

Prediction of cadmium and zinc concentration in wheat grain from soils affected by the application of phosphate fertilizers varying in Cd concentration

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Abstract Cadmium is an undesirable contaminant in phosphate fertilizer, and may represent a threat to food safety given its tendency to be taken up by plants and translocated into the edible parts. In this context, predicting wheat grain cadmium concentration from preliminary data would help to prevent exceeding the threshold values. Our study compared different approaches to estimate the concentrations of cadmium and zinc in wheat grains based on either soil solution chemistry of these elements, their quantities added to the soil and various soil parameters. Whereas the predictions based on soil solution chemistry show positive correlations between predicted and measured values of cadmium for some experimental sites, it was more difficult to predict grain cadmium concentrations in other sites. Reverse-wise, predictions based on applied cadmium and some soil parameters yielded systematically good correlations between predicted and measured values. The prediction of the concentration of zinc in wheat grains could not be achieved

as its content was neither related to the measured soil solution chemistry nor to the quantities of zinc applied to the soil. We suspect that zinc interacts with the phosphate fertilizer thus obscuring the regressions for plant uptake. The prediction of grain cadmium in wheat cultures is best achieved through empirical modeling from soil parameters and soil inputs rather than through estimates of the bioavailable fractions in the soil solution.

Keywords Phosphate fertilizer · Cadmium · Zinc · Chemical speciation · Wheat · Plant uptake

Introduction

Understanding cadmium uptake into plants and ultimately, preventing excessive transfer from soils to plant tissues intended for human consumption constitutes a daunting challenge. Soil cadmium is expected to increase progressively with its continuous application through its inadvertent presence as an undesirable contaminant in phosphate fertilizers, potentially increasing the risk of Cd accumulation in plants. Compared to most nutrients, cadmium has a relatively low mobility and it has been demonstrated that fertilizer applications can result in cadmium accumulation near the soil surface that serves as the major zone for plant nutrients (Hamon et al. 1998; Loganathan and Hedley 1997).

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The potential progressive accumulation of cadmium in agricultural soils may affect its accumulation in crops and is a potential cause for concern. In this respect, a critical load of cadmium in soil addressing human health effects through food intake was already computed based on the food quality criteria for its content in wheat grains (Brus et al. 2005; de Vries et al. 2004). The model uses regressions to link the cadmium content in wheat grains with either its free ion concentration in soil solution (de Vries et al. 2004) or its total concentration in soil and some soil parameters (Brus et al. 2005). In the first case, the free cadmium ion concentration may either be measured or estimated from other soil cadmium compartments and soil properties by regression or modeling (e.g., Sauvé 2002; Sauvé et al. 2000a, b).

The inference of cadmium phytoavailability from the free cadmium in solution relies on the mechanistic concept of the “free ion activity model” (Hough et al. 2005; Parker and Pedler 1997). Some limitations are highlighted for its difficulty in predicting metal phytoavailability through organic complexes co-transport, by non-equilibrium chemical interactions, by competitive uptake of others metals and by rhizospheric effects (Berkelaar and Hale 2003; Hassler et al. 2004; Parker et al. 2001). There is currently no biotic ligand model applicable to such agronomic soil-plant relations for plant tissue accumulations of metals (e.g. Antunes et al. 2006; Rachou and Sauvé 2008) nor do we have an alternate approach to account for the difficulties inherent in accounting for a dynamic component (Lehto et al. 2006; Nolan et al. 2005). The estimation of metal bioaccumulation using free ion concentrations in soil solution might still be the best partially mechanistic model currently available.

Accumulation of metals in plant tissues is also often predicted using totally empirical regression models linked to selected soil parameters (Brus et al. 2005; Adams et al. 2004; McLaughlin et al. 2006). This more simple estimation has the advantage of being independent of mechanistic hypotheses. In addition, it could enable us to account for interactions such as competition between metals that are not currently included in the free ion activity models for soils. Indeed, studies of competitive uptake of cadmium and zinc usually show significant interactions between these two elements, notably

antagonistic effects between the uptake of Cd^{2+} and Zn^{2+} (Hart et al. 2002; Jiao et al. 2004).

The study of low contamination levels encountered in most agricultural fields is a challenge since the range of concentration is limited and often close to the analytical detection limits. The soil chemistry and, even more so, the soil-plant transfer mechanisms observed at high contamination levels cannot be used to extrapolate what would happen under low contamination levels. The various processes involved at low and high concentrations are often quite different. Indeed, the ratio between dissolved metal concentrations and the quantity of reactive surface sites of the soils have proven to be important factors notably in the ageing processes of recently-contaminated soils.

In a previous paper, Lambert et al. (2007) described the shifts of dissolved cadmium and zinc concentrations in soils following the applications of different mono-ammonium phosphate (MAP) fertilizers. The MAP fertilizers used contained different levels of cadmium and increased levels of soil solution cadmium concentrations were observed for almost all MAP applications. In this study, we focus on parameters that can be used to predict Cd and Zn accumulation in wheat grains, as affected by Cd addition in phosphate fertilizer and soil characteristics under field conditions.

Materials and methods

Field setup

The experimental setup includes five agricultural sites from the Canadian prairies in Manitoba, Saskatchewan and Alberta (Table 1). Since 2002, a long-term experiment using annual broadcast applications of MAP fertilizers has been conducted. Three sources of MAP fertilizers were used to provide a wide range of cadmium concentrations. As determined by acid digestion, the phosphorus fertilizers contained $0.38 \text{ mg Cd kg}^{-1}$, $73.7 \text{ mg Cd kg}^{-1}$, and $211 \text{ mg Cd kg}^{-1}$ for fertilizers obtained from Ontario (Canada), North Carolina (USA) and Idaho (USA), respectively. They also contained $117 \text{ mg Zn kg}^{-1}$, $869 \text{ mg Zn kg}^{-1}$ and $3,500 \text{ mg Zn kg}^{-1}$, respectively.

Rates of phosphate applications were 0, 20, 40 and 80 kg P ha^{-1} . The 20 and 40 kg P ha^{-1} rates are representative of normal to high rates of what is

Table 1 Soil properties of the five sites

Soils	pH	Cd ($\mu\text{g g}^{-1}$)	Zn ($\mu\text{g g}^{-1}$)	OM (mg kg^{-1})	Clay (%)	Silt (%)	Sand (%)	CEC ($\text{cmol}(+) \text{kg}^{-1}$)	Iron (%)
Brandon (Manitoba)	7.7	0.28	69	28	36	34	30	34	0.79
Ellerslie (Alberta)	6.6	0.26	57	50	35	52	13	42	0.93
Ft. Sask. (Saskatchewan)	7.5	0.26	82	51	18	12	70	42	0.93
Phillips (Manitoba)	7.6	0.26	72	38	18	12	70	35	0.86
Sylvania (Manitoba)	6.5	0.20	50	30	18	12	70	20	0.87

usually applied for wheat production in Western Canada, whereas 80 kg P ha^{-1} is used to represent the effects of excessive inputs of fertilizers. A treatment without any phosphate fertilizer application serves as a control. The 10 treatments were replicated four times in a randomised complete block design for a total of 40 plots per site. Fertilizer treatments have been applied annually since 2002 and the crops were seeded each year following a durum wheat (*Triticum durum* Desf.)-flax (*Linum usitatissimum* L.)-durum wheat cropping sequence. Durum wheat received 80 kg N ha^{-1} N and flax received 60 kg N ha^{-1} as commercial urea fertilizer, side-banded at the time of seeding or pre-plant banded immediately prior to seeding, depending on the seeding equipment available. No other fertilizer nutrients were applied because the soils at the sites were sufficient in K, S, and micronutrients for optimum crop yield. Registered herbicides were applied as required for control of the weed spectrum present. Crops were harvested at maturity using a plot combine. Correlations in this paper are based on durum wheat grown in 2004, after 3 years of fertilizer applications.

Analyses

Soil analyses were conducted according to protocols described earlier (Lambert et al. 2007). Briefly, clay content was measured by hydrometer technique, total organic carbon by wet oxidation and potentiometric detection, cation exchange capacity by BaCl_2 displacement method and extractable iron by dithionite citrate extraction.

Soil solutions were obtained using water extractions with 5:1 liquid:soil ratio (50 ml:10 g) during 18 h and were then centrifuged 20 min at 4,400g. The supernatant was filtered through $0.45 \mu\text{m}$ cellulose

nitrate membranes and analyzed for anions (Cl^- , NO_3^- , SO_4^{2-} , and PO_4^{3-}) by ion chromatography with an NH_4^+ -saturated column and conductimetric detection, dissolved organic carbon with a Tekmar Dohrman Apollo 9000 TOC analyzer, pH by combined glass electrode and Cd and Zn by ICP-MS (Varian, UltraMass 700) with prior acidification to 2% using trace-metal grade HNO_3 .

The low cadmium concentrations in the soil water extracts and the potential interference from other metals complicates the use of the ion selective electrode or polarography to measure free ions in solution (Gulens 1987; Sauvé et al. 2000a, b; Sauvé and Parker 2005). These concentrations were therefore not analyzed but calculated from dissolved metal concentrations and solution chemistry.

Wheat (*Triticum durum* Desf.) cultures were harvested at seed maturity, dried at 60°C and a 500 mg subsample of the grain prepared by closed-vessel microwave digestion with nitric acid (6 ml). Cadmium was determined by transverse-heated platform graphite furnace equipped with longitudinal Zeeman background correction and zinc by flame atomic absorption using the recommended flame conditions with deuterium background correction as described in Gawalko et al. (2001).

Modeling

The free cadmium in solution was calculated using the speciation model Visual MINTEQ 2.40 (Gustafsson 2006). In addition to solution concentrations of cadmium and zinc, data for soluble anions (Cl^- , NO_3^- , SO_4^{2-} , and PO_4^{3-}), dissolved organic carbon, ionic strength and soil pH were computed. Both the Gaussian model and the Stockholm Humic model were compared to account for the role of

dissolved organic carbon. Free metal concentrations were then tested as predictors of bioaccumulated metals in wheat grains using simple linear regressions.

Dissolved metal fractions were also tested as possible predictors of the bioaccumulated fractions using simple linear regressions, first for each location taken individually and then for all sites combined together. The soil solution concentration of metals is believed to integrate a variety of factors such as the applied treatments, the soil chemistry and the geochemical context, and may therefore serve as better predictors of bioavailability or effects in the soil environment.

An empirical modeling of bioaccumulated cadmium and zinc was finally performed using stepwise multiple regressions. The variables were transformed with the logarithm to normalize the variances and to match a Freundlich relationship, as proposed between plant cadmium and soil cadmium (Brus et al. 2005).

$$\log Q_{\text{plant}} = a + b \times Q_{\text{soil}}$$

where Q_{plant} and Q_{soil} are the metal concentrations in plant tissues and total soil contents, respectively and where the intercept a represents the environmental factor formulated as:

$$a = \sum a_i \times X_i$$

with X_i is the studied parameter.

All statistical analyses were performed using SPSS 13.0 (SPSS Inc. 2004).

Results and discussion

Cd and Zn wheat grain contents

All the wheat grains grown on the control plots contained a cadmium concentration below 0.1 mg kg⁻¹ dry weight. The grain cadmium content increased with fertilizer addition and exceeded the 0.1 mg kg⁻¹ level for 45% of the 200 plots but remains below the 0.2 mg kg⁻¹ threshold level of the *Codex alimentarius* for all but two samples. The increase with fertilizer application was significant in three of the five sites when low P fertilizer rates were used and in all five sites when high P rates were applied. The same three ‘sensitive’ sites also showed higher Cd in the grains when low rather than high

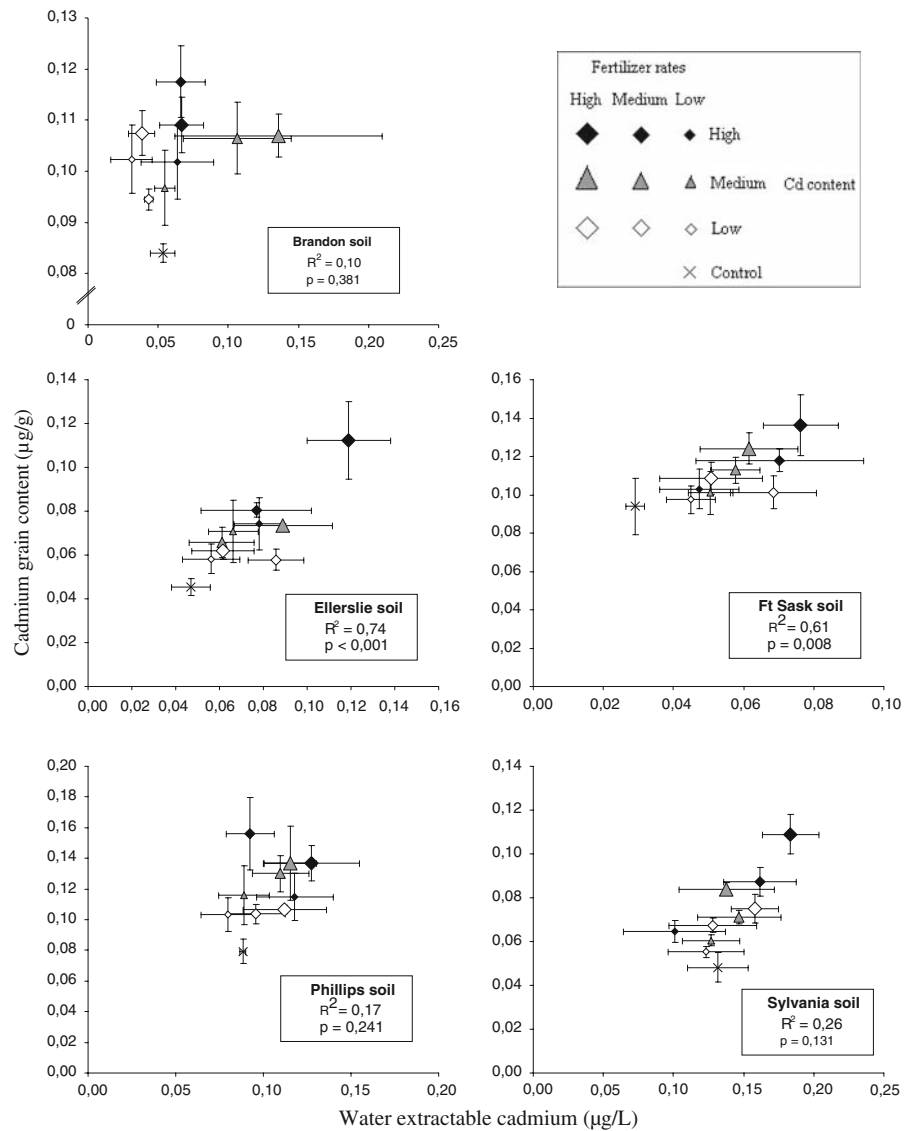
cadmium fertilizer sources were applied, while Cd concentration in the grain was increased at all five sites by application of the high cadmium fertilizer. Wheat grain yield also increased significantly ($P < 0.01$) at 4 of the 5 sites in 2004, with the maximum increase at each site ranging from 20 to 66% (data not presented). At the fifth site, grain yield was numerically higher with P fertilizer than without, but the difference was not statistically significant. As both grain yield and grain Cd concentration increased with P application, total Cd accumulation in the grain, as calculated by multiplying grain yield by the grain Cd concentration, also increased.

The zinc content of wheat grains was lower in all fertilized plots than in the control plots. This negative relation between plant Zn and phosphate addition is not new (Alloway 2004) but the explanation as to whether this is a chemical effect or a physiological effect is unresolved. There are some indications that phosphate additions reduce the solubility of zinc thus potentially limiting root uptake (Lambert et al. 2007). However, soil chemical effects and physiological impacts are intricate and difficult to separate. The three-way interaction among Cd, Zn and P for plant uptake complicates its investigation.

Free ion and dissolved concentrations as predictors

Simple linear regressions of grain cadmium against calculated free ionic cadmium yielded a significant but poor relation for all sites taken together. Taken separately, only two sites among the five sites studied present a significant regression fit of the grain Cd to its free ion concentration in the water extracts. Similar regressions made with dissolved cadmium concentrations rather than with free ion concentrations show, except for one soil, a better fit to the grain Cd values. The regressions are presented in Fig. 1. However, only the same two sites that showed a significant regression between grain Cd and free ion concentration in water extracts still demonstrate a significant regression with dissolved Cd concentrations. In our case, the calculated free ion concentrations fail to explain a large part of the variation in cadmium grain concentrations as would have been expected according to the free ion activity model. The calculated free cadmium activity was expected to give a better account of the geochemical context and to integrate the effects of the fertilizer

Fig. 1 Linear regression of bioaccumulated cadmium by soil water-extracted cadmium in then five experimental sites (mean values with standard errors)



treatments. The data actually show that the dissolved cadmium fraction is comparatively a slightly better predictor of the Cd grain concentrations than its calculated free ion activity.

Depending on the rates and grades of the fertilizer applications, cadmium from fertilizers may represent from a 10th and up to 50 times the content of the water-extractable cadmium in the soil when calculated over the top first 15 cm of the soil profile. In comparison, while the quantity of added cadmium ranges over more than two orders of magnitude among treatments, the increase of water-extractable cadmium in soils is limited to a factor from 1.25 for the lower cadmium additions up to 2 for the higher

cadmium additions. The buffering effect of the soil on the dissolved cadmium concentrations limits the range of variation between treatments to a level close to the variability observed between replicates.

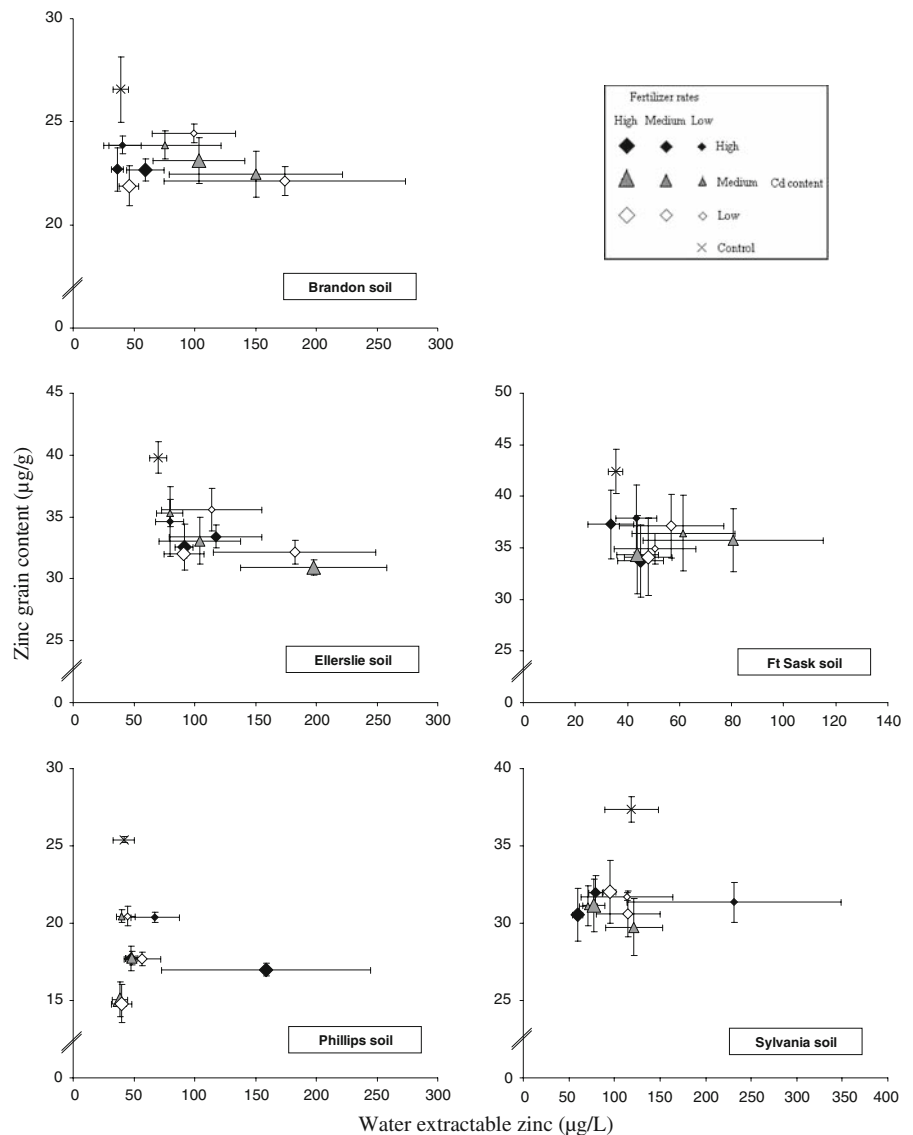
Indeed, the observed variability of dissolved cadmium among replicates, as illustrated in Fig. 1, is important relative to the variation among treatments. Regressions performed with each replicate values rather than with mean values do not show any significant relationships between grain Cd and dissolved Cd values. In addition, the natural variability of soil parameters such as pH among replicates varies by as much as 0.6 pH units. The integration of this variability in the chemical parameters of the water

extracts used for the free ion calculations seems to introduce an increased variability which may then reduce the usefulness of the free ion predictions of grain cadmium compared to dissolved cadmium.

Even if the observed variability seems to be the major limit to the prediction, it is important to recognize that the measured metal concentrations in the soil provide an indication of the metal concentration at a particular time. The measured metal concentrations do not systematically allow us to accurately predict the bioavailable fraction over a given time frame (as one would expect to happen over a growing season).

No relation comes out of the simple linear regressions of plant Zn with dissolved Zn. The main features of zinc uptake into grains are a negative relation with phosphate fertilizer applications as illustrated in Fig. 2. However, if lower grain concentrations of zinc are observed with increasing P applications, no clear decrease and even some local increase of water-extractable Zn can be observed. Albeit zinc is added as a contaminant in the phosphate fertilizers, it does not show a concomitant increase in the tissue concentrations as observed for cadmium. Its solubility is probably subjected to two opposite effects: the increase of total soil zinc

Fig. 2 Relation of plant zinc with water extracted zinc in five experimental sites (mean values and standard errors)



concentrations and a precipitation process with phosphate when phosphate fertilizers are added.

In the present case, it is suspected that the water extraction methodology may solubilize a somewhat larger fraction of soil zinc than what is normally found in the soil solution and this may therefore not adequately reflect the actual availability of zinc. This hypothesis is enforced by other data which show decreasing Zn concentrations with increasing fertilizer rates when measured using diffusive gradients in thin films (DGT) devices (Zhang et al. 1998; François et al. 2006). The high liquid-to-soil ratio combined with the end-over-end shaking during the water extraction contrasts with the simple contact equilibrium of soil and water before DGT measurements and may be the cause of an excessive zinc solubilization compared to what is actually phytoavailable.

Empirical modeling

The individual analysis of each site attempts to account for the intra-site soil parameters variability in addition to the variability due to the applied fertilizer treatments. Indeed, soil solution variables present a large variability which may certainly have an influence on the bioavailability of the metals. The results are presented in Table 2. The total yearly added cadmium is the main explanatory variable of the bioaccumulated cadmium for every site. In addition, three of these sites also have pH as predictor. Soil pH is slightly decreased by the addition of phosphate fertilizers and this will certainly impact the metal solubility and availability. Some influence of soluble anions is also observed. We can observe that Cl^- and PO_4^{3-} ions actually have a positive influence on the availability of cadmium, each in one site. Nitrate

ions, on the other hand, have a negative influence on plant uptake of cadmium in another site. However, it is difficult to conclude whether the variation of those ions have a direct influence on cadmium uptake or are marginal consequences of the treatment. Nevertheless, chloride ions are known to form complexes with cadmium which have been shown to enhance its phytoavailability (Smolders et al. 1998).

The interaction between cadmium and zinc for plant uptake is not highlighted in this study probably as a consequence of a higher interaction between P and Zn in soil solution.

Conversely to plant cadmium, tissue zinc concentrations do not present any prominent parameter common to all sites (Table 3). Soil pH however, is involved significantly in its explanation at three of the five sites. As was observed for cadmium, soil pH shows a negative influence on zinc availability. Soluble chloride ions represent a significant explanation as well being positively correlated with the tissue zinc concentrations.

In order to account for the geochemical context on the fate of phytoavailable metal fractions, multiple regressions that integrate the data from the five sites were also performed. Data about clay content, soil organic matter (SOM), cation exchange capacity (CEC) and iron oxide content were then added to the regressions. They represent a single measure for each site and so do not include slight variations within treatments and replicates at each site.

For cadmium, while added cadmium and soil pH remain among the best predictors of grain cadmium, clay content, SOM and CEC appear to explain a significant portion of the overall variability among sites. Clay content and SOM act as negative factors on cadmium bioaccumulation whereas CEC is a positive factor (Table 4).

For zinc, the comprehensive regression enforces the prominent role of soil pH on its bioavailability. Among the newly added soil parameters, only clay content shows a significant, yet negative impact on phytoavailability of zinc. The soluble anions NO_3^- and SO_4^{2-} are the only positive factors explaining a significant part of zinc bioavailability whereas chloride ions show no significant influence (Table 5).

Both for cadmium and zinc plant uptake, the empirical modeling yields a much better estimation compared to mechanistic modeling based on soil solution chemistry. The mechanistic prediction still

Table 2 Results of the multiple regression of bioaccumulated cadmium values in the five sites

Standardized coefficients Beta of the variables						
Sites	R_{adj}^2	Added Cd	pH	Cl^-	NO_3^-	PO_4^{3-}
Brandon	0.295	0.560				
Ellerslie	0.816	0.646	-0.358	0.445		
Ft. Sask.	0.509	0.413	-0.577			
Phillips	0.620	0.535	-0.540		-0.237	
Sylvania	0.735	0.544				0.502

Table 3 Results of the multiple regression of bioaccumulated zinc values in the five sites

Standardized coefficients Beta of the variables										
Sites	R_{adj}^2	pH	Added Zn	Cl^-	PO_4^{3-}	NO_3^-	SO_4^{2-}	Grain Cd	Soluble Zn	DOC
Brandon	0.41	-0.33						-0.41	-0.44	0.37
Ellerslie	0.47		-0.40	0.51		0.25				
Ft. Sask.	0.76	-0.74			-0.32		-0.40			
Phillips	0.40		-0.47	0.31	-0.43					
Sylvania	0.63	-0.34	-0.24	0.30		-0.30				

Table 4 Results of the multiple regression of bioaccumulated cadmium values over all sites

Standardized coefficients Beta of the variables									
R_{adj}^2	Added Cd	pH	SOM ^a	Clay content	CEC ^b	PO_4^{3-}	Cl^-	Soluble Cd	
0.73	0.46	-0.29	-1.27	-0.89	1.47	0.19	0.13	-0.11	

^a SOM, Soil organic matter

^b CEC, Cationic exchange capacity

Table 5 Results of the multiple regression of bioaccumulated zinc values over all sites

Standardized coefficients Beta of the variables							
R_{adj}^2	pH	NO_3^-	SO_4^{2-}	Added Zn	Clay content	Soluble Cd	Soluble Zn
0.73	-0.56	0.27	0.24	-0.14	-0.12	-0.22	-0.09

suffers some a lack of accuracy, notably in two aspects: on one side, the methodology that was used to measure dissolved metal fractions seems to give more reliable results for cadmium than for zinc; on the other side, the assessment of the free ion or soluble metals at a single sampling time does not necessarily match what occurs in the field over the growing season. This dynamic aspect cannot be accounted through simple water extracts.

The empirical modeling shows, on the contrary, that with a few key values based on soil chemistry, it is possible to have a good estimate of the magnitude of plant metal uptake and translocation into the wheat grains.

Conclusions

The total cadmium added to the soils and some key soil properties were better estimators of cadmium availability than an integrative parameter like water-extractable cadmium or even the calculated free metal species. pH, clay and soil organic matter contents

together with soluble anions (PO_4^{3-} , Cl^-) were the most indicative of the wheat grain Cd.

Cadmium taken up by the wheat grain was proportional to Cd added in the fertilizer each year. However we currently cannot differentiate between annual and cumulative effects.

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