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Spatial distribution and risk assessment of metals in agricultural soils

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ABSTRACT

The purpose of the presented study was to identify possible ecological and health risks by metal contamination in soil. More than 50,000 topsoil samples in agricultural soil were used to evaluate spatial concentrations and risks posed by selected metals on a national scale. Variograms and correlograms were used to identify metal spatial patterns and appropriate sampling distances. All metals were spatially dependent on short distances (up to 7 km). Optimal sampling densities to detect contamination at the local scale were estimated to be at around 1 sample per 0.5 km for Cd, Cu and Zn and 1.5–2 km for Pb, Hg and Ni based on Moran's index = 0.7. The concentrations of metals were partly influenced by precipitation and pH, but mostly by geology and industry. The Kriging method was used to create interpolated maps for individual metals. High concentrations of Cd, Pb and Zn were found in well-known mining areas (the Ore Mountains, the Upper Silesian Basin, the towns of Kutná Hora and Příbram). Elevated Ni and Hg concentrations resulted mainly from the nature of the parent rock material. Cu contamination was specifically influenced by Cu-based fungicides applied on soils where hop and wine are grown. Czech and European legal limits for various pH and soil textures were applied to identify potential risk areas. A relatively large area of agricultural soil (16%) is above the prevention limit for at least one metal. However, only a few localities exceed the limits with respect to food chain contamination and the inhibition of plant growth. Comparison of our results with European studies (LUCAS, GEMAS, FOREGS) points to the need for high density sampling in order to conduct accurate risk assessment and demonstrates that serious soil contamination happens (and needs monitoring) at the local and not the continental scale.

1. Introduction

Soil is an important repository for metals released into the environment as a result of human activity. Also, high metal values can occur due to a specific geology or due to the occurrence of ore deposits (Abrahams, 2002). Regarding human and plant health, metals can be both essential and non-essential micronutrients. Non-essential metals such as Cd, Hg or Pb can have potentially harmful effects on living organisms even at low concentration levels (Kabata-Pendias, 2011). Adverse effects in common plants include, among many others, chlorosis, dark green leaves, stunted foliage, and weak plant growth (Kabata-Pendias, 2011). Effects on human health mainly include allergy, nephrotoxicity, neuro-developmental disorders, cardiovascular toxicity, carcinogenicity, and damage to the reproductive system (Apostoli et al., 2006). Contamination of soils by metals can affect human health directly through ingestion, inhalation, or dermal contact, but mainly via the food chain (European Commission, 2011, 2012). For this reason, the contamination of agricultural soils and its consequences for food production and quality should be of a special concern.

Many limits on metals were developed to protect agricultural soils. Threshold values and other limits for metals have often been estimated as unique values for a country or a particular large area (Huber et al., 2008; Kibblewhite et al., 2008). However, it is recommended to define values according to environmental conditions because of their influence on the size of the metal bioavailable fraction (Albanese et al., 2015; Gawlik and Bidoglio, 2006; Johnson et al., 2012; Lado et al., 2008). Bioavailability is the key factor driving the toxic potential of metals in relation to the environment and living organisms. The environmental characteristics that affect metal levels and mobility in soil are, among others, geology, pH, cation exchange capacity, organic carbon content, soil texture, land use, and soil type.

The mapping of metal contents in soils is an important feature of metal contamination assessment.

Geochemical distribution maps of metals can reveal spatial patterns and, moreover, in the case of agricultural soils, can contribute to proper risk assessment and support the policy decision making process. However, mapping techniques require sufficient numbers of metal measurements which should be performed using the same method. For this purpose, several continental and regional programs have been set up to monitor metal contamination and/or to identify areas where monitoring at a more detailed scale is most justified. In the European sphere, these include the geochemical mapping projects FOREGS and GEMAS

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and soil monitoring program LUCAS. The FOREGS database contains >1500 randomly selected mineral soil samples from 26 European countries (Salminen et al., 1998); the GEMAS database includes >4100 agricultural soil samples collected from 33 European countries (Albanese et al., 2015; Ottesen et al., 2013; Reimann et al., 2014; Reimann et al., 2012; Tarvainen et al., 2012) and the LUCAS database, that was established for soil monitoring of regional variability across the European Union, contains almost 20,000 topsoil samples from 27 European countries (Tóth et al., 2016, 2013). The European mapping and monitoring programs are very important for the rough estimation of metal soil background values and gradients over a large area and enable country-to-country comparisons. However, low-resolution sampling cannot cover all conditions and sources at regional and local levels. The authors of the various European monitoring studies have mentioned the need for detailed regional studies to characterize local sources of contamination and the respective toxic potential of metals (Ottesen et al., 2013; Reimann et al., 2012; Tóth et al., 2016).

High-resolution studies focusing on metals and other soil parameters can also be found on the national scale, e.g. Spanish study that include 14,000 sediment and soil sites (IGME, Geochemical atlas of Spain, Atlas Geoquímico de España, 2012), monitoring in Cyprus with a density of 1 site per 1 km^2 on a grid of over 5350 sites (Cohen et al., 2011; Cohen et al., 2012); high density mapping of Northern Ireland (Johnson et al., 2005; Smyth and Johnson, 2011) or a national study conducted in England to establish normal background concentrations for some metals (Cd, Cu, Hg, Ni and Pb), based on >40,000 soil samples (Johnson et al., 2012) and varying sampling densities (1 site per 0.25 km^2 to 1 site per 25 km^2). Lower-resolution studies can be also found in European countries, e.g. the national soil monitoring network in France (Saby et al., 2011), which consists of 2200 sites on a 16 × 16 km grid; and a national study of 105 sites in Switzerland covering all major types of land-use and sampled every 5 years since 1984 (Desaules et al., 2010). Other studies on a regional level were performed in Spain in two river basins, the first in the Ebro River basin, with 624 sites sampled on an 8 × 8 km grid between 2003 and 2004 (Rodríguez Martín et al., 2009, 2006), and the second in the Duero River basin, with 729 sampling sites also collected on an 8 × 8 km grid (Nanos and Rodríguez Martín, 2012); and in Croatia within an area of 3700 km^2 and included 784 topsoil samples analyzed for basic metals (Romić et al., 2007).

The aims of this study were to assess the spatial variability of selected metals (Cd, Cu, Hg, Ni, Pb, and Zn) in agricultural soils with regard to contamination sources and to evaluate risks posed to the food chain and plant growth. The presented study takes advantage of a dense sampling scheme (>50,000 samples from the whole agricultural area of the Czech Republic), with at least one sample per 1 km^2. Such a high resolution design allows the consideration of various contamination sources, the selection of important factors influencing metals contamination in soil, and an appropriate sampling distance for each metal. With respect to sampling density and the size of the assessed area, this study is unique among national studies. Final maps were compared with available maps based on European-wide studies and possible uncertainties resulting from different sampling densities were considered.

2. Materials and methods

2.1. The sampling design and study area

The Czech program involving the agrochemical testing of soils is being conducted in order to supply farmers with information on contents of the main nutrients in soil, according to the Act on Fertilizers (Act No. 156/1998 Coll., as amended). Metal contents were analyzed in selected samples from the program of Agrochemical testing of soil in order to cover the whole area of agricultural soil in the Czech Republic. Soils were sampled according to Unified Soil Procedures Manual (Klement, 2014). For the purpose of the agrochemical testing, one composite sample consisted of 30 individual probes to depths of 30 cm and 15 cm in topsoil on arable land and grassland, respectively, was taken from the area of 7–10 ha. Samples for metal analyses were selected in order to cover each km^2 of agricultural soil. In cases of exceeding the limit values, all adjacent samples were additionally analyzed. This resulted in final density of 1 to 24 samples per 1 km^2 (Fig. 1). Under this sampling scheme, 59.2% of the country (approx. 46,000 km^2) was covered (41.8% of which is arable land and 17.4% grassland). A database containing >50,000 soil samples was subsequently created. The most important elements Cd, Cu, Hg, Ni, Pb and Zn were included in the study. The number of samples varied for individual metals, from 36,904 for Hg samples to 44,940 for Pb samples. Most of the data (83%) were collected during the period 1990–1994; the remaining samples were collected up to the year 2000. Soil texture was derived from digitized maps of Research Institute for Soil and Water Research and divided to two categories (light and standard texture) for evaluation of prevention and indication limits. Total organic carbon (TOC) was derived from Czech GIS maps (for more information see SI), and pH was measured directly in the samples.

The Czech Republic is a very heterogeneous geological area that contains almost all European geological substrates (Atlas map České republiky GEOČR 500, 1998), Fig. SI1. In total, 20 different geological substrates can be found in the studied area (9 of them are considered to be geologically anomalous and cover 28% of the area). A list of geological substrates with marked anomalous substrates can be found in Table SI1. Soils are acidic or neutral (median pH (KCl) = 6.4; pH ranges from 3.4 to 8.9) with a percentage of total organic carbon (TOC) ranging from 0.5% to 30% (the median value is 1.6%). Most agricultural soils in the Czech Republic receive from 550 mm to 650 mm of precipitation per year and are exposed to an average annual temperature of 7.5 °C. Statistics concerning climatic and soil properties are summarized in Table SI2. The main locations that are named throughout this article including industrial areas are shown in the Figure 2.

2.2. Chemical analysis

All samples were air-dried and sieved through a 2 mm sieve. Two methods of extraction were used: a) 10 g of sample were shaken in 100 ml of cold 2 M HNO_3 and subsequently 20 ml of extract were filtered for analysis (Zbíral, 2002); b) aqua regia extraction (ISO 11466). The contents of Cd, Cu, Hg, Ni, Pb and Zn were then analyzed by inductively coupled plasma mass spectrometry (ICP-MS) or atomic absorption spectroscopy (AAS). Hg was analyzed using a total mercury analyzer (TMA). pH was measured in KCl extraction. All the analyses were conducted in National reference laboratories of Central Institute for Supervising and Testing in Agriculture which are certified for chemical tests of soils according to CSN EN ISO/IEC 17043:2010. The limits of detections (LOD) for individual metal are presented in Table SI3.

2.3. Spatial analysis

Both the kriging interpolation method (ordinary kriging, OK) (Krige, 1952; Matheron, 1971) and Moran's spatial correlogram (Moran, 1950) were used to compute the spatial distribution of metal concentrations. Metals were not found to exhibit any clear anisotropic features and, therefore, isotropic variograms were employed to model the spatial pattern of metal concentrations. Empirical semivariograms were computed on log-transformed data to meet distribution criteria. Distances up to 30,000 m with 100 m classes were used. Each class contained all pairs within the given distance. Semivariances were fitted by the exponential semivariogram. The precision of the fit was evaluated on the basis of the coefficient of determination (R^2). Linear, spherical, and biexponential functions were also considered, but gave significantly worse results. Interpolated maps of metal concentrations based on variograms were used for spatial pattern visualization and the interpretation of possible contamination sources.