SOIL-DIFFUSIVE GRADIENT IN THIN FILMS PARTITION COEFFICIENTS ESTIMATE METAL BIOAVAILABILITY TO CROPS AT FERTILIZED FIELD SITES

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Abstract

Field trials in four distinct agricultural soils were conducted to examine changes to total recoverable and labile soil Cd and Ni concentrations with applications of commercial phosphate fertilizers. The edible portion of wheat and potato crops grown at the field plots were analyzed for recoverable Cd and Ni. Total recoverable Ni and Cd concentrations in agricultural soils increased by 10 and 22%, respectively, each year of the study at recommended application rates. Labile Cd and Ni were measured using diffusive gradients in thin films (DGT), a passive sampling device reported to estimate the plant bioavailable metal fraction. Nickel concentrations measured with DGT did not significantly change with treatment nor did they change over time. Cadmium concentrations measured with DGT increased with application rate and over time from 2003 to 2005, then decreased in 2006. Wheat grain Cd concentrations and Cd and Ni levels in tubers increased significantly with fertilizer treatment level. Grain and tuber Cd values exceeded the minimal risk levels for chronic oral exposure. At agronomical P-fertilizer application rates, 25% of plant samples deviated from the Cd minimal

risk levels. The present study reports the use of $K_{d\text{-}BIO}$, defined as the ratio of total recoverable metal to GT measured metal, as a significant indicator of crop metal accumulation in the edible portion. The $K_{d\text{-}BIO}$ values were well correlated with both grain and tuber concentrations over multiple growing seasons. Results from long-term field trials emphasize $K_{d\text{-}BIO}$ as a dynamic term that provides risk characterization information about the fate of Cd and Ni in aged, fertilized agricultural soils and crops.

INTRODUCTION

Phosphate fertilizers are responsible for significant metal contributions to agricultural soils globally each year [1]. A consistent relationship is lacking between metal accumulation in crops and soil metal fractions, yet understanding this relationship is critical to the protection of food supplies. Concerted efforts have been made to produce consistent and reliable methods and models to estimate crop uptake of metals from soil. Challenges include the lack of field studies, particularly those estimating metal fractions that are mobile and available for uptake into organisms, often referred to as bioavailable metal fractions [2,3].

The mobility of metals in soils is directly related to the partitioning between soil solid phase and solution phase [4], also defined as the distribution coefficient (K_d).

The K_d values in agricultural soils, in which metal levels are considered to be low, are not well characterized. This is due in part to discrepancies in sampling technique and analysis and large subsequent variability of available data [5]. Field trial data are needed following K_d values over time to capture changes in transient system conditions (e.g., wetting and drying cycles, tilling, cropping). Fixation, or aging, processes remove metal fractions from available soil pools and can be quantified by measuring decreases in labile metal over time [6]. Diffusive gradients in thin films (DGT) measure the labile metal or chemically active fraction in soils [7] and are reported to be a plant mimic of metal acquisition in the rhizosphere of a variety of species [8–11]. However, plants also access nonavailable pools [12–14] via active processes (e.g., organic acids, exudates). Therefore, a term such as K_d that incorporates changes in both mobile and fixed metal fractions may be useful in estimating metal uptake into crops.

The present study reports the calculation of $K_{d\text{-BIO}}$ values as the distribution between the total recoverable and DGT-measured Cd and Ni concentrations. In multiyear, multisite field trials, soils were treated with increasing applications of commercial phosphate fertilizers, beginning with typical agronomical rates. The present study tested whether changes in $K_{d\text{-BIO}}$ with fertilizer treatment and over time in aged soils were a good indicator of metal accumulation in wheat (*Triticum aestivum* L.) and potato (*Solanum tuberosum* L.) crops.

MATERIALS AND METHODS

Study area

Four agricultural field sites in Oregon, USA, were used for soil sampling and crop production. Differing climates, soil classifications, crop rotations, and agronomical practices distinguished each site. Selected characteristics of the soils used in the study are presented in Table1. An area of 1,012 m^2 was allocated for the four-year study duration at each research station and divided into a 4 × 4 randomized grid consisting of four treatment levels, each with four replicates. Two of the agricultural field sites were irrigated (designated irr-1 and irr-2), and two were dry land (dry-1 and dry-2).

Table 1.

Soil treatment

Commercially available fertilizers were screened for Cd and Ni content. Values for the ammonium sulfate control fertilizer, and ammonium phosphate treatment fertilizer are shown in Table 2. Control plots received a dose of the ammonium sulfate fertilizer based on typical agronomical application levels for the nitrogen needs for the soil type, irrigation practices, and crops to be grown at each site (oregonstate. edu/potatoes/fertilize.htm) [15,16]. Treatment plots received either a recommended agronomical rate (T1x), T2x, or T3x application of the ammonium phosphate fertilizer. All sites were thoroughly cultivated annually to

incorporate the fertilizer to a 22 cm depth using a disc. As per typical agronomical practice, post harvest wheat chaff was left on the field to inhibit erosion. All fields were tilled prior to the next season's planting. Soil additions of metal from fertilizer ranged from below limits of detection to 28 g/ha/year for Cd and 0.3 to 71 g/ha/year for Ni. At sites employing crop rotation, Cd and Ni soil inputs from fertilizer varied based on differing agronomical requirements each year.

Table 2.

Soil sampling

Soils were collected 5 to 10 months post fertilizer application either as an intact core from the organic matter (O) and surface soil (A) horizons (0–22 cm) using stainless steel soil probes (Art's Manufacturing&Supply), or for larger collection volume, using a stainless steel trowel. Sixteen core surface soil samples and 16 large-volume samples, each a composite of three subsamples, were collected at each field site. Large-volume samples, used for metal analysis with DGT, were neither dried nor ground, and were stored at less than −20°C until analysis.

Plants

Wheat and potatoes were grown following typical agronomical practices. Specific crops grown at each of the four field sites are listed in Table 1. Each year, 16 plant samples were collected from each site representing four replicates of each

of the four treatment groups. In 2005, dry-1 was fallow and no plant samples were collected. Wheat grain was harvested in late August using a mini-combine. Potatoes were collected using a small harvester and 12 randomly sampled potatoes from each replicate of each of the four treatments were composited and stored in mesh bags for transport to the laboratory. Composite samples were used to account for plant-to-plant variability and field heterogeneity. The wheat species and cultivars grown differed at some sites and interspecies comparisons were not analyzed in the present study. Crop species were selected based on communications with agricultural field research station directors based on annual crop productivity, availability, and weather and pest management forecasts.

MATERIALS AND METHODS

Total recoverable metal concentrations of surface soils and the edible portion of plant samples (grain and tuber) were determined using an adapted acid digestion from the U.S. Environmental Protection Agency 3050B (www.epa.gov/osw/hazard/testmethods/sw846/pdfs/3050b.pdf) [17]. Surface soils were dried and ground prior to digestion. Samples were analyzed by inductively coupled plasma mass spectrometry (PQ ExCell, Thermo Elemental). Moisture content, pH, percent organic matter, and cation exchange capacity were determined at the University of Idaho Analytical Sciences Laboratory.

Diffusive gradients in thin films

To duplicate 50 g aliquots of each soil, 18 MΩ cm water was added to achieve a 115% moisture level relative to the water holding capacity and equilibrated for 24 h. Diffusive gradient in thin films units (cap and piston design, DGT Research Ltd.) were deployed at room temperature for 72 h in one aliquot. The chelex resin was extracted with ultra pure 1 N HNO_3 and analyzed by inductively coupled plasma mass spectrometry. Soil solution samples were decanted and acidified. The mass of metal (M) accumulated on the resin gel per unit area was calculated using Equation 1. The time integrated DGT concentration was calculated using Equation 2.

(1) $M = C_{eluent} (V_{HNO3} + V_{gel}) / f_e$

Where C_{eluent} is the eluent concentration in micrograms per liter, V_{HNO3} is the volume of 1 N nitric acid used to extract metal from the resin, V_{gel} is the volume of the gel, and f_e is the elution factor. To calculate the time-integrated metal concentration in the DGT device (C_{DGT}), the following equation was used:

(2) $C_{DGT} = M\Delta g / (DtA)$

Where M is the mass of metal accumulated on the resin layer; Δg is 0.093 cm, or the thickness of the diffusive gel layer (~0.8 mm) plus the filter (~0.13 mm); D is the diffusion coefficient for each metal in pure water at 22°C; t is the deployment time (s), and A is the exposure area of the chelex resin (3.14 cm^2).

$K_{d\text{-BIO}}$ parameters

The present study adapted a calculation of a historical distribution coefficient (e.g., see [5,18,19]) using DGT measurements (Eqn. 3):

$$(3) \quad K_{d\text{-BIO}} = [metal]_{total\ recoverable} / [metal]_{DGT}$$

The total recoverable fraction is the acid-digested concentration of metal in surface soil (Cd_{total}, Ni_{total}), and Cd_{DGT} or Ni_{DGT} is the time-integrated metal concentration (averaged over 72 h) measured using DGT.

Quality control

Replicates, in addition to trip, field, and rinsate blanks, were collected at each field site. Laboratory quality control (QC) consisted of HNO_3 blanks, check standards, spikes, and certified reference materials 2711, 2710, 1640, 1515, and 1573a from the National Institute of Standards and Technology. 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 Cd in all certified reference materials was 99% ($n = 40$; certified reference materials: 2711, 99%; 2709, 97%; 1573a, 100%; 1640, 100%). For Ni, average recoveries were 98% ($n = 40$; certified reference materials: 2711, 101%; 2709, 96%; 1573a, 107%; 1640, 96%). In addition, an in-house reference soil was utilized in each

analytical run and irrigation waters were collected and analyzed for metal content each year from the irrigated sites.

Data analysis

SigmaPlot® 2003, version 8.0 (SPSS) was used for graphical representations. For statistical analyses, SigmaStat®, Version 3.1 (Systat Software) was used to determine treatment, and yearly effects. Minimum significance levels were $p < 0.05$.

RESULTS

Total recoverable Cd and Ni concentrations

Across all sites, significant increases in Cd_{total} were observed as fertilizer treatment level increased (Dunn's all-pairwise multiple comparison analysis [MCA], $p < 0.001$, $n = 192$) (Table 3). The average increase from the baseline Cd_{total}, taken from fields that were fallow in 2003, to T1x (2004–2006) was 43% averaged for all sites. Across all field sites for the typical agronomical (T1x) application rates, Cd_{total} increased an average of 22% each year following the first fertilizer applications in 2004. Taking into account the dilution to the fertilizer using the plot area and a 22 cm till depth, Cd soil loads for T1x ranged from 1 to 9 (mean 5) g/ha/year across all sites, significantly greater than the Cd load reported by McBride and Spiers [20] of 1 g/ha/year. Across all sites at T3x, an

averaged increase of 35% each year was observed following initial fertilizer applications.

These results contradict those of Jones et al. [21] who sampled soils from fields fertilized for 20 years under typical agronomical practices. The authors reported that 50-year projection models of fertilizer applications would increase total recoverable Cd by a maximum of 11.2% per year with the continuation of current practices. McBride and Spiers [20] reported that Cd accumulation in agricultural soils would take decades to occur with applications of a (6–24–24, N–P–K) phosphate fertilizer. Differing soil physical and chemical properties and site-by-site variances in soil nutrient needs may lead to increased Cd accumulation in agricultural soils, despite recommended phosphate fertilizer applications.

No notable increasing treatment effect was observed for Ni_{total} concentrations across all sites. However, significant Ni accumulation in soils over the three-year study was observed (Dunn's MCA, $p < 0.001$, $n = 192$). No differences of Ni_{total} concentrations between irrigated and dry sites were noted. Across all sites small increases in Ni_{total} concentrations from the baseline (2003) to 2004 of 4% for T1x and 5% for T3x was observed. At all sites, the average yearly increase of Ni_{total} concentrations after initial fertilizer application was 10% for T1x and 11% for T3x indicating little difference between treatment levels, but that Ni did accumulate in soils over time.

While total recoverable Cd and Ni concentrations increased in agricultural soils over time, they were in general, not well correlated with Cd and Ni concentrations found in wheat berries and potato. Results from Spearman rank order correlations across all sites and years, reveal no significant correlation between Cd_{plant} and Cd_{total} ($r^2 = 0.10$, $p = 0.17$), nor with Ni_{plant} and Ni_{total} ($r^2 = 0.08$, $p = 0.28$).

Table 3.

DGT Cd and Ni concentrations

Significant increases in Cd_{DGT} concentration with increasing fertilizer treatment were measured over the four-year study (Table 3). The treatment effect at both dry-1 and dry-2 sites averaged from 2004 to 2006, resulted in Cd_{DGT} values increasing 56 and 61%, respectively, from T1x to T3x (Holm–Sidak MCA, $p < 0.001$). Increasing trends were observed at irr-1 from 2004 to 2006. Compared with the Cd_{DGT} baseline results, T1x and T3x across all years contained 297 and 826% more Cd, respectively. Increases in labile Cd reflect Cd input from P fertilizer applications, as evidenced by significant correlations with Cd loads from fertilizer in regression analyses previously described [22]. Soil perturbation through tilling [23] may also have influenced labile Cd levels, considering all fields were fallow for at least one year before baseline measurements were taken.

In general, the Cd_{DGT} fractions did not increase in a dose response relationship each year. In 2005, the average Cd_{DGT} across all sites and treatments was significantly greater than all other years, including 2006 ($p < 0.001$). The increase in Cd_{DGT} in 2005 coincides with the lowest pH values observed at all sites, although typical agronomical field conditions were maintained. Soil pH has been shown to be an important factor in metal lability [24]. Soil-metal buffering and metal fixation over time under circumneutral, agricultural conditions also play a major role in determination of metal lability [25]. In a model developed by Hamon et al. [6], a 1.5% fixation of phytoavailable Cd occurred each year on plots that historically received phosphate fertilizer treatments. Fixation and/or release of labile Cd from a broad range of soils can be captured to some extent using DGT and may be an economically feasible alternative to radiolabeled studies.

Across all years and treatment levels, Cd_{DGT} at irrigated sites was double that of the dry sites, while Ni_{DGT} at irrigated sites was over three times that of dry sites (Dunn's MCA, $p < 0.05$). Significant increasing treatment effects in Ni_{DGT} at both irrigated sites were measured and increasing trends at the dry sites were observed. These results are consistent with the relative insolubility of Ni in noncontaminated soils, typical of human food cropping systems. Upon introduction to soil, rapid sorption of Ni occurs [26]. Following sorption, slow dissolution due to aging effects can increase labile Ni^{2+} [26]. However, in the present study, no significant yearly changes in Ni_{DGT} concentrations were

measured across all sites. Under field conditions, the DGT metal concentration was influenced by physical and chemical properties specific to the two irrigated sites. Hence, the irrigated sites were analyzed separately from the dry sites to evaluate changes in $K_{d\text{-BIO}}$.

Fertilizer treatment alters $K_{d\text{-BIO}}$ in aged soils

Decreases in $K_{d\text{-BIO}}$ were observed with increasing fertilizer treatment level for both Cd and Ni (Table 3). Across all sites, significant decreases from the baseline $K_{d\text{-BIO}}$ values for Cd and Ni were observed for T2x and T3x (2004 through 2006 composited; Dunn's MCA, $p < 0.001$, Cd; $p = 0.004$, Ni). Furthermore, significant differences were observed between $K_{d\text{-BIO}}$ values at irrigated and dry field sites for both Cd and Ni (Mann–Whitney rank sum test; $p < 0.001$, $n = 100$). One consideration is that decreases in pH with increasing treatment levels resulted in elevated labile metal concentrations. However, a significant decrease in pH was measured at the irrigated sites for the T3x application level only ($p < 0.05$). At the dry sites, pH values in general were low, but did not decrease with fertilizer treatment level and were not correlated with $K_{d\text{-BIO}}$ values for Cd or Ni ($r^2 < 0.45$).

No statistical differences were observed between the control and T1x $K_{d\text{-BIO}}$ for Cd and Ni. Although Cd_{total}, Cd_{DGT}, Ni_{total}, and Ni_{DGT} increased with treatment level, the magnitude of increase was similar between the control and T1x samples, resulting in $K_{d\text{-BIO}}$ ratios that were comparable. Alternatively, application of the

ammonium sulfate (control) fertilizer used in the present study may have contributed to the mobilization of fixed Cd already present in the agricultural soils. McLaughlin et al. [27] found that sulfate additions to agricultural soils via an ammonium sulfate fertilizer increased Cd solubility. Increased diffusion of Cd^{2+} ions through the diffusive gel of the DGT device may underestimate the increasing treatment effect and may in part help to explain the large increases in labile Cd from the baseline sampling event to 2004. Despite this potential caveat with the selection of a control fertilizer, maintaining typical agronomical practices, including consistent plant yields, was a critical objective of the present study.

Despite soils aging a minimum of five months post fertilizer application, increased ion activity may have resulted in competition between metals for sorption sites [28,29]. Phosphate fertilizer is water soluble and contains predominantly metal salts and crushed phosphate rock. Release of Cd from parent rock is time dependent; as the phosphate rock ages, more Cd is released [30]. Competition for available binding sites on soil solids has been shown to suppress sorption for both Cd and Ni [28,29] and may have increased metal lability. Irrigated fertilizers undergo faster dissolution than fertilizer applied at dry sites, and likely explained the downward shifts in irrigated $K_{d\text{-BIO}}$ values. Sastre et al. [25] recommended the use of field data to estimate K_d. The authors determined that K_d values in highly fertilized soils may be overestimated under laboratory conditions, with lower cationic background levels compared to real system conditions. Overall, similar

rates of decrease for irrigated and dry sites K_{d-BIO} values with increasing treatment level were observed, emphasizing the sensitivity of this ratio to small changes in soil microclimates.

K_{d-BIO} and Cd and Ni accumulation in plants

As previously described [22], Cd_{plant} increased significantly with increasing fertilizer applications. Ni_{plant} analyses resulted in significant treatment effect with potato at irr-1 and irr-2 where T3x tubers contained an average of 53 and 99% more Ni than the control, respectively. Despite recent evidence suggesting that Ni is involved in some plant enzymatic processes and may be essential [31], Ni has no known function in humans and is responsible for several adverse health outcomes in animals, including teratogenic and genotoxic effects at low doses (www.atsdr.cdc.gov/toxprofiles/tp5-c5.pdf) [32].

Plant Cd and Ni concentrations show good agreement with field derived K_{d-BIO} values (Fig. 1). These data emphasize one of the major benefits of utilizing a dynamic K_{d-BIO} term to assist in estimating metal accumulation in crops, in that K_{d-BIO} can potentially be useful in estimating accumulation irrespective of which crop is grown. K_{d-BIO} regression results for Cd_{plant} estimation were highly significant ($p < 0.001$) and explained 76% of the variance in Cd concentrations found in wheat grain and potato across all sites and years. Estimations were also significant for Ni ($p < 0.001$), but explained only 61% of the variance of Ni_{plant}. Regression models with traditional K_d measurements (total recoverable/soil solution metal

concentrations) resulted in poor agreement with plant Cd compared with $K_{d\text{-BIO}}$ results ($r^2 = 0.29$, $r = 0.54$; $p < 0.001$; $n = 175$). Ni K_d values also resulted in poor agreement with Ni_{plant} ($r^2 = 0.32$, $r = 0.57$; $p < 0.001$; $n = 150$) in part due to detection limit constraints with soil solution measurements, in which 15% of Ni samples were below detection limits.

Figure 1. Multiple years, crops, and sites regression of $\log_{(10)}K_{d\text{-BIO}}$(L/kg) with log plant (**A**) Cd (µg/kg, dry wt) and (**B**) Ni (mg/kg, dry wt) measured in wheat and potato from four agricultural field sites 2004 to 2006. A • symbol is used to represent wheat grain and a ▴ symbol is used for potato. The solid line represents a regression line and dashed lines represent the 95% confidence interval. For Cd, minimal risk levels (MRLs) based on a 0.2 µg/d/70 kg adult dry weight intake [36] are shown, including the intersection where plant Cd concentrations or corresponding $K_{d\text{-BIO}}$ will surpass the MRL. No oral MRL exists for Ni.

Regression analyses for both Cd and Ni in crops grown at irrigated sites resulted in a better fit with $K_{d\text{-BIO}}$ than crops grown at dry sites (irrigated: $r^2 = 0.49$, $r = 0.70$; dry: $r^2 = 0.16$; $r = 0.41$; $p < 0.01$). One explanation for the poor fit with $K_{d\text{-BIO}}$ at dry sites is that soluble and loosely absorbed metals are considered to be more available for plants [11]. Soils that received constant water input via irrigation presumably had more labile metal in solution, which was demonstrated

by irrigated wheat, which contained 38 and 47% more Cd and Ni, respectively, than dry wheat. Transpiration can also affect Cd accumulation in crops, and is controlled in part by soil moisture content. In a previous study, transpiration rates were shown to decrease with exposure to elevated Cd concentrations in nutrient solution [33]. However, recent evidence suggests that transpiration rates increase at noncontaminant levels typical of food cropping systems [34,35]. Van der Vliet et al. [34] also offer convincing evidence in support of the hypothesis that genetic variation between cultivars of wheat have a profound effect on the propensity for Cd translocation to grain. Overall, prediction of plant metal concentrations would have been skewed had total recoverable metal alone been used in the model. This was evidenced by the dry sites resulting in significantly greater total recoverable Cd and Ni concentrations than irrigated sites ($p < 0.001$ and $p < 0.008$, respectively), while plant metal concentrations were significantly lower at dry sites.

The $K_{d\text{-BIO}}$ measurements account for bioaccessible metal in the root zone, measured by DGT, in addition to nonlabile metal fractions accessible to plants. These attributes support the inclusion of a dynamic $K_{d\text{-BIO}}$ term in risk characterization models. Across all sites, 31% of wheat grain Cd levels surpassed the chronic oral minimal risk level (MRL) of 0.0002 mg Cd/kg person/d [36] (www.atsdr.cdc.gov/toxprofiles/tp5.html#bookmark15.), and 27% of those in exceedance were sampled at irrigated sites (Fig. 1A). Potatoes did not exceed

the MRL for Cd. Of the grain samples above the MRL, 73% were sampled from T2x or T3x treatment levels. However, many T1x samples were near, or surpassed the MRL. According to the regression model of the present study, only slight decreases in K_{d-BIO} could shift a significant fraction of plant samples into deviation under typical agronomical practices. For example, based on the Cd_{plant} and K_{d-BIO} MRL model, a 10% reduction in K_{d-BIO} values would result in a jump from 31 to 67% of grain samples in exceedance of the MRL for Cd.

Changes in K_{d-BIO} over time

To assess changes in K_{d-BIO} over the three-year study period, individual sites were compared. At all sites, Ni K_{d-BIO} values did not change significantly over the three-year study period. While Ni_{total} increased over time, Ni_{DGT} showed only nonsignificant increasing trends. In general, Ni binds tightly to soils and soluble Ni fractions rapidly decrease with time [37,38]. The soils used in the present study were aged a minimum of five months prior to sampling. Aging effects may explain the consistent Ni_{DGT} concentrations over time despite increased input. In general, decreases in Cd K_{d-BIO} 2003 to 2005, with 2005 being significantly less than all other years, were followed by an increase in 2006, irrespective of fertilizer treatment level (Fig. 2). Cd_{DGT} followed the opposite trend across all sites where small, albeit significant, increases were measured from 2003 to 2005, followed by a decrease in 2006.

Figure 2. Cd_{plant} concentrations (dry wt) plotted with changes in $\log_{(10)} K_{d\text{-BIO}}$ (Cd_{total}/Cd_{DGT})(L/kg) over time at agricultural field sites. T1x and T3x application levels are shown (Plant, $n = 16$) ($K_{d\text{-BIO}}$, $n = 4$). Two of the agricultural field sites were irrigated (designated irr-1, irr-2), and two were dry land (dry-1, dry-2). The • symbol represents $K_{d\text{-BIO}}$ for T1x, while the ○ symbol represents $K_{d\text{-BIO}}$ for T3x. The ▼ symbol represents plant concentration for T1x, while the ▽ represents plant concentration for T3x. Plant concentrations include wheat and potato data.

Capturing these changes in labile metal utilizing the $K_{d\text{-BIO}}$ relationship is critical for two reasons: Cd $K_{d\text{-BIO}}$ tracks well with multiple plant species over multiple growing seasons (Fig. 2) and $K_{d\text{-BIO}}$ measurements provide information about the environmental fate of Cd and Ni in agricultural systems. A consideration of the first critical finding is that crops take up a significant amount of the Cd that is put into the system. This is evidenced by regression results from a previous study, which show that soil-Cd load is an important factor in estimating plant Cd [22]. Advancements in metal fractionation tools, such as DGT, allow measurement of labile metal fractions in the root zone, which is critical to accurately capture the metal fraction that a plant encounters in the rhizosphere. In a risk assessment by Courchesne et al. [39], changes in soil microenvironments, such as the rhizosphere, were found to constitute a much larger impact on trace metal cycling with plants than metal measurements in bulk soil solution. Recently, Rengel and

Marschner examined the emergence of bioengineered crops that exuded significantly more chelating compounds to access nonavailable nutrient pools in soils [40]. While this may be important for increasing yields, the risk of enhanced metal accumulation exists. Especially as agricultural technology advances, it is important to define as clearly as possible the distinct relationships between labile metal and metal accumulated in the edible portion of a diversity of crops. $K_{\text{d-BIO}}$ values provided crop-specific information about the metal fraction that undergoes multiple transport phases to accumulate in the edible portion.

Regarding the second critical finding, information about changes in $K_{\text{d-BIO}}$ over time in transient systems, using typical agronomical practices, helps to supplement the current gap of field studies. Field validation data, including bioavailability assessment and accounting for natural variability within and between sites was recently emphasized as a target to improve soil risk characterization models [2]. Sustainable agricultural practices such as fallow years, crop rotation, and liming may allow time for metal fixation in soils or decrease labile metal concentrations [23]. Cadmium mobility is exponentially larger as a labile fraction in soil solution than bound to bulk soil. The lack of increasing labile Cd fractions, captured using $K_{\text{d-BIO}}$ values, may indicate a decreased risk of leaching. This idea is consistent with the results from Ingwersen and Streck [35] who found limited Cd horizontal mobility below 0.5 m

after 40 years of irrigation with wastewater. Hamon et al. [6] found no evidence of offsite movement of Cd after 50 years of single superphosphate applications.

The long-term implications are that Cd_{total} and Ni_{total} are increasing over time, despite being sampled from cropped fields—some loss of total recoverable metal may occur due to loss via biomass [21]. However, yearly fertilizer applications, atmospheric deposition, and practices such as tilling post harvest chaff, may replenish soil concentrations. Questions remain whether continuous Cd and Ni input to agricultural soils creates a situation in which a critical level will be reached. Studies are needed to define this critical level in distinct soil systems with distinct agronomical practices [41].

Acknowledgements

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