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Atmospheric distribution and deposition of mercury in the Idrija Hg mine region, Slovenia

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ABSTRACT

The atmospheric distribution and deposition of Hg in the area of the former Idrija Hg-mine, Slovenia, were investigated. Mapping of air Hg^0 concentrations was performed to assess the spatial distribution and major sources of mercury to the atmosphere in the area. In addition, analyses of mercury speciation in the air over Idrija were performed during a 4-day sampling campaign in September 2006 to better understand the fate and transformation of Hg in the atmosphere of this specific mercury polluted site. The speciation results were then compared to the results of mercury speciation in the wet and throughfall deposition sampled on a precipitation event basis from October 2006 to September 2007. The Hg^0 concentration in air was mostly below 10 ng m^{-3}, with the highest concentration in the area of the former smelter complex exceeding 5000 ng m^{-3}. Mercury-bearing airborne particles (TPM) seem to dominate the atmospheric Hg deposition, which revealed noticeable variations between precipitation events (11–76 ng m^{-2} day^{-1}), mostly as a function of the amount of precipitation. Hg in precipitation was largely (~50%) associated with the particulate phase (THg_P). No correlation was found between the THg_P and the dissolved phases (THg_D), suggesting that particulate phase Hg is mostly the result of dry deposition. In the throughfall, significantly higher (2–10 fold) Hg concentrations than in associated event precipitation were observed, mostly due to Hg in the particulate phase (~70% THg). As shown by SEM/EDXS microscopy, an important amount of mercury in the precipitation and throughfall samples is due to the presence of cinnabar particles as a result of the aeolian erosion of cinnabar-containing surfaces in the area.

1. Introduction

The Idrija mercury mine in south-western Slovenia was an important mercury production centre. In over 500 years, more than 12 million tons of Hg ore was excavated from this, the world's second largest Hg mine, from which 100 000 tons of elemental Hg and 7000 tons of cinnabar were extracted. During smelting of Hg ore an estimated amount of more than 35 000 tons of Hg was lost to the environment, mostly to the atmosphere as Hg^0 vapour and as particulate phase dumped into the River Idrijca or on its banks as smelting residues (Dizdarevič, 2001). Hence, Hg mining activities in Idrija have resulted in significant Hg contamination of surrounding local environments. While a relatively large number of observations of mercury dynamics in water, soils, sediments and biota for this important Hg contaminated site are available (e.g. Biester et al., 2000; Gnamuš et al., 2000; Horvat et al., 2002; Kocman et al., 2004; Žižek et al., 2007), the atmospheric distribution of mercury has only been addressed in a few studies (Gosar et al., 1997; Grönlund et al., 2005; Kotnik et al., 2005) and no data on atmospheric deposition are available so far.

However, the atmosphere plays an important role in the regional and global dispersion and deposition of mercury (Selin et al., 2007). It is known that mercury emitted from contaminated sites can be deposited locally or transported over long distances and deposited even at the most remote sites far from direct discharges of mercury (Lindberg et al., 2007). Before being deposited, atmospheric mercury can undergo various physical and chemical transformations that are controlled by the properties of different mercury species in the atmosphere. In the atmosphere, mercury exists primarily in inorganic form with two oxidation states: Hg^0 and Hg^{2+}. Gaseous elemental mercury (Hg^0) is relatively inert to chemical reactions with other atmospheric constituents. Its residence time is believed to be of the order of 1 year (Schroeder and Munthe, 1998). Therefore, once released to the atmosphere, it can be dispersed and transported over long distances before being deposited to terrestrial and aquatic ecosystems. Hg^{2+}, on the other hand, can be found in both the gaseous and the particulate phase bound in/to aerosols. Compared to Hg^0, Hg^{2+} has a much shorter lifetime in the atmosphere (from several days to a few weeks) (Lindqvist and Rodhe, 1985; Slemr et al., 1985). Hg^{2+} is a highly surface reactive species and deposits much faster than

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Hg^0 through both dry and wet processes (Lindberg and Stratton, 1998). To understand the regional budget of atmospheric Hg and the chemical and physical processes in the atmosphere, it is important to determine the spatial and temporal variability of atmospheric Hg concentrations, its speciation and deposition fluxes.

In the present study, atmospheric mercury distribution, and for the first time the speciation and deposition of mercury, was investigated in the Idrija Hg mine region, Slovenia. Mapping of air Hg^0 concentrations was performed to assess the spatial distribution and major sources of mercury to the atmosphere in the area. The influence of seasonal variations and changing weather conditions on Hg^0 distribution in air was also investigated. Furthermore, analyses of mercury speciation in the air over Idrija were performed to better understand the fate and transformation of mercury in the atmosphere of this specific mercury polluted site. Moreover, precipitation and throughfall samples were collected at different locations in the River Idrijca catchment in order to follow the amount, temporal variations and spatial distribution of the atmospheric deposition of mercury over the year.

2. Materials and methods

2.1. Site description

The area under investigation, the Idrija Hg mine region, covers the transitional zone between the Alps, the Dinaric Mountains and the Adriatic Sea (Fig. 1). The whole area is geomorphologically very heterogeneous, with a wide range of altitudes from 170 to more than 2000 m a.s.l. Forests cover as much as 80% of the surface, while the remaining 20% is mostly natural grassland with some pastures. The town of Idrija, where the mercury mine is located, lies 20 km from the source of the River Idrijca, on the alluvial plains at the confluence of the Nikova and the Idrijca. The study area has a warm humid temperate climate. The average air temperatures for those months representative of the seasonal meteorological variation in the domain are 0–2 °C in January, 6–10 °C in April, 16–22 °C in July and 8–12 °C in October. Concerning precipitation, all seasons receive approximately the same amount with no distinctive dry or wet periods. The transitional character of this area influences the climate the most. As the mountains (Julian Alps) block air circulation from the northern Adriatic Sea in a northerly direction, annual precipitation here is very high and ranges between 2000 and 3200 mm $year^{-1}$. High peaks and steep mountain slopes prevent air circulation in the valleys. The most common winds in this area follow the geography of the Idrijca valley.

Fig. 1. Study area and sampling sites.

2.2. Sampling and pre-analysis procedures

Air mapping of total elemental mercury in air was performed during three sampling campaigns (August 2006, October 2006 and July 2007) over the area between the towns of Idrija and the Spodnja Idrija (Fig. 1). A Lumex 915$^+$ absorbtion spectrometer installed in a car, together with a GPS instrument, was used. Both values (Hg concentration and geographical coordinates) were recorded by a portable computer through an appropriate software. During each campaign, elemental mercury in air was measured at more than 100 locations between 11 am and 3 pm. It should be noted that the measured values refer to 1.5 m above the road surface. The concentration values recorded at individual points were then smoothed into a geochemical map using a computer routine (GIS).

In September 2006, measurements of mercury speciation in air over the town of Idrija were performed during a 4-days sampling campaign. Different mercury species in air were collected by pumping the air through three different traps: a trap containing a quartz micro-fibre filter, a quartz glass tube containing gold powder and a quartz glass annular denuder impregnated with KCl. Samples were collected continuously with 12 h time resolution. Details about the procedure are given in Section 2.3.2.

Precipitation and throughfall sampling was designed based on the Bergerhoff type of sampler (German standard VDI 2119, 1996), recently validated by the European Committee for Standardisation (Brown et al., 2010). These wide-mouthed jar samplers used consist of a borosilicate glass collector bottle of 2 L volume with the horizontal opening of 120 mm resulting in a collecting area of 113 cm^2. The jars were mounted in a steel basket placed approximately 1.5 m above the ground and shielded from sunlight by wrapping in aluminium foil. The samplers were open for collection at all times. In this way, mercury deposited by both dry and wet deposition was collected. The length of the sampling period varied from 3 to 16 days, as the samples were collected on a precipitation event basis, which means from the beginning to the end of the precipitation event. Samples were obtained just after these events (usually within 4 h after the event). In total, 15 precipitation samples and 8 associated throughfall (beech forest) samples were collected in the town of Idrija from October 2006 to September 2007. Additional samplers were installed downstream along the River Idrijca, in Jagršče and Bača pri Modreju (Fig. 1). At these latter two locations, samples from two individual precipitation events that occurred on February and March 2007 were obtained. For both precipitation events, at the Jagršče location, throughfall samples in the beech forest were also collected. Collecting bottles were thoroughly cleaned before use by leaching in a 2% solution of HCl for a couple of days. In addition, bottle blanks were taken regularly to ensure that these remained within acceptable limits. Following sampling the sample collection vessels were closed and double sealed in plastic bags and immediately transported to the analytical laboratories where they were stored in the dark in a refrigerator until analysed. Additionally, event precipitation samples for stable oxygen and hydrogen isotopic composition were collected and stored separately. The amount of precipitation was recorded by weight in the laboratory.

2.3. Analytical methods

2.3.1. Determination of elemental mercury in air

Measurements of elemental mercury in air were performed using a portable RA-915$^+$ Zeeman Mercury Analyzer. Analyzer operation is based on differential atomic absorption spectrometry using high-frequency modulation of light polarisation. The detection limit of the instrument for ambient air, industrial and natural gases is 2 ng m^{-3} at a flow rate through the instrument of 20 L min^{-1}. The accuracy of the method is 20% (Sholupov and Ganeyev, 1995).

2.3.2. Mercury speciation in air

The experimental set-up used for mercury speciation in air was based on the work presented by Landis et al. (2002) with some adaptations. For divalent gaseous mercury (RGM) quartz glass annular denuders were used. Denuders (URG-2000-30CD) and inlets (URG-2000-30K, URG-2000-30PASS) were obtained from the URG company, USA. The denuders had a 25.4 cm active annular surface length with a 1 mm annular space and were coated with 2.4 M aqueous KCl solution. For total particulate mercury (TPM), a quartz micro-fibre filter (14 cm long, inner diameter 0.7 cm) was used (Lu et al., 1998). The filter was supported by a screen grid made from pure nickel. The sampling device serves as both particulate trap and pyrolyzer for airborne particulate species. Gaseous elemental mercury (GEM) was collected by Au-trap consisting of a quartz tube (14 cm long, inner diameter 0.4 cm) containing a powdered gold. All three traps were placed in sequence in an electrically heated housing (maintained at 50 °C) with the intake 1.5 m above the ground and air was pulled through the traps at a flow rate of 600–800 mL min^{-1} by a volumetrically flow-controlled pump. In this configuration, TPM was collected downstream of the