.1 – 27.3 mg/kg; Pb min/max = 3.63 – 44.4 mg/kg. Δ soil denotes the amount the soil trace metal concentration increases by with each application in soils with bulk densities of 1.13 and 1.4 t/m^3.

Table 4.8 Number of compost applications needed for As, Cu, and Pb to exceed their AsureQuality and NZS4454 concentration thresholds in the soil when comparing soils with bulk densities of between 1.13 and 1.4 t/m3 and minimum and maximum background trace metal c

[t.m.]	rate	Threshold AsureQuality				Threshold NZS4454			
		1.13		1.4		1.13		1.4	
		min	max	min	max	min	max	min	max
As									
13.28	13.00	86	0	87	0				
	26.00	43	0	44	0				
	51.00	22	0	23	0				
17.46	13.00	70	0	71	0				
	26.00	35	0	36	0				
	51.00	18	0	19	0				
Cu									
42.73	13.00	97	55	97	56	494	453	495	454
	26.00	49	28	49	29	247	227	248	228
	51.00	25	14	26	15	126	116	127	117
102.27	13.00	90	51	91	52	463	424	464	423
	26.00	45	26	46	27	232	212	233	213
	51.00	23	13	24	14	118	108	119	109
Pb									
95.08	13.00	149	118	150	119	187	156	188	161
	26.00	75	59	76	60	94	78	95	79
	51.00	38	31	39	32	48	40	49	41
117.64	13.00	113	90	114	91	142	118	143	119
	26.00	57	45	58	46	71	59	72	60
	51.00	29	23	30	24	37	31	37	32

Soil background metal concentrations: As min/max = 0.9 – 36.9 mg/kg; Cu min/max = 2.1 – 27.3 mg/kg; Pb min/max = 3.63 – 44.4 mg/kg.

Chapter 5

Discussion:

5.1   Trace metal concentration comparisons:

Concentrations of trace metals are commonly variable among different types of compost but also among municipal composts. The differences in trace metal concentrations between different composts are most likely due to differences in source material, composting procedure and sampling techniques at the time of sampling (Richard & Woodbury, 1992; Woodbury & Breslin, 1992)

As seen in table 5.1 Ding et al. (2017)completed a study of composts in the main provinces of China. The main feedstocks in their composts were mainly farming manures such as cattle, chicken and pig manure. The study had similar trace metal concentrations of As and Zn to the Living earth KSO compost, albeit a 384% higher concentration of Cd, 28% higher concentrations of Cr (potentially due to the Cr^{6+} being included), 51% higher Cu concentrations and 71% lower concentrations of Pb (lack of contaminants that would potentially be in MSW compost). The feedstocks are very different between these two composts and therefore most likely accounts for most of the differences in metal concentrations. The feedstock was mostly animal manure therefore could be assumed that the metals have elevated concentrations (As, Cu, Cd, Zn) due to the diets of the animals (F. Zhang et al., 2012).

The composts from the UK study by Dimambro, Lillywhite, and Rahn (2007) had a range of different feedstocks and composting procedures. The compost listed in table 5.1 (referred to as compost A in the study) consisted of only source separated kitchen and garden green waste with cardboard. The compost had similar levels of most trace metals but no data for As (assume insignificant concentrations present) and 35, 37, and 38% lower Cr, Pb, and Zn levels than the KSO compost respectively. The compost was found to consist of 0.1% glass as well as 0.4% plastic contaminants. Additionally, due to strict regulations in the UK regarding composts having contact with animal products it was kept in a vessel for an amount of time at high temperature (either at 70°C for an hour or 60°C for two days), before the process was repeated in a second vessel. After this the compost was kept in open windrows outside. This compost followed a similar procedure as the KSO compost but had marked differences in some trace metal concentrations suggesting the differences in feedstock could be the cause of the reduced Cr, Pb and Zn concentrations.

The study completed by Amlinger et al. (2004) was also completed in the UK, but from mechanically sorted MSW material as opposed to source separated material. Mechanical sorting is generally believed to be less effective than source separation, hence the increase in Pb, Zn and Cu when

compared to the source separated compost (Amlinger et al., 2004; Bardos, 2004; Richard & Woodbury, 1992). The KSO compost concentrations were similar to the concentrations obtained in the mechanically sorted data except for Pb and Ni which were 47%, 216% larger than the concentrations found in the KSO compost. Differences in concentration would most likely be related to the failure to separate out some materials however the fact that the KSO compost Pb concentrations are higher than the source separated compost as well (Table5.1) suggests that there may be another significant source of Pb other than what normally occurs in source separated compost. When source separated composts from ther studies on source separated material, th

Table 5.1 Comparison of trace metal concentrations of different composts

As	Cd	Cr	Cr^{6+}	Cu	Hg	Pb	Ni	Zn	Source
20.10	0.50	27.56	0.45	51.38	0.09	113.81	9.80	250.73	[1]Living Earth: KSO compost
16.33	2.42	35.52	nd	72.24	0.320	32.38	9.71	258	[2](Ding et al., 2017)
nd	0.41	16	nd	91	0.15	167	31	286	[3](Amlinger et al., 2004)
nd	0.47	17.9	nd	46.0	0.19	71.5	11.3	155	[4](Dimambro et al., 2007)

[1]compost in this study for comparison; [2]manure based compost; [3]mechanically sorted municipal composy; [4]source separated municipal compost

5.2   Correlations with As:

Arsenic was the only trace metal in KSO compost that increased above its 20 mg/kg threshold (as set by AsureQuality and NZS4454) as often as it did (40.2% of the total study time between 2013 and 2016, and every year) and as consistently (Figure 4.1), hence why the study focus was largely around variation in As concentration. Arsenic had significant correlations with the average temperature (r = -0.66, p<0.001), and the logs of Cu (r =0.348, p<0.05), Cr (r = 0.290, p<0.05) and Pb (r = p<0.01). The correlations between As and the other metals weren't strong but because of the large sample sizes (194 data points, d.f. = 192 and 54 data points for yearly data, d.f. = 52) these correlations were still significant.

5.2.1   Seasonal effect of As concentration:

Figure 4.1 and 4.2 shows there was a consistent trend from 2013 to 2016 where the As concentrations increased to a peak around week 25 to week 35 which roughly corresponds to the winter period (as mentioned in Chapter 3). Arsenic concentrations consistently shared a significant negative correlation with average temperature (p<0.001) suggesting a possible seasonal winter peak effect on the As concentrations in the KSO compost. The ANOVA completed further supported this and suggested that season had a significant effect on the concentration of As in compost (F = 37.32, d.f. = 2, p<0.001).

The apparent overall increase in As concentration later in the trial period (most pronounced in the significantly higher winter As concentration in 2016 than winters before) suggests an upward trend

As concentration in KSO compost with time. This could potentially be explained by accumulation of As in soil over time leading to an increased soil baseline level, but more likely points to anthropogenic causes of the increase in concentration. With the gradual increase in concentration incidence of the breaching of critical thresholds can only be expected to increase in future years, emphasising the need to establish what the cause is.

5.3 Potential sources of elevated trace metal concentrations:

5.3.1 CCA treated timber as a residential winter fuel source:

The burning of CCA treated timber as a residential winter heating fuel source could potentially be the source of the seasonal variation in As concentrations in the KSO compost. It is believed that the ash from these fires would be added to the residential green bins and composted as part of the KSO compost. It is generally believed that wood ash has benefits for the performance of compost when used at appropriate application rates as was found in a study by Kuba, Tscholl, Partl, Meyer, and Insam (2008), who found that an admixture of compost with up to 18% wood ash had no negative effects on the composting process and even improved performance. A home heating survey from Auckland found that up to 17% of local respondents were using timber offcuts (framing timber and fence post offcuts) which could potentially have been treated (Stones-Havas, 2014). Additionally, a study looking at the ambient air concentrations of Benzo(A)Pyrene (BaP) and As in New Zealand found a seasonal effect of As levels in the air in New Zealand urban areas where elevated concentrations were seen in and around July every year (Cavanagh, Davy, Ancelet, & Wilton, 2012). Source apportionment studies that looked at different materials present in particulate matter in a New Zealand town found little correlation between As and other trace metal concentrations in the particulate matter which doesn't suggest the source of the As to be from industrial activity such as smelting and coal combustion (Cavanagh et al., 2012). They found the As was more correlated with black carbon and potassium (K) which are common indicators for biomass burning and wood combustion (Fine, Cass, & Simoneit, 2001; Khalil & Rasmussen, 2003), which indicated that the As was potentially due to the burning of biomass and CCA contaminated wood due to the presence of As in the ash (Davy, Ancelet, Trompetter, Markwitz, & Weatherburn, 2012).

It could be assumed that similar results could be obtained in Christchurch, especially following the large-scale Christchurch rebuild due to the earthquakes in 2011 which would have resulted in a lot of surplus waste/damaged timber (treated and untreated) available for use as a heating source. Overall, more research would need to be done on the winter heating habits of Christchurch residents as well as the concentrations and chemical profiles of particulate matter in Christchurch to be sure whether this was a definite and substantial source of As in KSO compost. In terms of the correlations that

were completed, As is significantly correlated with both Cu (p<0.001) and Cr (p<0.01) and therefore the initial hypothesis cannot be rejected.

If CCA was the only source of As, Cu, and Cr in the municipal compost, then provided there was no volatilisation in Cr and Cu and only the amount mentioned earlier for As (2.3.4) then these trace metals would be found in the compost at a ratio of 1.06:1:1.75 (As:Cu:Cr). This would mean at 20.10mg/kg of As, only 18.96 mg/kg of Cu would be present and 33.18 mg/kg of Cr. While this value for Cu is lower than the actual recorded figure, the value for Cr is within 1 S.D. of the average. This could either suggest a slight difference in the CCA mixture ratio, resulting in some differences in ratios of As:Cu or that there is another significant source of Cu. Another potential source of Cu as well as other trace metals in particulate form could be from industrial sources such as high temperature metal smelting.

5.4   As, Cu, and Pb accumulation within soil:

The model quantified the effects of the main factors associated with the accumulation of trace metal in soil and explored a range of possible outcomes relevant to the Canterbury region. The factors of trace metal concentration within compost, application rate, soil density, and background trace metal concentrations were considered in the model. The main drawback of the model is the exclusion of losses of trace metals out of the soil system which could affect the accumulation rate of certain trace metals. In terms of As, Cu and Pb this isn't as much of a problem though as these metals are tightly adsorbed to the soil surfaces and therefore the losses out of the soil system would be negligible (Asher & Reay, 1979; Epstein et al., 1992; Meharg et al., 1994; O'Neill, 1990; Ullrich-Eberius et al., 1989). However, if the model were to be applied to trace metals that were not as tightly held in soil the model could lose some accuracy.

The model predicted As would reach its 20 mg/kg threshold in a range of applications between 0 and 155 in autumn and 0 and 87 in spring, however the lower limits were based on a soil that was already on or above threshold concentration before the initial application. Therefore, if the maximum background concentration soil is excluded for the purpose of indicating As accumulation and the next lowest figure used, it could be expected that threshold would be reached in between 26 – 155 applications if autumn produced compost was used or between 18 – 87 applications if spring produced compost was used. This translates to between 78 – 465 years and 54 and 261 years before the 20 mg/kg threshold is reached at 3 yearly application intervals for autumn and spring produced compost respectively. Copper thresholds (60, 300 mg/kg) were reached in 24 – 438 and 39 – 291 years for an autumn and spring produced compost respectively while Pb concentrations reached

threshold (200, 250 mg/kg) from 117 – 840, and 93 - 564 years for autumn and spring produced composts respectively. Out of the 3 metals, Cu would present the earliest problem followed by As, followed by Pb.

Possible management from the model outputs, the accumulation rates were lower for the autumn produced composts which suggests that it could be better for farmers to use the autumn produced composts as these result in lower accumulation rates and allowed for more applications before threshold concentrations rare reached. Additionally, as is already practised by Living Earth Ltd., the application of a bulking agent but for diluting the trace metal concentrations within the compost.

Chapter 6

Conclusions:

The objectives of this study were to ascertain whether any patterns could be found that could disprove the initial hypothesis, and to investigate potential issues arising from the application of the compost product to agricultural soils in terms of trace metal accumulation and subsequent human health, environmental or productivity issues.

The initial hypothesis was that the elevated As concentrations that Living Earth Ltd. had been finding was due to the burning of CCA treated timber and the subsequent addition of the ash to the residential green bins that get emptied as part of council kerbside bin collection. From the results in the study it was found the initial hypothesis could not be disproved.

The study found significant correlations between the concentrations of As, Cu, Cr and the average temperature in Christchurch. Arsenic was found to have significant positive correlations with both Cu and Cr as well as a negative correlation with average temperature. This suggested that as temperature decreased as would be expected in winter (leading to the increased incidence of residential heating use), the As concentrations in KSO compost increased. Copper and Cr didn't have significant correlations with temperature as consistently as As did however, they were still significantly positively correlated with As concentration. this could be assumed to be due to other sources that affected the concentrations of those trace metals within the compost.

The results for the correlations were only reinforced with the ANOVA completed on the effect of season on the concentration of As which found that season had a significant effect on the As concentration in KSO compost. The results showed that the As concentrations were significantly different between winter and summer and that a significant amount of this variation was due to season.

Appendix A

Yearly correlations:

A.1   2013:

Table A. 1 Trace metal correlations (r values) for the year 2013

2013	temp	Arsenic	Cadmium	Chromium	Chromium 6	Copper	Mercury	Lead	Nickel	Zinc
temp	1.000									
Arsenic	-0.724	1.000								
Cadmium	-0.260	0.246	1.000							
Chromium*	-0.023	0.029	0.116	1.000						
Chromium 6*	0.275	-0.220	-0.209	0.122	1.000					
Copper*	-0.668	0.661	0.468	0.164	-0.304	1.000				
Mercury*	0.042	-0.147	-0.165	-0.206	-0.115	-0.146	1.000			
Lead*	-0.446	0.665	0.140	0.238	-0.074	0.539	-0.146	1.000		
Nickel*	0.173	-0.186	0.057	0.850	0.000	-0.004	-0.289	0.068	1.000	
Zinc	0.016	0.119	-0.007	0.228	-0.159	0.078	-0.061	0.303	0.247	1.000

*log transformed

A.2   2014:

Table A. 2 Trace metal correlations (r values) for the year 2014

2014	temp	Arsenic	Cadmium	Chromium	Chromium 6	Copper	Mercury	Lead	Nickel	Zinc
temp	1.000									
Arsenic	-0.592	1.000								
Cadmium	-0.113	0.145	1.000							
Chromium*	0.219	-0.058	0.010	1.000						
Chromium 6*	0.193	-0.343	-0.207	-0.031	1.000					
Copper*	-0.085	0.165	-0.125	-0.189	-0.078	1.000				
Mercury*	-0.139	0.174	0.313	0.102	-0.108	-0.064	1.000			
Lead*	-0.386	0.351	0.096	-0.118	0.023	-0.105	0.400	1.000		
Nickel*	0.425	-0.265	-0.065	0.875	0.065	-0.113	0.086	-0.278	1.000	
Zinc	0.011	-0.134	-0.167	0.243	0.430	-0.009	-0.044	-0.038	0.254	1.000

*log transformed

A.3   2015:

Table A. 3 Trace metal correlations (r values) for the year 2015

2015	temp	Arsenic	Cadmium	Chromium	Chromium 6	Copper	Mercury	Lead	Nickel	Zinc
temp	1.00									
Arsenic	-0.64	1.00								
Cadmium	0.05	-0.22	1.00							
Chromium*	-0.31	0.41	-0.09	1.00						
Chromium 6*	0.22	-0.23	0.33	-0.08	1.00					
Copper*	-0.50	0.37	-0.03	0.29	0.19	1.00				
Mercury*	0.12	0.29	-0.39	-0.09	-0.27	-0.08	1.00			
Lead*	-0.03	0.41	-0.07	0.23	0.03	0.02	0.17	1.00		
Nickel*	-0.25	0.29	0.03	0.74	-0.12	0.13	-0.21	0.08	1.00	
Zinc	-0.05	0.41	-0.21	0.17	-0.21	0.23	0.38	0.36	0.16	1.00

*log transformed

A.4   2016:

Table A. 4 Trace metal correlations (r values) for the year 2016

2016	temp	Arsenic	Cadmium	Chromium	Chromium 6	Copper	Mercury	Lead	Nickel	Zinc
temp	1.000									
Arsenic	-0.702	1.000								
Cadmium	-0.149	0.243	1.000							
Chromium*	-0.427	0.775	0.272	1.000						
Chromium 6*	0.335	-0.272	-0.040	-0.190	1.000					
Copper*	0.021	0.196	0.279	0.288	0.106	1.000				
Mercury*	0.139	-0.175	-0.032	-0.210	0.180	-0.076	1.000			
Lead*	-0.419	0.484	0.099	0.386	-0.235	0.203	-0.317	1.000		
Nickel*	-0.005	0.215	0.066	0.495	-0.147	0.198	-0.253	0.188	1.000	
Zinc	0.015	0.166	0.330	0.348	0.026	0.359	0.077	0.158	0.295	1.000

*log transformed

References

Amlinger, F., Pollak, M., & Favoino, E. (2004). Heavy metals and organic compounds from wastes used as organic fertilisers. *Study on behalf of the European Commission, Directorate-General Environment, ENV. A, 2*.

Asher, C., & Reay, P. (1979). Arsenic uptake by barley seedlings. *Functional Plant Biology, 6*(4), 459-466.

Ashrafzadeh, S., Lehto, N. J., Oddy, G., McLaren, R. G., Kang, L., Dickinson, N. M., . . . Robinson, B. H. (2017). Heavy metals in suburban gardens and the implications of land-use change following a major earthquake. *Applied Geochemistry*. doi:http://dx.doi.org/10.1016/j.apgeochem.2017.04.009

AsureQuality. (2016). AsureQuality organic standard.   Retrieved from https://www.asurequality.com/assets/Organic-Files/organics-standard-2015-FULL-V6-Feb16.pdf

Bardos, P. (2004). Composting of mechanically segregated fractions of municipal solid waste–a review. *Falfield, Bristol: Sita Environmental Trust*.

Brady, N. C., & Weil, R. R. (1996). The nature and properties of soils.

Cavanagh, J., Davy, P., Ancelet, T., & Wilton, E. (2012). Beyond PM10: benzo (a) pyrene and As concentrations in New Zealand air. *Air Quality and Climate Change, 46*(2), 15.

Chaney, R. L., Mielke, H. W., & Sterrett, S. B. (1989). Speciation, mobility and bioavailability of soil lead. *Environ. Geochem. Health, 11*, 105-129.

Crecchio, C., Curci, M., Pizzigallo, M. D. R., Ricciuti, P., & Ruggiero, P. (2004). Effects of municipal solid waste compost amendments on soil enzyme activities and bacterial genetic diversity. *Soil Biology and Biochemistry, 36*(10), 1595-1605. doi:http://dx.doi.org/10.1016/j.soilbio.2004.07.016

Davy, P. K., Ancelet, T., Trompetter, W. J., Markwitz, A., & Weatherburn, D. C. (2012). Composition and source contributions of air particulate matter pollution in a New Zealand suburban town. *Atmospheric Pollution Research, 3*(1), 143-147.

deHaan, S. (1981). Results of municipal waste compost research over more than fifty years at the institute for soil fertility at Haren/Groningen, the Netherlands. *Netherlands Journal of Agricultural Science (Netherlands)*.

Dimambro, M., Lillywhite, R., & Rahn, C. (2007). The physical, chemical and microbial characteristics of biodegradable municipal waste derived composts. *Compost Science & Utilization, 15*(4), 243-252.

Ding, F., He, Z., Liu, S., Zhang, S., Zhao, F., Li, Q., & Stoffella, P. J. (2017). Heavy metals in composts of China: historical changes, regional variation, and potential impact on soil quality. *Environmental Science and Pollution Research, 24*(3), 3194-3209. doi:10.1007/s11356-016-8057-3

Epstein, E. (1996). *The science of composting*: CRC press.

Epstein, E., Chaney, R., Henry, C., & Logan, T. (1992). Trace elements in municipal solid waste compost. *Biomass and Bioenergy, 3*(3), 227-238.

Eriksen, G. N., Coale, F. J., & Bollero, G. A. (1999). Soil nitrogen dynamics and maize production in municipal solid waste amended soil. *Agronomy Journal, 91*(6), 1009-1016.

Fine, P. M., Cass, G. R., & Simoneit, B. R. (2001). Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the northeastern United States. *Environmental Science & Technology, 35*(13), 2665-2675.

Francis, G. S., & Knight, T. L. (1993). Long-term effects of conventional and no-tillage on selected soil properties and crop yields in Canterbury, New Zealand. *Soil and Tillage Research, 26*(3), 193-210. doi:10.1016/0167-1987(93)90044-P

Garcıa-Gil, J., Ceppi, S., Velasco, M., Polo, A., & Senesi, N. (2004). Long-term effects of amendment with municipal solid waste compost on the elemental and acidic functional group composition and pH-buffer capacity of soil humic acids. *Geoderma, 121*(1), 135-142.

Garcia, C., Moreno, J., Hernandez, T., Costa, F., & Polo, A. (1995). Effect of composting on sewage sludges contaminated with heavy metals. *Bioresource Technology, 53*(1), 13-19.

Gough, L. P. (1979). Element concentrations toxic to plants, animals, and man.

Hargreaves, J. C., Adl, M. S., & Warman, P. R. (2008). A review of the use of composted municipal solid waste in agriculture. *Agriculture, Ecosystems & Environment, 123*(1–3), 1-14. doi:http://dx.doi.org/10.1016/j.agee.2007.07.004

Harrison, D. F., Cameron, K. C., & McLaren, R. G. (1994). Effects of subsoil loosening on soil physical properties, plant root growth, and pasture yield. *New Zealand journal of agricultural research, 37*(4), 559-567. doi:10.1080/00288233.1994.9513095

He, X.-T., Logan, T. J., & Traina, S. J. (1995). Physical and chemical characteristics of selected US municipal solid waste composts. *Journal of environmental quality, 24*(3), 543-552.

He, X.-T., Traina, S. J., & Logan, T. J. (1992). Chemical Properties of Municipal Solid Waste Composts. *Journal of environmental quality, 21*, 318-329. doi:10.2134/jeq1992.00472425002100030003x

Hernando, S., Lobo, M., & Polo, A. (1989). Effect of the application of a municipal refuse compost on the physical and chemical properties of a soil. *Science of the total environment, 81*, 589-596.

Hicklenton, P. R., Rodd, V., & Warman, P. R. (2001). The effectiveness and consistency of source-separated municipal solid waste and bark composts as components of container growing media. *Scientia Horticulturae, 91*(3), 365-378.

Horrocks, A., Curtin, D., Tregurtha, C., & Meenken, E. (2016). Municipal Compost as a Nutrient Source for Organic Crop Production in New Zealand. *Agronomy, 6*(2), 35.

Horrocks, A., Tregurtha, C., & Meenken, E. (2015). Productivity, Profitability and N Fertiliser Reductions as a Result of Compost in an Arable Cropping Rotation. In R. O. Blu, S. M. M. Martinez, & S. P. Ospina (Eds.), *Ii International Symposium on Organic Matter Management and Compost Use in Horticulture* (Vol. 1076, pp. 51-67).

Houlbrooke, D. J., Paton, R. J., Littlejohn, R. P., & Morton, J. D. (2011). Land-use intensification in New Zealand: Effects on soil properties and pasture production. *Journal of Agricultural Science, 149*(3), 337-349. doi:10.1017/S0021859610000821

Iglesias-Jimenez, E., & Alvarez, C. (1993). Apparent availability of nitrogen in composted municipal refuse. *Biology and Fertility of Soils, 16*(4), 313-318.

Jakobsen, S. T. (1995). Aerobic decomposition of organic wastes 2. Value of compost as a fertilizer. *Resources, Conservation and Recycling, 13*(1), 57-71.

Kaldjian, P. (1988). *Characterization of Municipal Solid Wastes*. (EPA 530-Sw-88-033). U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response.

Khalil, M., & Rasmussen, R. (2003). Tracers of wood smoke. *Atmospheric Environment, 37*(9), 1211-1222.

Kuba, T., Tscholl, A., Partl, C., Meyer, K., & Insam, H. (2008). Wood ash admixture to organic wastes improves compost and its performance. *Agriculture Ecosystems & Environment, 127*(1-2), 43-49. doi:10.1016/j.agee.2008.02.012

Leita, L., & De Nobili, M. (1991). Water-soluble fractions of heavy metals during composting of municipal solid waste. *Journal of environmental quality, 20*(1), 73-78.

Logan, T., Henry, C., Schnoor, J. L., Overcash, M., & McAvoy, D. (1999). An assessment of health and environmental risks of trace elements and toxic organics in land-applied municipal solid waste compost. *Compost Science & Utilization, 7*(3), 38-53.

Marks, M., Williams, J., & Chumbley, C. (1980). *Field experiments testing the effects of metal contaminated sewage sludges on some vegetable crops.* Paper presented at the Inorganic pollution and agriculture. Proceedings of a Conference organised by the Agricultural Development and Advisory Service, April 1977.

McLaren, R. G., & Cameron, K. C. (1996). *Soil science: sustainable production and environmental protection*: Oxford University Press, USA.

Meharg, A., Naylor, J., & Macnair, M. (1994). Phosphorus nutrition of arsenate-tolerant and nontolerant phenotypes of velvetgrass. *Journal of environmental quality, 23*(2), 234-238.

Mertz, W., & Underwood, E. J. (1986). Trace elements in human and animal nutrition.

Mkhabela, M., & Warman, P. (2005). The influence of municipal solid waste compost on yield, soil phosphorus availability and uptake by two vegetable crops grown in a Pugwash sandy loam soil in Nova Scotia. *Agriculture, Ecosystems & Environment, 106*(1), 57-67.

Montemurro, F., Maiorana, M., Convertini, G., & Ferri, D. (2006). Compost organic amendments in fodder crops: effects on yield, nitrogen utilization and soil characteristics. *Compost Science & Utilization, 14*(2), 114-123.

Nagajyoti, P., Lee, K., & Sreekanth, T. (2010). Heavy metals, occurrence and toxicity for plants: a review. *Environmental Chemistry Letters, 8*(3), 199-216.

NIWA. (n.d.). *The national climate datebase: Christchurch Aero station.* Retrieved from: https://cliflo.niwa.co.nz

NZTPC. (2004). Hazard class description. Retrieved from http://www.nztpc.co.nz/hazardClassDescription.php

O'Neill, P. (1990). Arsenic. In B. J. Alloway (Ed.), *Heavy metals in soils* (pp. 83-99). New York: John Wiley & Sons.

Oliveira, H. (2012). Chromium as an environmental pollutant: insights on induced plant toxicity. *Journal of botany, 2012*.

Pankhurst, C., Doube, B. M., & Gupta, V. (1997). *Biological indicators of soil health*: Cab International Wallingford, UK.

Pascual, J., García, C., & Hernandez, T. (1999). Lasting microbiological and biochemical effects of the addition of municipal solid waste to an arid soil. *Biology and Fertility of Soils, 30*(1), 1-6.

Perucci, P. (1990). Effect of the addition of municipal solid-waste compost on microbial biomass and enzyme activities in soil. *Biology and Fertility of Soils, 10*(3), 221-226.

Peterson, P., Benson, L., & Zieve, R. (1981). Metalloids *Effect of heavy metal pollution on plants* (pp. 279-342): Springer.

Richard, T. L., & Woodbury, P. B. (1992). The impact of separation on heavy metal contaminants in municipal solid waste composts. . *Biomass & Bioenergy, 3*(3-4), 195-211. doi:10.1016/0961-9534(92)90026-m

Rogers, J. M., Stewart, M., Petrie, J. G., & Haynes, B. S. (2007). Deportment and management of metals produced during combustion of CCA-treated timbers. *Journal of hazardous materials, 139*(3), 500-505.

Sharma, V., Canditelli, M., Fortuna, F., & Cornacchia, G. (1997). Processing of urban and agro-industrial residues by aerobic composting. *Energy Conversion and Management, 38*(5), 453-478.

Standards_New_Zealand. (2003). *Chemical preservation of rounds and swan timber*. (NZS 3640:2003). Retrieved from https://shop.standards.govt.nz/catalog/3640%3A2003%28NZS%29/view

Standards_New_Zealand. (2005a). *Composts, soil conditioners and mulches.* (NZS4454:2005). Retrieved from https://shop.standards.govt.nz/catalog/4454%3A2005%28NZS%29/view

Standards_New_Zealand. (2005b). *General requirements of testing and calibration laboratories.* (NZS/ISO/IEC 17025:2005). Retrieved from https://shop.standards.govt.nz/catalog/17025%3A2005%28NZSISO%7CIEC%29/view

Steevens, D., Walsh, L., & Keeney, D. (1972). Arsenic phytotoxicity on a Plainfield sand as affected by ferric sulfate or aluminum sulfate. *Journal of environmental quality, 1*(3), 301-303.

Stones-Havas, T. (2014). *2012 Home heating survey results. Auckland Council technical report*. (TR2014/011).

Tchobanoglous, G., & Kreith, F. (2002). *Handbook of Solid Waste Management* (2 ed.). New York McGraw-Hill.

Tisdell, S. E., & Breslin, V. T. (1995). Characterization and leaching of elements from municipal solid waste compost. *Journal of environmental quality, 24*(5), 827-833.

Ullrich-Eberius, C., Sanz, A., & Novacky, A. (1989). Evaluation of arsenate-and vanadate-associated changes of electrical membrane potential and phosphate transport in Lemna gibba G1. *Journal of Experimental Botany*, 119-128.

Walter, I., Martínez, F., & Cuevas, G. (2006). Plant and soil responses to the application of composted MSW in a degraded, semiarid shrubland in central Spain. *Compost Science & Utilization, 14*(2), 147-154.

Webber, M., Soon, Y., Bates, T., & Haq, A. (1981). Copper toxicity to crops resulting from land application of sewage sludge *Copper in Animal Wastes and Sewage Sludge* (pp. 117-135): Springer.

Wolkowski, R. P. (2003). Nitrogen management considerations for landspreading municipal solid waste compost. *Journal of environmental quality, 32*(5), 1844-1850.

Woodbury, P. B., & Breslin, V. T. (1992). Assuring compost quality: suggestions for facility managers, regulators, and researchers. *Biomass and Bioenergy, 3*(3-4), 213-225.

Yousefi, J., Younesi, H., & Ghasempoury, S. M. (2013). Co-composting of Municipal Solid Waste with Sawdust: Improving Compost Quality. *Clean–Soil, Air, Water, 41*(2), 185-194.

Zennaro, M., Cristofori, F., Formigoni, D., Frignani, F., & Pavoni, B. (2005). Heavy metal contamination in compost. A possible solution. *Annali di chimica, 95*(3-4), 247-256.

Zhang, F., Li, Y., Yang, M., & Li, W. (2012). Content of heavy metals in animal feeds and manures from farms of different scales in northeast China. *International journal of environmental research and public health, 9*(8), 2658-2668.

Zhang, M., Heaney, D., Henriquez, B., Solberg, E., & Bittner, E. (2006). A four-year study on influence of biosolids/MSW cocompost application in less productive soils in Alberta: nutrient dynamics. *Compost Science & Utilization, 14*(1), 68-80.