The dynamics of heavy metals in plant–soil interactions

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1. Introduction

Heavy metal pollution is released into the environment by various anthropogenic activities, such as industrial manufacturing processes, domestic refuse and waste materials. Excess concentrations of heavy metals in soils have caused the disruption of natural terrestrial ecosystems (Wei et al., 2007; Yadav et al., 2009).

The bioavailability of metals in soil is a dynamic process that depends on specific combinations of chemical, biological, and environmental parameters (Li and Thornton, 2001; Peijnenburg and Jager, 2003; Panuccio et al., 2009).

Soil management can also change its physical, chemical, and biological characteristics, and as a result, different responses by biological activities to heavy metal toxicity can be observed. Also, the activities of microorganisms that promote plant growth can be altered by high concentrations of metals (Wani et al., 2007).

At high concentrations, all heavy metals have strong toxic effects and are regarded as environmental pollutants (Nedelkoska and Doran, 2000; Chehregani et al., 2005). Heavy metals are potentially toxic for plants: phytoxicity results in chlorosis, weak plant growth, yield depression, and may even be accompanied by reduced nutrient uptake, disorders in plant metabolism and, in leguminous plants, a reduced ability to fixate molecular nitrogen (Bazzaz et al., 1974; Chaudri et al., 2000; Broos et al., 2005; Dan et al., 2008). Soil pollution with heavy metals will lead to losses in agricultural yield and hazardous health effects as they enter into the food chain (Schickler and Caspi, 1999).

In heavy-metal-polluted soils, plant growth can be inhibited by metal absorption. However, some plant species are able to accumulate fairly large amounts of heavy metals without showing stress, which represents a potential risk for animals and humans (Oliver, 1997). Heavy metal uptake by crops growing in contaminated soil is a potential hazard to human health because of transmission in the food chain (Brun et al., 2001; Gincchio et al., 2002; Friesl et al., 2006). There is also concern with regard to heavy metal transmission through natural ecosystems (MacFarlane and Burchett, 2002; Walker et al., 2003). Parameters related to heavy metal uptake have been used as sensitive indicators of heavy metal toxicity (Nannipieri et al., 1997; Wilke, 1991). The toxicity of heavy metals in soil significantly varies with soil characteristics and the time elapsed after contamination (Doelman and Haanstra, 1984; Speir et al., 1995). Data from studies on the toxic effect of heavy metals on soils have been used to establish the concentrations at which heavy metals affect biological soil processes for regulatory purposes (Giller et al., 1998).

Although a large number of experimental studies have been carried out to analyze the negative effects of the accumulation of heavy metals in plants, little attention has been focused on mathematically formulating models capable of generally relating the concentration of heavy metals in the liquid phase of a soil and the concentration of heavy metals present in plants. In this work we model this relationship, and validate it by recently published experimental results.
2. Modeling

Many heavy metals are bioavailable in soil at natural pH levels. This mobility makes it possible for heavy metals to be absorbed by plants in forest and agricultural soils. Although chemical reactions in soil systems involve complex and diverse sequences of phenomena (Lindsay, 1979; Ulrich et al., 1980; Ulrich and Pankrath, 1983), De Leo et al. (1993) introduced a theoretical model of the interaction between soil acidity and forest dynamics when aluminum is mobilized with acid deposition, by focusing on the reaction:

\[ \text{Al(OH)}_3 + 3\text{H}^+ \rightarrow \text{Al}^{3+} + 3\text{H}_2\text{O} \]

Guala et al. (2009) simplified the parameters of the model by De Leo et al. making it possible for it to be experimentally validated without a loss of generality, and showed that the model also fits the interaction between soil acidity and the dynamics not only of forests but plants in general, when aluminum is mobilized with acid deposition. However, the presence of heavy metals in soils either as a result of natural processes or human activities may also imply similar general reactions such as the one proposed for Al, differentiated by the fact that other metals do not need low pH in order to become bioavailable. Therefore, this may lead us to consider the model as being applicable to other metals in soil, by modifying it in order to make it independent of the acid deposition, assuming the mobility of other heavy metals in natural pH levels in soil. Then, the generalized dominant reaction for any heavy metal M may be expressed as:

\[ \text{M(OH)}_n + n\text{H}^+ \rightarrow \text{M}^{n+} + n\text{H}_2\text{O} \]

In order to model the dynamic interaction between aluminum mobility due to soil acidity and plants, we can use the general mathematical expression of the model proposed by De Leo et al. (1993), further modified by Guala et al. (2009), namely:

\[
\begin{align*}
\frac{dT}{dt} &= T(h(T) - \mu(S)), \\
\frac{dS}{dt} &= \alpha A - h(T)S, \\
\frac{dA}{dt} &= \phi H - \beta A - \frac{\alpha A T}{p}, \\
\frac{dH}{dt} &= -\phi H - \beta H + \frac{W}{p}
\end{align*}
\]  

(1)

where T is the biomass of trees (kg m\(^{-2}\)), S is the concentration of Al\(^{3+}\) in trees (mg kg\(^{-1}\)), A and H are the concentrations of Al\(^{3+}\) (mg l\(^{-1}\)) and H\(^+\) (mg l\(^{-1}\)) in the soil solution, respectively. \(t\) is the time, \(W\) is the flux of protons to the soil during rain (mg m\(^{-2}\) year\(^{-1}\)), \(p\) is the available water for roots (mm) and \(\alpha\), \(\beta\) and \(\phi\) are coefficients of absorption (1 kg\(^{-1}\) year\(^{-1}\)), leaching (year\(^{-1}\)), reaction (year\(^{-1}\)), respectively. \(h(T)\) is the function of biomass net growth and \(\mu(S)\) is the function of mortality or metabolic inefficiency of trees due to the concentration of Al\(^{3+}\) they contain.

The net growth function was assumed by De Leo et al. (1993) to be of the form \(h(T) = a/(1 + bT)\), where coefficients \(a, b > 0\) are constant; and the bimodal \(h(T) = r(1 - T/k)\) as proposed by Guala et al. (2009). Although T originally referred to the biomass of trees, Guala et al. (2009) showed that it may also indicate some other physiological characteristics, and that Equation System (1) may also be applied to plants in general.

It is not easy to specify how heavy metals in soils determine metabolic inefficiency. Although the quantitative relationship between the concentration of heavy metals in soils and biomass production has been documented for some years, heavy metals do not seem to cause a notorious risk below a certain threshold, although the effects on different plant organs are detected.

In particular, the functional shape of the metabolic inefficiency and eventual mortality \(\mu(S)\) is assumed by De Leo et al. (1993) as:

\[ \mu(S) = \frac{c - fS}{e - S} \]

where in both cases \(c, f, e > 0\), \(S \in [0, e]\), \(S = e\) is the critical survival value. It does not mean plants can resist until \(S = e\), as this would only be only possible if \(\mu(S) = 0\) until \(S = e\), which would mean that plants are absolutely insensitive to any concentration below \(e\). Obviously, it is essential to choose the correct parameter values.

Although Equation System (1) was originally proposed to model the soil–plant interaction under aluminum mobility by acid conditions, we can reformulate the conditions of the last two equations for any disposed heavy metal M\(^{n+}\). Therefore, in equilibrium conditions the reformulated Equation System (1) could be rewritten as:

\[ 0 = T(h(T) - \mu(S)), \]
\[ 0 = \alpha M - h(T)S, \]
\[ 0 = \phi H - \beta M - \frac{\alpha M T}{p}. \]
\[ 0 = -\phi H - \beta H + \frac{W}{p} \]

(2)

where \(m\) is the atomic weight.

We do not focus directly on the mobility of aluminum due to the proton concentration \(H\) as a result of acid deposition \(W\), but instead on the availability of any deposited heavy metal M\(^{n+}\) beyond soil acidity conditions. Since disposed heavy metals are significantly available under natural acidity conditions in the liquid phase of soil and adsorbed by plants instead of being fixed by the soil matrix, we may neglect the two last expressions of Equation System (2) by focusing on the concentration of heavy metals M in the second equation of Equation System (2).

As a result, the system in equilibrium is expressed as:

\[ 0 = T(h(T) - \mu(S)), \]
\[ 0 = \alpha M - h(T)S, \]
\[ 0 = -\phi H - \beta M + \frac{W}{p} \]

(3)

Using Equation System (3), it is possible to calculate the relationship between the concentration of heavy metals in soil \(M\) and the concentration of heavy metals in plants \(S\). The expression yields:

\[ \alpha M = \mu(S)S \]

According to the definition of \(\mu(S)\) given above, the concentration of heavy metals in soil \(M\) as a function of the concentration of heavy metals in plants \(S\) is explicitly written as:

\[ M = \frac{1}{\alpha} \left[ \frac{-c + fS}{e - S} \right] S = \left[ \frac{-(c/\alpha) + (f/\alpha)S}{-e + S} \right] S \]

(4)

Coefficients \(c/\alpha, f/\alpha\) and \(e\) can be fitted by experimental results to establish the relationship between \(M\) and \(S\). Note that the relationship \(M - S\) is independent of the growth function \(h(T)\), which makes it possible to generalize the model to a wide range of plants. We can now test the model in order to verify whether Eq. (4) provides us with reliable results when we introduce realistic values. As can be clearly seen, determining the coefficients is a difficult process, and the known empirical methods yield widely deviating results (De Leo et al., 1993; Guala et al., 2009). Therefore, the model needs to be written in such a way that the relationship \(M - S\) may be inferred from fitting Eq. (4). This is possible by writing Eq. (4) in a general mathematical form, in which the constant terms are combined in aggregated coefficients to be fitted, i.e.

\[ M = \frac{-C_0S + C_1S^2}{-C_3 + S} \]

(5)

where \(C_1, C_2, C_3 > 0\).
However, many studies do not compare the heavy metal uptake to the concentration of heavy metals in equilibrium in soil M, but instead to the dose used to pollute the soil (Poulik, 1997; Moreno et al., 2006; Ryser and Sauder, 2006; Athar and Ahmad, 2002). In this case, we can define D as a proportional summation of the places where the heavy metal is located: the heavy metal uptake S, the heavy metal in soil solution M and the heavy metal adsorbed in the soil matrix (assuming a Freundlich linear relationship for the purpose of simplicity). In equilibrium this is D = k1S + k2M, where k1, k2 are the corresponding proportional coefficients for uptake and Freundlich adsorption, respectively. As M can be expressed in terms of S from Eq. (4), a simple algebraic calculation shows that D holds the same general mathematical form of Eq. (5). Therefore, we can validate the model fitting results shown either in terms of heavy metal equilibrium M or in terms of heavy metal dose D.

### 3. Results and discussions

In order to validate the model, we used a study (Benzarti et al., 2008) which measures the dynamic interaction between the level of heavy metals in soil and in plants such as alfalfa, lettuce, radish and the hyperaccumulator Thlaspi caerulescens for Cd, Cu and Zn.

Table 1 shows the results published by Benzarti et al. The corresponding coefficients of Eq. (5) are shown in Table 2. Poulik (1997) suggests a linear relationship for M–S (and D–S). However, although the behavior can be considered as linear far below the threshold of survival concentration e (equivalently, coefficient C3 of Eq. (5) and Table 2), linearity vanishes in the fitted function for all the experimental results when heavy metal levels increase. Coefficients C3 and C1 of our model suggest a more complex interaction as the concentration of heavy metals in plants S moves closer to the threshold, the linear fitting loses effectiveness and the nonlinear terms become relevant. These terms are important in order to reliably predict the threshold concentration e, after which plant survival is not possible, even when metabolic problems and plant death are supposed to occur before e.

The results shown in Table 2 would seem to indicate that the relevance of coefficient C1 is numerically negligible and should not be taken into account. This additional result suggests further revisions of the model. For instance, Guala et al. (2009) proposed another expression for µ(S) which varies slightly in mathematical terms, but which reflects a conceptually different idea about the growth of plants h(T) to that proposed by De Leo et al. (1993). Although h(T) does not explicitly appear after Eq. (3), expressions of h(T) and µ(S) are mutually dependent from the definition of Equation System (1). Therefore, further definitions of h(T) and µ(S) should be considered.

Benzarti et al. (2008, Table 1) shows that the last experimentally registered concentrations of Cd (expressed in mg kg⁻¹) in alfalfa, lettuce, radish and T. caerulescens are 174.7, 157.7, 268.8 and 366.2 mg kg⁻¹, respectively, corresponding to a dose of 1000 µM of Cd in soil. With regard to this, in Table 2 the model predicts plant death before 178.9, 165.9, 284.5 and 390.9 mg kg⁻¹, respectively. In the case of Cu (expressed in mg kg⁻¹) in alfalfa, lettuce, radish and T. caerulescens the last experimentally registered concentrations are 297.9, 284.5, 240.3 and 159.8 mg kg⁻¹, respectively, corresponding to dose of 1000 µM of Cu in soil. Table 2 shows that the model predicts plant death before 333, 321.4, 287.5 and 169.8 mg kg⁻¹, respectively.

### Table 1

Concentrations of Cd, Cu and Zn in plant tissues (mg kg⁻¹) (Benzarti et al., 2008).

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Dose (µM)</th>
<th>Alfalfa (mg kg⁻¹)</th>
<th>Lettuce (mg kg⁻¹)</th>
<th>Radish (mg kg⁻¹)</th>
<th>T. caerulescens (mg kg⁻¹)</th>
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<tr>
<td>Cd</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
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<td>0.1</td>
<td>7.00</td>
<td>7.18</td>
<td>7.431</td>
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<td>17.06</td>
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<td>12.74</td>
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<td>10</td>
<td>57.77</td>
<td>44.28</td>
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<tr>
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<td>100</td>
<td>144.2</td>
<td>108.5</td>
<td>195.7</td>
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<tr>
<td></td>
<td>1000</td>
<td>174.7</td>
<td>157.7</td>
<td>268.8</td>
<td>366.2</td>
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<td>1</td>
<td>9.39</td>
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<td>151.4</td>
<td>139.3</td>
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<td></td>
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<td>297.9</td>
<td>284.5</td>
<td>240.3</td>
<td>159.8</td>
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<tr>
<td>Zn</td>
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<td>14.46</td>
<td>20.94</td>
<td>18.18</td>
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<td>257.6</td>
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<td>423.7</td>
<td>464.5</td>
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<td>1000</td>
<td>583.3</td>
<td>677.9</td>
<td>699.3</td>
<td>1290.4</td>
</tr>
</tbody>
</table>

### Table 2

Value of the four aggregate coefficients corresponding to the simplified polynomial formula (C1S² – C2S)/(S – C3) for the Cd, Cu and Zn experiments (Benzarti et al., 2008).

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Coefficients</th>
<th>Alfalfa</th>
<th>Lettuce</th>
<th>Radish</th>
<th>T. caerulescens</th>
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<tbody>
<tr>
<td>Cd</td>
<td>C1</td>
<td>2.266 × 10⁻¹⁴</td>
<td>6.683 × 10⁻¹²</td>
<td>2.373 × 10⁻¹⁴</td>
<td>5.848 × 10⁻¹³</td>
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<tr>
<td></td>
<td>C2</td>
<td>24</td>
<td>51.72</td>
<td>43</td>
<td>67.5</td>
</tr>
<tr>
<td></td>
<td>C3</td>
<td>178.9</td>
<td>165.9</td>
<td>280.4</td>
<td>390.9</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.9896</td>
<td>0.9860</td>
<td>0.9778</td>
<td>0.9736</td>
</tr>
<tr>
<td>Cu</td>
<td>C1</td>
<td>2.361 × 10⁻¹³</td>
<td>4.486 × 10⁻¹²</td>
<td>2.338 × 10⁻¹⁴</td>
<td>2.337 × 10⁻¹⁴</td>
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<tr>
<td></td>
<td>C2</td>
<td>118</td>
<td>129.7</td>
<td>196.5</td>
<td>62.52</td>
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<td>333</td>
<td>321.4</td>
<td>287.5</td>
<td>169.8</td>
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<tr>
<td></td>
<td>R²</td>
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<td>0.9818</td>
<td>0.9683</td>
<td>0.9843</td>
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<tr>
<td>Zn</td>
<td>C1</td>
<td>5.851 × 10⁻¹⁰</td>
<td>2.339 × 10⁻¹⁰</td>
<td>1.333 × 10⁻¹¹</td>
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<td></td>
<td>C2</td>
<td>40.56</td>
<td>49.95</td>
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<tr>
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<td>C3</td>
<td>607</td>
<td>711.8</td>
<td>744.5</td>
<td>1349</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.9775</td>
<td>0.9694</td>
<td>0.9897</td>
<td>0.9859</td>
</tr>
</tbody>
</table>
respectively. The last concentrations of Zn (expressed in mg kg$^{-1}$) in alfalfa, lettuce, radish and _T. caerulescens_ are 583.3, 677.9, 699.3, 1290.4 mg kg$^{-1}$, respectively, corresponding to a dose of 1000 μM of Zn in soil. In Table 2 the prediction of plant death is before 607, 711.8, 744.5 and 1349 mg kg$^{-1}$, respectively. Note that Zn is the most absorbed metal out of the three tested. This is also reflected by the resistance predicted before dying. However, Cd and Cu exhibit diverse behavior according to the plant: while predicted survival for alfalfa, lettuce and radish is higher for Cu than Cd, the opposite is true for _T. caerulescens_.

Fig. 1 shows the results of the experimental fitting according to the proposed model. As can be seen, the figures present the threshold concentrations of heavy metals in plants S. These thresholds are represented by the coefficient $C_S$ of Eq. (5). It should be noted that these thresholds are not the “death point” of the plants, as metabolic problems and mortality appear before these points. Instead, they indicate the limit after which no plant of the given species under given conditions is expected to be found (De Leo et al., 1993; Guala et al., 2009).

4. Conclusions

The inhibition of plant growth due to concentrations of heavy metals can be predicted by a simple kinetic model. The model proposed in this study makes it possible to characterize the non-linear behavior of the soil–plant interaction with heavy metal pollution, in order to contribute towards establishing threshold values for the toxic effects of heavy metals on plants and eventual plant mortality, to avoid lethal levels of soil contamination, and to establish corrective strategies. The effects of heavy metals on plant development vary according to different soil characteristics, the type of plant and the metal. As a result, the model makes it possible to directly compare the relative fragility of different environments to the same pollutant. Finally, the effects of heavy metals on both plants and crops must be considered in order to establish the risk of these contaminants being transferred to the food chain. It is clear that the predictions should be experimentally confirmed in further studies, and before extrapolating the outcomes, it is necessary to take into account the high dependence of the results on pot-field, chemical, physical and environmental conditions.

Acknowledgements

This study was supported by the Xunta de Galicia in partnership with the University of Vigo through a Parga Pondal and Ángeles Alvarinho grant awarded to E.F. Covelo and F.A. Vega, respectively.

References


