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Environmental Contamination and Toxicology

Evaluation of Cd Uptake by Plants Estimated from Total Soil Cd, pH, and Organic Matter

F. Li,[1] M. Okazaki,[2] Q. Zhou[3]

[1] Faculty of Environment and Life Sciences, Liaoning University, Shenyang 110036, People's Republic of China
[2] Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan
[3] Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110036, People's Republic of China

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Numerous studies show that total soil cadmium content alone is not a good measure of short-term bioavailability and not a very useful tool to determine potential risks from soil contamination (Zhou *et al.* 1994; McBride 2002). In view of the fact that plants take up most nutrients from the soil solution, it is often assumed that the dissolved Cd is readily available to the organisms (Barber, 1984). The free Cd^{2+} ion or dissolved Cd in soil solution shows a relatively strong dependence on total soil Cd and soil pH (Sauvé *et al.* 2000). Thus, an equation of the general form given below has been obtained from Cd measured in dilute salt extracts from variably contaminated soils:

$$\log(\text{dissolved Cd}) = a + b \cdot \text{pH} + c \cdot \log(Cd_T) \qquad (1)$$

where Cd_T and pH are the total soil Cd concentration (mg/kg) and soil pH (in water), respectively. However, from the metal complexation theory which relates the metal activity of soil solution to the soil's pH, organic matter (OM) and total metal content (M_T), McBride *et al.* (1997) reported the following semiempirical equation:

$$pM = a + b \cdot (\text{soil pH}) + c \cdot \log(M_T OM^{-1}) \qquad (2)$$

where pM is the negative logarithm (to base 10) of the metal activity, and a, b and c are constants. The equation successfully predicted free Cu^{2+} activity in soils with a wide range of properties. Research has suggested that soil organic matter was not always, but often a statistically significant variable in predicting metal solubility from soil properties. There is evidence indicating that plant uptake of Cd decreased with an increase in soil organic matter (Eriksson, 1988), however, research by He and Singh (1993) suggests a positive relationship between soil organic matter and the bioavailability of total soil Cd.

Much attention has been paid to cadmium speciation and bioavailability in soils, as well as the relationship between the bioavailability of cadmium and soil properties. McBride (2002) tested actual predictions of Cd uptake by crops using combination of total soil Cd and soil pH. It shows that Cd uptake by leafy crops was estimated reasonably well. Although other factors, particularly soil texture, mineralogy and soil organic matter, are likely to affect the bioavailability of Cd in

Correspondence to: F. Y. Li

different soils, the lack of data for these soil parameters has limited tests of their significant controlling plant uptake. So far, it has been well established that Cd uptake by crops is dependent on total soil Cd, soil pH and soil organic matter content, however, actual prediction of Cd uptake by plants based simultaneously on these three soil parameters has not generally been tested. This study reanalyzed available data on the uptake of Cd by plants from soils, e.g., sewage-sludge-amended soils, urban soils and naturally developed soils by using Eq. (2).

MATERIALS AND METHODS

Data sets were selected from published literatures, where soil pH and organic matter content, as well as Cd concentration in the plant and soil have been reported. A statistical reanalysis of this data was done using multiple regression (Statistica, StatSoft Inc.1995), where the dependent variable was the logarithm (to base 10) of Cd concentration (mg/kg dry weight) in plant tissue, and the independent variables were soil pH, the logarithm (to base 10) of total soil Cd (Cd_T, mg/kg) to soil organic carbon content (C, g/kg) ratio. The objective was to determine whether a satisfactory estimate of aboveground plant tissue Cd could be made based on total soil Cd, pH and organic carbon content as suggested by the form of Eq. (2).

RESULTS AND DISCUSSION

The dependence of Cd uptake by lettuce on soil pH, total soil Cd and organic matter content was tested initially with the data set (40 individual measurements) for lettuce grown on long-term sewage sludge treated soil in Maryland, USA, which was presented by Brown *et al.* (1998). Studied soils in this research were maintained under both acidic (pH 5.0~5.4) and near-neutral (pH 6.2~6.9) pH conditions at several Cd contamination levels up to 5.7 mg/kg Cd in the topsoils. Soil organic carbon content ranged from 12.5 g/kg to 20.7 g/kg. The best-fit predictive equation was found by multiple regression analysis to be:

$$\log(\mathrm{Cd}_{\mathrm{lettuce}}) = 3.36 - 0.24\mathrm{pH} + 1.27\log\mathrm{Cd}_{\mathrm{T}} - 1.27\log\mathrm{C} \qquad (3)$$
$$\gamma = 0.961$$

with all parameters having a high level of significance ($P<0.0001$). The coefficient of independent variable C in Eq. (3) was negative, which shows that soil organic matter has a significantly protective effect on Cd uptake by lettuce. Herein, the constant of independent variable soil pH was negative, which represents that Cd uptake by lettuce decreased with the increment of soil pH.

The logarithms of the individual predicted (from Eq. (3)) and observed Cd concentrations in lettuce are plotted in Fig.1. In this case, the control treatments (labeled C) generally had greater potential for Cd uptake than the sludge treatments once pH, total soil Cd, and soil organic matter content were accounted for. This effect is evident in Fig. 1, the control plot data has shifted to positions generally below the best-fit line. In fact, when comparing control and sludge treatments with similarly low Cd levels in lettuce (data near the lower left-hand corner of Fig. (1)), Eq. (3) predicted greater potential for Cd uptake from the sludge

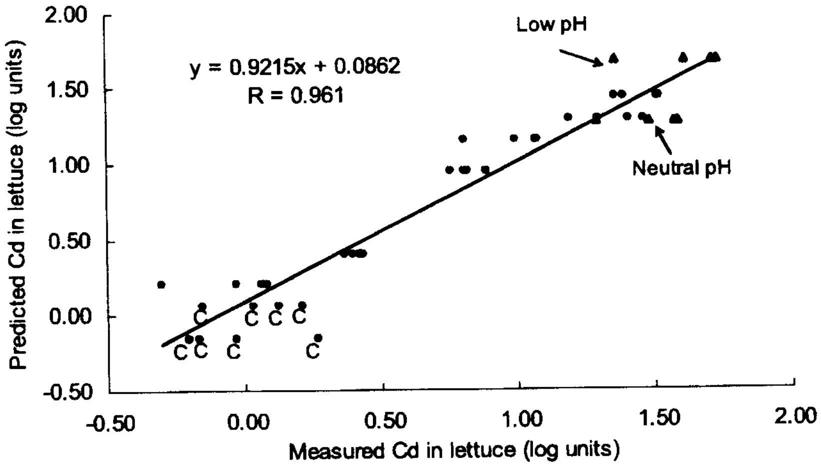

Figure 1. Predicted (by Eq. (3)) versus measured (Brown *et al.* 1998) Cd in lettuce (logarithm of tissue Cd in mg/kg units) grown on soils with and without sewage sludge. Data labeled by "C" denotes control plots without sludge application. The triangles denote data from unsludged plots where Cd had been applied in the form of soluble salt, rather than in sewage sludge.

treatments based on soil pH, total soil Cd and soil organic matter content alone. McBride (2002) attributed this to some evidence of a long-term sludge protective effect, which also was concluded by Brown *et al.* (1998). However, comparing control with Cd salt treatment, it seems that organic matter had a slight protection effect on Cd uptake at low Cd concentration levels in soil.

The triangles in Fig.1 represent Cd uptake data from experimental plots where Cd salts alone were applied. For both the acidic and neutral soil, the data fell close to the best-fit line, indicating that Eq. (3) estimates phytoavailability of Cd adequately when soil organic matter was accounted for. It shows that the sludge protection effect is present in soil under the condition of both low and neutral pH. On the basis of using the same literature, McBride (2002) concluded that strong bonding to sludge residues could not be expected in acidic soil and the sludge protection seemed to function near pH 7 regardless of soil organic matter. However, in this case, when soil organic matter was accounted for, data from the plots where only Cd salts were applied fell closer to best-fit line than the plots where only soil pH and total soil Cd were considered. It shows that organic matter does seem to have a protective impact on Cd uptake by crops under the condition of acidic or neutral pH.

The same approach to Cd uptake data was applied to a second experimental data set (23 individual measurements) for plants collected by the bulking of all vegetation at the sampling points from three inactive railway yards on the Island of Montréal, Québec, Canada (Ge Y. *et al.* 2000). In this case, soil pH (in water) ranged from 6.39 to 8.55, soil organic carbon content ranged from 13.9 to 150 mg/kg, and total soil Cd ranged from 1.0 to 13.3 mg/kg. The authors concluded that Cd uptake by

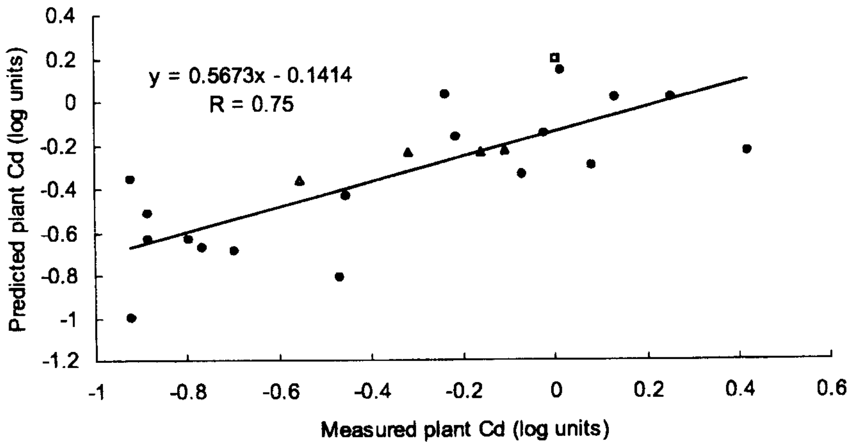

Figure 2. Predicted (by Eq. (4)) versus measured (Ge Y *et al.* 2000) Cd in plants (logarithm of plant Cd concentration in mg/kg units). Triangles represent soil sample with total soil Cd above 9.8 mg/kg and soil organic carbon above 100 mg/kg. The square represents soil sample with total soil Cd 10.6 mg/kg while soil organic carbon content was 24.8 mg/kg.

plants in situ could not be predicted by free, total dissolved and total soil Cd due to the bulking of all vegetation at the sampling points. The best-fit predictive equation was found by multiple regression analysis to be:

$$\log(Cd_{plant}) = 1.24 - 0.091pH + 0.77\log Cd_T - 0.77\log C \qquad (4)$$
$$\gamma = 0.75$$

with logarithm of total soil Cd to soil organic carbon ratio being most significant ($P<0.0001$), followed by the intercept ($P=0.152$) and soil pH ($P=0.340$). The weak significance of the pH can be attributed to the narrow pH range in the soils. Fig. 2 compares predicted and measured plant Cd (log values) based on Eq. (4).

Triangles in Fig. 2 represent that soil organic carbon content was above 100 mg/kg and also that total soil Cd concentration ranged highly from 9.8 mg/kg to 13.3 mg/kg. This indicates that plants grown in soils with high content of organic matter did have relatively low Cd concentration levels. However, the square in Fig.2 represents that soil sample (Point 1 in Yard 3) with total Cd concentration of 10.6 mg/kg and a organic carbon content of 24.8 mg/kg, which was substantially lower than that of soil samples plotted with triangles. Thus, plant Cd concentration was relatively higher compared with plants grown in soils labeled with triangles, which is evidence that soil organic content provided protection from Cd uptake by plants.

The importance of biosolids organic matter in the retention/sorption of Cd is an area of active discussion within scientific literatures, and conflicting evidence can be found suggesting the importance of organic matter breakdown in metal released from biosolids amended soils. The same approach to Cd uptake data was applied to

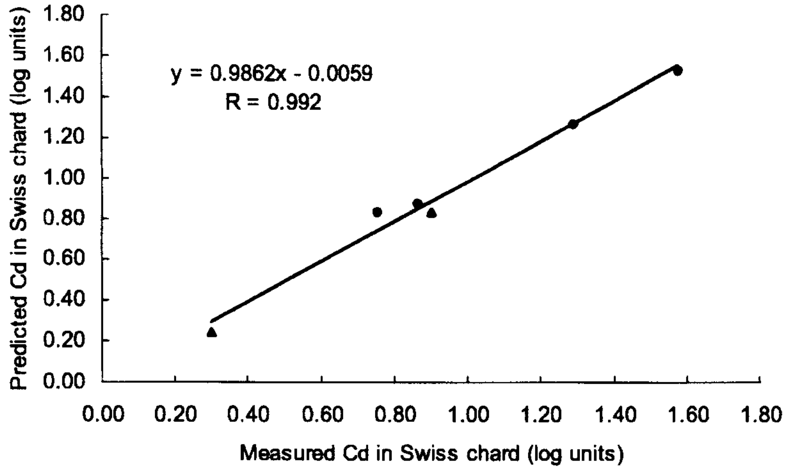

Figure 3. Predicted (by Eq. (5)) versus measured (Kim *et al.* 1988) Cd in Swiss chard (logarithm of tissue Cd in mg/kg units) grown in soils with and without sewage sludge. Triangles denote data from soils with naturally high Cd without sewage sludge.

the experiment (Kim *et al.* 1988), where Swiss chard was grown on calcareous and slightly alkaline soils (pH 6.5 to 7.9) in southern California, USA. This was a pot greenhouse experiment using six soils, two with naturally high levels of Cd (from the Santa Monica Mountains) and four from long-term sludge application sites. Data from this experiment was used to evaluate Cd bioavailability of naturally occurring Cd and of externally inputting Cd from biosolids, this produced the significant relationship:

$$\log(Cd_{Swiss\,chard}) = 5.83 - 0.19pH + 2.09\log Cd_T - 2.09\log C \qquad (5)$$
$$\gamma = 0.992$$

in this case, the coefficient of the intercept was most significant (P<0.001), followed by log Cd_T/C (P=0.0079) and soil pH (P=0.1535). McBride (2002) estimated Cd uptake by Swiss chard through combining total soil Cd with pH simultaneously, and attributed the weak significance of soil pH to the limited number of data and the narrow pH range in the soils. However, the coefficient of total soil Cd and organic matter in Eq. (5) was statistically significant for a P<0.01 level in Eq. (5). This indicates that the weak significance of soil pH might be due to the fact that soil organic matter has a stronger effect on controlling Cd uptake by crops when soil pH and organic matter were simultaneously accounted for. Fig. 3 compares predicted and observed Swiss chard Cd (log values) based on Eq. (5).

In Fig. 3, triangles represent plant Cd concentrations for the two naturally high-Cd (control) soils, and reveal no clear differences in the relative plant availability of Cd applied from sewage sludges compared with natural Cd, which was similar to the conclusion by McBride (2002). Although there has been debate for biosolids reducing Cd phytoavailability for many years, according to Eq. (5), soil organic matter was statistically significant and responsible for the reduction in phytoavailability of Cd. Thus, as organic material in biosolids decomposed, its Cd-binding function would be lost. This is evidence that the sludge treatment of soils may provide no long-term protection against Cd uptake in crops.

Regarding that the same cultivar, Swiss chard (*Beta vulgaris* var. cicla) was grown in the both experiments (by Lund *et al.* (1981) and Kim *et al.* (1988), respectively), herein, data sets for Swiss chard in the two experiments were pooled to evaluate Cd bioavailability of naturally occurring Cd and of externally inputting Cd from biosolids. This produced the significant relationship:

$$\log(Cd_{\text{Swiss chard}}) = 2.87 - 0.20\text{pH} + 0.42\log Cd_T - 0.42\log C \qquad (6)$$
$$\gamma = 0.813$$

in this case, the coefficient of $\log Cd_T/C$ was most significant (P=0.0084), followed by intercept (P=0.037) and soil pH (P=0.305). Although the soil pH range and the number of data increased by combining the two greenhouse experiments, the coefficient of soil pH was still weakly significant. This indicates that soil organic matter has a stronger effect on controlling Cd uptake by crops when soil pH and organic matter are simultaneously accounted for.

The logarithms of the individual predictions (from Eq. (6)) and observed concentrations of Cd in Swiss chard of both experiments (Kim *et al.* 1988; Lund *et al.* 1981) are plotted against one another in Fig. 4. In this case, all the sludge treatment plots data generally shifted to positions below the best-fit line once soil pH, total soil Cd and soil organic matter were accounted for. This reveals that the sludge treatment of soils provided no long-term protection against Cd uptake into crop. A comparison study of cadmium sulfate application to sludge-amended soils by Mahler *et al.* (1987) showed that Cd originating from sludge was still available for plant uptake, and it was essential to consider previous sludge application (cumulative Cd additions) in evaluating potential Cd accumulation by plants.

Metals bound by organic matter in biosolids amended soils can be released to soil solution due to decomposition of organic matter by soil microorganisms (Hooda and Alloway 1994). However, limited metal release can also be found in other published literature (Hyun *et al.* 1998). Many researchers concluded that the controversy lay in the determination of the behavior of the metals in the biosolids with aging, and the release of metals from biosolids into soils depending mainly on biosolids composition.

Stacey *et al.* (2000) observed that biosolids decomposed in soil and released metals to plant available pools even though it was considered to be aged. So far, it has been well known that the retention of metals in soils can be described by two dominant processes. One is that the metal is sorbed to the soil matrix as a readily exchangeable ion, and the other is that the metal is sorbed with a high affinity to specific sites on the soil matrix. The latter process includes the formation of inner- and outer-sphere complexes, surface precipitation, and incorporation of heavy metal ions into the mineral lattices of the soils which causes the metal to be strongly bound to the soil solid phase. However, the transport behavior of non-aged (freshly

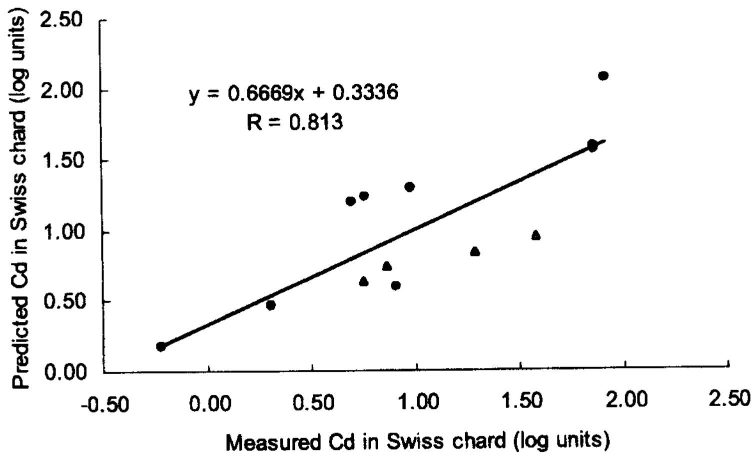

Figure 4. Predicted (by Eq. (6)) versus measured (Lund *et al.* 1981; Kim *et al.* 1988) Cd in Swiss chard (logarithm of tissue Cd in mg/kg units) grown in soils. Triangle represents data from soils amended with sewage sludge.

applied) and aged (indigenous) Cd was about the same in the humus Bh horizon and the transitional Bh/C horizon of sandy soil (Spodosol) (Seuntjens *et al.* 2001).

McBride (1995) reviewed toxic metal accumulation from agricultural use of sludge and summarized that organic matter was more effective than inorganic constituents in keeping Cd unavailable. Thus, in the long term, Cd added to soils by sewage sludge application may retain mobility, and not only cause harmful effects to humans through consumption but also adversely affect underlying aquifer.

The established equations based on the reanalysis of published literatures show that organic matter played a key role in keeping Cd unavailable in soil, whether in sludge amended soil or in naturally developed soil. Due to the input of organic matter to soils from sewage sludge application, there was no doubt that sludges initially provide a strong protection against Cd uptake by plants. Although debates exist about the permanent protective effect on Cd bioavailability in soil as regarded to the adsorption of Cd by inorganic constituents in sludges, none of the studies indicate that most soils were able to gradually convert a large portion of the added Cd to insoluble, unavailable form. As reviewed by McBride (1995), "Our best agricultural soils need to have their productivity and crop quality protected , not for 10, 20 or even 100 yr, but in perpetuity ". Still, it is essential for us to take a very cautious approach to the application of toxic metals in sludges and Cd input from other sources to agricultural soil.

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