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Uptake of ΣDDT, Arsenic, Cadmium, Copper, and Lead by Lettuce and Radish Grown in Contaminated Horticultural Soils

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Horticultural soils can contain elevated concentrations of selected trace elements and organochlorine pesticides as a result of long-term use of agrichemicals and soil amendments. A glasshouse study was undertaken to assess the uptake of weathered ΣDDT {sum of the *p*,*p*′- and *o*,*p*-isomers of DDT [1,1,1-trichloro-2,2-*bis*(*p*-chlorophenyl)ethane], DDE [1,1-dichloro-2,2-*bis*(*p*-chlorophenyl)ethylene] and DDD[1,1-dichloro-2,2-*bis*(*p*-chlorophenyl)ethane]}, arsenic (As), cadmium (Cd), copper (Cu), and lead (Pb) residues by lettuce (*Lactuca sativa*) and radish (*Raphanus sativus*) from field-aged New Zealand horticultural soils. Concentrations of ΣDDT, DDT, DDE, Cd, Cu, and Pb in lettuce increased with increasing soil concentrations. In radish, similar relationships were observed for ΣDDT, DDE, and Cu. The bioaccumulation factors were less than 1 with the exception of Cd and decreased with increasing soil concentrations. Lettuce Cd concentrations for plants grown on four out of 10 assayed soils were equivalent to or exceeded the New Zealand food standard for leafy vegetables of 0.1 mg kg^{-1} fresh weight. Concentrations of As, Pb, and ΣDDT did not exceed available food standards. Overall, these results demonstrate that aged residues of ΣDDT, As, Cd, Cu, and Pb in horticultural soils have remained phytoavailable. To be protective of human health, site-specific risk assessments and soil guideline derivations for residential settings with vegetable gardens need to consider the produce consumption pathway.

KEYWORDS: Phytoavailable; arsenic; cadmium; copper; lead; ΣDDT; lettuce; radish; orchard soils

INTRODUCTION

The historic use of agrichemicals and superphosphate fertilizers containing trace elements and organochlorine pesticides can result in contamination of horticultural land. Internationally, former horticultural land on the edge of urban areas is progressively being developed for residential subdivision, raising questions about the potential exposure of residents' to residual soil contaminants (*1*). Recent investigations have confirmed that former horticultural land in New Zealand (NZ) can contain elevated concentrations of arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), and ΣDDT as a result of agrichemical use (*2*). ΣDDT is the sum of the *p*,*p*′- and *o*,*p*-isomers of DDT [1,1,1-trichloro-2,2-*bis*(*p*-chlorophenyl)ethane] and their respective degradation products, *p*,*p*′- and *o*,*p*-DDE [1,1-dichloro-2,2-*bis*(*p*-chlorophenyl)ethylene] and *p*,*p*′- and *o*,*p*-DDD [1,1-dichloro-2,2-*bis*(*p*-chlorophenyl)ethane]. *p*,*p*′-DDT and *p*,*p*′-DDD were widely used as insecticides in NZ from the 1940s until the 1970s, replacing earlier lead arsenate insecticides. Arsenic was also the active ingredient in some herbicides. A range of Cu-based products have been historically and are currently used as fungicides, and Cd is a contaminant present in phosphate fertilizers (*2* and references therein). Exposure from the consumption of home-grown vegetables is one of the pathways considered by regulatory agencies when establishing soil guidelines protective of human health for residential settings and when undertaking site-specific risk assessments.

The uptake of contaminants by plants has been shown to vary with soil type, species of plant, contaminant concentration, and contaminant source (*3*–*5*). Few studies have measured the uptake of aged contaminants from horticultural soils, and only a limited number of studies have investigated the concurrent uptake of organic contaminants and trace elements (*5*). A limited number of previous studies have investigated trace element uptake by edible plants grown in NZ soils (*6, 7*). These studies indicate that field-aged trace elements in NZ horticultural soils are likely

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to be phytoavailable and warrant further investigation. While data on the uptake of aged ΣDDT residues by plants in NZ soils has not previously been published, studies from other countries have demonstrated that plants are able to accumulate trace elements and DDT residues from soil (*3, 8*). Previous studies investigating the plant uptake of trace elements and DDT have been principally carried out on Northern Hemisphere soils derived from basalts and formed by glacial activity. In comparison, soils in NZ tend to be younger volcanically derived soils dominated by tephra deposits. NZ soils also contain a higher proportion of variable charge minerals than Northern Hemisphere soils and can have high allophane and organic carbon contents (*9*). These broad differences in soil properties may affect the fate and behavior of DDT residues in NZ soils, particularly their phytoavailability.

In this study, we report an investigation of the uptake of ΣDDT, As, Cd, Cu, and Pb by two edible plant species, lettuce (*Lactuca sativa*) and radish (*Raphanus sativus*), grown in field-contaminated NZ soils. These vegetable varieties were selected as they are commonly grown in home gardens in NZ and are representative of root and leafy crops. The investigations reported in this paper were undertaken as part of a wider evaluation of the bioavailability and toxicity of aged contaminant residues in NZ horticultural soils.

Specific objectives of this investigation were (i) to determine if ΣDDT, DDT, DDE, As, Cd, Cu, and Pb in horticultural soils were available for uptake by common vegetable plants and, if so, to establish the relationship between plant tissue and soil contaminant concentrations and (ii) to calculate bioaccumulation factors (BAFs) for use in risk assessments for former horticultural land and to determine if concentrations of ΣDDT and trace elements in vegetables grown on former horticultural soils could exceed current NZ regulatory criteria.

MATERIALS AND METHODS

Soil Sampling. Representative composite bulk soil samples were collected from the A horizon (nominal depth, 15 cm) of four long-term horticultural properties (three pipfruit orchards and one vineyard) and four control sites (two regenerating native vegetation sites and two grazing paddocks) using a stainless steel spade within a 1 hectare block on each site using a "Z" sampling pattern. Additional contaminant concentrations (orchard 3 and orchard 4) were prepared by blending the soil from orchard 2 with the soil from the adjacent regenerating native vegetation site (bushblock 2).

Glasshouse Trial. The method for the plant trial was adapted from Gray et al. (*6*). Four replicate pots were prepared for each plant species and each soil by weighing sieved (<4 mm), field-moist soil [equivalent to 500 g dry weight (DW)] into a 15 cm diameter pot lined with polyethylene to prevent moisture loss and contact of the soils with the pots. Lettuce seedlings were grown from commercial seed (Yates) and planted as 13 day old seedlings, and radish seeds (Yates) were oversown and thinned to a maximum of five per pot at 10 days old. The pots were randomly placed on benches in a glasshouse, and the soil was maintained at 75% water-holding capacity (WHC) with deionized water. Supplementary lighting was not used, and the temperature was maintained between 10 and 25 °C with an average minimum temperature of 14 °C and an average maximum temperature of 24 °C obtained for the duration of the trial. The plants were fertilized twice during growth using a nutrient solution prepared from analytical grade reagents [NH_4NO_3, $Ca(H_2PO_4)_2 \cdot H_2O$, K_2HPO_4, K_2SO_4, and $MgSO_4 \cdot 7H_2O$] at an application rate equivalent to 100, 40, 60, 17, and 10 kg ha^{-1} of N, P, K, S, and Mg, respectively. Lettuces were harvested 43 days after germination, and the radishes were harvested after 35 days. Adhering soil particles were removed from all harvested plant parts by washing under running water, rinsing in distilled water, followed by a final rinse in either doubly distilled or deionized water. The plant material was freeze-dried (Dynavac Freeze Drier model FD12) and ground (Tecator Knifetec 1095 sample mill) in preparation for analysis.

DDT Analyses. *Soil.* DDT residues were analyzed using a method developed and modified from U.S. EPA Methods 3550C Ultrasonic extraction and 8081B Organochlorine Pesticides by Gas Chromatography (GC). The in-house standard operating protocol (SOP), registered by International Accreditation New Zealand, was optimized and validated for the extraction and analysis of organochlorine pesticides in sediments and soils (*10*). Oven-dried (30 °C, <2 mm) soil samples (10 g) were remoistened by the addition of 1 mL of distilled water and 1 mL of concentrated phosphoric acid. Sufficient Na_2SO_4 (10−20 g) to disperse sample aggregates was added, and the soils were thoroughly mixed by hand. All soil samples were spiked with the internal standard aldrin at a level representative of the expected DDT residue concentrations and extracted with 50 mL of 2:3 (v/v) acetone:hexane using sonication (30 min, Bandolin Sonorex 10P) followed by shaking on a rotary shaking table (300 rpm for 60 min). Following extraction, the hexane was partitioned by addition of Milli-Q water, an aliquot was purified using silica gel miniadsorption chromatography (Davisil, activated overnight at 130 °C), and the analytes were eluted with 2.5 mL of 20% ethyl-acetate in hexane. The SOP employed to analyze OC pesticides in soil and plant material incorporated quality assurance/quality control (QA/QC) procedures consistent with ISO 17025 operating principles. Each batch of samples (maximum 24 samples) included a solvent blank, solvent spike, control soil blank, and control soil spike. In-house QC soil samples were analyzed with each batch of samples, and one duplicate soil sample was analyzed for every 10 samples. All QA/QC samples were spiked with aldrin at an equivalent concentration of 0.250 mg kg^{-1}. The solvent spike and the control soil spike were spiked with a mixed organochlorine pesticide standard prepared in *iso*-octane to provide a soil concentration equivalent to 0.250 mg kg^{-1}.

Plant Tissue. Freeze-dried plant samples (0.5 g) were spiked with aldrin as an internal recovery standard and extracted with 15 mL of 2:3 (v/v) acetone:hexane using sonication (10 min) and rotary shaking (60 min at 300 rpm). The hexane and extracted DDT residues were recovered by partitioning against MilliQ water. The upper hexane layer was recovered, shake extraction was repeated two more times with 6 mL of hexane for 30 min, and the recovered hexane solutions were combined and dried by passing through a column of Na_2SO_4. The sample extract was reconstituted in dichloromethane, filtered through an 0.45 mm PVDF membrane acrodisc filter, and subjected to gel permeation chromatography (GPC) using a Shimadzu LC-10AT HPLC system connected to a Shimadzu SPD-10A UV detector and FRC-10A fraction collector. One milliliter of filtered DCM extract was injected onto two GPC columns (44 cm × 1 cm diameter columns packed with Biobeads Sx-8) connected in series and eluted with DCM at a flow rate of 1.4 mL/min. The eluting sample was collected in two separate volumetric fractions comprising lipids and organochlorine pesticides. The organochlorine pesticide fraction was blown to dryness using gentle heat and N_2, dissolved in hexane, and purified using florosil column chromatography. The purified extract was concentrated using N_2, exchanged into *iso*-octane, and diluted as necessary for analysis by GC-electron capture detection (ECD).

Each batch of plant samples included procedural blanks and solvent and control plant sample spikes as QC samples. The solvent and control plant tissue QA samples were spiked with a mixed organochlorine standard to provide a concentration equivalent to 100 μg kg^{-1} plant material. The internal recovery standard aldrin was spiked at an equivalent level of 200 μg kg^{-1} for lettuce samples and 100 μg kg^{-1} for radish hypocotyl and leaf samples.

All purified sample extracts were analyzed by GC-ECD (Varian 3600 CX, Varian 1078 split/splitless injector, and Varian 8200 CX autosampler). An Agilent HP-5 glass capillary column, 30 m × 0.25 mm i.d. × 0.25 mm phase thickness, was used to chromatographically separate the target compounds. The initial column temperature was held at 80 °C for 1 min, increased at 15 °C/min to 180 °C and held for 4 min, increased at 1.5 °C/min to 220 °C, and then increased at 50 °C/min to 320 °C, where it was held for 10 min. The injector and detector temperatures were held at 250 and 320 °C, respectively. A 1 μL aliquot

of sample extract was injected in purged-splitless mode with a splitless time of 45 s. Helium was used as a carrier gas at a flow rate of 1.2 mL/min and injector purge flow of 50 mL/min. Millenium acquisition software (Waters Corp.) was used to acquire and analyze the data using external standard calibration. The quantified results were not corrected for the recovery of the internal recovery standard (aldrin), and residue concentrations are reported on a DW basis.

The potential for DDT to degrade to DDE during high-temperature injection was recognized (*11*) and was monitored and assessed during each sample analysis run. An injection liner test mix containing *p*,*p*′-DDT, heptachlor, endrin, and endosulfan was analyzed immediately before and after each batch of samples to determine if these compounds were breaking down to their characteristic degradation products. If degradation of the compounds was observed, remedial maintenance of the GC injection system and analytical capillary column was carried out. Within each batch of samples being analyzed, sets of 20 samples were bracketed by a solvent blank and 5 and 50 ppb calibration standards. Individual compound responses for the *p*,*p*′- and *o*,*p*-isomers of DDT and DDE in the 5 and 50 ppb calibration response standards were compared throughout the course of a sample run to determine if DDT was degrading to DDE. If the relative response of the *p*,*p*′- and *o*,*p*-isomers of DDT were observed to decrease and/or the response of the *p*,*p*′- and *o*,*p*-isomers of DDE increased, the GC injector and capillary column underwent appropriate maintenance, and the affected samples were reanalyzed.

Trace Elements. *Soil.* Trace elements in soils (oven-dried at 30 °C, <2 mm) were extracted using U.S. EPA Method 200.2 Total Recoverable Metals. Briefly, 1 g of sample was digested with 4 mL of 50% HNO_3 and 10 mL of 20% HCl at 85 °C for 30 min. As and Cd were determined by inductively couple plasma mass spectrometry (ICP-MS) (Elan 6000), and Fe, Cu, and Pb were determined by ICP-optical emission spectroscopy (OES) (GBC Integra XL). A subset of the soil samples was analyzed for Cu and Pb using ICP-MS and ICP-OES, and good agreement was obtained between both sets of results. QA/QC measures included analysis of procedural blanks and replicates of a CRM soil (GBW07401), and one duplicate sample was analyzed for every 10 samples.

Plant Tissue. Freeze-dried and ground plant samples (0.5 g) were digested using a modification of the method of Hamon et al. (*12*). The samples were predigested in 5 mL of concentrated nitric acid overnight at room temperature followed by digestion at 100 °C in a digestion block (custom-made) for 1 h followed by 1 h at 120 °C. A procedural blank, one replicate of CRM GBW 7603 (bush branches and leaves) and one duplicate per 10 samples, was included in each batch of 40 samples. The plant digests were analyzed for As, Cd, Cu, Fe, and Pb by ICP-OES and ICP-MS as appropriate. The results reported for Fe in plant tissue and for Cu concentrations in radish leaves were determined using ICP-OES.

NZ Soil Bureau methods were used to determine the total organic carbon (TOC) content (Walkley−Black method), pH (1:2.5 soil:water ratio), Olsen P content (0.5 M $NaHCO_3$ at pH 8.5), and cation exchange capacity (CEC) (0.01 M silver thiourea) of the soils on air-dried and sieved (<2 mm) soils (*13*). The method of Konert and Vandenberghe (*14*) was used to prepare field-moist soils for particle size analysis, and the particle size was determined by laser diffraction analysis using a Malvern Instruments Mastersizer.

Statistical Analysis. Data were log-transformed as required for statistical analyses using customized Microsoft Excel worksheets and Minitab (version 14.20). To avoid overestimating plant tissue and soil concentrations of ΣDDT, zero was used for results less than the detection limits for both plant and soil analyses.

RESULTS AND DISCUSSION

Performance of Analytical Methods. The QA/QC data demonstrated robust performance of the analytical methods employed to measure the full range of analytes in soil and plant material. The 95% confidence intervals for mean recoveries of individual isomers of DDT, DDE, and DDD from spiked soil at 0.25 mg kg^{-1} were 110 ± 9 and 109 ± 15% for the two sample batches ($n = 2$). The 95% confidence intervals for the mean recovery of the internal standard aldrin from plant trial soil samples were 94 ± 7, 94 ± 1, and 76 ± 7% for samples spiked to 0.1, 5, and 25 mg kg^{-1} aldrin, respectively. The mean % relative standard deviation (RSD) for analysis of ΣDDT in duplicate plant trial soil samples was 15% ($n = 3$). Target analytes in all solvent blanks were below detection limits.

The mean % RSDs for ΣDDT from duplicate analyses of plant tissue samples were 15, 8, and 8.5% for lettuce leaves, radish hypocotyls, and radish leaves, respectively. The 95% confidence interval for mean recoveries of DDT compounds from plant tissue was 79 ± 7% at a spike rate of 200 μg kg^{-1} and ranged from 76 ± 4 to 135 ± 11% at a spike rate of 100 μg kg^{-1}. Mean recoveries of aldrin from plant tissue ranged from 64 to 103% for samples spiked to 200 μg kg^{-1} and from 41 to 104% for samples spiked to 100 μg kg^{-1}. A selection of radish leaf samples exhibiting low aldrin recoveries was reanalyzed to confirm the DDT compound levels, and the % RSD between the two sets of analyses was less than or equal to 23% for ΣDDT.

Method detection limits were determined from replicate analyses of spiked samples as recommended by the U.S. EPA (*15*). The calculated detection limit (DW) for the *o*,*p*′- and *p*,*p*′-isomers of DDT, DDE, and DDD was 2 μg kg^{-1} in plant tissue and 10 μg kg^{-1} in soil. Solution concentrations of target analytes less than 1 pg μL^{-1} were not quantified.

Similarly, the recovery of the analyzed trace elements in soil and plant CRMs was excellent with replicate analyses of reference samples providing acceptable levels of accuracy and precision by both instrumental methods. The mean values for copper and lead from the certified soil CRM (GBW07401) digests were 86 and 88% of the certified values when analyzed by ICP-OES and ranged from 96 to 116% when analyzed by ICP-MS. The recovery of target trace elements (excluding Cd) from plant CRM (GBW 7603 bush branches and leaves) ranged from 76 to 104% for plant samples analyzed by ICP-OES and from 73 to 111% for samples analyzed by ICP-MS. Replicate analysis ($n = 6$) of a second plant material CRM (GBW07604 poplar leaves) analyzed by ICP-OES provided 95% confidence intervals of 101 ± 1 and 100 ± 17% for the recovery of Cu and iron, respectively. Triplicate analyses of Cd in certified reference materials GBW 07604 (poplar leaves) and NIST SRM 1515 (apple leaves) were in agreement with the certified values.

ΣDDT in Lettuce and Radish Plants. Concentrations of aged ΣDDT residues in the experimental soils ranged from 17 to 12040 μg kg^{-1} (**Table 1**) and provided corresponding lettuce and radish hypocotyl ΣDDT concentrations of 0.16−1.93 μg kg^{-1} fresh weight (FW) and <0.12−11.5 μg kg^{-1} FW, respectively. There is a paucity of NZ data for organochlorine residues in vegetables with which to make comparisons. In a recent NZ total diet survey, *p*,*p*′-DDE concentrations of 30 and 5 μg kg^{-1} FW were measured in two zucchini samples (*16*). Root and leafy vegetables grown in a home garden on a former orchard in Hamilton, NZ, with a soil ΣDDT concentration of 11500 μg kg^{-1} contained *p*,*p*′-DDT concentrations ranging from <5 to 9 μg kg^{-1} FW (unpublished data supplied by Environment Waikato).

The plant tissue ΣDDT concentrations that we measured in vegetation are comparable to those reported for lettuce and radish and other vegetables in recent overseas studies. For example, concentrations of 0.32−1.15 and 0.28 μg kg^{-1} FW for *p*,*p*′-DDE and *p*,*p*′-DDT were measured in vegetables and vegetable products in the Canadian total diet survey for 1998/1999 (*17*). Mean ΣDDT concentrations of 0.06 and 0.45 and 1.44 μg kg^{-1} FW have been measured in lettuce and radish

Table 1. Concentrations of DDT Compounds (μg kg^{-1} DW) Measured in Treatment Soils[a]

treatment	*o,p′*-DDE	*p,p′*-DDE	*o,p′*-DDD	*p,p′*-DDD	*o,p′*-DDT	*p,p′*-DDT	ΣDDT
			horticulture				
orchard 1	64 ± 2	6289 ± 487	530 ± 34	789 ± 46	396 ± 10	3972 ± 108	12040
orchard 2[b]	26 ± 1	3367 ± 33	84 ± 3	292 ± 1	254 ± 6	4355 ± 70	8378
orchard 3[b]	21 ± 2	2670 ± 14	69 ± 2	229 ± 11	188 ± 10	3355 ± 99	6532
orchard 4[b]	13 ± 0.5	1575 ± 103	43 ± 0.4	138 ± 1	118 ± 3	2007 ± 139	3894
orchard 5[c]	<10	1978 ± 15	23 ± 4	139 ± 21	53 ± 2	1421 ± 519	3614
vineyard	<10	308 ± 41	<10	20 ± 3	12 ± 2	111 ± 20	451
			control				
bushblock 1	<10	17 ± 3	<10	<10	<10	<10	17
bushblock 2[b]	<10	141 ± 24	<10	<10	<10	163 ± 12	304
grazing 2[c]	<10	32 ± 20	<10	<10	<10	<10	32

[a] Results are reported as means ± standard errors ($n = 2$). Horticultural sites and their controls have the same superscript letter.

Table 2. Concentrations of DDT Compounds (μg kg^{-1} DW) Measured in Plant Tissue[a]

	o,p′-DDE	*p,p′*-DDE	*o,p′*-DDD	*p,p′*-DDD	*o,p′*-DDT	*p,p′*-DDT	ΣDDT
			lettuce				
orchard 1	<2	22 ± 1	<2	<2	<2	6 ± 0.2	28
orchard 2	<2	17 ± 1	<2	<2	<2	7 ± 0.4	24
orchard 3	<2	13 ± 1	<2	<2	<2	5 ± 1	18
orchard 4	<2	10 ± 1	<2	<2	<2	4 ± 0.3	14
orchard 5[b]	<2	10 ± 1	<2	<2	<2	<2	10
vineyard	<2	3 ± 0.1	<2	<2	<2	<2	3
bushblock 1	<2	3 ± 0.1	<2	<2	<2	<2	3
bushblock 2	<2	2 ± 0.1	<2	<2	<2	<2	2
grazing 1	NA[c]	NA	NA	NA	NA	NA	NA
grazing 2	<2	2 ± 0.2	<2	<2	<2	<2	2
			radish hypocotyl				
orchard 1	<2	124 ± 14	11 ± 1	12 ± 1	7 ± 0.5	36 ± 2	190
orchard 2	<2	77 ± 7	<2	4 ± 0.3	6 ± 0.2	44 ± 4	131
orchard 5	<2	46 ± 4	<2	<2	<2	9 ± 0.4	55
vineyard	<2	8 ± 1	<2	<2	<2	<2	8
bushblock 1	<2	<2	<2	<2	<2	<2	<2
bushblock 2	<2	3 ± 1	<2	<2	<2	<2	3
grazing 1	NA	NA	NA	NA	NA	NA	NA
grazing 2	<2	<2	<2	<2	<2	<2	<2
			radish leaf				
orchard 1	<2	53 ± 7	3 ± 1	4 ± 0.4	3 ± 0.2	14 ± 0.6	77
orchard 2	<2	33 ± 3	<2	<2	2 ± 1	16 ± 2	51
orchard 5	<2	26 ± 7	<2	<2	<2	5 ± 1	31
vineyard	<2	7 ± 0.5	<2	<2	<2	<2	7
bushblock 1	<2	3 ± 1	<2	<2	<2	<2	3
bushblock 2	<2	6 ± 1	<2	<2	<2	<2	6
grazing 1	NA	NA	NA	NA	NA	NA	NA
grazing 2	<2	3 ± 0.2	<2	<2	<2	<2	3

[a] Results are reported as means ± standard errors ($n = 4$). [b] $n = 3$ for this treatment. [c] Sample not analyzed.

grown in West Africa (*18*) and maximum ΣDDT levels of 31.7 and 39.5 μg kg^{-1} FW in lettuce and radish grown in Nanjing, China (*19*). Leeks grown in soil containing aged DDT residues (3.6 ± 0.6 μg kg^{-1} DDT and 3.5 ± 0.6 μg kg^{-1} DDE) contained 10 and 2.8 μg kg^{-1} of DDT and DDE, respectively, in the aerial parts (leaves and stem) at harvest (*20*).

The order of uptake for ΣDDT, *p,p′*-DDE, and *p,p′*-DDT on a DW basis was lettuce < radish leaf < radish hypocotyl for the three orchard soils (orchards 1, 2, and 5) used to grow both plant species (**Table 2**). The results for the bushblock, grazing, and vineyard soils are too low for a definitive trend to be identified. These differences in plant tissue ΣDDT concentrations are not explained by the mean plant lipid concentrations, which followed the order radish hypocotyl < radish leaf < lettuce. Other studies demonstrating plant uptake of aged organochlorine residues from soil have been unable to identify a pattern or mechanism that explains the differential uptake between plant species and distribution of contaminants within different tissues of a plant (*21*).

The main isomers of DDT detected in plant tissue were the *p,p′*-isomers of DDT and DDE (**Table 3**). In all plant tissues, the concentrations of *p,p′*-DDE significantly exceeded that of *p,p′*-DDT, even in the three soils where the concentration of *p,p′*-DDT was significantly higher than that of *p,p′*-DDE (refer to **Tables 1** and **2**). This is consistent with the results of previous studies that have demonstrated preferential uptake of *p,p′*-DDE into vegetables (*22*). These differences were significant for lettuce ($p < 0.002$), radish hypocotyl ($p < 0.03$), and radish leaf ($p < 0.01$) using a paired *t* test on log values. The QA/QC and GC performance monitoring systems that we implemented demonstrated that *p,p′*-DDT was not degraded to *p,p′*-DDE during GC analysis. The difference in *p,p′*-DDE/*p,p′*-DDT ratios between soil and plant can therefore be explained by three possible mechanisms: preferential uptake of DDE by the plants, degradation of DDT to DDE within the plant tissue, or enhanced degradation of DDT to DDE in the rhizosphere followed by preferential uptake of DDE. The preferential uptake of DDE by the experimental plants is most likely explained by the lower

Table 3. Concentrations of Trace Elements Measured in Plant Tissue (mg kg^{-1} DW)[a]

	As[b]	Cd	Cu	Pb	Fe
			lettuce		
orchard 1	<0.2	2.10 ± 0.14	12.1 ± 0.5	0.18 ± 0.02	63 ± 5
orchard 2	0.5 ± 0.01	1.93 ± 0.11	10.8 ± 0.4	0.39 ± 0.03	64 ± 2
orchard 3	0.4 ± 0.1	1.47 ± 0.03	9.9 ± 0.3	0.35 ± 0.03	62 ± 3
orchard 4	0.3 ± 0.01	1.23 ± 0.02	10.3 ± 0.2	0.32 ± 0.01	71 ± 1
orchard 5[c]	0.7 ± 0.2	1.49 ± 0.18	9.4 ± 0.8	0.53 ± 0.04	77 ± 4
vineyard	<0.4	1.25 ± 0.04	11.7 ± 0.4	0.32 ± 0.02	63 ± 3
bushblock 1	<0.4	0.51 ± 0.01	5.4 ± 0.3	0.19 ± 0.04	86 ± 3
bushblock 2	<0.2	0.30 ± 0.02	4.3 ± 0.3	0.16 ± 0.02	62 ± 2
grazing 1	<0.2	1.33 ± 0.06	4.8 ± 0.1	0.15 ± 0.01	66 ± 3
grazing 2	<0.4	0.82 ± 0.04	3.1 ± 0.1	0.14 ± 0.06	85 ± 6
			radish hypocotyl		
orchard 1	0.2 ± 0.1	0.45 ± 0.02	14.3 ± 0.2	0.12 ± 0.01	27 ± 1
orchard 2	1.5 ± 0.1	0.51 ± 0.02	18.0 ± 1.2	0.57 ± 0.04	46 ± 6
orchard 5	0.9 ± 0.1	0.50 ± 0.02	12.9 ± 0.7	0.97 ± 0.08	22 ± 1
vineyard	<0.4	0.35 ± 0.02	10.9 ± 0.8	1.30 ± 0.15	25 ± 2
bushblock 1	<0.4	0.30 ± 0.08	3.8 ± 0.2	0.22 ± 0.02	39 ± 2
bushblock 2	0.2 ± 0.01	0.34 ± 0.07	3.1 ± 0.1	0.76 ± 0.09	49 ± 4
grazing 1	<0.2	0.24 ± 0.01	2.5 ± 0.1	0.13 ± 0.01	39 ± 4
grazing 2	<0.4	0.54 ± 0.05	2.0 ± 0.1	0.07 ± 0.01	28 ± 1
radish leaf					
orchard 1	0.2 ± 0.03	0.81 ± 0.03	34.0 ± 1.6	0.18 ± 0.01	66 ± 4
orchard 2	0.7 ± 0.03	1.11 ± 0.03	40.0 ± 2.4	0.29 ± 0.02	55 ± 4
orchard 5	NA[d]	NA	23.4 ± 2.1	NA	75 ± 3
vineyard	NA	NA	20.3 ± 0.7	NA	81 ± 2
bushblock 1	NA	NA	6.3 ± 0.2	NA	99 ± 6
bushblock 2	<0.2	0.37 ± 0.04	4.0 ± 0.2	0.30 ± 0.03	96 ± 5
grazing 1	NA	NA	3.0 ± 0.1	NA	83 ± 2
grazing 2	NA	NA	3.2 ± 0.2	NA	94 ± 2

[a] Results are reported as means ± standard errors ($n = 4$). [b] Samples were analyzed for As in two batches with differing detection limits. [c] $n = 3$ for this treatment. [d] Sample not analyzed.

K_{ow} and K_{oc} values that combine to increase the solubility and bioavailability of DDE as compared to DDT.

DDT and other recalcitrant organochlorine compounds have been reported to be transformed by plant cell cultures including lettuce (*23, 24*). However, these experiments were conducted under specific optimized laboratory conditions, and while we cannot exclude the possibility that DDT underwent some degree of transformation to DDE within the plants used in our experiments, preferential uptake of DDE by plants is a more plausible explanation.

There was a significant linear correlation ($p < 0.001$) between the mean soil and mean plant tissue concentrations for ΣDDT and the principle metabolite *p,p′*-DDE (**Figure 1**). The concentration of *p,p′*-DDT in lettuce also increased with increasing soil concentration, but there were insufficient data points above the detection level to determine if similar relationships existed for radish. This relationship has been previously reported for carrots and potatoes grown in soil contaminated with DDT (*22*).

Tissue concentrations of both *p,p′*-DDT and *p,p′*-DDE increased with increasing soil concentration, indicating that plant uptake had occurred. Several mechanisms have been identified for plant uptake of persistent organic pollutants from contaminated soil including: root uptake and translocation through the xylem, uptake from the vapor phase via the leaves and roots, and adhesion of soil particles (*25*). The experimental design employed in this study did not allow the pathways of root uptake and translocation to be distinguished from vapor phase uptake of *p,p′*-DDT and *p,p′*-DDE, so we have to assume that a combination of these pathways contributed to the ΣDDT concentrations measured in the plant tissue.

The inclusion and subsequent extraction of DDT residues associated with soil particles are unlikely to present a significant source of DDT residues in the plant tissues. To minimize this possibility, the plant tissues were thoroughly washed to remove any adhering soil particles before freeze drying and analysis. The effectiveness of the plant washing procedure was verified by plant Fe levels, which were analyzed as a tracer for soil particles adhering to plant surfaces. The Fe concentrations measured in plant tissues (**Table 3**) were within the normal range of 29−130 mg Fe kg^{-1} DW in vegetables (*26*). Convincingly, the *p,p′*-DDE:*p,p′*-DDT ratios for the plant tissue were consistently higher than those measured for the soil, demonstrating that adhering soil particles were not the main source of *p,p′*-DDE and *p,p′*-DDT in the plant material.

Volatilization from soils is a recognized source of DDT and other organochlorine pesticides in ambient air, and vegetation has been shown to take up persistent organochlorines from the vapor phase (*27*). Volatilization and vapor phase uptake of DDT by plants in our experiments cannot be excluded, as the soil in each pot was not covered, the plants formed a canopy over the soil, and ΣDDT compounds in the glasshouse air were not measured. The consistent low concentration of ΣDDT in plants grown in control soil treatments indicates that it is unlikely volatilization of ΣDDT from higher level contaminated soil treatments and deposition to plants in other treatments occurred.

Plant uptake of *p,p′*-DDE and *p,p′*-DDT into above-ground parts of lettuce and radish indicate that root uptake and translocation of the aged DDT residues into plant tissues occurred in our experiments. This conclusion is confirmed by previous studies demonstrating root uptake and translocation of persistent chlorinated organic contaminants (*8, 28*). Recent studies propose that root exudates released by plants mobilize soil-aged organochlorine pesticides to enhance their uptake by plants (*5, 29*).

Determining the exact uptake mechanism of aged DDT residues to the plants is not critical to the outcomes of the experiment reported here. Regardless of which mechanism dominated uptake, the lettuce and radish plants accumulated DDT residues from the soil. This indicates that despite a considerable period of weathering and aging in field soils, a fraction of these historical DDT residues remain bioavailable and continue to present a potential hazard to ecosystems and human health.

Trace Element Concentrations in Plants. The maximum plant tissue trace element concentrations followed the order Fe > Cu > Cd > As > Pb for lettuce, radish leaf, and radish hypocotyls (**Table 3**). Plant tissue concentrations were generally within the ranges reported in the literature for lettuce and radish grown in potted soils (*6, 30–33*) and field trials (*34*) with comparable contaminant levels (**Table 4**).

The concentrations of As, Cu, and Pb were higher in radish than lettuce. In contrast, the concentration of Cd was greater in lettuce than radish. Trace element concentrations in the plants and individual components followed the order: radish hypocotyls > lettuce leaves > radish leaves, for As; lettuce leaves > radish leaves > radish hypocotyls, for Cd; radish leaves > radish hypocotyls > lettuce leaves, for Cu; and radish hypocotyls > lettuce leaves > radish leaves, for Pb.

The order of uptake that we obtained for As and Cd in our experiments agrees with previous studies (*32, 33, 35–37*). The order of plant uptake for Cu and Pb from soil is consistent with the results of Sauvé et al. (*38*) but contrasts to other studies reporting higher levels of Cu and Pb in lettuce than in radish hypocotyls (*35, 39*). The higher level of Pb in lettuce obtained in previous experiments may be influenced by aerial deposition of Pb, a mechanism excluded in our experiments. Our results

Table 4. Trace Element and Chemical and Physical Soil Characteristics for Plant Assay Soils[a]

soil	As	Cd	Cu	Pb	OlsenP	Fe	Mn	% TOC	pH	CEC	% clay	% silt	% sand
						horticulture							
orchard 1	15.2	0.54	366	59	89	22215	271	5.4	5.65	24	26	64	10
orchard 2[b]	35.6	0.38	314	116	85	11001	350	3.1	5.88	16	33	57	10
orchard 3[b]	28.0	0.30	243	97	65	11845	326	3.1	5.72	14	26	49	25
orchard 4[b]	18.3	0.23	160	67	41	10712	269	3.7	5.55	12	27	54	19
orchard 5[c]	5.6	0.24	73	78	56	2743	77	3.1	5.65	8	21	64	14
vineyard	2.1	0.16	117	57	40	9825	131	3.4	5.45	8	34	59	7
						control							
bushblock 1	1.7	0.04	18	10	6	9767	39	2.9	5.74	11	31	58	11
bushblock 2[b]	1.7	0.03	12	16	5	10428	177	3.6	5.03	12	18	46	36
grazing 1	2.3	0.28	17	34	12	25950	393	5.6	5.67	21	28	67	5
grazing 2[c]	0.4	0.09	3	4	9	2962	82	3.2	5.74	7	20	62	17

[a] Units are mg kg^{-1} for trace elements, Fe, Mn, and Olsen P, and the CEC is reported as me/100 g. Horticulture soils and their controls have the same superscript letter.

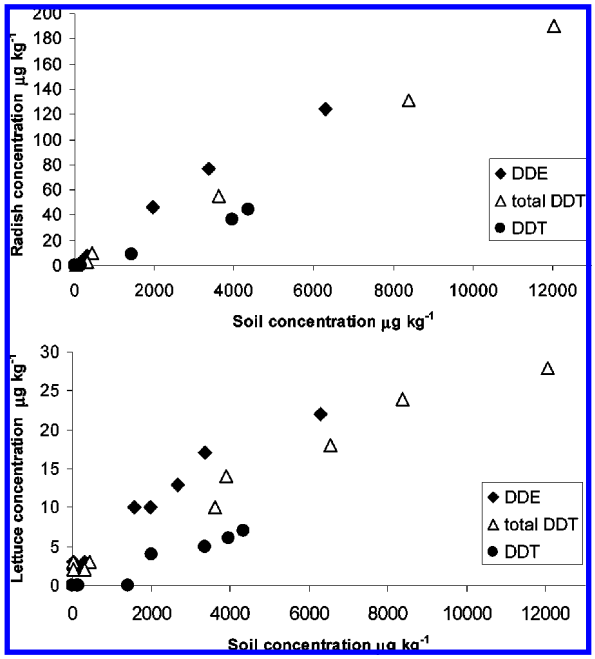

Figure 1. Relationship between radish hypocotyl, lettuce and soil ΣDDT, and *p,p′*-DDE and *p,p′*-DDT concentrations (μg kg^{-1} DW).

of higher concentrations of Cu in radish leaves vs hypocotyls are confirmed by previous studies (*4, 33, 36*) and may be due to differing physiological requirements for Cu between radish hypocotyls and leaves.

Relationship with Soil Concentrations. Our experiments demonstrated a significant linear relationship between the total concentrations of Cd, Cu, and Pb in soil and lettuce leaves, soil Cu and radish hypocotyl, but not for Cd and Pb (**Table 5**). These significant correlations are consistent with previous reports of increased trace element concentrations in plant tissues with increasing soil concentrations for spiked, aged, and pasture soils (*6, 40, 41*).

Our finding that radish concentrations of Cd and Pb were not related to soil concentrations is confirmed by Samsøe-Petersen et al. (*42*) for Cd and Aten et al. (*43*) for Pb but contrasts to other studies demonstrating increasing radish leaf and root concentrations with increasing soil Cd and Pb concentrations (*7, 30*). A possible explanation for the difference between our study and these previous reports is their use of soils with higher contaminant concentrations. Additionally, several of the reported studies utilized soils collected either from within the same contaminated site or from a more limited geographic area, reducing the influence of varying soil physicochemical properties on contaminant uptake.

Table 5. Linear Regression Equations for Relationships between Plant Tissue and Soil Contaminant Concentrations[a]

regression equation	R^2	p
lettuce		
$\log Cd_{plant} = 0.624 \times \log Cd_{soil} + 0.521$	0.95	<0.001
$\log Cu_{plant} = 0.295 \times \log Cu_{soil} + 0.350$	0.92	<0.001
$\log Pb_{plant} = 0.326 \times \log Pb_{soil} - 1.12$	0.55	0.009
$\log Pb_{plant} = 0.434 \times \log Pb_{soil} - 0.701 \times \log CEC - 0.520$	0.90	<0.001
$\Sigma DDT_{plant} = 0.0023 \times \Sigma DDT_{soil} + 2.54$	0.98	<0.001
$DDE_{plant} = 0.0034 \times DDE_{soil} + 2.93$	0.95	<0.001
radish hypocotyl		
$\log Cd_{plant} = 0.083 \times \log Cd_{soil} - 0.340$	0.0	0.472
$\log Cd_{plant} = 0.267 \times \log Cd_{soil} - 1.01 \times \log TOC - 0.756 \times clay + 1.45$	0.65	0.069
$\log Cu_{plant} = 0.506 \times \log Cu_{soil} - 0.034$	0.90	0.000
$\log Pb_{plant} = 0.726 \times \log Pb_{soil} - 1.07 \times pH - 2.83 \times \log TOC + 6.06$	0.93	0.003
$\Sigma DDT_{plant} = 0.0158 \times \Sigma DDT_{soil} - 0.70$	1.00	<0.001
$DDE_{plant} = 0.0202 \times DDE_{soil} + 1.78$	0.99	<0.001
radish leaf		
$\log Cu_{plant} = 0.621 \times \log Cu_{soil} + 0.007$	0.88	<0.001
$\log Cu_{plant} = 0.700 \times \log Cu_{soil} - 0.451 \times \log Fe_{soil} + 1.67$	0.99	<0.001
$\Sigma DDT_{plant} = 0.006 \times \Sigma DDT_{soil} + 4.20$	0.99	<0.001
$DDE_{plant} = 0.008 \times DDE_{soil} + 4.81$	0.98	<0.001

[a] Units are mg kg^{-1} DW for trace elements and μg kg^{-1} DW for DDT compounds; *p,p′*-isomers of DDT and DDE.

Soil concentrations of Cd and Pb alone did not account for their variability in radish hypocotyls and tissues. Soil organic carbon (*6, 37*) and pH (*44*) have been indentified to control phytoavailabiity of Cd in NZ soils. Multiple regression analysis of our data excluded soil pH as a significant in plant uptake of Cd. The incorporation of soil % TOC and % clay improved the fit of the linear regression model from 0 to 65.2%, but it remained insignificant ($p < 0.069$). The small size of the data set (**Table 4**) and the limited range of soil Cd concentrations (0.03−0.54 mg kg^{-1}) may have precluded the identification of controlling soil properties.

An improved linear regression fit between soil Pb and uptake by lettuce was obtained by the addition of CEC and for uptake by radish hypocotyls by the addition of soil pH and % TOC. These findings are consistent with a recent study identifying these soil properties as controlling variables for the phytoavailability of Pb in soil (*45*).

BAFs. BAFs are used to compare relative uptake values obtained from different studies and to derive soil quality guidelines protective of human exposure through vegetable consumption (*46, 47*). We calculated BAFs from our experi-

Table 6. BAFs for Uptake of Aged ΣDDT Residues and Trace Elements by Lettuce and Radish

	p,p′-DDE	*p,p′*-DDT	ΣDDT	As	Cd	Cu	Pb
			lettuce				
orchard 1	0.003	0.002	0.002	NC[a]	3.88	0.03	0.003
orchard 2	0.005	0.002	0.003	0.01	5.09	0.03	0.003
orchard 3	0.005	0.001	0.003	0.01	4.90	0.04	0.004
orchard 4	0.006	0.002	0.004	0.01	5.33	0.06	0.005
orchard 5	0.005	NC	0.003	0.13	6.20	0.13	0.007
vineyard	0.010	NC	0.007	NC	7.79	0.10	0.006
bushblock 1	0.176	NC	0.176	NC	12.82	0.30	0.020
bushblock 2	0.014	NC	0.007	NC	9.94	0.35	0.010
grazing 1	NA[b]	NA	NA	NC	4.74	0.28	0.004
grazing 2	0.063	NC	0.063	NC	9.06	0.93	0.036
			radish hypocotyl				
orchard 1	0.020	0.009	0.016	0.01	0.82	0.04	0.002
orchard 2	0.023	0.010	0.016	0.04	1.34	0.06	0.005
orchard 5	0.023	0.006	0.015	0.17	2.09	0.18	0.013
vineyard	0.026	NC	0.018	NC	2.20	0.09	0.023
bushblock 1	NC	NC	NC	NC	7.54	0.21	0.023
bushblock 2	0.021	NC	0.010	0.12	11.41	0.25	0.048
grazing 1	NA	NA	NA	NC	0.85	0.15	0.004
grazing 2	NC	NC	NC	NC	6.02	0.60	0.013
			radish leaf				
orchard 1	0.008	0.004	0.006	0.01	1.49	0.09	0.003
orchard 2	0.010	0.004	0.006	0.02	2.91	0.13	0.002
orchard 5	0.013	0.004	0.009	NA	NA	0.32	NA
vineyard	0.023	NA	0.016	NA	NA	0.17	NA
bushblock 1	0.176	NA	0.176	NA	NA	0.35	NA
bushblock 2	0.042	NA	0.020	NC	12.41	0.32	0.019
grazing 1	NA	NA	NA	NC	NA	0.18	NA
grazing 2	0.094	NA	0.094	NC	NA	0.94	NA

[a] Not calculated as residue not detected in plant tissue. [b] Not calculated as plant tissue not analyzed.

mental data by dividing the DW tissue concentration of contaminants by their respective soil concentration (**Table 6**).

BAFs calculated for the uptake of aged DDT residues by lettuce and radish in our experiments (**Table 6**) were less than 1, indicating that radish and lettuce were not bioaccumulating *p,p′*-DDT and *p,p′*-DDE under the specified experimental conditions. Our BAFs are comparable to those previously reported for plants (0.00035−0.08; median, 0.028) by the U.S. EPA (*47*), 10 plant species selected for their ability to phytoextract heavy metals from soil (mean BAF value for *p,p′*-DDE of 0.18) (*3*). The BAFs that we obtained from aged historically contaminated soils are comparable to those obtained from experiments using soils with shorter aging periods. Similar BAFs (0.014−0.036) for uptake of DDT by radish from soils 3 years after DDT application are obtained from the results reported by Lichenstein (*48*).

The BAFs obtained for trace element uptake by lettuce and radish were generally comparable with those reported in the literature for lettuce and radish grown on soils containing comparable trace element concentrations (*40, 42*) and uptake factors used by regulatory agencies to determine soil criteria (*46, 47*). The relative order of the BAFs of Cd > Cu > As > Pb was similar to the order of uptake reported for lettuce grown in biosolid amended soil (*41*).

Pearson's correlation analysis was used to determine significant relationships between BAFs and soil contaminant concentration and soil properties. The BAFs for ΣDDT and *p,p′*-DDE for lettuce and radish leaves decreased with increasing soil concentration (**Table 7**). The BAFs for lettuce uptake of measured trace elements decreased with increasing soil concentration, as did those for Cd and Cu in radish hypocotyls and Cu in radish leaves (**Table 8**). These results are consistent with previous studies that have observed decreasing uptake of trace element and DDT by plants with increasing soil concentration (*48, 49*). Two possible explanations for the observed decrease in BAFs with increasing soil concentration are (i) a limited number of binding sites for transport of contaminants physically limits uptake and (ii) the most available contaminant pool is taken up first with replenishment being kinetically limited.

The BAF for ΣDDT uptake by radish hypocotyl was inversely related to % sand ($p < 0.01$) (**Table 7**). In comparison, Beall and Nash (*50*) and Lichenstein (*48*) reported that the phytoavailability of DDT decreased with increasing soil organic matter content. There were no other significant relationships between BAFs for plant uptake of ΣDDT and *p,p′*-DDE and soil properties; however, the small size of the data set may have masked significant relationships.

For lettuce, significant inverse relationships were found between the BAFs for Cd, Cu, Pb, and Olsen P, and significant inverse relationships were found between the BAFs for lettuce uptake of Cd and Pb and soil properties including Fe, Mn, and CEC (**Table 8**). The Olsen P concentration was inversely related to the BAFs for Cu uptake by radish hypocotyls and leaves, as well as the BAFs for Cd and Pb uptake by radish hypocotyls. These significant inverse correlations between BAFs and soil properties could also be explained by a significant correlation between the soil property of interest and the total soil concentration, with the exception of the significant correlation between the BAF for lettuce uptake of Pb and the CEC ($p < 0.05$). The CEC is a key soil property that can enhance adsorption and hence reduce the bioavailability of trace elements in soil (*26*).

The observed decrease in BAFs with increasing soil contaminant concentration has implications for site-specific risk assessments and the derivation of soil criteria. To avoid under- or overestimating tissue contaminant concentrations, the BAF values chosen to estimate vegetable contaminant concentrations need to be derived from studies with comparable soil contaminant concentrations.

Comparison to Regulatory Standards. Plant tissue concentrations of accumulated contaminants were compared to NZ and international standards for contaminants in leafy and root vegetables. To enable comparison with regulatory standards, DW concentrations were converted to FW concentrations. Food standards are not set for Cu as a contaminant because it is regarded as a nutrient.

The ΣDDT levels measured in lettuce (0.0002−0.002 mg kg^{-1} FW) and radish (<0.0001−0.01 mg kg^{-1} FW) in our experiments did not exceed the United States action level for lettuce of 0.5 mg kg^{-1}, the Canadian MRL for vegetables of 0.5 mg kg^{-1}, the European MRL for vegetables of 0.05 mg kg^{-1}, the Codex alimentarius EMRL of 0.2 mg kg^{-1} for carrots, or the default NZ standard of 0.1 mg kg^{-1} FW (*51*). This may be a consequence of lettuce and radish being fast growing crops, the hydrophobicity of DDT residues limiting their uptake into these high water content vegetables, or the high sorption affinities of DDT residues for soil organic matter.

The concentration of Cd in lettuce grown on four of the ten experimental soils were equivalent to or exceeded the current NZ standard (*51*) for Cd in leafy vegetables (0.1 mg kg^{-1} FW), and a further four treatments exceeded 50% of this value. While plant tissue Pb concentrations in edible parts of the lettuce and radish plants did not exceed any of the food standards, Pb concentrations in radish hypocotyls were equal to or greater than half the standard for Pb levels in root vegetables of 0.1 mg kg^{-1} FW in three of the assayed soils (orchard 5, vineyard, and bushblock 2).

Table 7. Pearson's Correlation Coefficients for Relationships between Plant BAFs and Soil Trace Element Concentrations and Physical Characteristics (Log Transformed Variables)[a]

	soil lettuce ($n = 10$)			radish hypocotyl ($n = 8$)			radish leaf ($n = 8$)	
	Cd_{BAF}	Cu_{BAF}	Pb_{BAF}	Cd_{BAF}	Cu_{BAF}	Pb_{BAF}	Cu_{BAF}	Zn_{BAF}
Cd_{total}	**−0.943*****	**−0.744***	**−0.77****	**−0.96*****	**−0.722**	**−0.891****	−0.669	−0.7
Cu_{total}	**−0.696***	**−0.994*****	**−0.857****	−0.676	**−0.952*****	−0.577	**−0.871****	−0.54
Pb_{total}	**−0.743***	**−0.899*****	**−0.93*****	**−0.729***	**−0.837****	−0.526	**−0.828**	−0.55
Olsen P	**−0.783****	**−0.891*****	**−0.755**	**−0.766***	**−0.790***	−0.646	−0.668	−0.445
pH	−0.334	−0.262	−0.073	−0.481	−0.201	−0.58	−0.085	−0.37
% TOC	−0.572	−0.113	−0.44	−0.628	−0.416	−0.678	−0.544	−0.68
CEC	**−0.658***	−0.501	**−0.682***	−0.605	−0.663	**−0.754***	**−0.761***	**-0.85***
% clay	−0.203	−0.496	−0.41	−0.473	−0.598	−0.343	−0.577	−0.6
% silt	−0.231	0.129	0.057	−0.678	−0.167	−0.643	−0.121	−0.35
% sand	0.24	0.087	0.228	**0.745***	0.482	0.589	0.514	0.699
Mn	**−0.811****	−0.572	**−0.797****	−0.667	−0.585	−0.645	−0.683	**−0.81***
Fe	−0.456	−0.417	−0.62	−0.476	−0.619	−0.525	**−0.753***	**−0.82***

[a] Significant relationships are presented in bold. *$p < 0.05$, **$p < 0.01$, and ***$p < 0.001$.

Table 8. Pearson's Correlation Coefficients for Relationships Between BAFs for ΣDDT and the *p,p′*-DDE vs Soil ΣDDT and *p,p′*-DDE Concentrations (Log Values) and Soil Properties[a]

	lettuce ($n = 9$)	radish ($n = 5$)	radish leaf ($n = 7$)
	BAFs for ΣDDT		
ΣDDT	**−0.817****	0.483	**−0.809***
Olsen P	−0.611	0.706	−0.623
% TOC	−0.348	0.061	−0.397
pH	0.230	0.766	0.234
CEC	−0.271	0.051	−0.268
% clay	0.126	0.771	0.133
% silt	0.162	0.844	0.003
% sand	−0.192	**−0.995*****	−0.089
Fe	−0.205	0.011	−0.180
Mn	−0.625	0.081	−0.602
	BAFs for *p,p′*-DDE		
p,p′-DDE	**−0.802****	−0.329	**−0.818***
Olsen P	−0.615	−0.169	−0.671
% TOC	−0.351	−0.741	−0.405
pH	0.221	0.142	0.149
CEC	−0.272	−0.803	−0.279
% clay	0.125	0.578	0.096
% silt	0.151	0.138	−0.083
% sand	−0.183	−0.429	−0.009
Fe	−0.205	−0.647	−0.182
Mn	−0.624	−0.411	−0.607

[a] Significant correlations are presented in bold. *$p < 0.05$, **$p < 0.01$, and ***$p < 0.001$.

It is significant that Cd concentrations in lettuce exceeded the current NZ standard for Cd in leafy vegetables at soil concentrations much lower than the maximum value reported for a NZ orchard soil of 1.5 mg kg^{-1} (*2*). Exceedances of the food standard for Pb could also occur as the maximum soil Pb concentrations used in our uptake experiments were below the maximum Pb concentration reported for a NZ orchard soil of 340 mg kg^{-1} (*52*) and the current NZ guideline for Pb in high-contact residential soils of 400 mg kg^{-1} (*53*).

It should be noted that although food standards are used as proxies for risk, an exceedance of one or more food standards does not necessarily denote unacceptable risk to persons consuming that food. Risk is assessed in relation to how total intakes over the whole diet compare with tolerable intake limits, such as the provisional tolerable weekly intake (PTWI) for Cd (*54*). However, the regulatory significance of food standard exceedances is that such food is technically noncompliant with a protective standard and should be excluded from human food chains.

The measured concentrations of ΣDDT, As, Cd, Cu, and Pb in the plant tissues demonstrate that aged contaminants present in former NZ horticultural soils remain phytoavailable despite a considerable period of aging. Concentrations of Cd in lettuce exceeded the current NZ food standard for Cd in leafy vegetables and concentrations of Pb in radish exceeded 50% of the current food standards for vegetables for several of the assayed soils. Significant relationships between the plant tissue and the soil contaminant concentrations were observed for ΣDDT and *p,p′*-DDE in all plant parts, Cu in radish hypocotyls and leaves, and Cd and Cu in lettuce leaves. These observed significant and linear relationships indicate that plant tissue concentrations will continue to increase with increasing soil contaminant concentrations and could reach levels exceeding NZ and international standards for Cd and ΣDDT designed to protect human health. Our findings demonstrate that the produce consumption pathway should be considered as part of site-specific risk assessments and soil guideline derivation for settings where vegetable gardens are likely to be present. However, care is needed with the selection of BAFs for use in site-specific risk assessments and derivation of soil guidelines to ensure that human exposure from vegetable consumption is appropriately characterized and is robust.

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