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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

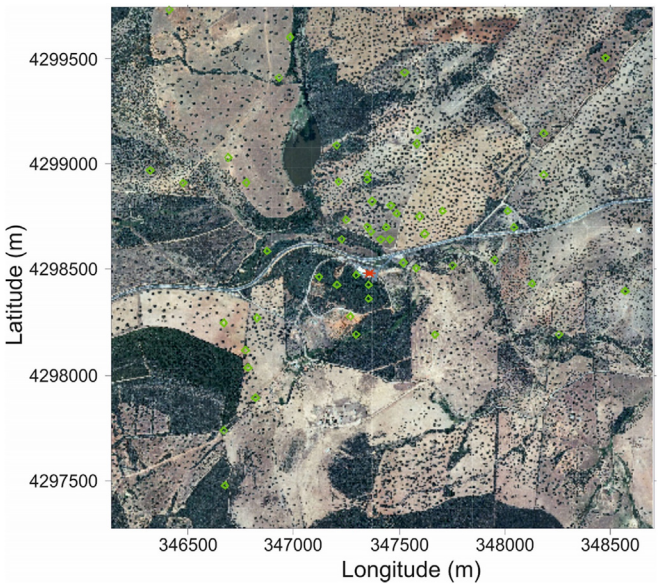

Fig. 1. Sampling map for the survey carried out in Las Cuevas area. Red asterisk corresponds to the main Hg source: the mercury storage center. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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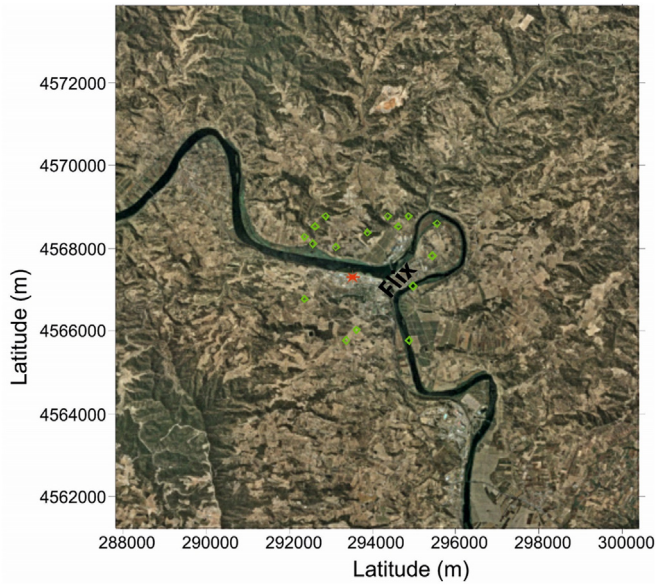

Fig. 2. Sampling map for the survey carried out in the Flix area. The red asterisk corresponds to the location of the chlor-alkali plant. The Flix urban area is also indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

height of 1.5 m, which is considered to be the reference value for the human exposition to the contaminant by inhalation. This technology and the corresponding methodology has been widely probed and described (Esbrí et al., 2015).

3.1.2. Sampling procedure of mercury in soil

Three soil samples per year were collected in the same sampling stations that the air measurements, taking out the soils up to a depth of 30 cm after eliminating the external 5 cm. Collected samples were immediately stored in hermetic plastic bags. Before analysis, the soil samples were dried at room temperature and further disaggregated and sieved with a mesh size of 2 mm. Reported values correspond to the average of the collected samples in the studied period. For mercury quantification, samples between 20 and 30 mg were calcined into a pyrolytic chamber RP-91C at 800 °C, and the vaporized mercury was driven to the LUMEX equipment and measured at a $\lambda = 254$ nm.

3.1.3. Biomonitoring of mercury concentration

For Las Cuevas survey, the lichen *Ramalina* was selected as bioindicator. The use of this specie for atmospheric metals monitoring has been previously described by several authors (Branquinho et al., 1999; Bermudez et al., 2009; Cercasov et al., 2002; González et al., 1996 and Walther et al., 1990). Samples within 1–2 g were taken with tweezers from branches of acorn tree (*Quercus rotundifolia*) at a height of 1.5–2.0 m, Lichens were further stored in paper bags and kept refrigerated until the analysis.

Besides, the kinetic of mercury accumulation of the Ramalina lichen was studied by transplanting *Ramalina* from a clean area, Los Montes de Toledo (Toledo, South-Central Spain). 7 lichens were transplanted per each specific sampling station close to that of the native one. The total sample was obtained from all transplanted lichens following the above procedure. Samples were taken at different moments: 10, 45 and 92 days. These sampling periods were selected in order to obtain stable measurements and to give the lichens time enough to recover from the stress caused by transportation and sowing (Kono and Tomiyasu, 2009).

At Flix area, the used lichen specie was the *Xanthoria parietina Thalli*. This is, as *Ramalina*, an epiphyte lichen extensively used in monitoring of atmospheric metallic pollutants (Cuny et al., 2004; Gür and Yaprak, 2011; Loppi et al., 2006; Scerbo et al., 2002; Vannini et al., 2014). Therefore, it was sampled, also from trees and shrub vegetation, using the same methodology as for Las Cuevas survey.

Before analysis, lichens samples were frozen and further lyophilized in a Telstar cryodos-50 equipment in order to achieve a complete water removal. The mercury in lichens was analyzed three times by using the LUMEX equipment provided with a pyrolytic chamber.

3.2. Samples analysis

The analytical technique used for solid samples (soil and lichens) was the atomic absorption spectrometry with Zeeman effect and high frequency modulation (ZAAS-HFM), using a Lumex RA-915+ device with RP-91C pyrolitical attachment (Sholupov et al., 2004). This is a widely used technique to analyze total mercury concentration in geological and biological samples (Amorós et al., 2014; Verestiuc et al., 2015) in a wide range of concentrations and detection limits of 0.5 ng kg^{-1} (geological samples) and 2 ng kg^{-1} (biological samples).

In order to check the validity of the procedure, we ran analytical tests (Standard Addition Method, using the NIST 2710, NIST 2711, and BCR 146R standards; see below) on single (lichens) and composite (lichens plus a known amount of a standard) samples. The results showed that background correction effectively inhibited any major distortion (e.g., plant: *Eleocharis palustris* (L.) Roemer & Schultes: n = 4 runs, variation on Hg concentration = 0.3%). Quality control at the laboratory was accomplished by analyzing replicated samples to check precision, whereas accuracy was obtained by using certified standards: (SRM) NIST 2710, (SRM) NIST 2711, and BCR 146R.

4. Results

4.1. Mercury concentration in air and soil

As commented above, two sites with different mercury sources were evaluated: the Las Cuevas and the Flix areas. The main goal was checking the biomonitoring capacity of lichens for different mercury sources. Fig. 3 shows the GM concentration as function of the location coordinates.

Three maximum concentration of mercury can be observed (Fig. 3a), which correspond with the location of mercury storage center and two old mine dumps. The highest GM value is found in the mercury storage center (110 ng m^{-3}), which is related with the handling of mercury that evaporates during the filling of the mercury containers for further selling. This value is smaller than that recommended by the US EPA as a human health risk for long term exposition (300 ng m^{-3}) (US EPA, 2007). The rest of the area presents a stable emission or dispersion pattern of GM with values within 20–40 ng m^{-3}. The Flix area (Fig. 3b) shows two GM peaks in the vicinity of the chlor-alkali plant: the concentrations in these points are higher than 1500 ng m^{-3}, which considerably overpass the US EPA (2007) recommended limit. GM concentrations sharply decrease from the chlor-alkali plant to the town area, to reach mercury concentration close to cero to the East of this. According to these mercury values in the atmosphere, it is possible to say that the Flix area is more contaminated for mercury than the mining area of Las Cuevas in Almadén.

The relationship between the GM and mercury contents in the soils are represented by curves that are concave upward in shape for both areas (Fig. 4).

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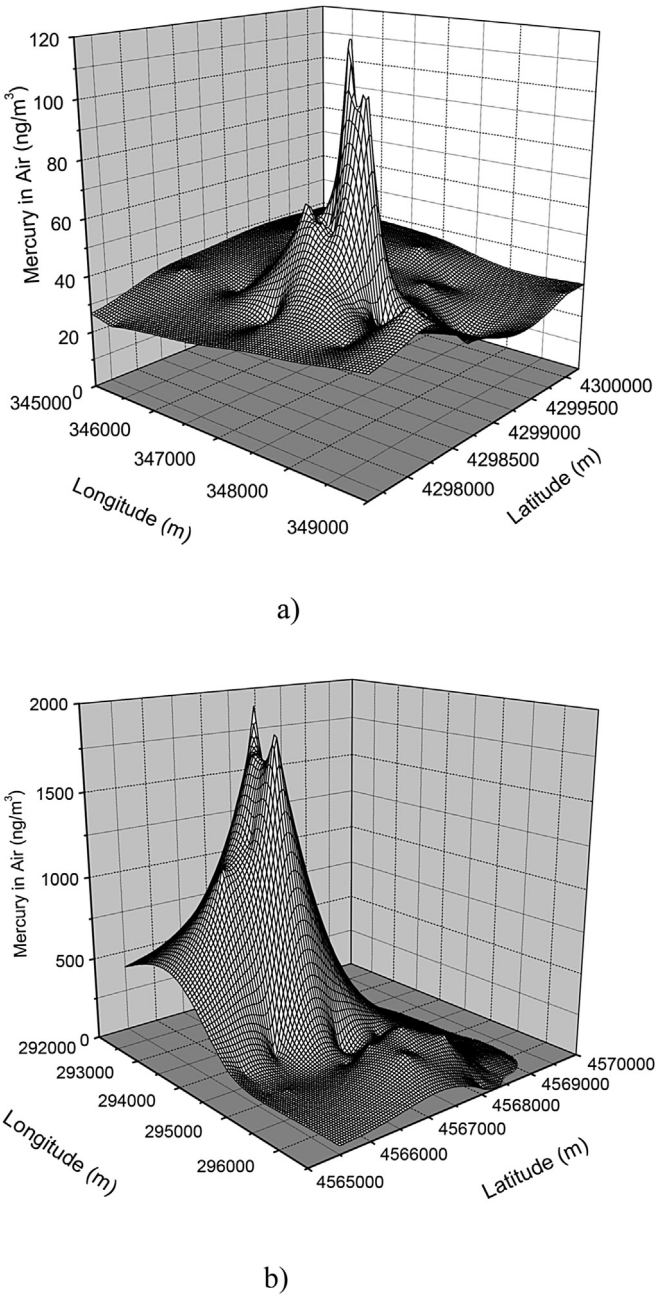

Fig. 3. Mercury concentration in air. a) Las Cuevas area; b) Flix area.

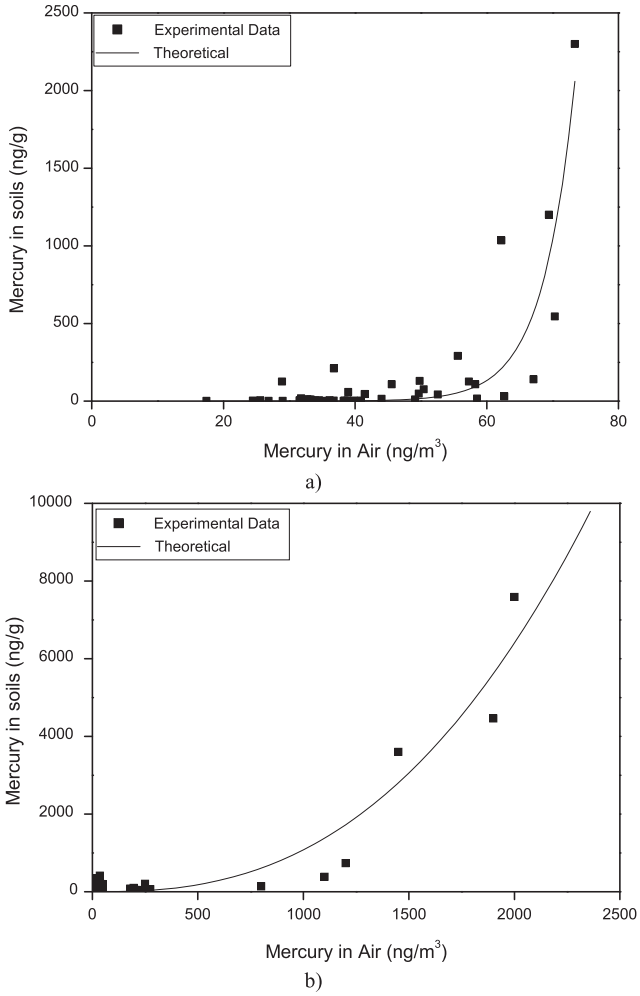

Fig. 4. Relationship between mercury in air and soils. a) Las Cuevas area, b) Flix area.

According to Fig. 4, for low values of the GM concentration, the mercury in soils is practically neglected but once the inflection point is reached, the concentration in the soil sharply grows up. These inflections points for Las Cuevas and Flix correspond to 60 and 1000 ng m^{-3} and 153 and 1080 ng g^{-1}, in air and soil respectively. Hence, the mercury vapor is more easily released from the soils in Flix than from soils in Las Cuevas, because soils from Las Cuevas, containing 2500 ng g^{-1}, are able to emit only 75 ng m^{-3}, whereas soils in Flix, having the same concentration, emit 20 times that value. This could be related with the differences in the characteristics of both soils since Las Cuevas is constituted mainly by natural contaminated soils while the soils in Flix are contaminated from the mercury emitted by the CAP. Important variations in the mercury vaporization from different soils were observed by During et al. (2009) and they also attributed these differences to the soils characteristics (pore size distribution, substrate type, surface type, Hg concentration, etc).

4.2. Mercury concentration in native lichens in the studied areas

The distribution of bioaccumulated mercury concentrations in native lichens were studied by using the lichens *Ramalina* and *Xanthoria* for the Las Cuevas and the Flix areas, respectively. These data were analyzed versus the mercury concentration in air (Fig. 5), being the GM for each lichen sampling site obtained from the matrix data of Fig. 3.

As expected, the closer to the source, the higher the mercury concentration in the lichens. On the other hand, the values of mercury concentration in *Xanthoria* lichens are similar to those found by Grangeon et al. (2012) when studying the same lichen also in the surroundings of a CAP in Grenoble (France) and those reported by Balarama et al. (2003) when using the *Parmelia sulcata* lichen in the vicinity of a mercury thermometer-making factory situated in a southern state of India.

The mercury concentration in *Ramalina* lichens increase sharply with the mercury in gas, while the mercury concentration in *Xanthoria* ones is directly proportional to GM (Fig. 5).

Additionally, the tendency of the mercury concentration in lichens (q_L) versus the mercury gas concentration (GM) was fitted to a potential equation. This behavior was also observed in other lichens such as the *Lepisorus thunbergianus* (Kono and Tomiyasu,

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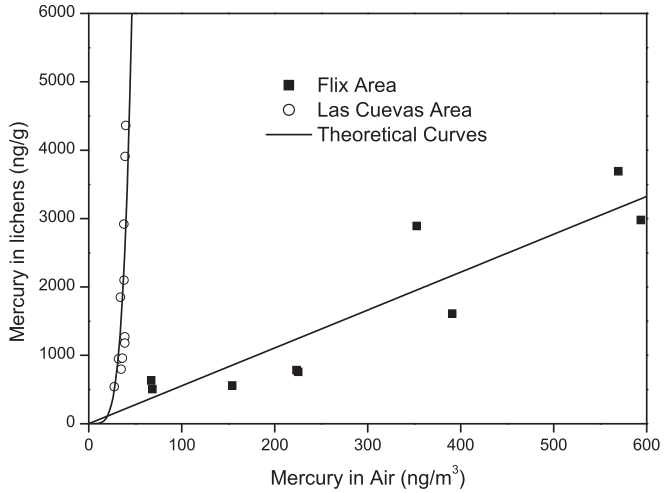

Fig. 5. Relationship between mercury in air and bioaccumulated mercury in the native lichens: (o) Las Cuevas area; (■) Flix area.

2009). Considering that the mercury in lichens reaches an equilibrium with the mercury in air, this can be described by a Freundlich equation (Equation (1)), indicating that lichens behave as a solid having good characteristic for being used in adsorption processes with unlimited sorption sites (Chern and Chien, 2002; Freundlich and Heller, 1939).

$$q_L = k_F \cdot GM^n \quad (1)$$

where k_F is the Freundlich constant and n is a parameter that define the lichen heterogeneity.

Fitting parameters q_L and n for the systems GM and mercury in the lichens from Las Cuevas and Flix are shown in Table 1.

The value of n higher than one for the adsorption of *Ramalina* lichen confirms that its mercury uptake is strongly dependent on GM concentration while the n value of *Xanthoria* lichen equal to one, indicates that qL is proportional to the atmospheric mercury concentration.

The difference in the q_L-GM equilibrium of the studied cases could be due to the tissues and morphological differences between the studied lichens and also to the forms of mercury that are emitted in both of these regions. Attending to the GM concentration, it was expected that the lichen *Xanthoria* located in Flix loaded a larger amount of mercury than *Ramalina* from Las Cuevas; since the higher the GM concentration, the higher the final mercury uptake in lichens (Vannini et al., 2014). Balarama et al., 2003 studied the speciation of the mercury uptake by the lichen *Parmelia sulcata* from an elemental mercury source and found that from a total of mercury of 8 mg kg^{-1} in the lichen, only 0.1 mg kg^{-1} was elemental mercury. These results indicate that lichens convert the Hg^0 into inorganic form Hg^{2+}. As commented above, the chlor-alkali of Flix emits Hg^0, although some oxidants present in the region could convert part of it to reactive mercury (Fernández et al., 2000). In the same way, the mercury emitted in Las Cuevas, an area with a low concentration of oxidants to transform the Hg^0 to Hg(II), is mainly elemental mercury or Hg-p. Hence, in both areas Hg^0 is the most predominant species, indicating that the huge difference observed in the mercury uptake for the studied lichens must be related with the lichen characteristics.

Table 1
Freundlich parameter values for the equilibrium of mercury in both phases solid (in lichens) and gas in both areas.

Area	k_F (ngg^{-1}) (m^3 ng^{-1})^n	n
Las Cuevas	$6.7169 \cdot 10^{-5}$	4.75
Flix	5.5416	1.00

4.3. Mercury concentration in transplanted lichens in Las Cuevas area

Fig. 6 shows several examples of the kinetics of mercury bioaccumulation in the *Ramalina* lichens in the Las Cuevas area, plotting the ratio between the lichen mercury concentrations at each time (q_t) and its initial mercury concentration (q_L^0) respect to the sowing time.

As can be observed, this kinetics follow straight lines whose slopes are dependent on the sampling station. Vannini et al. (2014) found the same linear increase with time for the mercury uptake by three different lichens (Pseudevernia furfucacea, Xanthoria parietina and Evernia prunastri). They presented a model in which the mercury in lichens is only dependent on the gaseous mercury concentration previous to reach the lichen saturation. Nevertheless, the observed saturation for long exposure time is not considered in the proposed model. This saturation was also observed in this work using the native lichens. Hence, a boundary condition taking into account the established equilibrium between lichen and GM must be considered.

In this way, the accumulation of mercury into the lichen was fitted to a first order kinetic model, depending on the previous established equilibrium between the q_L and MG. This mercury accumulation in the lichen can be described as follows:

$$\frac{d(m_L \cdot q_t)}{dt} = k_l \cdot a \cdot (q_L - q_t) \cdot m_L \quad (2)$$

where m_L is the mass of lichen (g), q_t is lichen the mercury concentration for a specific time (ng g^{-1}), k_l is the overall mass transfer rate coefficient based on the gas phase resistance (m day^{-1}), and *a* is the lichen mass transfer area exposed to the air per lichen gram (m^2 m^{-3} g^{-1}).

k_l and a are constants dependent on the lichen and sampling station. Taking into account that only one lichen specie is used, both constants can be joined in only one, named k_{la} which will only depend on the sampling station. Integrating Equation (2), the following expression is obtained:

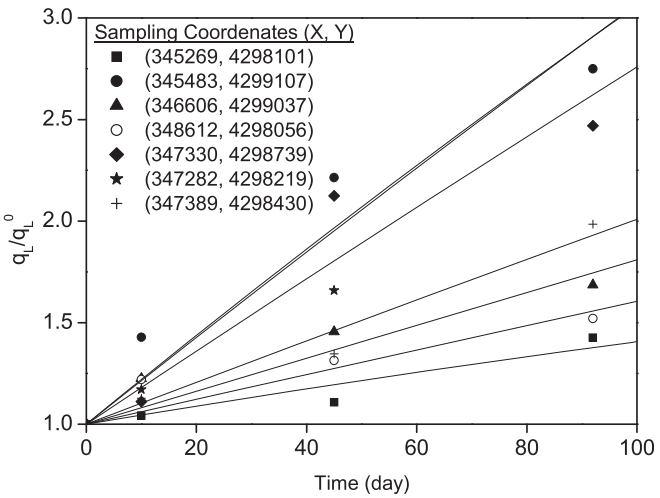

Fig. 6. Kinetic curves for the different sampling stations of the *Ramalina* lichen in Las Cuevas area.

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$$\frac{q_t}{q_L} = \left(1 - e^{-k_{la}t}\right) + \frac{q_L^0}{q_L} \cdot e^{-k_{la}t} \quad (3)$$

Values of k_{la} are represented as function of the specific coordinates of longitude and latitude of the Las Cuevas area.

These constants are independent on the mercury concentration in the gas phase, being mainly dependent on the atmospheric conditions such as wind speed, temperature, humidity and precipitation. The highest values appear in the zone of predominant wind flow (south-west), becoming the mercury uptake by lichens the result of the convective regimen (Fig. 7).

It is possible to observe that the storage mercury center and the dumps present a low wind influence, being the mercury uptake by lichens located in this region controlled by the equilibrium, in agreement with the highest concentration in the gas phase. Thus, this biomonitoring system could be explained by the theory of mass transfer phenomena.

5. Conclusions

Atmospheric mercury concentrations in Las Cuevas are smaller than the recommended US EPA value whereas this value is overpassed in Flix, what mainly occurs in the vicinity of the chlor-alkali plant. Concave upward curves were obtained comparing the mercury concentration in air and soil in both areas, observing that for lower values of soils concentrations the GM is practically neglected. Once the inflection point is reached, the GM sharply grows up. It was found that mercury was more easily released from the soil in Flix than soils Las Cuevas and can be mainly attributed to the source nature.

The performed studies by using native lichens *Ramalina* and *Xanthoria* in Las Cuevas and Flix, respectively, showed that *Ramalina* is able to accumulate larger amounts of mercury than *Xanthoria*. It was also found that the content of mercury in lichens in respect to the mercury in gas followed a Freundlich type equation, indicating that the equilibrium between both phases was established.

Transplanted *Ramalina* lichens 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 constant for each sampling station were calculated. As it was expected, these values increased in the predominant wind flow direction. Hence, lichens can be considered as good biomonitors for studies in contaminated regions with elemental traces.

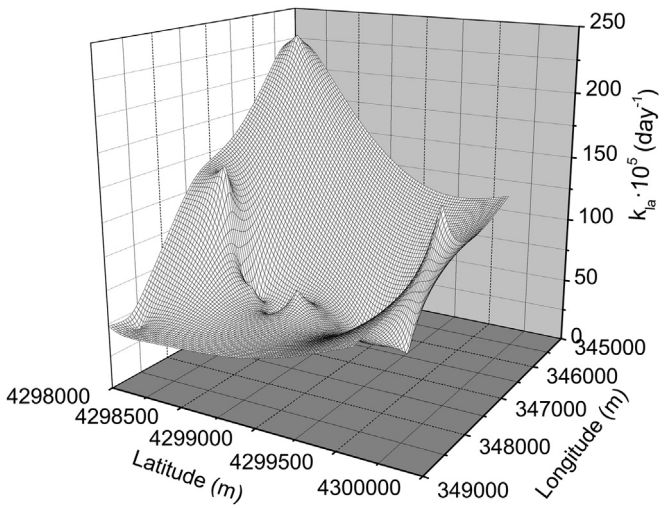

Fig. 7. Values of the mass-transfer coefficient in Las Cuevas area.

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References

Agnan, Y., Séjalon-Delmas, N., Claustres, A., Probst, A., 2015. Investigation of spatial and temporal metal atmospheric deposition in France through lichen and moss bioaccumulation over one century. Sci. Total. Environ. 529, 285–296.
Amorós, J.A., Esbrí, J.M., García-Navarro, F.J., Pérez- Reyes, C., Bravo, S., Villaseñor, B., Higueras, P., 2014. Variations in mercury and other trace elements contents in soil and in vine leaves from the Almadén Hg-mining district. J. Soils Sediments 14, 773–777.
Balarama, M.V., Karunasagar, D., Arunachalam, J., 2003. Study of mercury pollution near a thermometer factory using lichens and mosses. Environ. Pollut. 124, 357–360.
Bargagli, R., Barghigiani, C., 1991. Lichen biomonitoring of mercury emission and deposition in mining, geothermal and volcanic areas of Italy. Environ. Monit. Assess. 16, 265–275.
Bargagli, R., Monaci, F.F., Borghini, F., Bravi, F.F., Agnorelli, C., 2002. Mosses and lichens as biomonitors of trace metals. A comparison study on hypnum cupressiforme and Parmelia caperata in a former mining district in Italy. Environ. Pollut. 116, 279–287.
Bergamaschi, L., Rizzio, E., Giaveri, G., Loppi, S., Gallorini, M., 2007. Comparison between the accumulation capacity of four lichen species transplanted to an urban site. Environ. Pollut. 148, 468–476.
Bermudez, G.M.A., Rodriguez, J.H., Pignata, M.L., 2009. Comparison of the air pollution biomonitoring ability of three Tillandsia species and the lichen Ramalina celastri in Argentina. Environ. Res. 109, 6–14.
Branquinho, C., Catarino, F., Brown, D.H., Pereira, M.J., Soares, A., 1999. Improving the use of lichens as biomonitors of atmospheric metal pollution. Sci. Total. Environ. 232, 67–77.
Carmona, M., Llanos, W., Higueras, P., Kocmand, D., 2013. Mercury emissions in equilibrium: a novel approach for the quantification of mercury emissions from contaminated soils. Anal. Methods 5, 2793–2801.
Cercasov, V., Pantelică, A., Sălăgean, M., Caniglia, G., Scarlat, A., 2002. Comparative study of the suitability of three lichen species to trace-element air monitoring. Environ. Pollut. 119, 129–139.
Chern, J.M., Chien, Y.W., 2002. Adsorption of nitrophenol onto activated carbon: isotherms and breakthrough curves. Water Res. 36, 247–255.
Conti, M.E., Cecchetti, G., 2001. Biological monitoring: lichens as bioindicators of air pollution assessment – a review. Environ. Pollut. 114, 471–492.
Cuny, D., Davranche, L., Thomas, P., Kempa, M., van Haluwyn, C., 2004. Spatial and temporal variations of trace element contents in Xanthoria Parietina Thalli collected in a highly industrialized area in Northern France as an element for a future epidemiological study. J. Atmos. Chem. 49, 391–401.
Davies, F., Notcutt, G., 1996. Biomonitoring of atmospheric mercury in the vicinity of Kilauea, Hawaii. Water Air Soil Pollut. 86, 275–281.
During, A., Rinklebe, J., Böhme, F., Wennrich, R., Stärk, H., Mothers, S., Laing, G.D., Schulz, E., Neue, H., 2009. Mercury volatilization from three floodplain soils at the Central Elbe River, Germany. Soil. Sediment. Contam. 18, 429–444.
Esbrí, J.M., López-Berdonces, M.A., Fernández-Calderón, S., Higueras, P., Díez, S., 2015. Atmospheric mercury pollution around a chlor-alkali plant in Flix (NE Spain): an integrated analysis. Environ. Sci. Pollut. R. 22, 4842–4850.
European Commission, 2010. 2010. Review of the Community Strategy Concerning Mercury. COM, p. 723 (final).
Fernández, J.A., Aboal, J.R., Carballeira, A., 2000. Use of native and transplanted mosses as complementary techniques for biomonitoring mercury around and industrial facility. Sci. Total Environ. 256, 151–161.
Ferrara, R., Maserti, B.E., Andersson, M., Edner, H., Ragnarson, P., Svanberg, S., Hernandez, A., 1998. Atmospheric mercury concentrations and fluxes in the Almaden district (Spain). Atmos. Environ. 32, 3897–3904.
Freundlich, H., Heller, W., 1939. On adsorption in solution. J. Am. Chem. Soc. 61, 2228.
García-Sánchez, A., Contreras, F., Adams, M., Santos, F., 2006. Atmospheric mercury emissions from polluted gold mining areas (Venezuela). Environ. Geochem. Health 28, 529–540.
Garty, J., 2001. Biomonitoring atmospheric heavy metals with lichens: theory and application. Crit. Rev. Plant Sci. 20, 309–371.
Giordano, S., Adamo, P., Sorbo, S., Vingiani, S., 2005. Atmospheric trace metal pollution in the Naples urban area based on results from moss and lichen bags. Environ. Pollut. 136, 431–442.
González, C.M., Casanovas, S.S., Pignata, M.L., 1996. Biomonitoring of air pollutants from traffic and industries employing Ramalina ecklonii (Spreng.) Mey. and Flot. in Córdoba, Argentina. Environ. Pollut. 91, 269–277.

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Gosar, M., Pirc, S., Šajn, R., Bidovec, M., Mashyanov, N.R., Sholupov, S.E., 1997. Distribution of mercury in the atmosphere over Idrija, Slovenia. Environ. Geochem. Health 19, 101–110.

Grangeon, S., Guédron, S., Asta, J., Sarret, G., Charlet, L., 2012. Lichen and soil as indicators of an atmospheric mercury contamination in the vicinity of a chlor-alkali plant (Grenoble, France). Ecol. Indic. 13, 178–183.

Gür, F., Yaprak, G., 2011. Biomonitoring of metals in the vicinity of Soma coal-fired power plant in western Anatolia, Turkey using the epiphytic lichen, Xanthoria parietina. J. Environ. Sci. Health Part A 46, 1503–1511.

Hernández, A., Jébrak, M., Higueras, P., Oyarzun, R., Morata, D., Munhá, J., 1999. The Almaden mercury mining district, Spain. Miner. Deposita 34, 539–548.

Higueras, P., Oyarzun, R., Lunar, R., Sierra, J., Parras, J., 1999. The Las Cuevas mercury deposit, Almadén district (Spain): unusual case of deep-seated advanced argillic alteration related to mercury mineralization. Min. Deposita 34, 211–214.

Higueras, P., Oyarzun, R., Lillo, J., Sánchez-Hernández, J.C., Molina, J.A., Esbrí, J.M., Lorenzo, S., 2006. The Almadén district (Spain): Anatomy of one of the world's largest Hg-contaminated sites. Sci. Total Environ. 356, 112–124.

Higueras, P., Oyarzun, R., Kotnik, J., Esbrí, J.M., Martínez-Coronado, A., Horvat, M., López-Berdonces, M.A., Llanos, W., Vaselli, O., Nisi, B., Mashyanov, N., Ryzov, V., Spiric, Z., Panichev, N., McCrindle, R., Feng, X., Fu, X., Lillo, J., Loredo, J., García, M.E., Alfonso, P., Villegas, K., Palacios, S., Oyarzún, J., Maturana, H., Contreras, F., Adams, M., Ribeiro-Guevara, S., Niecenski, L.F., Giammanco, S., Huremović, J., 2014. A compilation of field surveys on gaseous elemental mercury (GEM) from contrasting environmental settings in Europe, South America, South Africa and China: separating fads from facts. Environ.Geochem. Health 36, 713–734.

Ikingura, J.R., Akagi, H., Mujumba, J., Messo, C., 2006. Environmental assessment of mercury dispersion, transformation and bioavailability on the Lake Victoria Goldfields, Tanzania. J. Environ. Manage. 81, 167–173.

Kauppi, M., 1976. Fruticose lichen transplant technique for air pollution experiments. Flora 165, 407–414.

Kim, K.-H., Mishra, V.K., Hong, S., 2006. The rapid and continuous monitoring of gaseous elemental mercury (GEM) behavior in ambient air. Atmos. Environ. 40, 3281–3293.

Kono, Y., Tomiyasu, T., 2009. Biomonitoring of atmospheric mercury levels with the apiphytic fern Lepisorus thunbergianus (Polypodiaceae). Chemosphere 77, 1387–1392.

Llanos, W., Higueras, P., Oyarzun, R., Esbrí, J.M., López-Berdonces, M.A., García-Noguero, E.M., Martínez-Coronado, A., 2010. The MERSADE (European Union) project: testing procedures and environmental impact for the safe storage of liquid mercury in the Almadén district. Spain. Sci. Total Environ. 408, 4901–4905.

Lodenius, M., 2013. Use of plants for biomonitoring of airborne mercury in contaminated areas. Environ. Res. 125, 113–123.

López-Berdonces, M.A., 2009. Propuesta metodológica de sistema de biomonitorización de mercurio atmosférico basado en líquenes. Degree Dissertation. University of Castilla-La Mancha, 56 pg. In Spanish.

Loppi, S., 2000. Lichen biomonitoring as a tool for assessing air quality in geothermal areas. In: Proceedings World Geothermal Congress, pp. 645–648.

Loppi, S., Bonini, I., 2000. Lichens and mosses as biomonitors of trace elements in areas with thermal springs and fumarole activity (Mt. Amiata, central Italy). Chemosphere 41, 1333–1336.

Loppi, S., Nelli, L., Ancora, S., Bargagli, R., 1997. Passive monitoring of trace elements by means of tree leaves, epiphytic lichens and bark substrate. Environ. Monit. Assess. 45, 81–88.

Loppi, S., Pacioni, G., Olivieri, N., Di Giacomo, F., 1998. Accumulation of trace metals in the lichen Evernia prunastri transplanted at biomonitoring sites in Central Italy. Bryologist 101, 451–454.

Loppi, S., Paoli, L., Gaggi, C., 2006. Diversity of epiphytic lichens and Hg contents of Xanthoria parietina thalli as monitors of geothermal air pollution in the Mt. Amiata area (Central Italy). J. Atmos. Chem. 53, 93–105.

Munteanu, V., Munteanu, G., 2007. Biomonitoring of mercury pollution: a case of study from the Dnister River. Ecol. Indic. 7, 489–496.

Nannoni, F., Santolini, R., Protano, G., 2015. Heavy element accumulation in Evernia prunastri lichen transplants around a municipal solid waste landfill in central Italy. Waste Manage. 43, 353–362.

Saupé, F., 1990. Geology of the Almaden mercury deposit, province of Ciudad real. Spain Econ. Geol. 85, 482–510.

Scerbo, R., Possenti, l., Lampugnani, L., Ristori, T., Barale, R., Barghigiani, C., 1999. Lichen (Xabthoria Parietina) biomonitoring of trace element contamination and air quality assessment in Livorno Province (Tuscany, Italy). Sci. Total Environ. 241, 91–106.

Scerbo, R., Ristori, T., Possenti, L., Lampugnani, L., Barale, R., Barghigiani, C., 2002. Lichen (Xanthoria parietina) biomonitoring of trace element contamination and air quality assessment in Pisa Province (Tuscany, Italy). Sci. Total Environ. 286, 27–40.

Sholupov, S., Pogarev, S., Ryzhov, V., Mashyanov, N., Stroganov, A., 2004. Zeeman atomic absorption spectrometer RA-915+ for direct determination of mercury in air and complex matrix samples. Fuel Process. Technol. 85, 473–485.

Southworth, G.R., Lindberg, S.E., Zhang, H., Anscombe, F.R., 2004. Fugitive mercury emissions from a chlor-alkali factory: sources and fluxes to the atmosphere. Atmos. Environ. 38, 597–611.

US EPA, 2007. Mercury, Elemental Reference Concentration for Chronic Inhalation Exposure (RfC). http://www.epa.gov/teach/chem_summ/mercury_elem_summary.pdf (accessed 30.01.16).

Vannini, A., Nicolardi, V., Bargagli, R., Loppi, S., 2014. Estimating atmospheric mercury concentrations with Lichens. Environ. Sci. Technol. 48, 8754–8759.

Verestiuc, P.C., Breaban, I.G., Tucaliuc, O.M., Nemtoi, G., Cretescu, I., 2015. Assessment of mercury level in leaves and soils in urban landscape of Iasi. In: International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, 2. SGEM, pp. 57–64.

Walther, D.A., Ramelow, G.J., Beck, J.N., Young, J.C., Callahan, J.D., Maroon, M.F., 1990. Temporal changes in metal levels of the lichens Parmotrema praesorediosum and Ramalina stenospora, Southwest Louisiana. Water Air Soil Pollut. 53, 189–200.

Zhu, J., Wang, D., Liu, X., Zhang, Y., 2011. Mercury fluxes from air/surface interfaces in paddy field and dry land. Appl. Geochem. 26, 249–255.

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