REGULAR ARTICLE

Trace element uptake dynamics for maize (*Zea mays* L.) grown under field conditions

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Abstract

Background and aims The trace element uptake process of plants is a key factor in assessing the risks of trace element build-up in agricultural soils. Scarce information exists on the trace element dynamic uptake of plants grown in the field, especially on those potentially hazardous. In this study, the uptake process of As, Cd, Cu, and Zn in maize plants was quantified and characterized throughout the entire season.

Methods Along two seasons, the uptake dynamics of field-grown maize plants in absorbing the soil borne trace elements was examined. Biomass production and the concentration of the elements in plant and soil solution samples were determined. A kinetic model was employed to characterize the uptake by plants.

Results The kinetic parameters of the uptake process, maximum cumulative uptake rate, U_{max}, time to reach 50 % of U_{max}, t_{U50}, and reciprocal of the uptake rate, b_U when followed throughout the season in terms of the plant's growing degree days remained constant between seasons and were element specific. In spite of the large amount biomass produced, maize plants extracted minute quantities of Cd and As. Increasing cumulative uptake rates of As, Cd, Cu, and Zn from the soil took place primarily in the early half of the growing season when the biomass accumulation was still less than 50 % of the maximum harvested biomass. The element-specific plant uptake factor (PUF), which denote the partition of trace elements between the soil solution and plant phases, decreased following

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a first-order kinetics along the growing period, did not show any significant difference between seasons, and, at maturity stage, followed the sequence Cd≥Zn>Cu≥As.

Conclusions The uptake process of the elements was adequately described by the kinetic model, showing similar patterns but different magnitude and distribution in the plant. The extraction of Cd and As by plants is low in comparison to common inputs through fertilizer applications into maize production systems, indicating potential risk of trace element accumulation in soils. The *PUF* may be estimated according to the kinetics parameters of the uptake process. On a per-unit-soil solution element basis, Cd and Zn would be more susceptible to the soil-to-plant transfer than As and Cu.

Introduction

Trace elements, in metallic and metalloid forms, are ubiquitous in the terrestrial environment. While many are essential for the livelihood of biota in minute quantities, practically all of them have adverse biochemical effects if thresholds are exceeded (Pierzynski et al. 2005). Through anthropogenic activities, trace elements accumulate and become enriched in terrestrial ecosystems, thus entering the soil-plant continuum and being inadvertently transferred along the food chain to harm humans and foraging animals. Global circulation and atmospheric fallouts, mineral extraction and smelting, industrial emission, fertilizer application, and waste disposal are common modes of their transmissions (Chang and Page 2000; Dach and Starmans 2005; Nicholson et al. 2003).

Plant uptake would be a key process to evaluate environmental risks of trace element accumulation in soils. However, there are comparatively few studies that monitored the trace elements uptake dynamics for field-grown plants, especially of potentially hazardous elements. The concentrations of trace elements in harvested plant tissues may be experimentally related to those of the corresponding soils on which the plants were grown (Guttormsen et al. 1995; Huang et al. 2006). In risk assessment, the plant uptake of trace element from soils is customarily characterized by a linear transfer coefficient namely the plant uptake

factor, *PUF* (L soil solution kg^{-1} biomass), based on experimental data that:

$$PUF = C_{plant}/C_{ss} \tag{1}$$

where C_{plant} denotes the trace element concentration in plant tissues (mg kg^{-1}) and C_{ss} denotes the trace element concentration of the soil solution in which the plants were grown (mg L^{-1}). Soil solution concentration is considered a good predictor of metal bioavailability (Gerritse et al. 1983; Kabata-Pendias and Pendias 2001). Free metal activity in the soil solution has been suggested to be the best indicator of metal bioavailability (Minnich et al. 1987; Parker et al. 1995), however, it is more difficult to determinate on a routine basis. In turn, C_{ss} can be estimated through a linear trace element distribution coefficient, K_d (L kg^{-1}) that:

$$K_d = C_{total}/C_{ss} \tag{2}$$

where C_{total} denoted the total trace element concentration of soil (mg kg^{-1}). The distribution coefficient strongly depend on soil properties like pH, clay and organic matter content, involves the global trace element-soil interactions, and has been used to assess the fate of metals in soils (Sauvé et al. 2000).

The element-specific *PUF* of a plant species is considered to be constant at a given time (e.g., harvest) and soil conditions, and can be obtained from outcomes of cultivating plants under field conditions (Huang et al. 2006; Soriano and Fereres 2003) or short-term potting cultures (Lehoczky et al. 2006; Lorenz et al. 1997). Chen et al. (2009a) showed that *PUF* of selected food crops grown in fields in California exhibited a normal distribution with rather narrow data dispersions.

The transfer factor described by Eq. 1, *PUF*, is empirical in nature. It indicates steady state conditions and a linear mass transfer of trace elements between those in the soil solution and those absorbed by plants, and it doesn't take into consideration the dynamic interactions between root and soil in the nutrient absorption process. Besides, the trace element uptake rates vary among elements (Mullins and Sommers 1986), chemical species of an element (Abedin et al. 2002; Habbas and Meharg 2008), and due to soil environment conditions (Perriguey et al. 2008).

Conceptual considerations

Michaelis-Menten kinetic model has been used to characterize dynamics of elemental uptake by plants:

$$J = \frac{J_{\max} \times C_{ss}}{K_m + C_{ss}} \qquad (3)$$

where J (mg cm^{-1} root day^{-1}) is the trace element influx rate of plant root and is a function of trace element concentration in the solution phase, C_{ss} (in this case µgL^{-1}), J_{max} (mg cm^{-1} root day^{-1}) is the maximum solute uptake influx, and K_m (mgL^{-1})=C_{ss} when J=0.5 x J_{max} is the root permeability coefficient. The C_{ss} is an overall result of the processes governing the chemical reactions of trace element in soils. The parameters J_{max} and K_m represented characteristics of the plants and are considered constant for a plant species. The cumulative plant uptake rate, $U(t)$ (µg cm^{-3} soil day^{-1}) of time t, is obtained when uptake influx, J, is multiplied by the root density, $R(t)$ (cm root cm^{-3} soil), that is a function of time, t:

$$U(t) = R(t) \times J = R(t) \times \frac{J_{\max} \times C_{ss}}{K_m + C_{ss}} \qquad (4)$$

The total uptake is obtained by integrating Eq. 4 over the growing period as the root density is a function of time, t.

The Michaelis-Menten kinetic model empirically depicts the processes through which plants absorb nutrients and contaminants (Darrah and Staunton 2000; Silberbush et al. 2005). However, this approach is problematic for modeling the uptake process under realistic conditions. It was challenging to adopt this model for crops growing under the field conditions (BassiriRad et al. 1999). The J_{max} and K_m have been obtained customarily under a steady state condition over a short growth period in laboratory settings (e.g., Abedin et al. 2002; Mullins and Sommers 1986). However, the uptake in the field is a dynamic non-steady-state process that depends on the growing conditions, plant age, and nutrient status (Steingrobe and Schenk 1994, and references therein). During the growing season, the root density and thus the total element uptake rise in proportion with time. It is difficult to measure the root density, and there is not a simple and accurate field-based technique to assess the time dependent change in root density (Tudoreanu and Phillips 2004).

Typically, the plant growth can be divided into phases of early accelerating, exponential, and final saturation growth stages toward maturity. The plant biomass and root density grow accordingly. The increase in the above-ground biomass (BM) over time generally follows a sigmoidal trend so that:

$$BM(t) = \frac{BM_{\max}}{1 + \exp^{\frac{-(t - t_{BM50})}{b_{BM}}}} \qquad (5)$$

where $BM(t)$ is the cumulative biomass at time t of the growing season, BM_{max} is the maximum biomass (kg ha^{-1}) at the time of harvest, b_{BM} (time unit) is the reciprocal of the growth rate, and t_{BM50} is the time for plant to reach 50 % of BM_{max}. To minimize effects on plant growth due to fluctuations of ambient temperatures, the plant growing time can be expressed in terms of cumulative plant growing degree days (GDD, °C-day). By normalizing the time scale in terms of plant GDD, t_{BM50} (in °C-day) can be considered as a constant for a given species. In this manner, the BM_{max} may be estimated by measuring the plant biomass, $BM(t)$, at any time t (in °C-day). Assuming that plant uptake is proportional to the biomass of growing plants, the trace element cumulative uptake rate could be determined as (Chen et al. 2009b):

$$U(t) = \frac{U_{\max}}{1 + \exp^{\frac{-(t - t_{U50})}{b_U}}} \qquad (6)$$

where $U(t)$ and U_{max} (gha^{-1}day^1) denote the cumulative uptake rate of trace element at time t and at time of harvest, respectively, b_U (time unit) was the reciprocal of the uptake rate, and t_{U50} is the time for plant to reach 50 % of U_{max}. Again, t_{U50} can be expressed in terms of GDD.

By integrating the Michaelis-Menten and the uptake kinetics models, Chen et al. (2008, 2009b) characterized the Cd uptake by lettuce (*Lactuca sativa* L.) plants grown on an Entisol. The root density of growing plant is a function of its above ground biomass. With this assumption, the Eq. 4 can be written in terms of time-dependent changes in biomass, $BM(t)$, as follows:

$$U(t) = BM(t) \times R_{root-shoot} \times \frac{J_{\max} \times C_{ss}}{K_m + C_{ss}} \qquad (7)$$

where $U(t)$ represents the cumulative plant uptake rate at time t after seeding and $R_{root\text{-}shoot}$, the root-to-shoot ratio (cm root kg^{-1} biomass), is a constant. This way it was possible to relate the actual uptake rates to the Michaelis-Menten parameters.

The total uptake (U) at time t can be obtained from the element content in the plant tissue (mgkg^{-1}) and the corresponding biomass, $BM(t)$. By integrating Eq. 7, the change of the element content in the plant tissue with time can be obtained:

$$C_{plant}(t) = C_{ss} \times PUF_0 \times \exp^{-b_{PUF} \times t} \tag{8a}$$

$$PUF(t) = PUF_0 \times^{-b_{PUF} \times t} \tag{8b}$$

where $PUF(t)$ is the plant uptake factor as a function of time and PUF_0 represents a hypothetical PUF that is the PUF when $t=0$, and b_{PUF} is an equation parameter. Experimental data showed that PUF for grain maize at time close to maturity stage tends to reach a stable minimum value (Molina 2009), thus PUF(t) can be better described as:

$$PUF(t) = PUF_h + A \times^{-b_{PUF} \times t} \tag{9}$$

where PUF_h is the PUF at time when the transfer from soil to plant completes (harvest), A is an equation parameter, and $PUF_h + A = PUF_0$, i.e., the theoretical PUF at $t=0$. These equations illustrate the dynamic process of trace element uptake by growing plants and characterize the kinetics of trace element transfer from soils to plants.

Different absorption mechanisms and distribution of trace elements within plants may be described, depending on the element, the plant type, and the phonological stage (Prasad 1997). The model represented by the Eqs. 6–8 was evaluated by Chen et al. (2009b) only for Cd uptake in field-cultivated lettuce (leafy vegetable). Consequently, the model has not been applied to compare different trace elements or tested on a different plant species (e.g., cereals).

Objectives

We hypothesize that plant uptake of soil borne trace elements is a time-dependent dynamic process, and develop the following field scale experiment and use

the outcomes to: i) quantify and characterize As, Cd, Cu, and Zn absorption of maize (Zea mays L.) over the growing season, and ii) evaluate the kinetics of trace element uptake process. These elements present different environmental health challenges as they cross the soil—plant inter phase (WHO 2009).

Materials and methods

Site description

The field experiments were set up at a large scale production farm located in San Pedro (34º01'S, 71º22'W), Región Metropolitana, central Chile. The average annual rainfall is 350 mm and average daily temperature was 13.9 °C. The soil is a Mollisol (Mixed, thermic, Ultic Haploxerolls) with high natural fertility and it is typical of the region where maize is intensely cultivated. The site had been under conventional tillage maize cultivation since 1993 and received heavy fertilizer and herbicide applications. The phosphorus (P) fertilizers used over the years had been mono-ammonium phosphate (MAP) and triple superphosphate (TSP) that were the highest in As, Cd, Cu, and Zn contents among fertilizers commonly used in Chilean croplands (Molina et al. 2009). A central pivot irrigation system was employed.

Crop management

During two following growing seasons, a 0.14-ha area within the production field was selected for the experiment. Grain maize (var. Mycogen 2878) was sown in mid October with 0.75 m distance between rows and at an average population of 95,000 plants ha^{-1}. Typical cultivation practices were followed. Fertilizers were applied at rates of 400 kgNha^{-1} as urea, 65.5 kg P ha^{-1} as MAP, and 150 kgKha^{-1} as potassium chloride (KCl). The MAP and KCl, accounting for 7 % of the total N and 100 % of the total P and K fertilizer inputs, were applied at time of planting. The urea was applied in 6 split applications through the central pivot irrigation system. The total irrigation ranged between 650–700 mmha^{-1}.

The GDD were calculated according to:

$$GDD = \sum_1^n (T_m - T_b) \tag{10}$$

where T_m is the average daily air temperature (°C), T_b is the physiological base temperature for maize growth (10 °C), and n is the number of growing days; (T_m - T_b)=0 °C if T_m<10 °C and (T_m - T_b)=20 °C if T_m> 30 °C. The crops were harvested toward the end of March when plant growth accumulated between 1,320–1,380 GDD.

Soil and plant sampling and analysis

Above-ground plant biomass samples were taken 6 to 7 times during the course of a growing season. The first sample was taken at plant growth stage of 3–4 leaves. Each time, composite tissue samples consisting of three plants in a row were obtained at three randomly selected locations in the experimental plot. The plant material was separated into two portions namely stem + leaves and ears, washed with a diluted HCl solution, rinsed with double-distilled water, and dried at 65° until reaching constant weight. The dried plant material was then ground to pass a screen with 0.5-mm openings and sub-sampled. Aliquots of 0.5±0.001 g ground plant tissue were microwave digested in Teflon pressure bomb with 4 ml HNO$_3$ (65 %), 4 ml H$_2$O$_2$ (30 %) and 2 ml deionized water according to USEPA Method 3052 (USEPA 1996). The Cd content of the digests was determined by graphite furnace-atomic absorption spectroscopy and As content of the digests was determined by hydride-generation atomic absorption spectroscopy. The copper and Zn contents were determined by inductively coupled plasma-optical emission spectroscopy.

Composite soil samples were taken from the plow layer (0–25 cm depth), passed through a screen with 2-mm openings, and air-dried. The samples were characterized according to procedures outlined in the *Methods of Soil Analysis* of American Society of Agronomy (Page et al. 1982): determinations of soil texture by the hydrometer method, pH and electrical conductivity in extracts of 1:2.5 (w/v) soil to water ratio, organic carbon by chromic acid digestion, exchangeable bases by equilibrating with ammonium acetate at pH=7.0, and CaCO$_3$ equivalent by the gravimetric method (Table 1). At the beginning of each season, soil samples (three replicates) were taken and the soil solution concentration (C$_{ss}$) of trace elements was

Table 1 Selected properties of the soil

Parameter	Measurement
Soil Texture	Clay loam[a]
Sand	35.0 (%)
Silt	25.2 (%)
Clay	39.8 (%)
pH$_{H2O}$	5.6
Electrical conductivity	0.14 (dS m^{-1})
Sum of bases	16.8 (cmol kg^{-1})
Organic matter	2.9 (%)
CaCO$_3$ equivalent	1.8 (%)

[a] According to USDA soil classification

estimated by equilibrating soil and water mixtures (soil-to-water ratio of 1:0.5) for 48 h in an orbital shaker rotating at 40 rpm (Chen et al. 2007). After the equilibrium, samples were centrifuged and filtered. The concentration of As, Cd, Cu and Zn were determined on the solutions by the same analytical methods as the plant tissue digests.

Quality control and assurance

Quality of analysis was assured by comparison with certified standard reference materials SRM 2709 (soil), SRM 1547 (peach leaves) and SRM 1640 (water) from the US National Institute of Standards and Technology (NIST). The analysis was repeated if deviation was >10 %. To ensure the precision of the analysis, each sample was digested and analyzed in duplicate. The concentrations of the replicates were compared and the analysis was repeated if the replicate difference was >10 %. Spiked samples were also used to establish if matrix interference was causing amplification or decrease in sample response.

Data analysis

The experimental data were fitted to the model equations using a non-linear regression procedure using SigmaPlot 10.0 (Systat Software Inc.). Statistical comparisons between seasons and among different elements were done by comparing the confidence intervals (CI, 95 % probability) of the equations' parameters as estimated by the non-linear regression procedure.

Table 2 Trace element contents (mean concentration ± standard deviation) and partition coefficients (K$_d$) of the experimental soil

Element	Total, C_{total}, (mgkg^{-1})	Solution, $C_{sol,}$ (mgL^{-1})	K$_d$ (Lkg^{-1})
As	9.1±1.0	$1.74 \times 10^{-3} \pm 1.8 \times 10^{-4}$	5,230
Cd	0.27±0.026	$2.19 \times 10^{-4} \pm 5.6 \times 10^{-5}$	1,230
Cu	32.3±2.4	0.229±0.043	141
Zn	65.4±3.0	0.255±0.052	286

Results

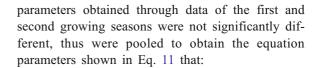### Trace element contents of the soil

The total As, Cd, Cu, and Zn contents of the soil (Table 2), C_{total}, were well within the concentration range for soils under agricultural cultivations around the world (Kabata-Pendias and Pendias 2001). Trace element concentration of the soil solution, C_{ss}, representing the extent of readily plant available As, Cd, Cu, and Zn of the soil, were a small fraction of the respective total amount (Table 2) and the kinetics of their dissolution from solid phases would expected to be slow (Chen et al. 2006). The Cd and As in soil solution phase represented less than 0.042 % and the Cu and Zn in soil solution phase represented less than 0.36 % of their respective total contents.

For all trace elements, no significant differences ($p < 0.01$) were recorded for C_{ss} when compared at the beginning of the two consecutive seasons. The same was valid for soil pH and EC (data not shown). Even when it is well recognized that C_{ss} in the rizosphere may change throughout the season due to the influence of roots on soil pH, organic acids concentration, and water content (Gobran et al. 2001), the bulk soil solution concentration is less sensitive to such effects. Chen et al. (2009b) observed that bulk Cd-C_{ss} slightly varied over the growing season, with no significant effect of time in a soil cultivated with lettuce. Thus, for modeling purposes, the bulk C_{ss} could be considered constant.

The K_d values were comparable in magnitude to those of agricultural soils reported elsewhere (Chen et al. 2009a) and were considerably lower than those of the soils contaminated by anthropogenic activities (Sauvé et al. 2000).

Biomass production and trace element uptake

The above-ground biomass production grew according to Eq. 5 in which $R^2 = 0.99$. The equation parameters obtained through data of the first and second growing seasons were not significantly different, thus were pooled to obtain the equation parameters shown in Eq. 11 that:

$$BM(t) = \frac{BM_{max}}{1 + \exp^{\frac{-(t-795)}{187}}} \quad (11)$$

For maize, the time (GDD) to reach 50 % maximum biomass, t_{BM50}, was 795 °C-day and the exponential biomass growth rate (GDD^{-1}), b_{BM}, was 187 °C-day^{-1}. Based on Eq. 11, the biomass yield of maize can be tracked and the maximum biomass yield can be obtained by simply measuring the biomass at time t during the course of a growing season and set t to the targeted harvesting growing degree days of the plant.

When maize plants were harvested, the concentrations of As and Cd in the shoot + leaves portion were approximately one order of magnitude higher than those of the ear portion while the concentrations of Cu and Zn in shoot + leaves portion were comparable to those of the ear portion (Table 3). In Table 3, the concentration range over the growing season was temporally classified to depict the gradually decreased trace element concentrations of plant tissue over time. The element concentrations of both the shoot + leaves and ears portions of maize were the highest at the early stage of their formations and decreased over the time until shortly before harvesting.

Table 3 Trace elements in maize plants: Concentration range (mgkg^{-1}) from beginning (3–4 leaves growth stage) to end of the growing season

Plant part	As	Cd	Cu	Zn
Shoot + leaves	0.053–0.024	0.045–0.019	9.6–2.9	38.3–14.1
Corn ears	0.016–<0.009[a]	0.016–<0.005[a]	3.6–1.6	32.5–15.0

[a] Limit of detection

The trace element uptake rate (Fig. 1), $U(t)$, followed the same pattern of the cumulative increase of plant biomass and fitted the model described by Eq. 6 (Table 4). The maximum
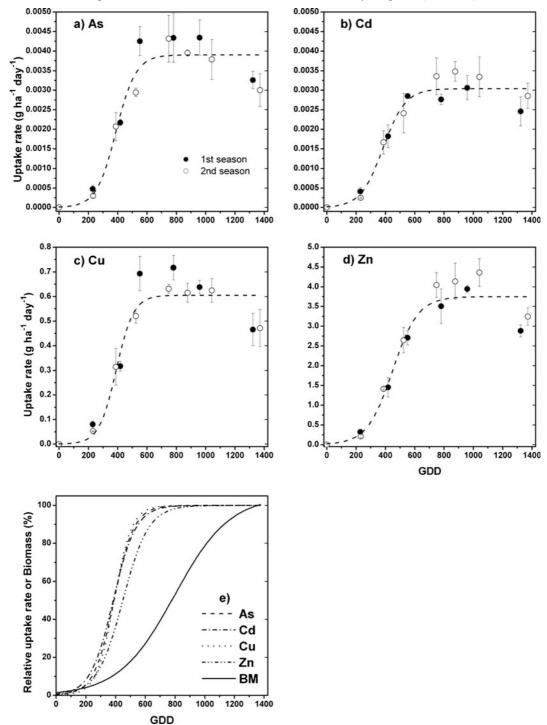

Fig. 1 Trace element cumulative uptake rate (a-b), and relative biomass accumulation (BM) and element uptake (e) of maize plants as a function of growing degree days (GDD) showing mean and standard deviation of experimental data and depictions according to Eqs. 5 and 6

Table 4 Trace element uptake kinetics (Eq. 6) for maize plants. U_{max} maximum cumulative uptake rate, t_{U50} time to reach a 50 % of U_{max}, b_U reciprocal of the uptake rate, *GDD* growing degree days. ± indicates confidence interval (95 %)

Kinetic parameters	As	Cd	Cu	Zn
U_{max} (gha^{-1}day^{-1})	$3.9\times10^{-3}\pm0.3\times10^{-3}$	$3.0\times10^{-3}\pm0.1\times10^{-3}$	0.61 ± 0.03	3.75 ± 0.17
t_{U50} (*GDD*)	389 ± 25	384 ± 20	390 ± 24	449 ± 24
b_U (*GDD*)	67.5 ± 23.8	76.7 ± 18.0	59.1 ± 24.5	86.6 ± 23.4
R^2	0.917	0.950	0.906	0.940

[a] Calculated according to Eq. 8

uptake rate, U_{max}, were 3.9×10^{-3}, 3.0×10^{-3}, 0.61, and 3.8 gha^{-1}day^{-1} for As, Cd, Cu, and Zn, respectively. The patterns of $U(t)$ vs. t (GDD) plots for As, Cd, Cu, and Zn were virtually the same. For all of the elements, the $U(t)$ exhibited a notable dip at the time of harvest, comparing to that of the previous sampling date (Fig. 1a through d). The discrepancy might be attributed to the loss of basal leaves as the plants drying out resulting to an underestimation of biomass thus the maximum uptake rate at harvest, U_{max}. During the seedling stage from 0 to 200 degree days, the plant uptake of trace elements was low due to the limited root density. The trace elements started to accumulate in the plant tissue in the exponential manner according to the biomass growth from 200 to 600 degree days. Afterwards, the cumulative uptake rate leveled off and reached the U_{max}. For As, Cd, and Cu, the U_{max} was reached at 600 to 700 degree days during the R1 anthesis (silking) stage of plants. The U_{max} for Zn was reached approximately 7 days later at 700 to 800 degree days when the plants were between the R2 blister and R3 kernel stages coinciding with the t_{BM50} for cumulative biomass (Eq. 11).

Plant uptake factor

The PUF of As, Cd, Cu, and Zn decreased exponentially over the growing season (Fig. 2) according to Eq. 9 (Table 5) showing that biomass accumulation is faster than the root absorption and transfer of the elements to the above-ground biomass of plants (mass dilution effect). When the time was normalized in terms of *GDD*, the PUF remained fairly consistent over the two growing seasons and was well described by this first order reaction model (Fig. 2). The PUF decreased

approximately 7.2, 6.3, 7.6, and 3.6 times for As, Cd, Cu and Zn, respectively, from the early growing stages to harvest time. From seeding to the R2 stage (700 GDD), the PUF followed the sequence: Cd>Zn>Cu>As. From the R2 stage, when the maximum uptake rate for Zn was reached, the sequence was: Cd≥Zn>Cu≥As (Fig. 2e, Table 5).

Discussion

Trace element uptake

The concentrations of As, Cd, and Cu in the shoot + leaves portion were consistently higher than those in the ear portion throughout the season, indicating that there were physiological barriers that hinder the passage of these elements from stem + leaves to the ears, especially for As and Cd. In the case of Zn, there appeared to have a remobilization of this element from other parts of plants to the ears (Petruzzelli et al. 1989). At harvest, the percentage of trace elements in the ears, in relation to the total uptake, showed that Zn>Cu>Cd>As (Fig. 3, Table 6) in that As and Cd contents of the ears represented less than 9 % and 20 % of the total plant uptake, respectively. The trace metals that play a role as micronutrients, Cu and Zn, in the stem + leaves and ears portions were approximately 45 to 55 % splits. Maize plants extracted small amounts of trace elements from soils. In spite of the large biomass production, the total uptake of trace elements by maize averaged 0.52, 0.43, 77.1, and 520 gha^{-1}year^{-1} for As, Cd, Cu, and Zn, respectively (Table 6). It is interesting to note that for As and Cd these amounts are considerably lower than their annual inputs through P fertilizer applications for typical
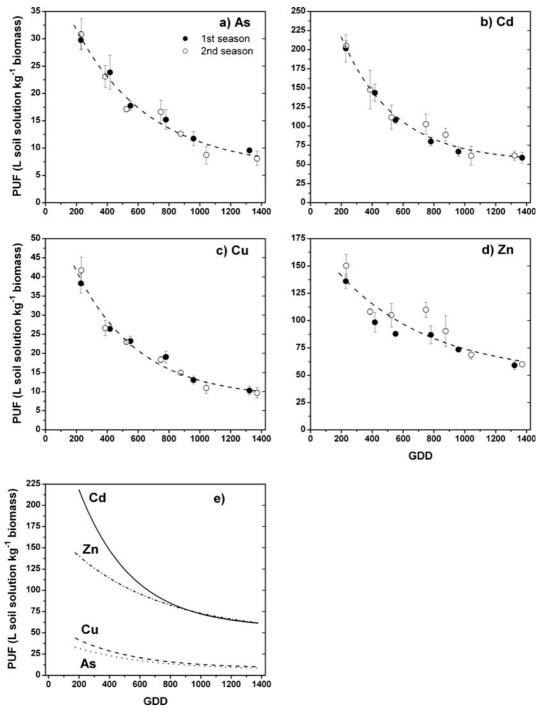
Fig. 2 Plant uptake factor (PUF) as function of growing degree days (*GDD*) for maize plants showing mean and standard deviation of experimental data and depictions according to Eq. 9

high-yield maize production system in Chile that fell in the range of 3.6 to 6.4 g As ha^{-1} and 1.2 to 17.4 g Cd ha^{-1} (Molina et al. 2009). Potentially, the harmful trace elements may accumulate in the cropland soils under long-term cultivation. This situation is not always valid for Cu and Zn, whose balances in a maize-cultivated soil (soil accumulation), can be positive or negative strongly

Table 5 Kinetics of trace element plant uptake factors, PUF (Eq. 9), for maize plants. PUF_0 theoretical PUF at t=0, PUF_h=PUF at time close to harvest. ± indicates confidence interval (95 %)

Kinetic parameters	As	Cd	Cu	Zn
$PUF_0 = PUF_h + A$ (L soil solution kg^{-1} BM)	44.6±8.5	341±28	62.8±11.3	177±55.9
PUF_h (L soil solution kg^{-1} BM)	6.3±3.7	53.8±6.4	8.3±3.5	49.8±22.7
b_{PUF} (GDD)	$2.06\times10^{-3}\pm0.74\times10^{-3}$	$2.86\times10^{-3}\pm0.71\times10^{-3}$	$2.46\times10^{-3}\pm0.74\times10^{-3}$	$1.66\times10^{-3}\pm0.91\times10^{-3}$
R^2	0.973	0.982	0.977	0.849

depending on the trace element content of applied fertilizers (Molina 2009).

Increasing uptake rates of As, Cd, Cu, and Zn from soils took place primarily in the early half of the growing season when the biomass accumulation was still less than 50 % of the maximum harvested biomass (Fig. 1). The uptake rate then reach a stable maximum value (U_{max}) which is governed by the increment of biomass and a lower accumulation of trace element per unit of plant biomass. The absorbed trace elements would then be redistributed inside the increasing plant tissue biomass during the later stage of growth. Even when As and Cd have no relevance in terms of plant nutrition, their uptake patterns are similar to Cu and Zn.

Plant uptake factor

The drop of the PUF has been attributed to a greater root competition, decrease in the activity of both mature and young roots, and/or greater proportion of lower-activity mature roots in relation to younger roots as the plants develop to maturity (Barber 1995; Mengel and Barber 1974a). It was early demonstrated that the root density in maize plants tends to decrease from flowering to maturity stage (Mengel and Barber 1974b). Consequentially, the element uptake potential also decreases along the season. Even when no significant differences were noted between the kinetics of the drop of the PUF, represented by b_{PUF}, this parameter was lower for Zn in comparison to the other metals (Table 5) indicating a relative lower decrease of Zn-PUF along the season in comparison to the other elements. Because of the greater transfer to ear biomass (Fig. 3), the active absorption of Zn is kept over time and the absorption activity is higher in relation the other three elements. These results agree with those reported by Karlen et al. (1988), who observed that more Zn was accumulated during grain fill than that was
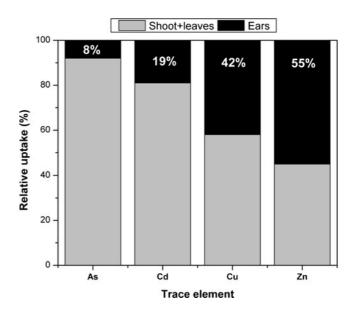
Fig. 3 Trace element distribution in harvested maize plants

Table 6 Trace elements in maize plants: Total uptake (gha^{-1}) at harvest time. Mean±standard deviation

Plant part	As	Cd	Cu	Zn
Shoot + leaves	0.470±0.029	0.360±0.024	45.2±4.8	236±26
Corn ears	0.040±0.023	0.080±0.022	32.2±4.1	286±17
Whole plant	0.520±0.030	0.430±0.046	77.1±5.0	520±43

lost from vegetative parts, which indicated that the ability of maize roots to uptake Zn is kept along the growing season.

The absorption of As, Cu, and Zn in plants is mainly active (Abedin et al. 2002 Bowen 1987; Reid 2001). In the case of Cd both passive and active mechanisms can be involved (Harris and Taylor 2004; Smeyers-Verbeke et al. 1978). At the beginning of the vegetative stage Cd showed a bioavailability notably higher in comparison to the other elements. At the end of the season, the availability of Cd, as assessed by the PUF, is comparable to that of Zn (Fig. 2; Table 5). According to Reid (2001), the membrane cation transporters of roots have a wide range of substrates which allow the absorption of non-essential elements, like Cd, through the channels for other cations with lower selectivity such as Ca, Cu, Fe, and Zn. In our experiment, As was the element with lowest bioavailability. The transfer of As from roots to above-ground biomass is limited in plants (Kabata-Pendias and Pendias 2001). In addition, the soil in this study has received the application of high doses of P fertilizers, and the As absorption by roots may be limited in presence of high levels of available P because of the competition of arsenate and phosphate (Gulz et al. 2005), the dominating forms of theses anions under aerated soil conditions.

Conceptually, PUF illustrates the partition of a trace element between those present in soil solution and those taking up by growing plants. In this regard, the PUF should denote the partition at the end of the soil-to-plant transferring process, PUF$_h$, i.e., when the plants matured. Therefore, for a specific element, the PUF$_h$ may be written in terms of the kinetic parameters of the uptake process as:

$$PUF_h = \frac{\frac{U_{max}}{BM_{max}}}{C_{ss}} \times days \qquad (12a)$$

$$PUF_h = \frac{\frac{U_t \times \left(1 + e^{\frac{-(t-t_{U50})}{b_U}}\right)}{BM_t \times \left(1 + e^{\frac{-(t-t_{BM50})}{b_{BM}}}\right)}}{C_{ss}} \times days \qquad (12b)$$

in which, *days* indicate the number of days to harvest.

Judging the data presented in Fig. 2 and Table 5, the PUF of Cd and Zn were at least one order of magnitude greater that those of As and Cu. On a per-unit-soil solution element basis, Cd and Zn would be more susceptible to the soil-to-plant transfer than As and Cu.

In our experiment and in a previously reported work (Chen et al. 2009b)2009b), the trace element uptake rates were related to its soil solution concentration. The kinetic parameters of the model accounted for the change of the plants' ability to uptake the elements during the growing season and allowed comparisons among them. It is well recognized that the pH, the presence of competing cations and complexing agents (i.e., soluble organic matter) in the soil solution can influence the uptake rates, making more difficult and complex the predictions of metal bioavailability. Protons and cations compete for the absorption sites at root surfaces, while complexation changes the bioavailability by competing with the plant roots for the metal (Hough et al. 2005; Kalis et al. 2006; Kunhikrishnan et al. 2011; Perriguey et al. 2008). Additionally, it has been demonstrated that trace element free concentration or activity does not necessarily improve the prediction of metal uptake by plants when compared with data obtained from total soil solution concentration (e.g., Hough et al. 2005). On this regard, the model used in this work needs to be tested on different soil types and conditions to evaluate its applicability in a wide range of agro-ecosystems, and, if necessary, analytical determinations and model calculations could be incorporated to estimate, in the soil solution, the metal speciation and to include the mentioned

soil solution factors. However, once the best indicator of metal bioavailability is defined, the model implementation and parametization remains the same.

Conclusions

We used the maize plants grown in production fields to illustrate and compare the uptake dynamics of soil borne trace elements namely As, Cd, Cu and Zn.

1. The kinetic parameters of the uptake process, maximum cumulative uptake rate, U_{max}, time to reach 50 % of U_{max}, t_{U50}, and reciprocal of the uptake rates of, b_U when followed throughout the season in terms of the plant's growing degree days remained constant between seasons and was element specific.

2. Increasing cumulative uptake rate of As, Cd, Cu, and Zn from soils took place primarily in the early half of the growing season when the biomass accumulation was still less than 50 % of the maximum biomass harvested. The uptake rate then tend to stabilize and the absorbed trace elements were redistributed in later half of the growing season as the biomass continued to accumulate.

3. The plant uptake factor, PUF, which denote the partition of trace elements between the soil solution and plant phases, decreased following a first-order kinetics along the growing period and did not show any significant difference between seasons. This bioaccumulation index may be estimated according to the kinetics parameters of the trace element uptake process.

4. On a per-unit-soil solution element basis, Cd and Zn would be more susceptible to the soil-to-plant transfer than As and Cu.

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