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Temporal Changes in Cd Sorption and Plant Bioavailability in Compost-Amended Soils

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Abstract: The application of Cd-contaminated phosphate fertiliser has enriched concentrations of this non-essential element in many agricultural soils. Consequently, concentrations of the metal in some agricultural products exceed the Maximum Limit in foods. Composts can reduce the transfer of Cd from soil to plants; however, it is unclear how long this beneficial effect endures. We aimed to determine temporal changes of phytoavailable Cd in two market garden soils (an Allophanic Orthic Granular Soil and a Recent Silt Loam). Soils were amended with either municipal green waste compost or sawdust and animal waste compost at a rate of 2.5% *w/w* under three incubation regimes: at 19 °C, at 30 °C, and at 30 °C with additional N added as urea at 0.6 g urea/kg soil added over 1 year. Each replicate was sampled after 1, 5, 9, 13, 21, 31, and 49 weeks, and phytoavailable Cd was estimated through 0.05 M Ca(NO₃)₂ extraction. Seed potato (*Solanum tuberosum*), 'Nadine' variety, was grown in the Pukekohe Allophanic Orthic Granular Soil, freshly amended with municipal compost and the same soil aged for one year. The concentration of Cd in all samples was analysed using an ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometer). The C concentration in the soil—compost mixtures decreased over the year, with the greatest decreases occurring in the soils incubated at 30 °C with added N. Unexpectedly, the concentration of Ca(NO₃)₂-extractable Cd in the compost-amended soils did not increase over time and in some cases even decreased. This was confirmed through a pot experiment, which showed the Cd concentration in potato was reduced by 50% in both the freshly amended soil and the amended soil aged for one year. Cadmium immobilisation in soils might be due to both the sorption of Cd by organic matter and the occlusion of sorbed Cd by oxy-hydroxides of iron and aluminium. Over 49 weeks, soluble Cd does not increase as organic matter oxidises. The application of municipal compost to soil will reduce both plant Cd solubility and plant Cd uptake for at least one year in the soils tested.

Keywords: Ca(NO₃)₂-extractable Cd; incubation; potato; organic amendment



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1. Introduction

Cadmium (Cd) is a non-essential trace element that is present at elevated concentrations in many agricultural soils [1,2]. It occurs naturally as a contaminant in all phosphate rocks. Rock phosphate originating from igneous rocks contains Cd concentrations of 0.7–30 mg/kg P [3], whereas rock phosphate refined from sedimentary rocks may contain Cd concentrations >556 mg/kg P [4] and accounts for between 85 and 90% of world P production [3]. The use of Cd-containing phosphate fertiliser to sustain agricultural produc-

tivity has resulted in an enrichment of Cd in agricultural soils worldwide [2,5,6]. Elevated Cd in soil is a key driver of increased Cd concentration in plant tissue and foodstuffs [7–13].

Most Cd in soil is bound to the solid phase, with relatively low concentrations present in soil solution [14]. Soil K_d (sorbed/solution Cd quotient) values for silt loam soils range from 50 to 200 and from pH 5 to 6.5 [15,16]. Nevertheless, soil-borne Cd is readily taken up by plants [17] and then transferred to animals and humans through plant consumption [18,19]. Exceedances of food safety standards have been reported in vegetables worldwide [10,20–22]. The availability of soil Cd for uptake by plants (i.e., phytoavailability) largely depends on the amount of metal that exists as a soluble species, which is a function of the total concentration as well as physicochemical and biological properties of the soils [2].

Some 55–90% of Cd in soil solution is present as free metal ion Cd^{2+} [23]. Cadmium may occur as cationic species, $CdCl^+$, $CdOH^+$, $CdHCO_3^+$, and $CdHS^+$; and as anionic species, $CdCl_3^-$, $Cd(OH)_3$, $Cd(OH)_4^{2-}$, and $Cd(HS)_4^{2-}$ [2]. It also forms complexes with organic ligands, such as low-molecular-weight organic acids, fulvates, and humates [2]. The most phytoavailable species in soil solution are Cd^{2+} and $CdCl^+$ [24]. Phytoavailability of soluble Cd is also affected by plant nutrients (especially Ca, Zn, and Cl^-), as well as pH, ionic strength, and aeration [25]. Most studies report reduced plant uptake at high soil pH, presumably due to increased K_D values [26,27]. However, some studies have shown an increase in plant Cd uptake at high pH, despite reduced Cd concentrations in soil solution. The drivers underlying these effects are complex and difficult to disentangle: Zn deficiency at high soil pH may result in an increase in the expression of Zn transporter proteins that can facilitate Cd uptake [28]. Increased Cd solubility at higher Ca^{2+} ion concentrations following liming may also play a role [1,29]. Increased activity of $CdCl^+$ species activity in saline soils has also been associated with elevated Cd concentrations in wheat (*Triticum aestivum* cv. Halberd) and Swiss chard (*Beta vulgaris* cv. Foodhook Giant) [13,30].

The addition of organic matter to soil as carbonaceous amendments can reduce Cd uptake by plants [1,31–35] through binding Cd into less phytoavailable solid phase species [16,34,36]. Following the application of 2–5% compost, Al Mamun et al. [37] reported a reduction in Cd concentration in potato tubers (*Solanum tuberosum*) by 29–66%, depending on the compost. Compost made from mixtures of food waste, lawn clippings, tree prunings, sawdust, and animal offal effectively reduced Cd solubility in batch sorption experiments, which was associated with significantly decreased Cd uptake by *Allium cepa* L., *Spinacia oleracea* L., and *Lactuca sativa* L. of up to 60% [15]. Shuman et al. [38] reported that the larger surface area of humified organic matter removes Cd from soil solution making it less available to *Zea mays* L. Inorganic components in compost, particularly Fe and Al (oxyhydr)oxides, may further reduce Cd solubility and thence plant uptake [39].

The organic matter in the compost can be degraded by soil microorganisms, so it may be expected that the abundance and nature of functional group ligands that bind Cd in soils would change over time. However, there is a lacuna of information on the rate of change of the Cd-binding capacity of composts over time following their addition to soil. Karaca [40] showed that soils amended with mushroom compost and grape mark (added at rates of 2%, 4%, and 8%) retained their ability to bind Cd, even after incubation at 25 °C for six months. Similarly, Lee et al. [34] showed in a greenhouse study that the reduction in DTPA-extractable Cd resulting from hog manure application persisted for at least six months.

It was hypothesised that the bound Cd in composts will be released into soil solution as the compost decomposes and that its phytoavailability will, therefore, increase. Depending on environmental conditions, compost manufacturers recommend that compost be added annually to triennially to maintain the soil's organic matter content [41]. Therefore, most Cd that is bound to the compost is likely to be released over this timeframe. To test this hypothesis, this research sought to fulfil two objectives. The first objective was to determine the temporal changes in $Ca(NO_3)_2$ -extractable Cd in two soils amended with composts of different provenances under contrasting incubation regimes over one year. The second

objective was to compare the transfer of Cd from a soil to potatoes grown in a pot trial using freshly amended compost and the same soil a year later.

2. Materials and Methods

2.1. Soil Sample Collection

Two distinct soils were collected from market gardens in New Zealand: an Allophanic Orthic Granular Soil from Pukekohe ($37^{\circ}13'18.92''$ S $174^{\circ}52'5.94''$ E) and a Recent Silt Loam from Levin ($40^{\circ}38'17.49''$ S $175^{\circ}14'23.61''$ E) in the North Island of New Zealand. Henceforth, these soils will be referred to as 'Pukekohe soil' and 'Levin soil', respectively. Soils were collected from within the plough layer (top 0.25 m) and were dried, ground, sieved (7 mm mesh), and their chemical properties determined (Tables 1 and 2). Cadmium concentrations in the Pukekohe and Levin soils were 1.45 mg/kg and 0.47 mg/kg, respectively, at the time of collection. One year before the experiment, a subset of the Pukekohe soil was amended with municipal compost (2.5% *w/w*, as reported by Al Mamun et al. [37]), and another subset of the Pukekohe soil and a subset of the Levin soil were spiked with Cd (as the sulphate salt) to increase their Cd concentrations by ca. 1 mg/kg. All soils were left to incubate in pots in a greenhouse where they were watered occasionally. Following spiking, Cd concentrations in the Pukekohe and Levin soils had increased to 2.08 (± 0.09) mg/kg and 0.99 (± 0.05) mg/kg, respectively.

Table 1. Chemical properties and elemental concentrations (mg/kg unless otherwise indicated) of the materials used in the experiments. Values in brackets represent the standard error of the mean ($n = 3$).

Properties	Municipal Compost (Living Earth Compost)	Sawdust Compost (Parkhouse Compost)	Pukekohe Soil	Levin Soil
pH (H ₂ O)	7.4	7.0	6.0	6.5
CEC (cmol _c /kg)	45 (<1)	47 (<1)	22 *	15 *
C (%)	21	21	2.1 *	1.2 *
N (%)	2.3	1.6	0.23 *	0.13
P	4178 (37)	5159 (227)	3414 (26)	2247 (20)
S	2644 (27)	3610 (70)	491 (6)	296 (1)
Ca=	24,903 (588)	37,416 (1456)	4147 (117)	7008 (99)
Mg	4177 (16)	2186 (34)	2400 (95)	2873 (43)
K	14,938 (33)	5412 (67)	1951 (59)	2242 (54)
B (mg/kg)	20 *	<1	33 (0)	9 (0)
Cd	0.70 (0.10)	0.45 (0.10)	1.45 (0.03)	0.47 (0.01)
Cu	59 (1)	25 (1)	65 (1)	20 (0.2)
Zn	310 (11)	34 (2)	173 (1)	67 (1)
Cr	28 (1)	37 (1)	40 (2)	15 (0.3)
Ni	9.3 (1)	5.2 (0.1)	25 (1)	7.4 (0.5)
Fe	12,472 (261)	8218 (2030)	44,606 (96)	22,729 (1527)
Al	9534 (164)	8126 (147)	93,008 (476)	32,412 (1188)

* data from Hill Laboratories, New Zealand.

Table 2. Extractable [0.05 M Ca(NO₃)₂] concentrations (mg/kg) of selected elements from the Pukekohe and Levin soils. Values in brackets represent the standard error of the mean (n = 5).

Element	Pukekohe Soil	Levin Soil
Cd	0.011 (0.003)	0.008 (0.002)
Cu	0.13 (0.02)	0.12 (0.01)
Zn	0.38 (0.06)	0.18 (0.02)
Ni	0.090 (0.012)	0.014 (0.002)
Fe	0.65 (0.20)	0.51 (0.04)
Al	0.82 (0.20)	0.49 (0.04)

2.2. Collection of Composts

We collected municipal compost from Living Earth Ltd. (Christchurch, New Zealand). The source materials for this compost were mainly lawn clippings, tree prunings, and food waste. Hereafter, this compost will be referred to as MC (Municipal Compost). The second compost, manufactured from sawdust and animal residues (manure and carcasses), was obtained from Parkhouse Garden Supplies (Christchurch, New Zealand). Hereafter, this compost will be referred to as SC (Sawdust Compost). Table 1 shows the chemical properties of the composts.

2.3. Incubation Experiment

The two composts were mixed into separate subsets of the spiked soils at a rate of 2.5% w/w (Table 3). This corresponds to a rate of 50 t/ha (assuming a plough depth of 15 cm and bulk density 1.3 gm/cm³), after Horrocks et al. [42]. Each soil had a control where no compost was applied. For each soil and soil–compost mixture, three incubation regimes were imposed under dark conditions. These sought to simulate a typical soil temperature (T-19, incubation at 19 °C) that might be encountered in temperate regions, as well as extreme cases intended to maximise microbially driven soil C turnover using incubations at 30 °C with and without N added as urea (T-30+N and T-30, respectively). Each treatment was replicated thrice.

Table 3. Summary of experimental design.

Soil—Compost Mixture	Treatments (n = 3)
Levin soil control (no compost)	T-19, T-30, T-30+N
Levin soil + 2.5% municipal compost	T-19, T-30, T-30+N
Levin soil + 2.5% sawdust compost	T-19, T-30, T-30+N
Pukekohe soil control (no compost)	T-19, T-30, T-30+N
Pukekohe soil + 2.5% municipal compost	T-19, T-30, T-30+N
Pukekohe soil + 2.5% sawdust compost	T-19, T-30, T-30+N
T-19 = Incubated at 19 °C	
T-30 = Incubated at 30 °C,	
T-30+N = Incubated at 30 °C with added Urea-N.	

The experiment started on 11th March 2014. Analytical-grade urea (N₂H₄CO LabServ™, Biolab Aust. Ltd., Hindmarsh, Australia) was applied in T-30+N experimental units in three separate applications on weeks 1, 5, and 13 as a source of N for microorganisms to enhance the microbial activity in soils. A total of 413 mg of urea (dissolved in 10 mL of water) was added to the N treatments, which was equivalent to an N addition rate of 200 kg/ha.

The soils and soil–compost mixtures were mixed twice a week, and their moisture content was maintained at 25% through compensating for lost weight with deionized water. Each replicate was sampled after 1, 5, 9, 13, 21, 31, and 49 weeks, where 40 g of soil was collected from each box. The change in organic matter (soil or soil with compost) was

determined through measuring total C. We did not determine CO₂ emissions from the soils. The samples were dried in an oven at 70 °C until a constant weight was obtained (<5 days) and sieved (2 mm nylon mesh) for chemical characterisation (see Section 2.5).

2.4. Pot Trial

Al Mamun et al. [37] measured Cd uptake by potatoes from a Pukekohe soil, freshly amended with MC. Subsets of unamended and MC-amended soils (rate of 2.5% *w/w*) left-over from the work of Al Mamun et al. [37] a year prior (and now 'aged') were transferred into 5 kg plastic pots. Each treatment was replicated thrice. The pots were placed in a randomised block design in the Plant Growth Unit at Lincoln University. Seed potato (*Solanum tuberosum*; var: 'Nadine') was obtained from Morton and Smith DWE, Christchurch, New Zealand. Seed potatoes were sprouted in moist trays covered with black polythene. After one week, the plants were transferred to individual pots and grown for nine weeks, during which the pots were watered regularly while maintaining the moisture content below the soils' maximum water holding capacity to avoid excessive drainage. The tubers had formed by the end of the growth period and the shoots were showing signs of chlorosis, at which point the tubers were gently removed from the soil to avoid scratching (and, hence, soil contamination). They were then washed thrice with tap water, dried using paper towels, and weighed to get the fresh weight of the potato tubers. The tubers were then washed thrice with reverse osmosis water and thrice with deionized water. The peel (1–2 mm thickness) was separated with a clean stainless peeler. The peeled tubers were divided into quarters, placed in paper bags, and dried in an oven at 70 °C until a constant weight was obtained. The dry weights were recorded, after which the tubers were ground using a Retsch ZM200 grinder (Düsseldorf, Germany) and stored in sealed plastic vials.

2.5. Chemical Analyses

Soil pH was measured at a soil–water ratio of 1:2.5 [43] using a SevenEasy™ pH sensor (Mettler Toledo, Hamilton, New Zealand). Total C (forthwith C_T) and N concentrations were analysed in soil and compost samples using an Elementar Vario Max CN elemental analyser (Elementar®™, Langensfeld, Germany). Cation exchange capacity of the original materials was measured using the 0.01 M silver thiourea (AgTU) method [43]. Samples (0.70 g of dry soil with 35 mL of 0.01 M AgTU in a 50 mL vial) were placed on an end-over-end shaker for 16 h, followed by centrifuging for 10 min at 2000 rpm. The supernatant was filtered through a Whatman no. 40 filter and analysed for silver (Ag) using the ICP-OES.

Cadmium extractable through 0.05 M Ca(NO₃)₂ was used to provide a general estimate of Cd phytoavailability [44,45]. Briefly, 5 g of soil was mixed with 30 mL of 0.05 M Ca(NO₃)₂ and agitated using a vortex mixer for 3 min, shaken on an end-over-end shaker for 2 h, and centrifuged at 3000 rpm for 10 min. The supernatant was filtered through a Whatman no. 52 filter paper into 30 mL vials and analysed using ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometer), Varian 720, Palo Alto, CA, USA.

Pseudo-total elemental analyses of soil and plant samples were carried out using microwave digestion in 8 mL of Aristar™ nitric acid (± 69%), after which the digest was diluted with milliQ water to a volume of 25 mL and filtered using Whatman no. 52 filter paper [46]. The concentrations of B, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mo, Mn, Na, P, S, and Zn were determined using ICP-OES (Varian 720, Palo Alto, CA, USA).

The Certified Reference materials (soil and plant material, International Soil analytical Exchange—ISE 921 and International Plant analytical Exchange IPE 100, Wageningen University, Wageningen, The Netherlands) were analysed to confirm recovery of elements in the digests.

2.6. Statistical Analysis

Data were analysed using Minitab® 17 (Minitab Inc., State College, PA, USA) and Microsoft Excel 2013. Data were tested for normality, and log-normally distributed data

were log transformed prior to analysis. Significant differences were assessed using Analysis of Variance (ANOVA) with a post-hoc Fisher's test. Correlation analyses were used to determine significant temporal trends in extractable elements. The level of significance for both tests was set at 0.05.

3. Results

3.1. Changes in Total Carbon Concentration with Time

The addition of municipal compost and sawdust compost at 2.5% *w/w* initially increased C_T in the soils by 0.65% and 0.75%, respectively. However, by week 49, C_T in soil and soil–compost mixtures had significantly decreased in all treatments (control, municipal compost, and sawdust compost) in both soils (Figure 1A–F). In general, the magnitude of decrease followed the order $T-19 < T-30 < T-30+N$, indicating that the organic matter degradation was more rapid at higher temperatures and with added N. While the differences in C_T between T-30 and T-30+N soils were generally not significant throughout the incubation (Pukekohe soil + MC after 21 weeks was the exception), the difference was significant between the T-19 soil and the other two treatments in most soils after 13 weeks. Some treatments had a small but significant increase in C_T during weeks 5–13 (Figure 1, Table S1).

3.2. Effect of Composts on Extractable Cadmium and Other Elements

The $\text{Ca}(\text{NO}_3)_2$ -extractable Cd concentrations in both the treatments and the controls decreased overall during the 49 week incubation. The reduction was greater in the two compost-amended soils than in the control soils (Figure 2). However, within that time $\text{Ca}(\text{NO}_3)_2$ -extractable Cd concentrations increased significantly between weeks 2 and 10, before decreasing to achieve a net reduction. At the end of the incubation, the extractable Cd concentration in the compost treatments had decreased to between 23 and 89% of the control soils, with the greatest reduction in both soils generally achieved in the warmer incubations (Figure 2).

In contrast to Cd, the composts had little effect on the $\text{Ca}(\text{NO}_3)_2$ -extractable Cu, Mg, Mn, and P, while there were significant increases in $\text{Ca}(\text{NO}_3)_2$ -extractable K, Na, and S (Tables S3 and S5–S10). Both composts increased the $\text{Ca}(\text{NO}_3)_2$ -extractable Zn in the Levin soil but not the Pukekohe soil (Table S11). Regarding the temporal changes in $\text{Ca}(\text{NO}_3)_2$ -extractable elements, the concentrations of Cu, K, Mn, Na, P, S, and Zn followed a similar pattern to Cd in that they either remained unchanged or significantly decreased during the experimental period. In contrast, concentrations of Fe significantly increased (Table S4). Aluminium mostly remained unchanged or significantly increased in the Pukekohe soil (Table S2). Magnesium remained unchanged throughout the experiment (Table S6). The urea application to the soils and soil–compost mixtures decreased the pH of soils by ca. 0.4 pH units (Table S1).

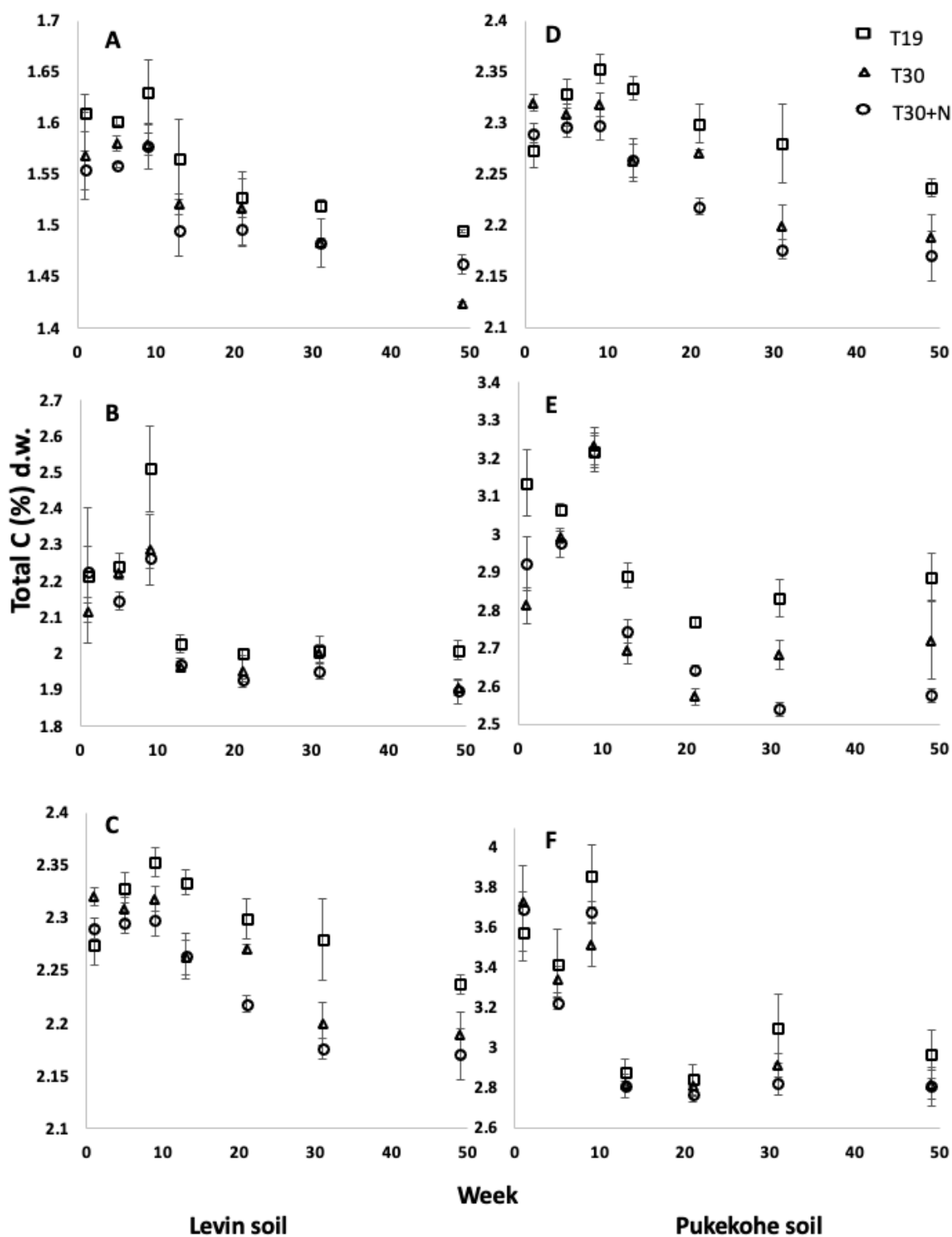


Figure 1. Changes of total C (C_T) in soils with time in treatments T-19, T-30, and T-30+N ((A) Levin soil control, (B) Levin soil+MC, (C) Levin soil+SC, (D) Pukekohe soil control, (E) Pukekohe soil+MC, (F) Pukekohe soil+SC). Error bars represent the standard error of the mean (n = 3).

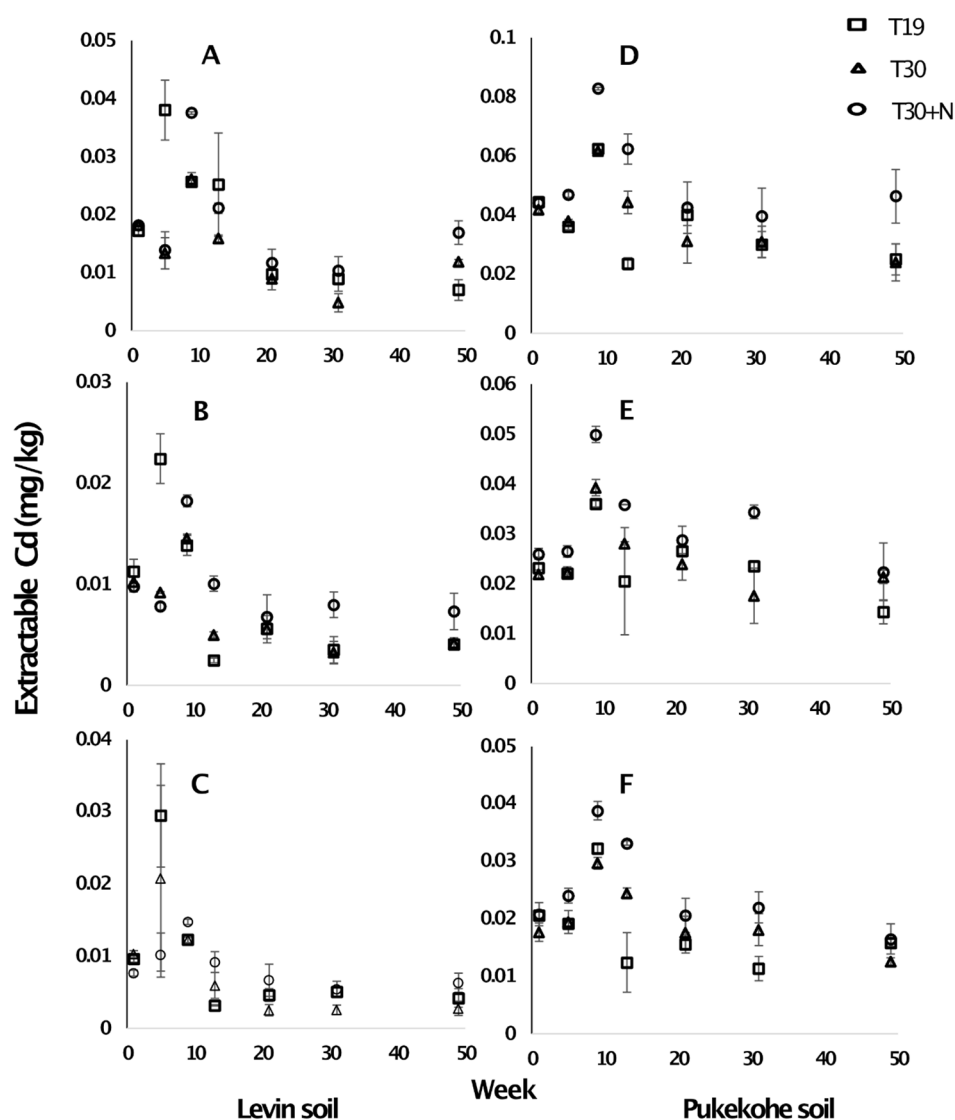


Figure 2. Changes in $\text{Ca}(\text{NO}_3)_2$ -Extractable Cd with time in treatments T-19, T-30, and T-30+N ((A) Levin soil control, (B) Levin soil+MC, (C) Levin soil+SC, (D) Pukekohe soil control, (E) Pukekohe soil+MC, (F) Pukekohe soil+SC). Error bars represent the standard error of the mean ($n = 3$).

3.3. Accumulation of Cd and Other Elements by Potato Grown in Incubated Soils

Cadmium uptake by the potatoes grown in both of the MC-amended soils (freshly amended and aged soil) was about half of the control soils (Table 4). The concentration of Cd in the peeled potato tubers ranged from 0.011 to 0.044 mg/kg dry weight (d.w.), equivalent to 0.002–0.008 mg/kg fresh weight, which is well below the Maximum Limit of 0.1 mg/kg F.W. stated in the Food Standards of Australia and New Zealand (FSANZ) standard 1.4.1 and EU legislation (EU 1881/2006). Comparing the freshly amended soil with aged soil, there was a significant decrease in Cd in both the controls and the compost-amended soil. This decrease mirrors the results of the $\text{Ca}(\text{NO}_3)_2$ extractions. Unlike the extractions, there was no significant increase in Fe uptake into the potato tuber.

Table 4. Mean elemental concentrations (mg/kg DW) in the peeled tubers grown in a freshly amended compost-treated soil [37] and an “aged” soil that had been amended with compost for 1 year, and total C and Ca(NO₃)₂-extractable Cd concentrations in Pukekohe soils. The different letters (A–D) show where differences between means are significant.

Treatments	Freshly-Amended Soil #		Soils Aged for 1 Year	
Parameters	Control	Municipal Compost	Control	Municipal Compost
Cd	0.040 (0.003) ^A	0.020 (0.011) ^B	0.020 (0.001) ^B	0.011 (0.001) ^C
B	7.40 (0.04) ^A	7.33 (0.3) ^A	5 (0.5) ^B	6 (0.2) ^B
Ca	419 (65) ^A	289 (15) ^B	247 (11) ^B	357 (40) ^{AB}
Cu	6.1 (0.3)	6.4 (0.4)	5.7 (0.5)	5.5 (0.1)
Fe	23 (2) ^A	21 (0.2) ^{AB}	19 (1) ^{AB}	18 (1) ^B
K	20811 (424) ^A	21565 (705) ^A	21833 (408) ^A	20256 (544) ^B
Mg	1268 (72) ^B	1253 (39) ^B	1465 (46) ^A	1244 (103) ^B
Mn	6.7 (0.7) ^A	6.7 (0.2) ^A	6.2 (0.3) ^A	4.8 (0.4) ^B
Mo	0.6 (0.05) ^B	1.4 (0.2) ^A	0.8 (0.2) ^B	1.5 (0.1) ^A
Na	87 (16) ^B	153 (1) ^A	75 (8) ^B	163 (19) ^A
P	3356 (179) ^{AB}	3245 (60) ^B	3521 (106) ^A	3351 (26) ^{AB}
S	1248 (71) ^{BC}	1214 (37) ^B	1606 (68) ^A	1336 (84) ^{BC}
Zn	20 (2)	19 (1)	17 (0.3)	16 (0.5)
Extractable Cd in soil	0.011 (0.003) ^A	0.002 (0.000) ^B	<0.001	<0.001
Total C in soil (%)	2.29 (0.02) ^C	3.0 (0.01) ^A	2.0 (0.01) ^D	2.4 (0.01) ^B

Data from Al Mamun et al. [37].

4. Discussion

The overall decrease in the total carbon concentration of all the soils and soil–compost mixtures shows the mineralization of organic matter (either from the compost or the original soil) by microorganisms, and is consistent with other compost-amended soil incubation studies that have used measurements of CO₂ production to show this [47,48]. The greater decrease at higher temperatures with added N was expected due to the increased microbial activity under these conditions [49,50]. The brief and small increase in C_T in all treatments between weeks 5 and 10 was most likely due to the rapid mineralization of oxygen-rich, low-molecular-weight moieties such as carbohydrates that are easily consumed by soil microorganisms [51], thus briefly increasing the C concentration, particularly in the compost-amended soils.

We did not measure the change in CEC in our soils. Other authors have reported a general reduction in the soils’ organic matter results in a decrease of the soils’ CEC [52], which would lead to a concomitant increase in cation solubility. Nevertheless, the decomposition of composts has also been reported to produce humic substances with a higher CEC [53,54], which would be consistent with our finding that the solubility of Cd and other elements either remained unchanged or even decreased in the compost-treated soils. The elements whose Ca(NO₃)₂-extractable concentrations decreased commonly exist as both cations (Cd, Cu, K, Na, and Zn) and oxyanions (P and S) in aerobic soils [55]. Therefore, changes in the charges of functional groups in the organic matter over time is unlikely to have had a significant impact on the solubility of those elements. The Cd results are consistent with previous studies where EDTA and DTPA-extractable Cd in compost-amended soils were lower than in corresponding control soils up to 6 months after application [40]. In a phytoremediation/phytostabilisation operation on heavily contaminated soils, compost addition led to an improvement in biodiversity after five years [56]. The lack of consistent differences in the Ca(NO₃)₂-extractable Cd across the different temperature and nitrogen addition treatments (T-19, T-30, and T-30+N) indicates that the aforementioned breakdown of labile organic materials did not affect the sorption of Cd to these significantly. Increased formation of strong organo–Cd associations in the ageing compost [57] may also have contributed to the metal immobilisation.

The significant increases in $\text{Ca}(\text{NO}_3)_2$ -extractable Fe and Al concentrations suggest that the decreases in the extractable concentrations of most elements could have been partly an artefact of the experimental conditions. The regular mechanical disturbance of the moist soils will have disrupted soil aggregates [55,58,59] that would have maintained high surface areas of reactive surfaces for binding elements and high concentrations of colloidal Fe and Al [60]. These colloids may have occluded sorbed elements and thus reduced their solubility. This may have also occurred with colloidal organic matter liberated from aggregates whose re-attachment and coating of reactive surfaces would have further reduced the solubility of elements sorbed onto those surfaces. This process is a well-recognised mechanism for stabilising organic matter in soils [61–63].

In the field, mechanical disturbance of aggregates may occur following repeated ploughing. Previous studies on the role of ploughing on the solubility and phytoavailability of elements in soil have shown contradicting results. Lavado et al. [60] observed in a field trial that DTPA-extractable Cd concentrations did not change due to mechanical disturbance. In contrast, EDTA-extractable Cd was shown to have decreased due to mechanical disturbance for soils treated under laboratory conditions [55], which agreed with the reports of reduced Cd uptake in field-grown plants where the soils had not been subject to mechanical disturbance when compared to plants grown on mechanically disturbed soils.

The Cd concentrations in the potatoes grown here are generally below the previously reported range of concentrations (0.040–0.113 mg/kg D.W.) across different field-grown potato varieties grown in the Pukekohe region [64]. In the aged soils, the concentrations were less than 18% of the same varietal (“Nadine”) grown in the field [64]. These differences may be partly due to fresh fertiliser (including Cd) inputs to the field soils during the growing season; however, differences in Cd uptake by that variety between different regions has also been recognised as having an influence, with significantly greater uptake at lower latitudes [64]. The cooler air temperature during the growth in the austral winter may also have reduced Cd uptake in the pot trial, when compared to the field-grown potatoes that are grown mainly in the summer [65]. The reduced uptake of Cd into potato tubers in the aged compost-amended soils reflected the low extractable concentrations of the metal in the same soils. These results suggest that MC can significantly reduce phytoavailability of Cd both in soils that have been freshly amended and one year later, after the reactive organic matter fractions in the compost have been mineralized. This agrees with the results from a previous pot trial that showed a significant reduction in the Cd concentration in the grain, leaf, and stem of wheat plants six months after compost addition [36]. The fact that these effects persist for up to a year, despite a gradual loss of C from soils, suggest that natural soil processes and mechanical disturbance may be converting compost into forms that either directly bind Cd to them, rendering Cd sorbed onto mineral fractions inert, or both. Potentially, leaching losses from the pots may have contributed to the reduction in Cd uptake by potatoes. However, other authors have shown that Cd leaching is negligible. For example, Gray et al. [66] reported leaching losses of 0.27–0.86 g/ha/yr from New Zealand soils, representing < 0.05% of the total Cd loading of the soil (assuming an average concentration of 0.89 mg/kg [67], a depth of 0.15 m, and a density of 1.5 g/cm³).

5. Conclusions

The addition of composts to soil reduces the $\text{Ca}(\text{NO}_3)_2$ -extractable Cd concentrations compared to the control. While incubation with mechanical disturbance and the addition of urea resulted in a significant decrease in the soil carbon concentrations, there was no corresponding increase in $\text{Ca}(\text{NO}_3)_2$ -extractable Cd, and the plant uptake of Cd remained either unchanged or decreased over a one-year incubation period. The lack of increase in $\text{Ca}(\text{NO}_3)_2$ -extractable Cd may be partly due to the experimental conditions, which included regular mechanical disturbance, potentially occluding Cd and other elements attached to the surfaces of soil colloids. Future work should identify the formation of mineral-associated organic carbon in the compost-amended soil and elucidate the fraction

of organic matter that binds Cd in these compost-amended soils. Furthermore, field trials could confirm the longevity of compost-bound Cd in agricultural soils.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/soilsystems7040107/s1>, Table S1: pH over time (week) in Levin soil and Pukekohe with and without composts. SE is the standard error of the mean (n = 3); Table S2: Extractable Al (mg/kg) over time (week) in Levin soil and Pukekohe with and without composts. SE is the standard error of the mean (n = 3); Table S3: Extractable Cu (mg/kg) over time (week) in Levin soil and Pukekohe with and without composts. SE is the standard error of the mean (n = 3); Table S4: Extractable Fe (mg/kg) over time (week) in Levin soil and Pukekohe with and without composts. SE is the standard error of the mean (n = 3); Table S5: Extractable K (mg/kg) over time (week) in Levin soil and Pukekohe with and without composts. SE is the standard error of the mean (n = 3); Table S6: Extractable Mg (mg/kg) over time (week) in Levin soil and Pukekohe with and without composts. SE is the standard error of the mean (n = 3); Table S7: Extractable Mn (mg/kg) over time (week) in Levin soil and Pukekohe with and without composts. SE is the standard error of the mean (n = 3); Table S8: Extractable Na (mg/kg) over time (week) in Levin soil and Pukekohe with and without composts. SE is the standard error of the mean (n = 3); Table S9: Extractable P (mg/kg) over time (week) in Levin soil and Pukekohe with and without composts. SE is the standard error of the mean (n = 3); Table S10: Extractable S (mg/kg) over time (week) in Levin soil and Pukekohe with and without composts. SE is the standard error of the mean (n = 3); Table S11: Extractable Zn (mg/kg) over time (week) in Levin soil and Pukekohe with and without composts. SE is the standard error of the mean (n = 3); Table S12: Fisher's post hoc test of the data used in Figure 1 (A–F). Values with the same capital letters in the rows are not significantly different. Values with the same lower-case letters in the columns are not significantly different. The “*” indicates no significant difference; Table S13: Fisher's post hoc test of the data used in Figure 2 (A–F). Values with the same capital letters in the rows are not significantly different. Values with the same lower-case letters in the columns are not significantly different. The “*” indicates no significant difference.

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