

Modeling the accumulation of As, Cd, Cu, Pb and Zn in grasses (*Agrostis* sp. and *Poa* sp.) and stinging nettle (*Urtica dioica*) on selected sites taking into account soil physico-chemical properties

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Abstract. The effect of soil properties on the accumulation of metals in two vegetation types was evaluated at 10 sites with a wide variation in soil physicochemical properties pH, organic carbon, clay percentage, total soil metal concentration and exchangeable soil metal content. Accumulation modeling was conducted for grasses (*Agrostis* sp. and *Poa* sp.) and stinging nettle (*Urtica dioica*).

Keywords: Metals, vegetation, soil characteristics, bioavailability

Introduction

Soil is an important factor in the terrestrial food web to which all fauna and flora is directly or indirectly linked. An excess of metals are introduced to ecosystems via anthropogenic processes. Metals with no natural, biological function also called non-essential metals (cadmium (Cd), lead (Pb)) or essential metals (arsenic (As), Copper (Cu) and zinc (Zn)) present in soils at high concentration poses a risk due to their accumulation in food webs while their toxic effects disrupts the existing biological balance (Celechovska et al., 2008). The degree to which metals are available for plant uptake and further accumulation in the food web strongly depends on the degree of pollution and soil physico-chemical properties (Franz et al., 2008). It has been shown that bioavailability is affected by soil properties such as pH, organic matter content or clay content (van Wezel et al., 2003) however in most studies accumulation modeling in food webs are based on total metal concentrations and not so much on the bioavailable or exchangeable fraction. To address this we selected and characterized soils with a wide variation in soil properties and a broad range of metal concentrations, we sampled in grassland and forest sites for grasses and nettle and extracted the total and exchangeable metal fractions from sampled soils. Our main aim was to build soil-plant transfer models taking into account changing soil properties to see if it is indeed possible to predict the level of metal accumulation in grasses and nettle.

Materials and Methods

From the mid 1950ties-70ties, zinc and lead were refined in the northern regions of Flanders; during extraction volatile metals condensed on dust particles and were subsequently expelled into the air. As a result these emissions polluted a wide spread area. Even though emission is nowadays close to zero the persistent character of metals ensures their long term presences in contaminated soils (OVAM, 2008). Samples were collected in and around Antwerp: Wilrijk (Fort 6), Mortsel (Fort 4) Hoboken (Fort 8, Hobokense Polder, Petroleum Zuid and Zorgvliet Park), Brasschaat (Park), Olen (Olens Broek), Limburg (Hageven nature reserve) but also in Noyelles-Godault (Metaleurop Nord), France. All sites consisted of grasslands interfered with patches of forest, samples were collected on both forest and grassland to see if different accumulation patterns occurred. Soil-plant regression models were derived for As, Cd, Cu, Pb and Zn to estimate the concentrations in grasses (*Agrostis* sp. and *Poa* sp.) and nettle (*Urtica dioica*) taking into account soil characteristics (total metal concentrations in soil, the bioavailable metal fraction, pH, organic matter content and clay% <2 μ m). Soil was collected from the top 10 cm, after removal of visible upper litter layer. The soil was stored in a poly-ethylene bag at -20 °C prior to metal analysis. The pH was assessed within 24 h of collection. Samples of stinging nettle and grasses, which were dominant species at all sites, were sampled. Samples were placed into

brown paper bags and directly dried at 60°C.

Soil samples were dried at 60°C for one week. Samples were sieved with a 2mm sieve to remove roots and other debris. Soil organic carbon (OC) content was determined by the loss of ignition (LOI) method, soil pH was measured after addition of a potassium chloride (KCl) solution using a field pH meter (DeHach). Clay content was determined by a particle size analyser which calculates grain size with the GRADISTAT program and lastly calcium chloride extractions (CaCl₂ 0.01M) was used for extracting the exchangeable metal fraction. Metals concentrations were measured using an inductively coupled plasma mass spectrometer (ICP-MS). Soil samples were digested with aqua-regia (HNO₃ and HCl ratio 1:3) in a microwave in teflon vessels (ETHOS 900 Microwave Labstation, Milestone, Italy). After dry, the vegetation was powdered with a pestle and mortar after which samples were soaked in acid for one week and lastly digested with the aqua-regia method in an open hot plate. Samples were analyzed for arsenic (As), cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) using inductively coupled plasma - optical emission spectrometer (ICP-OES). When concentrations were below detection limits, analyses were performed with an ICP-MS. All concentrations are reported as dry weight concentrations. For quality assurance, reference samples light and sandy soil (BCR-142R) and sewage sludge (BCR-146R) was used and for vegetation white clover (BCR-402) and hay powder (BCR 129) respectively were analysed (Mester et al., 2003).

Differences between sites and vegetation types were analyzed with Analysis of Variance (ANOVA), using GraphPad Prism 5. For the modeling multiple linear regressions (SigmaPlot 11.0) was used. To obtain normality of the data they were transformed into their natural logarithm prior to statistical analysis.

Results and discussion

For all sites pH showed a significant correlation with clay percentage (P=0.001) while pH showed no significant correlation with organic carbon. Metal accumulation (total metal fraction) appeared to be similar in both grasses and nettle except for Pb; where nettle accumulated more than grasses. No significant differences between forest and grassland sites in metal content was observed however at Fort 8 (one of the more polluted sites) the forest sites showed significantly higher metal concentration than the grassland sites. Even though Pb generally occurs in organic complexes and is thus not available for uptake by vegetation significant models could be constructed. Other metals that showed significant modeling potential were As in nettle (log [As] soil p<0.001 and log OC p=0.006), Cd in grass (log [Cd] in soil p=0.003, OC p=0.003 and clay % <2µm p<0.001), Cu in grass (pH p<0.001 and nettle log [Cu] soil p<0.001, OC p=0.019), Zn in grass log [Zn] soil p<0.001, pH <0.001 and log clay % <2µm p=0.031.

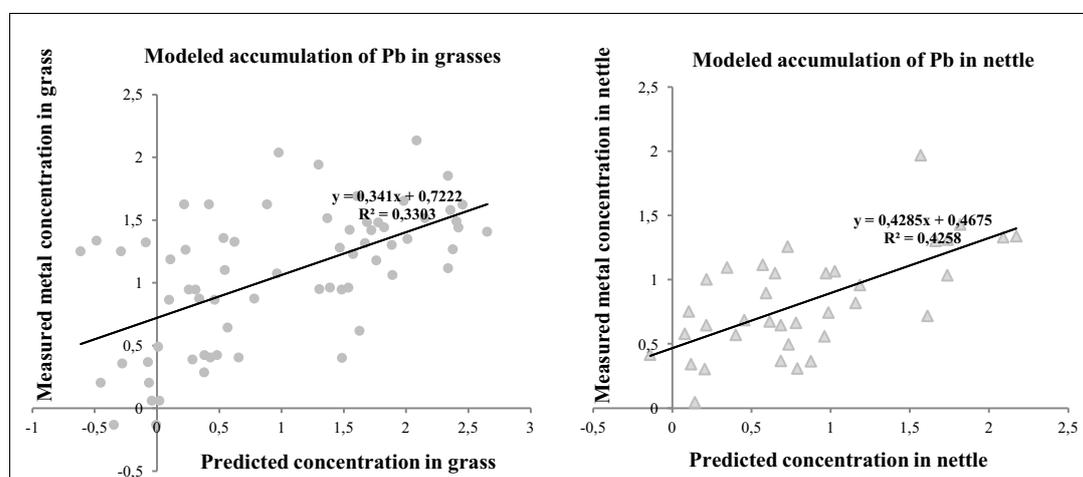


Fig. 1. Modeled outcome of Pb accumulation in grasses; $[Pb] \mu\text{g/g Grass} = 0,280 + (0,717 * \log [Pb] \mu\text{g/g SOIL}) - (0,0891 * \text{pH}) + (0,551 * \log \text{OC}) - (1,327 * \log \text{clay } \% (<2\mu\text{m}))$ and stinging nettle (*Urtica dioica*): $[Pb] \mu\text{g/g Nettle} = -0,214 + (0,736 * \log [Pb] \mu\text{g/g SOIL}) - (0,0282 * \text{pH}) - (0,322 * \log \text{OC}) - (0,438 * \log \text{clay } \% (<2\mu\text{m}))$

Conclusion

The advantage of using models like the ones proposed here is that it facilitates extrapolation to soils of various origins, with different physicochemical properties, and possibly to other plant species; furthermore such model predictions underpin the correctness of field measurements, since field accumulation data can show large variability.

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