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Research article

The role of native lichens in the biomonitoring of gaseous mercury at contaminated sites

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ABSTRACT

Contamination by atmospheric mercury has been assessed in two different areas from Spain (Las Cuevas, Ciudad Real and Flix, Tarragona) using lichens as biomonitors. The relationship established between mercury contents in the soils and the gaseous mercury (GM) was also observed. It was found that the GM is highest in the vicinity of the source and it is dispersed depending on of the distance to the source and the wind directions. The mercury concentration in the gas phase in Flix was higher than that found in Las Cuevas and also higher than the value that the US EPA recommended. The mercury bioaccumulation in the native lichens from genders *Ramalina* and *Xanthoria* were used as biomonitors for absorbing mercury in Las Cuevas and Flix, respectively. The mercury uptake by *Ramalina* was higher than the amount accumulated by *Xanthoria*, a difference that was mainly due to the lichen characteristics. The content of mercury in lichens in relation to the mercury in gas was fitted by a Freundlich type equation, indicating that the equilibrium between both phases was established. Besides, transplanted *Ramalina* lichen in Las Cuevas allowed to obtain the kinetic of mercury uptake. A kinetic model of first order based on the equilibrium was proposed and the mass transfer constants for each sampling station were estimated. As it was expected, these values increased with the predominant wind flow direction.

1. Introduction

Mercury is one of the less abundant elements on earth but one of the most eco-toxic pollutants due to its high capacity of accumulation in living organism and its persistence in the environment (Munteanu and Munteanu, 2007). As a pollutant, Hg is emitted to the atmosphere from anthropogenic or natural processes. Natural sources are volcanoes, soil erosion and oceans, whereas anthropogenic ones include all the emissions derived from human activities such as: fossil fuel consumption, gold mining activities, chemical industry, paints, paper mills, metal or cement production, insecticides and fungicides (Grangeon et al., 2012; Scerbo et al., 1999). It can be found in the atmosphere predominantly in its elemental gaseous form Hg^0 (>90–99%) (Kono and Tomiyasu, 2009), being the other forms, reactive gaseous mercury RGM and mercury bound to particles (Hg-p). Hg^0 can react with oxidants (eg. O_3) oxidizing it and transforming it to Hg(II), which is rapidly deposited locally in the same way than Hg-p by wet or dry depositions, whereas Hg^0 is only affected by dry depositions (Grangeon et al., 2012; Fernández et al., 2000). Soluble RGM or Hg-p in water is transformed into different organic species and mainly methylmercury (CH_3Hg^+), an extremely toxic compound that is bioaccumulated by fish (Lodenius, 2013; Carmona et al., 2013). Therefore, the measurement of mercury dispersion and concentration has become a matter of concern in most of the developed countries and important efforts has been employed in this field (European Commission, 2010).

Mercury monitoring can be performed by technical collectors or by living organisms (biomonitoring). Monitoring of atmospheric mercury on the basis of direct instrumental measurements is easy and reliable, and a great number of studies deal with this question (García-Sánchez et al., 2006; Gosar et al., 1997; Higueras et al.,

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2014; Kim et al., 2006; Southworth et al., 2004; Zhu et al., 2011). However, instrumental measurements require instrumental availability during longtime spans in order to study the temporal and/or geographic distribution of the pollutant. Mercury biomonitoring present many advantages such as the possibility of long-term monitoring without spreading high cost equipment. Also, it gives more accurate information of the spatial mercury distribution, their effective surface is considerably larger than those from technical ones, detect most of the mercury species and indicate the changes in the ecosystems (Lodenius, 2013; Bergamaschi et al., 2007).

Lichens are often used for biomonitoring in the environment because they pick up nutrients directly from air, retaining a large amount of trace elements (Agnan et al., 2015; Balarama et al., 2003; Conti and Cecchetti, 2001; Garty, 2001; Giordano et al., 2005). They are specially used for mercury measurements due to their sensitivity to estimate its biological effects for supplying information about atmospheric mercury and also on its reaction products in a quick and inexpensive way (Davies and Notcutt, 1996; Bargagli and Barghigiani, 1991; Bargagli et al., 2002; Grangeon et al., 2012; Loppi et al., 1997; Loppi and Bonini, 2000; Loppi, 2000; Ikingura et al., 2006). Lichens are able of direct accumulation of elements from the atmosphere in their tissues and on their whole external surface (Scerbo et al., 1999). On the other hand, the use of transplanted lichens (Kauppi, 1976; Loppi et al., 1998; Nannoni et al., 2015) may offer better possibilities, including the one of electing the monitoring sites, and carrying out surveys with specific duration.

In previous works, López-Berdonces (2009) and Esbrí et al. (2015) offer some data on the usage of these organisms for the Almadén mercury mining district (AMMD) (South Central Spain), where Las Cuevas is located, and for the surroundings of the Flix chlor-alkali plant, respectively. Our study examines the possibilities of usage of lichens as a tool to assess the atmospheric mercury contamination associated to both natural and anthropogenic sources of this pollutant.

The main objective of this study was to set a methodology for a general mercury monitoring for different mercury sources, based in the analysis of contents of this element in native lichens present in the Las Cuevas and in Flix area. These data were used in order to find the equilibrium relationship between the GM and the mercury into the lichen. Besides, kinetic of mercury uptake was also checked in Las Cuevas area and a model based on the equilibrium was established. To accomplish this general objective, the following partial objectives were considered:

i) Analyses of the gas and soil mercury concentrations in the studied areas.
ii) Characterization of a real distribution of mercury bioaccumulated in native lichens.
iii) Study of the influence of the mercury source in the lichens mercury bioaccumulation, comparing the results from the Las Cuevas and Flix areas.
iv) Development of the kinetic model of mercury accumulation by lichens in the Las Cuevas area using transplanted lichens from non-contaminated areas.

2. Study areas

Almadén mining district is located in central part of Iberian Peninsula, 300 Km south west of Madrid. The area is part of the "*Meseta Sur*", which has a Mediterranean climate with hot summers and cold winters; with an annual average of precipitations of 400 mm. The average temperature ranges from 1 to 8 °C in January to 17–31 °C in July. Almadén mining district is considered as one of the most important mercury deposits in the world (Saupé, 1990; Hernández et al., 1999). Ferrara et al. (1998), Higueras et al. (2006) and Llanos et al. (2010) documented mercury presence in the local and regional atmosphere, based on instrumental measurements. One of the most significant mercury sources of this area is the Las Cuevas complex, due to the presence of an important mercury storage center and the fact that this area is constituted by an old mercury mine and two dumps. Higueras et al. (1999) and Llanos et al. (2010) describe extensively this area from the geological and environmental points of view, respectively.

The second study area is the Flix area. It is located in Tarragona province, northeast Spain. In this area, the contaminated soils and the chlor-alkali plant (CAP), located very close to the Flix urban area, are important sources for gaseous mercury. Esbrí et al. (2015) studied this area and found very high levels of mercury as an atmospheric pollutant and also in local soils. It is important to point out that CAPs represent approximately a 2% of the total anthropogenic mercury emitted to the atmosphere. The mercury form emitted from these plants is elemental mercury that escapes from the cathode in electrolytic cells that produce chlorine and caustic soda from NaCl (Grangeon et al., 2012).

3. Material and methods

3.1. Samples collection and preparation

In this work, mechanical collectors and lichens have been used for mercury monitoring in air and soil, obtaining samples from 2007 to 2012. Both collection methods for gas or solid samples, are described in the Subsections 3.1.1 and 3.1.2 and the maps showing the sampling locations for Las Cuevas and Flix are shown in Figs. 1 and 2, respectively.

3.1.1. Mercury gas measurement

Mercury gas samples were collected and analyzed by using a LUMEX RA-915+. This equipment gives a measurement of mercury gas per second. The analyses were performed during 120 s/day, 3 days per week. Reported values are the average for each sampling station during the studied period. The MG was measured at a

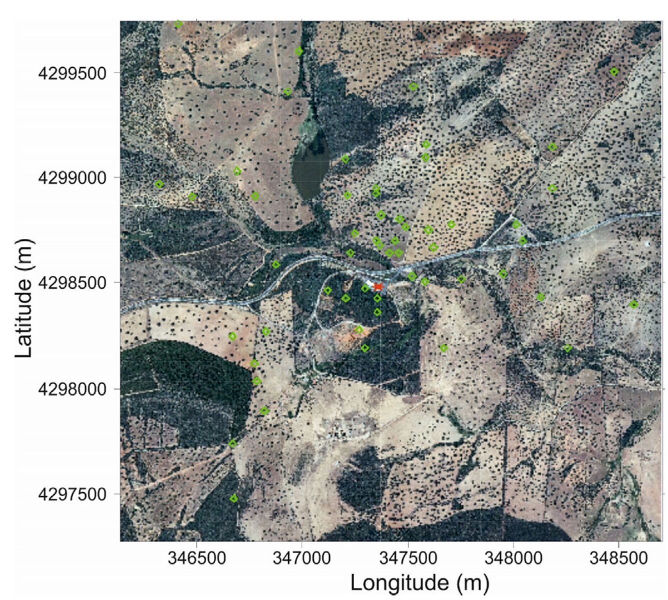

Fig. 1. Sampling map for the survey carried out in Las Cuevas area. Red asterisk corresponds to the main Hg source: the mercury storage center. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)