DGT estimates cadmium accumulation in wheat and potato from phosphate fertilizer applications

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Abstract

Cadmium is a common impurity in phosphatic fertilizers and may contribute to soil Cd accumulation. Changes in total and bioavailable Cd burdens to agricultural soils and the potential for plant Cd accumulation resulting from fertilizer input was investigated. Three year field studies were conducted using three dose levels of cadmium-rich, commercial, phosphate fertilizers applied at four agricultural sites. Labile Cd concentrations, measured using the passive sampling device Diffusive Gradients in Thin Films (Cd_{DGT}), increased with increasing fertilizer application rates. Cd also accumulated in the edible portion of wheat and potato crops grown at the sites, and showed strong positive dose response with fertilizer treatment. Regression models were calculated for each site, year, and for individual crops. Model comparisons indicated that soil physical and chemical parameters in addition to soil Cd fractions, were important determinants of Cd_{DGT}. Significant factors contributing to Cd_{DGT} concentrations were Cd from fertilizer input ($Cd_{fertilizer}$), pH, cation exchange capacity (CEC), and total recoverable Cd (Cd_{total}). Important factors used to determine Cd concentrations in wheat grain (Cd_{wheat}) and in potato (Cd_{potato}) were as follows: Cd_{wheat}:$Cd_{fertilizer}$, and Cd_{DGT}; and Cd_{potato}:$Cd_{fertilizer}$, Cd_{DGT}, % O.M. The effective concentration, C_E, calculated from DGT did not correlate well with Cd_{wheat} or with Cd_{potato}. Direct measurements of Cd_{DGT}correlated better with Cd found in edible plant tissue. The modeling approach presented in this study helps to estimate Cd accumulation in plant tissue over multiple years and in distinct agricultural soil systems.

Keywords

Cadmium; Bioavailability; Diffusive Gradients in Thin Films (DGT); Field experiments; Plant

1. Introduction

Many commercially available fertilizers and soil amendments contain variable levels of non-nutritive metals, such as Cd, arising from multiple sources including parent rock and the use of waste product as fertilizer (McLaughlin et al., 1996 and Raven and Loeppert, 1997). Studies of the long-term effect of applying Cd-rich fertilizers to soils have resulted in mixed and conflicting conclusions, making it difficult to establish risk parameters for non-nutritive metals in fertilizer (USEPA, 1999). Previous studies have employed a one-time use of soil highly contaminated with Cd, leaving unanswered questions about Cd bioavailability in agricultural settings, where Cd concentrations are considerably lower. Cd spiked soils show much higher transfer rates to plants, than in soils in which the metals have aged (Chaudri et al., 2007 and Huang et al., 2004) and are not realistic in agricultural field studies. In addition, physical and chemical properties may differ significantly in agricultural soils subjected to repetitive tilling and irrigation, which influences Cd availability to crops (Mench, 1998).

The primary route for Cd exposure in humans is through ingestion of foods (Norvell et al., 2000). Although levels of tolerable intake of many toxic metals from foods have been established (Van Urk and Marquenie, 1989), no maximum allowable concentrations for toxic metals in non-contaminated, agricultural soils have been defined (USEPA, 2003). One reason for the lack of a standard is that the relationship between soil–metal concentration and the amount of metal found in the edible portion of crops is not well defined. Individual crops acquire nutrients at variable rates and translocation of non-nutritive constituents is not necessarily uniform across species. Furthermore, edible plant tissues consumed may receive nutrients via different routes (eg. xylem vs. phloem). These nuances complicate plant metal uptake efforts and the total soil metal concentration is often an unreliable indicator of plant metal concentration. Another reason for a lack of a standard is the need for an accurate and universal technique to mimic or model plant metal accumulation.

Researchers have found some success relating soil metal fractions to Cd plant concentrations utilizing soil extraction methods and measurements of free ion activities (Chaudri et al., 2007, Morel, 1983 and Sukkariyah et al., 2005), though the impact of metal uptake by plants followed by metal resupply from soil solid phase to soil solution has been largely ignored (Zhang et al., 2001). In this study we attempt to link soil–metal bioaccessibility, defined as the metal fraction in the rhizosphere potentially available for plant acquisition, with soil–metal bioavailability, defined as the extent to which bioaccessible metals absorb onto, or into, and across biological membranes of organisms (USEPA, 2007). Labile Cd species have been shown to be bioaccessible to plants (Degryse et al., 2006 and Zhao et al., 2002). Increases in labile Cd from continuous fertilizer application may lead to changes in plant Cd accumulation. As plants assimilate nutrients via organic and inorganic acquisition, the Cd fraction in the rhizosphere becomes depleted, initiating a release of Cd from surrounding soil surficial sites, and creating the potential for increased plant Cd uptake (Evans, 1989).

One way to measure the solid phase resupply of the labile Cd fraction is with Diffusive Gradient Thin Films (DGT). DGT is a diffusion driven passive sampling device developed and used for quantitative determination of labile metals in situ (Davison and Zhang, 1994). The focus of sampling by DGT is on the speciation and ultimately the bioaccessibility of metals rather than the traditional method of determining their mere presence as measured by a total recoverable concentration. Labile metal is removed from the soil solution by binding to the chelex resin. In this way, DGT is effectively acting as a mimic for a plant root. Labile metal species measured with DGT more accurately reflect metal bioaccessibility and bioavailability to plants than measurement of ion activities alone (Davison et al., 2000, Nolan et al., 2005, Zhang et al., 2001 and Zhang et al., 2004).

It is therefore of great importance to define the bioavailable fraction of metals in agricultural soils (USEPA, 2007). Previous bioavailability studies have focused on application of biosolids, or reclaimed irrigation waters (USEPA, 1999), while few looked at phosphate fertilizers as a source of continuous metal input into agricultural systems. The majority of studies measured Cd fractions found in bulk solution to delineate correlations with plant (Chaudri et al., 2001 and Degryse et al., 2006). We hypothesize that the labile Cd fraction captured by DGT increases with dose-dependent phosphate fertilizer applications and is a good predictor of Cd uptake into wheat grain and potato.

2. Experimental section

2.1. Study area

Soils were collected from four agricultural field locations in the state of Oregon, USA. Sampling locations represent distinct agricultural systems defined by distinct climates, soil classifications, crop rotations, and agronomy practices. Selected characteristics of the sites are presented in Table 1. At each sampling location, an area of 1012 m^2 was allocated and divided into a 4 × 4 randomized grid consisting of four treatment levels (dose), each with four replicates.

Table 1.

2.2. Soil treatment

Commercially available fertilizers were used for field dosing. Dosing consisted of a control and three Cd-rich treatment levels. The control (C) was a 1× application rate with a non metal-rich ammonium sulfate commercial fertilizer (21-0-0-24, N–P–K–S). Treatment level 1× (T1×) was a 1× application rate of a commercially available, Cd-rich, phosphatic fertilizer (16-21-0 N–P–K), followed by T2×, and T3×. Application rates are based on typical agronomical application levels for the nitrogen needs for the soil type, irrigation practices, and crops to be grown at each site. (Hart et al., 2000 and Hemphil, 2006). Each year T1×–T3× Cd soil loads from fertilizer input may be very different at each site based on the aforementioned agronomic factors. Average concentrations of Cd in the control fertilizers were 0.007 (± 0.003), < 0.00012, and 0.27 (± 0.2) mg/kg 2004–2006 respectively. Average concentrations in treatment fertilizers were 20 (± 1.5), 49 (± 1.1), and 52 (± 3.5) mg/kg 2004–2006 respectively.

2.3. Sample collection

Soils were collected at harvest approximately 5–10 months post fertilizer application. Surface and DGT soils were collected within the field grid from each of the treatment replicate plots. If crops were present, soils were collected from spaces in between individual plants. Overall, 16 total surface soil, DGT soil and plant samples, four samples per treatment level, from each of the four field treatment replicates were collected from each site for a total of N = 64 of each type of sample collected from the four different field sites.

2.4. Surface soils

Surface soils were collected as an intact core from the O and A horizons (0–22 cm) using stainless steel soil probes (AMS inc., American Falls, ID, USA). By sampling in these horizons, we aimed to access the soil that would most likely be in contact with plant roots. Each treatment replicate represents a composite of three sub-sample cores collected from distinct spots within the replicate plot area and composited into one sample to capture field heterogeneity within each treatment plot and replicate.

2.5. Diffusive Gradient in Thin Film Soils

Surface soils (0–22 cm) were collected for DGT deployment using a stainless steel trowel. A composite of three sub-samples were taken from each treatment replicate to account for soil heterogeneity. To preserve the natural biota of the soil, samples were neither dried nor ground. DGT soils were placed in clean plastic bags, and stored at < − 20 °C until analysis. Side-by-side aliquots were removed from the sample to simultaneously test for DGT measured and soil solution metal concentrations.

2.6. Plant

Wheat (Triticum aestivum L.) and potatoes (Solanum tuberosum) were grown following typical agronomical practices (Table 1.). Sixteen plant samples, representing four replicates of each of the four treatment groups, were harvested once a year from each site for analysis. Wheat grain was harvested using a mini-combine, allowing individual replicates from each treatment to be sampled. Similarly, twelve potatoes were randomly sampled and composited from each replicate using a small potato harvesting machine for a total of 192 potatoes from one field site per season (12 □ 16). Although wheat species and cultivar differences in Cd accumulation have been identified (McLaughlin et al., 1996), comparisons were not incorporated into the analysis for this study. The wheat varieties grown were known to be the most common and widely used for each specific field site for each year based on communication with the agricultural research station directors. No statistically significant change in crop yield was seen at Klamath, Hermiston, or Columbia for the study duration. No change in yield was measured at Willamette, except in 2006, where T3× yield was significantly greater than the control ($P < 0.05$, $N = 16$).

2.7. Methods

Total recoverable metal concentrations of surface soils and the edible portion of plant samples were determined using an acid digestion as adapted from EPA methods 3050B and 7020 (USEPA, 1996). Potatoes were washed and lightly scoured under ultra pure water. Wheat kernels and potatoes with skin were dried and ground prior to homogenization and acid digestion. Samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (PQ ExCell, Thermo Elemental, Waltham, MA, USA). Soil sub-samples were sent to the University of Idaho Analytical Sciences Laboratory (Moscow, ID, USA) and analyzed for general fertility including pH, P, K, percent organic matter (% O.M.), nitrate ($NO_3{-}N$), ammonium ($NH_4{-}N$), CEC (Table 1.), and particle density (not shown).

2.8. DGT deployment and sample analysis

DGT soils were brought to room temperature (21 °C) prior to use. Room temperature soils (~ 50 g) were mixed in duplicate with 18 MW cm water to achieve a 115% moisture level based on the water holding capacity. After a 24 h equilibration, DGT units (DGT Research Ltd., Lancaster, Lancashire, UK) were deployed according to Zhang and Davison for 72 h and the time integrated metal concentration accumulated in the DGT device was calculated according to Zhang and Davison (1995).

2.9. Calculation of C_E

The effective concentration (C_E) takes into account not only the concentration of metal accumulated on the resin in the DGT, but also the amount of metal that is resupplied to the soil solution from solid phase metal pools (Zhang et al., 2001). C_E is determined by using the DIFS model (DGT Induced Fluxes in Sediments) as previously described (Harper et al., 2000 and Sochaczewski et al., 2007). The input variables required to calculate C_E were distribution coefficient (K_d), soil solution concentration, soil density, soil porosity, and diffusion coefficients of Cd in pure water (D). K_d was defined as the distribution between the total recoverable, acid digested Cd fraction in soil and the soil solution Cd fraction as described above. With the exception of D, each of these parameters was measured directly for each site and applied to the model for more precise, site specific, calculation of C_E.

2.10. Quality control

Field and laboratory quality control (QC) samples comprise at least 15% of each analytical run. Trip, field, and rinsate blanks were below limits of quantification. Certified reference materials (CRMs) were purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). Soil CRMs included 2710 Montana Highly elevated soil, 2711 Montana Moderately elevated soil, and 2709 San Joaquin soil. For DGT and soil solution analysis, CRM 1640 Natural Waters was used. Plant CRMs included 1515 Apple Leaf, and 1573a Tomato Leaf. Blank samples ($N = 104$) and rinsate blanks ($N = 4$) were below detection limits. The average percent recovery for all check standards was 97% ($N = 63$). Average spike recoveries were ≥ 90% ($N = 10$). The average percent recovery for all CRMs was 99% ($N = 40$; CRMs: 2711, 99%; 2709, 97%; 1573a, 100%; and 1640, 100%). Irrigation waters were sampled each year from Klamath and Hermiston ($N = 22$/site).

2.11. Data analysis

For graphical representations, SigmaPlot 2003 for Windows, Version 8.0 (SPSS Inc., Chicago IL, USA) was used. Sigma Stat for Windows, Version 3.1 (Systat Software, Inc., San Jose, CA, USA) was used to determine one-way analysis of variance (ANOVA, Holm–Sidak method), the Pearson product moment correlation parametric test, and multiple linear regressions (MLR). The ANOVA determined treatment and yearly effects. The MLR was used for multivariate modeling to detect variables that are correlative with cadmium concentration in the DGT device and in plant. Significance levels for all statistical analyses were set at $P < 0.05$.

3. Results and discussion

3.1. Bioaccessible Cd measured by DGT

Cd soil additions through fertilizer applications were small compared with other studies, and dose steps were low to more closely simulate typical agricultural practices. Despite this challenge, increasing Cd_{DGT}concentration with fertilizer treatment was seen at three out of four sites. At the Klamath and Hermiston (irrigated) sites, T3× samples contained 64 and 46% greater Cd_{DGT} than the control groups ($P < 0.001$), while T3× samples at Columbia and Willamette (dry) sites measured 62 and 47% more Cd_{DGT} than the controls over the four year study period ($P = 0.01$). An increasing trend in Cd_{DGT} was seen at Klamath 2004–2006, but was not statistically significant. These increases in Cd_{DGT}, albeit slight, provide evidence that DGT measures increases in labile metal with dose increases at non-contaminated field sites. Using ANOVA, all-pairwise multiple comparison procedures (Holm–Sidak method), yearly treatment effects were measured at Hermiston, Columbia, and Willamette as shown in Fig. 1.

Fig. 1.

DGT measured Cd response 2003–2006. Significant treatment effect in Cd_{DGT} per year is noted by an asterisk. Dose step significance levels are indicated with lower case letters, $P<0.05$, $N = 4$.

For all sites, Cd_{DGT} concentrations were linearly correlated with Cd soil loads from fertilizer input ($Cd_{fertilizer}$) (average $R^2 = 0.69$; $P < 0.05$). However, at the highest loads at all sites in 2006, Cd_{DGT} did not reflect the $Cd_{fertilizer}$ increase. In 2003–04, averages of Cd_{DGT} were 16 and 27% for those measured in 2005 respectively. Yet in 2006, Cd_{DGT} levels dropped to 51% for those observed in 2005. In addition, Cd_{DGT}concentrations were similar across soil types, in spite of nearly double the $Cd_{fertilizer}$ at Hermiston and Willamette in 2005–06, suggesting significant influence from soil physical and chemical factors.

It is well known that soil properties can alter Cd mobility (Chaudri et al., 2001 and Sauve et al., 2000). To evaluate the combined effect of other variables on Cd_{DGT}, multiple linear regression (MLR) models were derived for each year, at each site, and for individual plant species. Included in the model were the following parameters: total recoverable Cd (Cd_{total}), pH, % O.M., CEC, Cu and Zn in soil solution (Cu_{soln}, Zn_{soln}), Cu and Zn in irrigation waters (Cu_{irr}, Zn_{irr}), and $Cd_{fertilizer}$. Cd_{DGT} is well correlated with Cd concentration in soil solution (Cd_{soln}) ($R^2 = 0.70$, $P < 0.0001$, $N = 180$). To avoid issues of collinearity, Cd_{soln} was not included in the Cd_{DGT} regression models. Organic matter, pH, and CEC have been defined as key critical factors that influence Cd mobility in soils (Lee et al., 1996). Interactions between Cu and Zn fractions and Cd in agricultural soil systems are not well understood. Conflicting results show both antagonistic (Tsang and Lo, 2006 and Welch et al., 1999) and enhanced accumulation of Cd in crops (Papoyan et al., 2007) in the presence of Cu and Zn. Inclusion of these metals in MLR models assists in characterizing the soils and promotes a better mechanistic understanding of how the presence of Cu and Zn soil fractions, lead to decreased or enhanced uptake of Cd in crops. Common soil characterization factors found to be significantly correlated with Cd_{DGT} across all sites were % O.M., CEC, pH, Cd_{total}, and Cu_{soln}. The site specific regression equations for significantly correlative factors of Cd_{DGT} are shown in Table 2A.

Table 2.

3.1.1. Dry sites

Increased soil binding sites, via the presence of organic matter for example, may have increased Cd sorption to soil particulates (Evans, 1989). Increased sorption may have masked the Cd_{DGT} treatment effect at the Columbia and Willamette sites in 2004. A slight reduction in pH with $Cd_{fertilizer}$ input was observed at Columbia between the control and T3× ($P < 0.05$), while no significant pH decrease was measured at Willamette with fertilizer treatment. For all years, Cd_{DGT} levels at Columbia were similar to the other field sites, despite $Cd_{fertilizer}$ values that were half of those of all the other sites. While low pH measurements may have increased Cd_{DGT}, no treatment effect was observed. The lowest observed pH values of the study were measured at Columbia in 2006, and pH was identified as a significantly correlative factor with Cd_{DGT} that year. Silt loam soils at the Willamette field are rich in clay minerals and have moderate organic matter content. Significant correlative factors of Cd_{DGT} at Willamette were CEC, and % O.M. As per typical agronomical practices at Willamette, the experimental field plot was amended with lime post harvest in 2005 due to low pH values. Cd concentrations in lime samples were below our method detection limit. However, the addition of lime has been shown to decrease labile Cd and likely decreased the magnitude of treatment effect observed in Cd_{DGT} at Willamette in 2006 (Christensen, 1984). This claim is further substantiated by observed increases in Cd_{total} each year across all treatments Willamette (data not shown).

3.1.2. Irrigated sites

Values of pH decreased with increased fertilizer treatment level, however, reductions were not incremental. Significant pH decreases were only seen at the T3× application level ($P < 0.05$) with all years averaged. pH is recognized as a principle factor affecting metal solubility (Suave et al., 2000) and fertilizer amendments to soils can lead to decreases in pH (Lorenz et al., 1994). Indeed, pH and CEC were important variables which explained Cd_{DGT} concentrations at Klamath and Hermiston. Cd_{total} was a significant factor in explaining the Cd_{DGT} observed at Hermiston in 2005–2006. This is reasonable due to the lack of binding sites via low % O.M., CEC, and clay mineral content, typical of Adkins fine sandy loam soil found at the Hermiston field site. For the interpretation of the relationship between Cd_{DGT} and Cu_{soln} at Klamath and Hermiston we proceeded with caution, since no significant Cd_{DGT} treatment effect was observed at these sites for the specified years. Klamath and Hermiston soils contained on average double the Cu_{soln} compared to the dry sites and significant correlations with Cd_{DGT} were measured at these sites. Correlations are likely explained by common influences of soil properties that affect each metal in a similar way.

Copper is not thought to directly compete with Cd for root binding sites, since essential Cu uptake channels already exist (Colangelo and Guerinot, 2006). However, Cu may bind tightly to soil surficial sites that would otherwise have been occupied by Cd (Tsang and Lo, 2006). These nuances of varied soil physical and chemical parameters and their potential to influence Cd_{DGT}, support the need for a comprehensive approach to estimate metal risk in soil systems.

In addition to the use of soil characterization parameters to procure information about the fate of soil Cd, another factor of vital importance is Cd loads to agricultural soils from fertilizer application ($Cd_{fertilizer}$). It has been shown that the application of phosphatic fertilizers is a major contributor of Cd to agricultural systems (McLaughlin et al., 1996) and little off-site movement, via leaching occurs (Hamon et al., 1998). The fertilizers used in this study were within state regulatory statutes for maximum allowable Cd content. Although regulation of Cd content in phosphatic fertilizers is a positive step, the question remains whether agronomically relevant applications of legally acceptable Cd-containing fertilizers result in Cd accumulation in the edible portion of crops. To determine the contribution of $Cd_{fertilizer}$ to bioaccessible soil Cd fractions, as measured by DGT, $Cd_{fertilizer}$ was also included in the MLR models. In 2004, $Cd_{fertilizer}$ was not significantly correlated with background corrected Cd_{DGT} concentrations at any of the field sites. However, $Cd_{fertilizer}$showed strong significant correlations at both irrigated sites in 2005–06 and at Willamette in 2006, suggesting that labile Cd increase in soils occurred at a slow rate. This is not surprising considering the limited metal addition via agronomically relevant fertilizer applications. The regression equations for significantly correlative factors of Cd_{DGT} including $Cd_{fertilizer}$ are shown in Table 2B.

3.2. Cd measured in edible plant tissue

At non-contaminated sites, with agronomically relevant phosphatic fertilizer applications, Cd was found to be present in the edible portion of wheat and potato crops (Fig. 2). Wheat grain has been shown to accumulate significant amounts of Cd, while even higher levels are found in leafy vegetables and potatoes (Taylor et al., 1998). The total recoverable Cd concentration in plant (Cd_{plant}), µg/kg dry weight, ranged from 22 to 161 in wheat, and 63–283 in potato. Dose dependent relationships between Cd_{plant} and fertilizer treatment levels were found at Willamette, Klamath and Hermiston. At the Columbia site, a crop rotation schedule of wheat–fallow–wheat was followed. No treatment effect was observed at Columbia for the 2004 or 2006 winter wheat analysis.

Fig. 2.

Plant cadmium concentrations (µg/kg, dry weight) and Cd soil loads by treatment level from four agricultural field sites. Significant treatment effect is noted with an asterisk and dose step significance levels are indicated with lower case letters.

3.2.1. Irrigated sites

Klamath potatoes T3× resulted in an average of 33% greater Cd concentration than the control group ($P = 0.001$), while T3× for wheat 2005 and 06, contained 23 and 30% more Cd than the control, respectively ($P = 0.01$). At the Hermiston sampling site, a wheat–potato–wheat rotation was followed. At Hermiston in 2004, no significant treatment effect was measured for wheat and reflected the lowest $Cd_{fertilizer}$ input for all years. In 2005–06, T3× potatoes contained 38 and 50% greater Cd than the control respectively ($P = 0.01$). These results are in contrast to other studies that found no increases in grain Cd with fertilizer addition to soils (Jones and Johnston, 1989 and Mortvedt, 1987). The authors attributed the lack of grain Cd accumulation to either no treatment effect, or the lack of due to increasing yield with increased P application. In the current study, no significant difference in yield between treatment levels was observed at all sites for all years, except in 2006 at Willamette, where a slight increase in grain yield was measured between T3× and the control.

3.2.2. Dry sites

At Willamette 2004–05 wheat T3× measured 39 and 36% greater Cd than the control groups. No treatment effect was observed at Willamette in 2006, despite having the largest $Cd_{fertilizer}$ input that year for all sites. The decrease in Cd_{plant} is likely an artifact of increased pH at Willamette from lime application in the fall of 2005. Increasing Cd input generally resulted in increasing Cd_{plant} at three out of four sites. However, similar to Cd_{DGT}, plant Cd uptake has been shown to vary widely with slight changes in soil physical and chemical parameters (Bergkvist and Jarvis, 2004 and Wang et al., 2006).

MLR models were utilized to determine factors important in estimating Cd_{plant}. Factors included in the models were: Cd_{total}, Cd_{soln}, Cd_{DGT}, pH, % O.M., CEC, Cu_{DGT}, Cu_{soln}, Cu_{irr}, Zn_{DGT}, Zn_{soln}, and Zn_{irr}. Regression equations for significantly correlative factors of Cd_{plant} are shown in Table 2C. Collinear parameters were removed from the analysis as indicated by a variance inflation factor greater than 4. Common soil characterization factors found to describe Cd_{plant} reasonably well were % O.M., CEC, pH, Cd_{DGT}, Cd_{total}, Cd_{soln}, and Zn_{irr}. Soil pH is the most notable of the parameters affecting Cd availability to crops (Lofts et al., 2004). Indeed, pH was a significant factor in 44% of the regression models generated with our data. As expected, decreases in soil pH correlated with increases in Cd_{plant}. Soil % O.M. surprisingly showed positive correlations with Cd_{plant} at Klamath all years. Metals bound to organic complexes in solution are readily taken up by durum wheat (Krishnamurti and Naidu, 2000). Wang et al. found that O.M. was positively correlated with Cd increases in Chinese cabbage, spinach, and cole (Wang et al., 2004). Pinto et al. found that while the presence of O.M. decreased Cd in solution, the Cd concentration in sorghum shoot increased (Pinto et al., 2004). Zn_{irr} was a significant factor and was negatively correlated with wheat at Klamath in 2005. One hypothesis is that Zn and Cd are bioaccessible to plants via a similar transport mechanism (Hart et al., 2002), thereby creating a competitive environment for the two metals in the rhizosphere. Cd fractions were also significantly correlated with Cd_{plant}, including Cd_{total}, Cd_{soln}, and Cd_{DGT}. By design, DGT is intended to mimic metal uptake via diffusion at the root level, thereby offering a partial mechanistic comparison for DGT/plant metal uptake. Cd_{DGT} was found to be an important variable, especially for the estimation of Cd in irrigated crops.

MLR model results including the addition of $Cd_{fertilizer}$ are shown in Table 2D. Correlation coefficients tended to improve with the inclusion of $Cd_{fertilizer}$, providing further supporting evidence of phosphatic fertilizer as a major source of Cd in wheat grain and potato at typical agricultural sites with low soil Cd concentrations. After taking into account the other Cd fractions in the Cd_{plant} model, Cd_{DGT} was the only significant factor after the addition of $Cd_{fertilizer}$.

3.3. Plant Cd accumulation as a function of the effective concentration C_E

Previous studies have utilized DGT and the DIFS model to calculate C_E. C_E has been used to predict metal uptake into spinach, ryegrass, barley root, tomato shoot, and pepperwort (Almas et al., 2006, Nowack et al., 2004, Zhang et al., 2001 and Zhao et al., 2006). Plant active processes for nutrient assimilation, such as exudation of organic acids, are not considered in the DIFS model. In spite of this, root and shoot concentrations are often well correlated with C_E (Vandenhove et al., 2007, Zhang et al., 2001 and Zhao et al., 2006). Little is known about how C_E will correlate with wheat grain and potato. Calculated C_E values were nearly two times larger for irrigated sites than non irrigated sites (0.78 (± 0.83), 0.45 (± 0.37) µg/L respectively). Cd concentrations in irrigated wheat correlated better with C_E ($R = 0.45$, $P < 0.001$, $N = 60$) than Cd in dry wheat ($R = 0.22$, $P = 0.09$, $N = 80$). C_E was also not well correlated with Cd in potato ($R = 0.36$,$P = 0.06$, $N = 32$). The use of DGT and C_E to estimate Cd accumulation in crops appears to be species specific, with notable differences between wheat and potato Cd estimations. Almas et al. also found differences in agreement with Cd uptake and C_E between spinach and ryegrass, with ryegrass showing stronger correlation (Almas et al., 2006).

3.4. Composite regression models estimate Cd_{plant} accumulation

MLR models were created to determine variables that correlate best with Cd_{wheat} over all years at all sites. That is, included in the model for wheat were variables from all of the sites for each year that wheat was grown. The MLR model included the same variables used to predict Cd_{wheat} with the addition of C_E. The regression equations for the most significantly correlative factors of Cd found in irrigated and non-irrigated (dry) wheat are shown in Eqs. (1) and (2).

Equations

(1) $\log Cd_{irrigated\ wheat} = 2.0 + (0.26 \log Cd_{DGT}) + 0.0091\ Cd_{fertilizer})$

(2) $\log Cd_{dry\ wheat} = 1.6 + (0.0075\ Cd_{fertilizer})$

For $Cd_{irrigated\ wheat}$, (Eq. (1)) these two factors explain 69% of the Cd found in the grain ($N = 60$; $R^2 = 0.48$; $P < 0.001$). $Cd_{dry\ wheat}$ (Eq. (2)) MLR analysis resulted in only $Cd_{fertilizer}$ as a significant factor, yet accounted for 50% of Cd in non-irrigated grain ($N = 80$; $R^2 = 0.25$; $P < 0.001$). Regression models for Cd_{potato} were not combined into one equation due to large differences in Cd concentration between potatoes grown at the Klamath and Hermiston sites. Despite having loads nearly double those applied at Klamath, Hermiston potatoes contained less than 50% of the Cd concentration compared with Klamath potatoes. Overall, the calculated C_E was not a significant factor in the estimation of Cd_{wheat} at irrigated or dry sites, nor with Cd_{potato}. Previous studies showed that wheat stover, including roots and stalk, contained more Cd than wheat grain, indicating that translocation capabilities of plants to edible portions play an important role for potential human Cd exposure through food intake (WSDA, 2001). Both wheat grain and tubers receive the bulk of their organic and inorganic content via phloem transport along source-sink gradients (Wardlaw, 1990). For soil Cd, this involves initial root uptake, transfer to the xylem in the root stele and a further transfer from xylem to phloem along the pathway from root to grain or root to tuber (Herren and Feller, 1997 and Van der Vliet et al., 2007). The Cd content of both these edible tissues is thus subject to additional constraints on transport, when compared to a leafy crop such as lettuce.

3.5. Appraisal of long-term soil Cd concentrations and plant Cd accumulation

Low-level fertilizer-based Cd applications distinguish this study, resulting in agronomically and environmentally relevant soil Cd levels at non-contaminated, agricultural field sites. The results from this study may be used to determine allowable concentrations of Cd in commercial fertilizers as well as determine Cd accumulation in two globally important crops at realistic application levels. Projections to define ‘critical limits’ of soil metal burdens based on long-term metal addition to soils was recently identified as a goal of the uppermost importance (Lofts et al., 2007) and real-system field data are needed to aggrandize and ameliorate current projection models. While considering plant uptake of metals and potential human risk, results from current models often vary considerably due to site specific and crop differences, particularly plant species in which translocation at a distance to the edible portion occurs. In this case, DGT was utilized as an effective tool to measure the kinetically labile soil metal pools, but was only marginally predictive of Cd found in the edible portion of wheat and potato crops. Conversely, DGT metal correlation with crops with little translocation distance have been successful, leading to questions about whether additional correction factor terms could be included in the DIFS model to incorporate a larger range of plant species. We agree that future research incorporating the bio-distribution coefficients of metals in surface soils, DGT, and plant is warranted to better define the potential for human Cd consumption risk.

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References

A.R. Almas, P. Lombnaes, T.A. Sogn, J. Mulder. Speciation of Cd and Zn in contaminated soils assessed by DGT-DIFS, and WHAM/Model VI in relation to uptake by spinach and ryegrass. Chemosphere, 62 (2006), pp. 1647–1655

P. Bergkvist, N. Jarvis. Modeling organic carbon dynamics and cadmium fate in long-term sludge-amended soil. J Environ Qual, 33 (2004), p. 181

A.M. Chaudri, C.M.G. Allain, S.H. Badawy, M.L. Adams, S.P. McGrath, B.J. Chambers. Cadmium content of wheat grain from a long-term field experiment with sewage sludge. J Environ Qual, 30 (2001), p. 1575

A. Chaudri, S. McGrath, P. Gibbs, B. Chambers, C. Carlton-Smith, A. Godley et al. Cadmium availability to wheat grain in soils treated with sewage sludge or metal salts. Chemosphere, 66 (2007), pp. 1415–1423

T.H. Christensen. Cadmium soil sorption at low concentrations: I. Effect of time, cadmium load, pH and calcium. Water Air Soil Pollut, 21 (1984), pp. 105–114

E.P. Colangelo, M.L. Guerinot. Put the metal to the petal: metal uptake and transport throughout plants. Curr Opin Plant Biol, 9 (2006), pp. 322–330

W. Davison, H. Zhang. In situ speciation measurements of trace components in natural waters using thin-film gels

Nature, 367 (1994), pp. 546–548

W. Davison, P.S. Hooda, H. Zhang, A.C. Edwards. DGT measured fluxes as surrogates for uptake of metals by plants

Adv Environ Res, 3 (2000), pp. 550–555

F. Degryse, E. Smolder, R. Merckx. Labile Cd complexes increase cd availability to plants. Environ Sci Technol, 40 (2006), pp. 830–836

L.J. Evans. Chemistry of metal retention by soils. Environ Sci Technol, 23 (1989), pp. 1046–1056

R.E. Hamon, M.J. McLaughlin, R. Naidu, R. Correll. Long-term changes in cadmium bioavailability in soil. Environ Sci Technol, 32 (1998), pp. 3699–3703

M.P. Harper, W. Davison, W. Tych. DIFS—a modelling and simulation tool for DGT induced trace metal remobilisation in sediments and soils. Environ Model Softw, 14 (2000), pp. 55–66

J. Hart, N.W. Christensen, T.L. Jackson, R. Karow, W.E. Kronstad. Winter wheat fertilizer guide, Oregon State University, Corvallis, OR (2000), pp. 1–3

J.J. Hart, R.M. Welch, W.A. Norvell, L.V. Kochian. Transport interactions between cadmium and zinc in roots of bread and durum wheat seedlings. Plant Physiol, 116 (2002), pp. 73–78

D. Hemphil. Potato information exchange: fertilization and liming, Oregon State University, Corvallis, OR (2006)

T. Herren, U. Feller. Transport of cadmium via xylem and phloem in maturing wheat shoots: comparison with the translocation of zinc, strontium, and rubidium. Ann Bot, 80 (1997), pp. 623–628

B. Huang, S. Kuo, R. Bembenek. Availability of cadmium in some phosphorus fertilizers to field-grown lettuce. Water Air Soil Pollut, 158 (2004), pp. 37–51

K.C. Jones, A.E. Johnston. Cadmium in cereal grain and herbage from long-term experimental plots at Rothamsted, UK. Environ Pollut, 57 (1989), pp. 199–216

G.S.R. Krishnamurti, R. Naidu. Speciation and phytoavailability of cadmium in selected surface soils of South Australia. Aust J Soil Res, 38 (2000), pp. 991–1004

S.Z. Lee, H.E. Allen, C.P. Huang, D.L. Sparks, P.F. Sanders, W.J.G.M. Peijnenburg. Predicting soil–water partition coefficients for cadmium. Environ Sci Technol, 30 (1996), pp. 3418–3424

S. Lofts, D.J. Spurgeon, D. Svendsen, E. Tipping. Deriving soil critical limits for Cu, Zn, Cd and Pb: a method based on free ion concentrations. Environ Sci Technol, 38 (2004), pp. 3623–3631

S. Lofts, P. Chapman, R. Dwyer, M.J. McLaughlin, I. Schoeters, S.C. Sheppard et al.. Critical loads of metals and other trace elements to terrestrial environments. Environ Sci Technol, 41 (2007), pp. 6326–6331

S.E. Lorenz, R.E. Hamon, S.P. McGrath, P.E. Holm, T.H. Christensen. Application of fertilizer cations affect cadmium and zinc concentrations in soil solutions and uptake by plants. Eur J Soil Sci, 45 (1994), pp. 159–165

M.J. McLaughlin, K.G. Tiller, R. Naidu, D.P. Stevens. Review: the behaviour and environmental impact of contaminants in fertilizers

Aust J Soil Res, 34 (1996), pp. 1–54

M.J. Mench. Cadmium availability to plants in relation to major long-term changes in agronomy systems. Agric Ecosyst Environ, 67 (1998), pp. 175–187

F. Morel. Principles of aquatic chemistry. John Wiley & Sons, New York (1983)

J.J. Mortvedt. Cadmium levels in soils and plants from some long-term soil fertility experiments in the United States of America. J Environ Qual, 16 (1987), pp. 137–142

A.L. Nolan, H. Zhang, M.J. McLaughlin. Prediction of zinc, cadmium, lead, and copper availability to wheat in contiminated soils using chemical speciation, Diffusive Gradients in Thin Films, extraction, and isotopic dilution techniques. J Environ Qual, 34 (2005), pp. 496–507

W. Norvell, J. Wu, D.G. Hopkins, R.M. Welch. Association of cadmium in durum wheat grain with soil chloride and chelate-extractable soil cadmium. Soil Sci Soc Am J, 64 (2000), pp. 2162–2168

B. Nowack, S. Koehler, R. Schulin. Use of Diffusive Gradients in Thin Films (DGT) in undisturbed field soils. Environ Sci Technol, 38 (2004), pp. 1133–1138

A. Papoyan, M. Pineros, L.V. Kochian. Plant Cd^{2+} and Zn^{2+} status effects on root and shoot heavy metal accumulation inThlaspi caerulescens. New Phytol, 175 (2007), pp. 51–58

A.P. Pinto, A.M. Mota, A.D. Varennes, F.C. Pinto. Influence of organic matter on the uptake of cadmium, zinc, copper and iron by sorghum plants. Sci Total Environ, 326 (2004), pp. 239–247

K.P. Raven, R.H. Loeppert. Trace element composition of fertilizers and soil amendments. J Environ Qual, 26 (1997), pp. 551–557

S. Sauve, W. Hendershot, H.E. Allen. Soil-solution partitioning of metals in contaminated soils: dependence in pH, total metal burden, and organic matter. Environ Sci Technol, 34 (2000), pp. 1125–1131

L. Sochaczewski, W. Tych, B. Davison, H. Zhang. 2D DGT induced fluxes in sediments and soils (2D DIFS). Environ Model Softw, 22 (2007), pp. 14–23

S. Suave, W. Hendershot, H.E. Allen. Solid-solution partitioning of metals in contaminated soils: dependence on pH, total metal burden, and organic matter. Environ Sci Technol, 34 (2000), pp. 1125–1131

B.F. Sukkariyah, G. Evanylo, L. Zelazny, R.L. Chaney. Cadmium, copper, nickel, and zinc availability in a biosolids-amended piedmont soil years after application. J Environ Qual, 34 (2005), pp. 2255–2262

J. Taylor, R. DeWoskin, F. Ennever. Toxicological profile for cadmium. Agency for toxic substances and disease registry, Atlanta (1998), p. 439

D.C.W. Tsang, I.M.C. Lo. Competitive Cu and Cd sorption and transport in soils: a combined batch kinetics, column, and sequential extraction study. Environ Sci Technol, 40 (2006), pp. 6655–6661

USEPA. Method 3050B: acid digestion of sediments, sludges, and soils. Test methods for evaluating solid waste (3rd ed.), U.S. EPA, Washington, DC (1996) 2nd update

USEPA. Estimating risk from contaminants contained in agricultural fertilizers: Draft Report, United States Environmental Protection Agency, Office of Solid Waste, Washington, DC (1999)

USEPA. Executive summary: guidance for developing ecological soil screening levels (Eco-SSLs), United States Environmental Protection Agency, Office of Solid Waste, Washington, DC (2003)

USEPA. Framework for metals risk assessment, United States Environmental Protection Agency, Washington DC (2007), p. 172

H. Vandenhove, K. Antunes, J. Wannijn, L. Dunquene, M. Van Hees. Method of Diffusive Gradients in Thin Films (DGT) compared with other soil testing methods to predict uranium phytoavailability. Sci Total Environ, 373 (2007), pp. 542–555

L. Van der Vliet, C. Peterson, B. Hale. Cd accumulation in roots and shoots of durum wheat: the roles of transpiration rate and apoplastic bypass. J Exp Bot, 58 (2007), pp. 2939–2947

G. Van Urk, J.M. Marquenie. Environmental behaviour of cadmium: WHO are at risk and why, World Health Organization: Heavy Metals in the Environment, vol. 11, Geneva (1989), pp. 456–459

X.P. Wang, X.Q. Shan, S.Z. Zhang, B. Wen. A model for evaluation of the phytoavailability of trace elements to vegetables under the field conditions. Chemosphere, 55 (2004), pp. 811–822

A.S. Wang, J.S. Angle, R.L. Chaney, T.A. Delorme, R.D. Reeves. Soil pH effects on uptake of Cd and Zn by Thlaspi caerulescens

Plant Soil, 281 (2006), pp. 325–337

I.F. Wardlaw. The control of carbon partitioning in plants. New Phytol, 116 (1990), pp. 341–381

R.M. Welch, J.J. Hart, W.A. Norvell, L.A. Sullivan, L.V. Kochian. Effects of nutrient solution zinc activity on net uptake, translocation, and root export of cadmium and zinc by separated sections of intact durum wheat (Triticum turgidum L. vardurum) seedling roots. Plant Soil, 208 (1999), pp. 243–250

WSDA. A report on the plant uptake of metals from fertilizers, Washinton State Department of Agriculture, Olympia (2001), pp. 1–23

H. Zhang, W. Davison. Performance characteristics of the technique of diffusion gradients in thin-films (DGT) for the measurement of trace metals in aqueous solution. Anal Chem, 67 (1995), pp. 3391–3400

H. Zhang, F.J. Zhao, B. Sun, W. Davison, S. McGrath. A new method to measure effective soil solution concentration predicts copper availability to plants. Environ Sci Technol, 35 (2001), pp. 2602–2607

H. Zhang, E. Lombi, E. Smolders, S. McGrath. Zn availability in field contaminated and spiked soils. Environ Sci Technol, 38 (2004), pp. 2608–3613

F.J. Zhao, R.E. Hamon, E. Lombi, M.J. McLaughlin, S.P. McGrath. Characteristics of cadmium uptake in two contrasting ecotypes of the hyperaccumulatorThlaspi caerulescens. J Exp Bot, 53 (2002), pp. 535–543

F. Zhao, C.P. Rooney, H. Zhang, S. McGrath. Comparison of soil solution speciation and diffusive gradients in thin-films measurements as an indicator of copper bioavailability to plants. Environ Toxicol Chem, 25 (2006), pp. 733–742