Journal of Geochemical Exploration 167 (2016) 38–48

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/gexplo

Distribution pattern of mercury in the Slovenian soil: Geochemical mapping based on multiple geochemical datasets

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ARTICLE INFO

Article history:
Received 18 January 2016
Revised 6 May 2016
Accepted 8 May 2016
Available online 11 May 2016

Keywords:
Soil
Mercury distribution
Geochemical mapping
Idrija mine
Slovenia

ABSTRACT

A regional geochemical survey was conducted, covering the entire territory of Slovenia. Medium-density soil sampling was performed in a 5 × 5 km grid, mercury concentrations were analysed and a map of mercury spatial distribution was constructed. The determined mercury concentrations revealed an important difference between the western and the eastern parts of the country. A huge anomaly in the western part is the consequence of environmental contamination due to the 500-year history of mining and ore processing in the Idrija mercury mine and partly due to Hg containing rocks on outcrops. Slightly elevated Hg concentrations revealed in the Ljubljana-Kranj and Celje basins indicate urban pollution due to industry, traffic and the use of mercury-containing products. It was established that, besides anthropogenic impacts, lithological and climatic characteristics that determine the type of soil also influence the distribution of mercury in soils. The data were compared to a previously conducted low-density geochemical survey (sampling grid 25 × 25 km, $n = 54$) and to the regional geochemical data set supplemented by local high-density sampling data (irregular grid, $n = 2835$). Comparing high-, medium- and low-sample density surveys, it was shown that higher sampling density allows the identification and characterization of anthropogenic influences on a local scale, while medium- and low-density sampling reveal general trends in the mercury spatial distribution, but are not appropriate for identifying local contamination in industrial regions and urban areas.

1. Introduction

Mercury is a trace element naturally present in the environment, from both natural and anthropogenic sources, and is highly toxic (Clarkson and Magos, 2006; Harada, 1995; Nance et al., 2012). In Europe, a EU mercury strategy was launched in 2005 (ec.europa.eu/environment/chemicals/mercury) and it includes 20 measures to reduce mercury emissions, cut supply and demand, and protect against exposure, especially to the methylmercury found in fish. In October 2013, the Minamata Convention on Mercury was signed, with the main goal to reduce human exposure to mercury (UNEP, 2013).

1.1. Hg sources

Natural sources of mercury include the weathering of mercury-containing rocks, volcanic eruptions and geothermal activity. Anthropogenic emissions include mercury that is released from fuels, raw materials or uses in products or industrial processes. Globally, small-scale gold mining is the largest source of anthropogenic mercury emissions, followed closely by coal combustion. Other large sources of emissions are the production of non-ferrous metals and cement (UNEP, 2013). Currently, about 30% of annual emissions of mercury to air come from anthropogenic sources and 10% from natural geological sources. The rest (60%) is from reemissions of previously released mercury that has built up over decades and centuries in surface soils and oceans. Current mercury emissions from anthropogenic sources are estimated to be 1960 tonnes annually, while annual re-emissions of mercury are 4000–6300 tonnes (Mason et al., 2012; UNEP, 2013).

In Europe, coal-fired power plants (CFPP) are the largest stationary anthropogenic source of mercury emissions (Weem, 2011). Mercury is volatilized during combustion and released in its elemental form Hg(0). Subsequent cooling of the flue gas and interaction of Hg(0) with other flue-gas constituents, such as chlorine and unburned carbon, will result in the partial transformation of Hg(0) to oxidized forms of mercury Hg(2+), and a proportion of the mercury will be adsorbed onto fly ash particles Hg(P). As a result, coal-combustion flue gas contains varying percentages of Hg(P), Hg(2+), and Hg(0) (Gharebaghi et al., 2011; Weem, 2011).

Another important source of Hg pollution is the use of mercury in agriculture. Although the use of mercury as seed dressing (antimicrobial and fungicidal chemicals applied prior to planting) was prohibited many years ago, pesticides, fertilizers, sewage sludge and irrigation water remain a source of mercury pollution (Hseu et al., 2010). Sources

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http://dx.doi.org/10.1016/j.gexplo.2016.05.005

of mercury also include industrial processes and consumer products. Due to its special properties, including high density and a high rate of thermal expansion, mercury is often used in barometers and thermometers. It can also be combined with other metals to create special alloys called amalgams. Gold and silver amalgams have been used in dentistry for fillings, and tin amalgams are commonly used in production of mirrors. Mercury can be found in many different lamps, including 'black lights,' and is used in the industrial production of chlorine and sodium hydroxide (Environment Canada, http://www.ec.gc.ca/mercure-mercury/).

1.2. Main Hg sources in Slovenia

Low density soil and sediment geochemical survey in Slovenia was presented by Pirc et al. (1994). Geochemical maps show in both media an extended anthropogenic halo around Idrija mercury mine and indications of a differing Hg backgrounds between the western and the eastern part of the country, and indications of man-made anomalies were also observed through the country (Pirc et al., 1994). The Idrija area is strongly enriched with mercury due to mineralized rocks and mining and ore processing, and was the focus of many detailed investigations over the last decades (Bavec, 2015; Bavec and Gosar, 2016; Bavec et al., 2014, 2015, 2016; Biester et al., 1999, 2000; Covelli et al., 1999, 2001; Gosar, 2004; Gosar and Šajn, 2001, 2003; Gosar et al., 1997, 2002, 2006; Grönlund et al., 2005; Hess, 1993; Hines et al., 2006; Horvat et al., 1999, 2003; Kocman and Horvat, 2011; Kocman et al., 2004, 2011; Teršič, 2010, 2011; Teršič and Gosar, 2013; Teršič et al., 2011a, 2011b, 2014; Žibret and Gosar, 2005). During 500 years of mercury production in Idrija, approximately 40,000 tonnes of Hg were released into the environment (Cigale, 2006; Miklavčič, 1999; Mlakar, 1974). Non-point source mercury emissions occurring over one year from the Idrijca River catchment were estimated by Kocman and Horvat (2011). The results of modelling revealed that, annually, approximately 51 kg of mercury are emitted from contaminated surfaces into the Idrijca river catchment (640 km^2). In addition, it was estimated that at least additional 17–34 kg of mercury are emitted annually from the most important point source of mercury (the ancient roasting complex) into the atmosphere (Kocman and Horvat, 2011). Other sources of mercury for 2001 were identified by Svetina et al. (2002) and included: coal-fired power plants, dental amalgams, products of the electric industry (batteries, lamps, measuring devices as thermometers, manometers, barometers), chemicals, the cement industry, incineration and waste treatment. The main sources of mercury were divided into the following categories: the use of mercury in industrial processes (the chemical industry, the electrical industry, cement production), consumer products containing mercury, waste incineration, cremation and hazardous waste disposal. Annual emission of Hg in Slovenia into the environment from these sources was estimated to be 1620 kg in 2001; 900 kg was deposited as waste, 630 kg escaped into the air and 90 kg into the water (Svetina et al., 2002). Pirc and Budkovič (1996) also recognized the use of explosives containing Hg fulminate during the First World War as a Hg source in the area of Soča (Isonzo) front (west Slovenia).

In the present study mercury concentrations and regional distribution of mercury in the topsoil across the whole territory of Slovenia were estimated and a geochemical map of mercury distribution was elaborated. The data from Slovenia were compared to data from the whole of Europe. The main purpose of this study was to define a geochemical baseline for mercury in Slovenia, so that it will serve as a timeline for monitoring future changes. In addition, the objectives of the study were to identify the regional differences caused by and the environmental implications of anthropogenic activities, to establish whether the mercury geochemical anomaly caused by the Idrija mine is also reflected in the regional mercury distribution and to determine whether any geochemical anomalies exist at other known mercury sources.

To evaluate the differences in determined Hg geochemical anomalies between low- and medium-density sampling, the data for Hg concentrations in soils from this medium-density geochemical survey (sampling grid 5 × 5 km) were compared to a previously performed low-density geochemical survey (sampling grid 25 × 25 km, Šajn, 1999) and to the regional geochemical data set supplemented by local high-density sampling data (irregular grid, $n = 2835$). In addition, geochemical maps of non-transformed data were compared to the maps of data normalized by Box–Cox transformation (Box and Cox, 1964). Since many statistical techniques are sensitive to non-normally distributed data, the Box–Cox transformation was performed. The Box—Cox transformation improves this feature, especially for the skewness and level of normality of the data sets.

1.3. The study area

Slovenia is situated in Central Europe (Fig. 1) and covers an area of 20,273 km^2. In Slovenia, 4 geographical units meet: the Alps, the Pannonian Basin, the Dinarides and the Mediterranean; this fact is reflected in the great diversity of its geology, climate, relief, vegetation and pedological characteristics (Repe, 2004). The interaction of three major climate systems (Continental, Alpine and sub-Mediterranean) in the territory of Slovenia strongly influences the country's precipitation regime. The average density of the watercourses in Slovenia is 1.33 km per square km, among the highest density found in Europe. In Slovenia, the average annual precipitation is 1570 mm (Hrvatin, 2004). The spatial variability of the precipitation is high—the annual precipitation sum varies from 800 mm in the northeastern part of the country to >3500 mm in the northwest (www.arso.gov.si). Because of its diversity and distinct variation over short distances, bedrock is the most important pedogenetic factor in Slovenia (Repe, 2004). Divided by lithological type, 49.25% of Slovenian territory is composed of clastic rocks, 39.31% of carbonate rocks, and 4.27% of a mixture of the two. Metamorphic rocks comprise 3.9% of Slovenian territory, pyroclastic rocks 1.78% and the smallest area (1.49%) is occupied by igneous rocks (Komac, 2005). Slovenia is characterized by carbonate rock and the corresponding karst surfaces. In the highest parts of Slovenia (alpine and subalpine Slovenia) poorly developed regolith, shallow rendzina on carbonate rock or ranker on a silicate bedrock occur. Rendzinas, thin soils with A–C or A–R profiles, which form on limestone and dolomites, are the most widespread soil type, covering 24% of the territory. Older type soils with a developed cambic B-horizon; these are brown soils overlying hard carbonate rocks and terra rossa (both Chromic Cambisols according to FAO classification), which cover 14% of the Slovenian territory, eutric brown soils (Eutric Cambisols, 14%) and distric brown soils (Distric Cambisols, 16%). Eutric brown soils are developed in the valleys and basins of central Slovenia (Ljubljana basin, Celje basin) and compose the most fertile Slovenian agricultural land (Vrščaj et al., 2005). Various types of leptosols (lithic, umbric, rendzic), cambisols, luvisols, fluvisols, and histosols are found in alpine and subalpine Slovenia, according to the international FAO classification. In Sub-Mediterranean Slovenia mainly shallow rendzina, brown forest soil, and—in the Kras region as a special form—a distinctly red terra rossa soil type is developed (Vrščaj et al., 2005). Due to the abundance of surface waters and the relatively flat surface, the most gleyed and pseudogleyed soils in Slovenia are found in northeastern Slovenia. As a result of the flat surface, this is the most important agricultural area of Slovenia (Repe, 2004).

For the purpose of our study, Slovenia was divided into several natural units based on the units defined by Poljak (1987) by the geographical and geological characteristics of the Slovenian territory. The following 6 natural units were used in this study for the interpretation of statistical results and Hg distribution: Alps, Western Prealps, Eastern Prealps, Dinarides, Interior basins and Pannonian basin (Fig. 2). The description of natural units that follows is summarized after Poljak (1987). The **Alps** occupy the northern part of Slovenia and consist of several