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Development and comparison of regression models for the uptake of metals into various field crops

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ABSTRACT

Field crops represent one of the highest contributions to dietary metal exposure. The aim of this study was to develop specific regression models for the uptake of metals into various field crops and to compare the usability of other available models. We analysed samples of potato, hop, maize, barley, wheat, rape seed, and grass from 66 agricultural sites. The influence of measured soil concentrations and soil factors (pH, organic carbon, content of silt and clay) on the plant concentrations of Cd, Cr, Cu, Mo, Ni, Pb and Zn was evaluated. Bioconcentration factors (BCF) and plant-specific metal models (PSMM) developed from multivariate regressions were calculated. The explained variability of the models was from 19 to 64% and correlations between measured and predicted concentrations were between 0.43 and 0.90. The developed hop and rapeseed models are new in this field. Available models from literature showed inaccurate results, except for Cd; the modelling efficiency was mostly around zero. The use of interaction terms between parameters can significantly improve plant-specific models.

1. Introduction

The presence of metals in soils is of either geochemical or anthropogenic origin. Soil enrichment by human activity can lead to elevated concentrations of metals, with unfavourable effects on environmental biota and humans (US-EPA, 2007). Direct anthropogenic sources of metals entering the environment are fertilizers and pesticides, industrial effluents, sewage sludge, and atmospheric deposition (Guala et al., 2010; Haygarth,P. and Jones, 1992). The exposure of humans to some metals is known to be associated with a wide range of health effects. Cadmium and lead, which are highly toxic, are the most closely monitored elements and exhibit several acute and chronic effects (Bradl, 2005; Conor, 1991; Oliver, 1997). Chromium is an essential element in trivalent form and toxic in hexavalent form. Both forms are potential human carcinogens (Nriagu and Nieboer, 1988). The intake of other elements such as copper, molybdenum, zinc and nickel is not typically associated with adverse health effects. All, except for nickel, are essential elements with several adverse effects appearing only at high doses (US-EPA, 2007).

The extent of the toxic effect depends on the amount of metal entering the human body. The exposure pathways that contribute most to human health risks depend on the exact form of land use and the particular chemicals under consideration. Usually, the most important avenues of exposure are the consumption of contaminated food, the inhalation of suspended air particles, the direct ingestion of soil, and the consumption of contaminated drinking water (Bradl, 2005; Conor, 1991). In some cases, usually in the vicinity of industry or traffic, the air pathway plays the major role. In other cases, dietary exposure is the predominant form of exposure for most metals (Qu et al., 2012). It is possible to estimate exposure *via* the ingestion of dust and soil if the inhalation and ingestion rates are known (Hough et al., 2005), while the estimation of dietary exposure is more difficult because of variability in the contamination of different commodities and in the eating habits of individuals. In the Czech Republic, a dietary survey is performed every two years and many market food commodities are investigated. According to this study, exposure to all monitored metals mostly arises from the consumption of potatoes and grain products (e.g. rolls, bread, dumplings, and flour) (NIPH, 2013). Field crops are among the food commodities which contribute most to human metal exposure. Crop-specific prediction models are a reasonable tool to estimate potential dietary risks across larger areas. Some models work with site-specific conditions, but often fail when used

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to predict uptake rates under different conditions (Legind and Trapp, 2010; US-EPA, 2007). The simple estimation of bioconcentration factors (BCF) can serve as a rough insight into the range of heavy metal uptake, but it does not reflect more detailed site-specific conditions. A more complex approach is represented by regression models, in which concentrations of metals in plants are predicted by various soil parameters, mostly the total concentration of a metal in soil, soil pH, and organic carbon (Adams et al., 2004; Bešter et al., 2013; EC-DGI, 2000; Eriksson et al., 1996; Hough, 2002; Chaudri et al., 2007; Jackson and Alloway, 1992; Legind and Trapp, 2010; Otte et al., 2001; Waegeneers et al., 2011). Nevertheless, other models have revealed further important parameters – for example, clay content, the dry weight of the plant (Otte et al., 2001), the concentrations of other metals in the soil (Eriksson et al., 1996), and interaction terms between variables, which might reveal other than the measured soil properties (Tudoreanu and Phillips, 2004). Cadmium is a metal which is typically monitored and modelled; a model by Hough (2002) and the RIVM model by Otte et al. (2001) also include Cu, Ni, Pb and Zn. The selection of the field crop depends on the purpose of the study. Commonly investigated plant crops are cereals (wheat, barley) (Adams et al., 2004; EC-DGI, 2000; Eriksson et al., 1996; Hough, 2002; Chaudri et al., 2007), root vegetables (carrots) (EC-DGI, 2000; Legind and Trapp, 2010), leafy vegetables (cabbage, lettuce) (Jackson and Alloway, 1992; Legind and Trapp, 2010), potatoes and maize (Tudoreanu and Phillips, 2004).

In the Czech Republic, the basal monitoring of soils, undertaken by the Central Institute for Supervising and Testing in Agriculture (CISTA), can be used for such model building under defined conditions. The aim of this study was to evaluate measured soil concentrations and soil factors and their influence on metal concentrations in different agricultural plants for several metals from the Czech monitoring database by developing a novel regression model. Such a model might be well-suited to the preliminary risk assessment of larger areas such as the whole of the Czech Republic. Other available models with similar soil conditions and concentration levels were used for comparison.

2. Materials and methods

2.1. Sampling and analysis

Soil samples were collected from agricultural sites included in the basal monitoring of soils in the Czech Republic by CISTA at irregular times from 1992 to 2009 (Poláková et al., 2010). Sampling sites were selected to represent the proportions of soil types in the Czech Republic and to be equally distributed across the whole country. The Czech Republic represents a relatively small area of 78 869 km^2 but has a heterogeneous landscape covering many environmental gradients typical of the whole central European region. Elevation ranges between 250 and 700 m (average = 450 m). Mean annual air temperatures mostly vary between 5.5 and 9 °C with a winter minimum at around −20 °C and maximum summer values of between 30 and 35 °C (Komprda et al., 2013). A plot was defined as a rectangle of dimensions 25 × 40 m. Disturbed soil samples were used to determinate chemical and physico-chemical soil properties. The collection of samples was undertaken along diagonals (an X pattern); four partial samples were taken from topsoil using a zig-zag pattern (according to the thickness of the horizon, maximally to 30 cm). The physical properties of soil, grain size composition, organic carbon content, and pH were determined according to ISO 17025. Detailed determination is described elsewhere (Poláková et al., 2010). Metals were extracted in aqua regia (AR) and their concentrations measured by an ICP OES spectrometer (Pb, Cd) and an AAS spectrophotometer (other metals). Values under the limit of detection were replaced with half of limit. The measured soil properties are summarized in Table SI1. Plant samples were collected at the same sites and from the same plots used in the CISTA monitoring program for soil samples. The products collected from each sampled plot were the main ones, i.e. grains, potato tubers, rape seed, and pasture grass. In total, 175 samples of wheat, 80 of barley, 21 of potato, 13 of hops, 13 of maize, 57 of rape, and 171 of grass from 64 different agricultural areas were collected. Grass samples were divided into the first (spring/early summer, n = 105) and second (late summer, n = 66) mowings. The distribution of sampling sites across the Czech Republic is illustrated in Figure SI1. Samples were weighed, air-dried, and homogenized. Metal concentrations in plant samples were determined in the same way as for soil samples. Some plant samples were collected in the same localities as soil samples, but in a different year. The soil and plant samples were paired according to sampling site and year of sampling. The time separation for most paired samples was no longer than 3 years.

2.2. Data and statistical analysis

First, regression models collected from literature sources were used for the prediction and subsequent comparison of metal concentrations based on our data set.

For the main comparison of predicted concentrations in field crops, available complex models based on regression equations involving various physical–chemical properties of soil were used. Only models for relevant crops and using input parameters determined in our dataset were investigated (Table 1). Model inputs are summarized in Table SI2. All compared models parameters overlapped with parameters measured in our study area. The success with which the models fitted the measured concentrations was evaluated by model efficiency (EF) calculated by the following equation:

$$EF = 1 - \frac{\sum (C_{model} - C_{measured})^2}{\sum \left(C_{measured} - \overline{C}\right)^2}, \tag{1}$$

the model strength was determined by the mean normalized average error (MNAE) given by

$$MNAE = \frac{\sum(|C_{model} - C_{measured}|/C_{measured})}{n}, \tag{2}$$

and the model bias was calculated by mean normalized bias (MNB) given by

$$MNB = \frac{\sum(C_{model} - C_{measured})}{\sum C_{measured}}, \tag{3}$$

where C_{model} is the predicted concentration given by the model, $C_{measured}$ is the measured concentration, $\overline{C}$ is the mean of measured concentration, and n represents the number of observations.

Subsequently, the transfer (bioconcentration) factor (BCF) was calculated as the simplest model for predicting uptake into crops:

$$\mathrm{BCF}_{\mathrm{metal}} = \frac{M_{plant}}{M_{soil}}, \tag{4}$$

where M_{plant} is the metal concentration in the plant and M_{soil} is the total metal concentration in the soil.

Then, the collected data including concentrations of metals in soils and plants together with soil properties were used to develop plant-specific regression models for individual metals (PSMM).