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Assessment of environmental and health risks in former polymetallic ore mining and smelting area, Slovakia: Spatial distribution and accumulation of mercury in four different ecosystems

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ABSTRACT

Former long-term mining and smelting of pollymetallic ores in the Middle Spiš area caused a serious contamination problem of the environment with heavy metals and metalloids, especially mercury (Hg). Several studies have reported concentration of Hg in the area but this paper provides first detailed characterization of Hg contamination of different environmental components in agricultural, forest, grassland and urban ecosystems. The ecosystems are in different distances from emission sources – former mercury and copper smelting plants in NE Slovakia. Total Hg content was studied in soil/substrate samples (n = 234) and characteristic biological samples (*Athyrium filix-femina* (L.) Roth, *Macrolepiota procera* (Scop.) Singer, *Boletus edulis* Bull., *Cyanoboletus pulverulentus* (Opat.) Gelardi, Vizzini & Simonini, *Triticum aestivum* (L.), *Poa pratensis* (L.)) (n = 234) collected in the above-mentioned ecosystems. The level of contamination and environmental risks were assessed by contamination factor (C_f), index of geoaccumulation (I_{geo}) and potential environmental risk index (*PER*). To determine the level of transition of Hg from abiotic to biotic environment, bioconcentration factor (*BCF*) was used. To determine a health risk resulting from regular and long-term consumption of the locally available species, the results of the Hg content were compared with the Provisional Tolerable Weekly Intake (PTWI) for Hg defined by World Health Organization. The results suggest that almost 63% of the area belong to the very high risk category and 80% of the sampling sites shown very high contamination factor. Geoaccumulation index showed that almost 30% of the area is very strongly contaminated and only 8% is not contaminated with Hg. Spearman's correlation relationship confirmed that the values of *PER*, *BCF*, C_f and I_{geo} decreased with an increasing distance from the pollution source. The percentage of contribution to PTWI ranged between 5.76–69.0% for adults and 11.5–138% for children. Mushroom *M. procera* showed the highest %PTWI among the tested biological samples. Studied ecotoxicological parameters showed high level of health risk for population living in the area. Consumption of the crops grown in the area and mainly edible wild mushrooms might negatively affect the health of the consumers in the long-term.

1. Introduction

Mercury (Hg) represents one of the most toxic inorganic pollutants due to its wide distribution, high persistency in ecosystems and bioaccumulation ability in food chain (Douay et al., 2013; Zhang et al., 2012). Hg contamination level of the environment increases with increasing industrialization and urbanization. The contamination arises from various sources, such as mining and smelting activities (Hough et al., 2004), transportation, burning of waste, etc. (Omar et al., 2007). Several studies dealt with the issue in the last two decades (Angelovičová and Fazekašová, 2014; Árvay et al., 2014; Árvay et al., 2015; Dadová et al., 2016; Kalač et al., 1996; Santos-Santos et al., 2006; Zhang et al., 2012), focusing on the distribution and accumulation of Hg in various environments in areas of former mining and smelting activities. Topsoil somewhere in the world, due to geogenic anomalies and/or Hg ore (HgS) mining and smelting or as by-side contaminant in

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Cu-ores smelting, is the most mercury affected part of the terrestrial ecosystems (Tomáš et al., 2012; Tomiyasu et al., 2017; Xiao et al., 2017). This can result in high concentrations of Hg accumulated in plants and especially mushrooms, which are highly efficient in its uptake from topsoil and bioconcentration in their bodies (e.g. *M. procera, Boletus* spp.) (Árvay et al., 2015; Falandysz et al., 2017; Fu et al., 2008; Luo et al., 2011; Melgar et al., 2009; Zheng et al., 2013). Soil is characterized by its biological activity of important socio-economic functions, particularly food production, which creates a substantial risk of contaminants transition from the abiotic to biotic environment (Kelepertzis, 2014).

Mining and smelting activities represent the greatest risk for the individual environmental components, resulting in an increased contamination of soil/substrate and plants and/or edible wild mushrooms by Hg and thus provide the main entrance of this contaminant to the food chain (Bermudez et al., 2011; Douay et al., 2013; Finster et al., 2004; Kňažická et al., 2013; Mleczek et al., 2013, 2015; Wang et al., 2005). The consumption of crops grown on mercury (and other heavy metals) contaminated soils, as well as ingestion or inhalation of the contaminated soil particles are the main ways of the Hg and heavy metals entering the human body (Cambra et al., 1999; Cui et al., 2004; Dudka and Miller, 1999; Nabulo et al., 2010).

The territory of Slovakia is characterized by numerous sites with an increased natural, but mainly anthropogenic Hg content resulting from mining and smelting activities since Middle Ages. The studied area of the Middle Spiš region is located in the north-eastern part of Slovakia. All environmental components in the area are mercury-burdened (Demková et al., 2017). The largest emission source used to be an ore treatment plant in Rudňany, operated until 1993. The plant processed a Hg rich ore (cinabarit and siderite) mined from the nearby mines. The history of the Hg mining and smelting dates to the second half of the 19th century, however, Hg was mined here since the 13th century. During this period, several hundred tons of Hg was obtained here, with a huge amount released to the environment, due to imperfect technology. Approximately 142 t of Hg were emitted to the environment during 1963–1988 (Hronec et al., 1992). The emitted Hg was translocated in direction of the prevailing south-eastern winds and extremely affected the quality of the environment around 10 km from the emission source (Angelovičová and Fazekašová, 2014; Árvay et al., 2014). Another source of Hg in the area has been a copper smelter in Krompachy (eastern part of the studied area) located 15 km to the east from the emission source in Rudňany. The company processed copper ore (containing Hg) mined nearby (southeast part of the area) during 1938–1988 (Demková et al., 2017; Hronec et al., 1992).

The aim of the present study is to (1) determine the Hg contamination of topsoil and biological samples (BS) that represent four basic ecosystems of the studied area, (2) to evaluate ecological risks of Hg by applying contamination factor (C_f) according to Hakanson (1980), index of geoaccumulation (I_{geo}), potential environmental risk index (*PER*) and bioconcentration factor (*BCF*) in individual ecosystems, (3) to assess the health risk resulting from the consumption of the studied species by applying Provisional Tolerable Weekly Intake (PTWI).

2. Materials and methods

2.1. Study area

The area of the Middle Spiš region is located in the north-eastern part of Slovakia (Fig. 1). It is characterized by montane topography. The average annual temperature is 6.8 °C (January: − 6.2 °C, July: 17.0 °C). Precipitation ranges from 590 to 800 mm. Geomorphological nature of the area is shaped by the prevailing south-western winds (Rudňany) and west and/or east winds (Krompachy). The size of the area is 586 km^2, forests cover more than 70% of the area. The subject of the study is an impact of the former emission sources in Rudňany (48°23'04.23"N, 20°40'39.79"E) and Krompachy (48°54'50"N, 20°52'26"E) on the level of Hg contamination of various ecosystems. Geochemical character of the area (volcanic origin), together with several hundred years long tradition of mining and metalworking predisposes the Middle Spiš region to high levels of contamination of all environmental components by heavy metals and metalloids (mostly As, Cd, Cu, Fe, Hg, Mn, Pb and Zn). There are also tailing ponds and dumps of the mined and processed polymetallic ores representing secondary source of contamination. Sludge from the plant smelter in Rudňany is stored in a pond located nearby. It is characterized by a high content of various heavy metals. The average content of Hg was 49.3 ± 2.21 mg kg^{-1} in dry weight (DW) and represents currently the largest source of Hg in the area (Árvay et al., 2013). Sludge from the Krompachy plant is stored in a pond in Slovinky (SE of the study area). The content of Hg in sludge was 3.35 mg kg^{-1} DW (Angelovičová et al., 2014).

2.2. Sample collection and preparation

Topsoil (0–0.1 m) samples (n = 234) and corresponding number of plant and mushroom samples representing different ecosystems (agricultural: n = 20, grassland: n = 57, forest: n = 132 and urban: n = 25) of the studied area were collected in the period of 2012–2014. The sampling points were determined by two methods. The first method aimed to determine the effect of prevailing winds on the atmospheric distribution of Hg from the main emission source (ES) in Rudňany (n = 142). The individual sampling points were set in sixteen lines of the direction vectors (N, NNE, NE, ENE, E, EN, NNE, NE, ENE, E, ESE, SE, SSE, S, SSW, SW, WSW, W, WNW, NW and NNW). The distance among the sampling points from the ES was one kilometre up to the sixth kilometre and from there the sampling points distance was 2 km. In the second method, the sampling points were chosen randomly in three areas. There were 46 sampling points in the western part (National Park Slovak Paradise), 18 sampling points in the southern part and 28 sampling points in the eastern part of the region (Fig. 1).

After the collection, the soil/substrate samples were temporarily stored in plastic sealable bags. Under the laboratory conditions, the samples were air-dried at room temperature for 3 weeks. Afterwards, they were cleaned of rough particles and sieved through a mesh sieve (2 mm). The biological samples were defined according to the type of ecosystem, from which they were collected. Two types of samples were collected in forest ecosystems: *A. filix-femina* (n = 73) and edible wild mushrooms (n = 59): *M. procera* (n = 30), *B. edulis* (n = 22) and *C. pulverulentus* (n = 7). Samples of *P. pratensis* (n = 82) were collected in grassland ecosystem and residential area and *T. aestivum* grain samples (n = 20) were collected in agricultural ecosystems. The plant samples were temporarily stored in paper bags. Prior to the analyses, the plant samples were washed by deionized water and afterwards dried in a hot air oven Venticel 111 (BMT, a.s., Czech Republic) at 40 °C to the constant weight for approximately 22 h. Subsequently, the plant material was homogenized to powder using cutting mill Pulverisette 19 (Fritsch, GmbH, Idar-Oberstein, Germany) and stored in plastic bags prior to the analyses. The mushroom samples were cleaned from debris and they were divided into cap and stem and oven-dried in Venticel 111 at 40 °C for approximately 24 h. The oven-dried samples were homogenized to powder in agate mortar and stored in plastic bags until the analyses.

2.3. Samples analysis

2.3.1. Exchangeable pH determination

Exchangeable soil reaction was determined in all soil/substrate samples. In an 100 mL plastic bottle, 20 g of soil and 50 mL of $CaCl_2$ (Sigma-Aldrich, spol. s r. o., Bratislava, Slovakia) (c = 0.01 mol L^{-1}) solution was mixed. The suspension was shaken in Unimax 2010 horizontal shaker (Heidolph Instruments, GmbH, Schwabach, Germany) for 20 min. Afterwards, the samples were filtered through filter paper