MERCURY BIOMONITORING WITH MOSS FROM THE ALMADÉN MINING DISTRICT, SOUTH CENTRAL SPAIN

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ABSTRACT: The migration of chemical elements in the environment is inevitable. Therefore, the elements that can cause damage to human health must constantly be observed. Mercury is one of the elements whose toxicity imposes persistent monitoring. For this reason, there are a couple of active and passive monitoring methods to observe its behavior. Like other vegetation, mosses accumulate mercury in their structure which is related to the concentration of this element in the air. Mosses are highly valued for observation purposes in Almadén. The town is famous for the largest mercury deposit in the world and thus requires constant monitoring.

Keywords: mercury, mosses, biomonitoring, Almadén, thermal speciation.

БИОМОНИТОРИНГ НА ЖИВАК С МЪХОВЕ ОТ МИННИЯ РАЙОН НА АЛМАДЕН, ЮЖНАТА ЧАСТ НА ЦЕНТРАЛНА ИСПАНИЯ

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РЕЗЮМЕ. Миграцията на химическите елементи в околната среда е неизбежна. Следователно тези елементи, които могат да застрашат човешкото здраве, трябва да бъдат следени постоянно. Живакът е един от тези елементи, чиято токсичност налага непрестанен мониторинг. Поради тази причина има няколко активни и пасивни методи за мониторинг, с които да се следи поведението на токсичните елементи. Подобно на друга растителност, мъховете приемат живак от въздуха и го натрупват в своята структура. Концентрацията на живак във въздуха е свързана със съдържанието му в мъховете. Тяхната полза е високо ценена за наблюдение на Алмаден – най-голямото живачно находище в света.

Ключови думи: живак, мъхове, биомониторинг, Алмаден, термично сортиране.

Introduction

Mosses are highly adaptable and widespread in nature. They have the ability to uptake airborne heavy metals and POPs from the atmosphere which makes them highly valued for passive biomonitoring (Bargagli, 2016). Atmospheric mercury is in a dynamic equilibrium with moss tissues, reflecting variations of total gaseous mercury in their concentrations on mosses tissues (Boquete et al., 2013). There are a great number of studies applying this capacity of mosses to biomonitor atmospheric mercury, not only mercury dispersion patterns around mercury mining sites (Huckabee et al., 1983; Plouffe et al., 2004; Qiu et al., 2005; Ping et al. 2008) or industrial areas (Boquete et al., 2013; Varela et al., 2014), but also on a larger scale to an entire country like Norway (Steinnes et al., 2003) or on a still larger scale to a whole continent like Europe (Harmens et al., 2010, 2015). There are protocols to make biomonitoring studies using mosses (Frontasyeva et al., 2014), and a lot of discussions on whether these protocols are adequate and based on scientific criteria or not (Fernandez et al., 2015). Nowadays, biomonitoring atmospheric mercury using mosses is a common issue. One of the most important places requiring constant monitoring on the ambient is the Almadén district area (Esbri et al., 2016). The mercury in the ore body is in the form of cinnabar (HgS). The district is about 300 km^2 with an estimated total content of mercury before mining of around 250 000 t. The mining works in the district began in Roman times, around 2000 years ago, and continued without interruption until 2003. In 2005, the European Union forbade the mining and production of mercury because of its toxicity. Depending on the form and bond related with the other elements, mercury can be extremely poisonous or not so toxic. Nowadays, the mine is reclaimed and has a status of a world heritage site in the list of UNESCO (UNESCO, 2012). It is well-known that mining industry cannot extract all the useful compounds of the ore bodies. Also, the way of extraction of mercury through evaporation and liquefaction emits a huge amount of Hg which is accumulated in the surrounding soils (Higueras et al., 2006). In the atmosphere, 95% of mercury can be found as Hg^0 which is a stable and highly mobile form (Schroeder and Munthe, 1998). The significantly smaller amount is in the water-soluble state which is characterized by low mobility because of its reaction with gaseous compounds, such as $HgCl_2$, HgO. Based on laboratory experiments, it has been proved that mosses take up Hg^0 rapidly and linearly and that the metal becomes strongly bound with almost no losses for a couple of weeks. The reason for this retention is that the accepted Hg^0 is transformed into water-soluble Hg^{2+}[cita]. Because of the volatile character and mobility of mercury, the area requires constant monitoring to ensure the health of the citizens of the town.

Materials and methods

Sampling network was designed to cover populated areas, the main atmospheric mercury source (Almadén mining center), secondary sources (cinnabar monuments or polluted roads), and local background locations. Figure 1 displays sampling areas, sampling points, and TGM measurement points on the Almadén area.

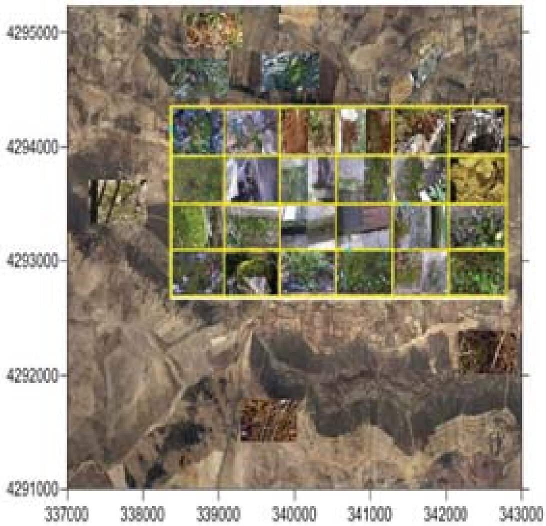

Fig. 1. Sampling network with the sampling moss

In order to acquire realistic information about TGM contents in the atmosphere of Almadén, It was necessary to make air measurements in day and night hours. These measurements were carried out by Atomic Absorption Spectrometry using Lumex RΔ - 915+ equipment that takes 1 TGM data and is able to detect mercury concentrations between 2 ng m^{-3} and 25,000 ng m^{-3}. The seasonal change can strongly affect the survey (Esbri et al., 2016). Spring is the most suitable season for collecting mosses because they are wet and newborn, and TGM has higher contents than in autumn and winter. The mosses for this survey were collected in April of 2017. Mercury accumulation becomes bigger in time. To avoid this, only the youngest and greenest mosses were taken. Samples were collected from each square of the coordinate network plus some extra material to close the anomaly area. Figure 1 represents the place and the species of moss samples. According to Fernandez et al., (2015) there is a difference in atmospheric moss uptake depending on the moss species. For this survey, only the average concentrations are taken.

The samples were temporarily stored in a carton envelope with the help of a chemical spoon and using nitrile gloves. They were brought to the laboratory on the same day. The samples were immediately washed and dried in a laboratory oven at 35ºC for 7 days. The mosses were washed carefully with ultra pure water. The inclusion of ash and soil particles in the moss body may influence the final result. To avoid inaccuracies as much as possible, soil particles were removed carefully. Immediately after washing, samples were put in polypropylene jars and left in the laboratory drying oven until they completely dried. Samples stayed in the oven for one week under the temperature of 35 ^{0}C. This temperature was required because of the volatile character of Hg, to avoid losses of mercury. After this week, samples were sealed with parafilm. To prevent the growth of microorganisms, the samples were put into a fridge at a temperature of below -15^{o}C. After all these steps, the samples were ready for analyses. The sample had to be homogenized and put into flasks.

The total mercury analysis was achieved by Atomic Absorption Spectrometry, using a Lumex RA-915+ equipment; with its PYRO-915 pyrolysis attachment BCR-62 CRM was analyzed simultaneously to ensure the quality of measurements.

Results

For this survey, 39 moss samples were taken, collected around the whole area and the expected main gaseous mercury source in the eastern part of the town. Table 1 represents the average concentration in each sample. According to Fernandez (2002b), the essential number of samples must not be less than 30. Sample №17 of section C1 is with extremely high concentration of around 800 ppm. The reason for that anomaly level is the cinnabar rock with extremely rich liquid mercury.

The concentration of mercury in the air is different throughout the hours of day and night. This strong variability has influence over the uptake rates in mosses. The influence of weathering conditions, too, affects Hg concentrations. To better understand this variability, the air measurements are taken throughout day and night. The result of them is shown in Figure 3. Red spot №1 is exactly under the mine so that it is expected to be with high concentrations. Two reasons may have influence on the results for red spot №2 – the windrose and the outcrop. There is a polluted road east of the town that is covered with residues from the ore which create the anomaly in №3.

According to the results from the mosses, the mercury pollution is stronger in the first 300 m near the mine. One of the main reasons is the fact that this area is very rich in mercury and a big amount of it is still in the soil. The second reason is the way of extraction through frying of the ore. The results were expected which confirm that the pollution in area is strictly observed and that moss biomonitoring is sensible and in accordance with active monitoring techniques.

Table 1.
Main mercury data of studied sites

Sector	TGM (ng m^{-3})	Sector	TGM (ng m^{-3})
F3	43.5	B2	159.6
F1	46.9	D1	92.0
E1	88.2	D1	112.8
BB	98.5	D2	78.0
F3	0.3	D2	47.4
F4	80.1	E3	63.5
E4	100.5	E3	55.3
AA	93.4	D3	86.5
A3	0	D3	136.7
A4	0	C3	139.7
D4	27.1	C3	145.9
C4	85.1	B3	173.3
B4	91.8	MA 001 Residencial area	55.2
B3	47.3	MA 00 University	47.1
C2	138.2	AA	127.0
C1	227.7	BB	35.8
A1	37.8	BB1	28.6
CASTLE OF VIRGEN	102.6	BB2	6.6
A2	153.8	CC	35.2
B1	180.2		

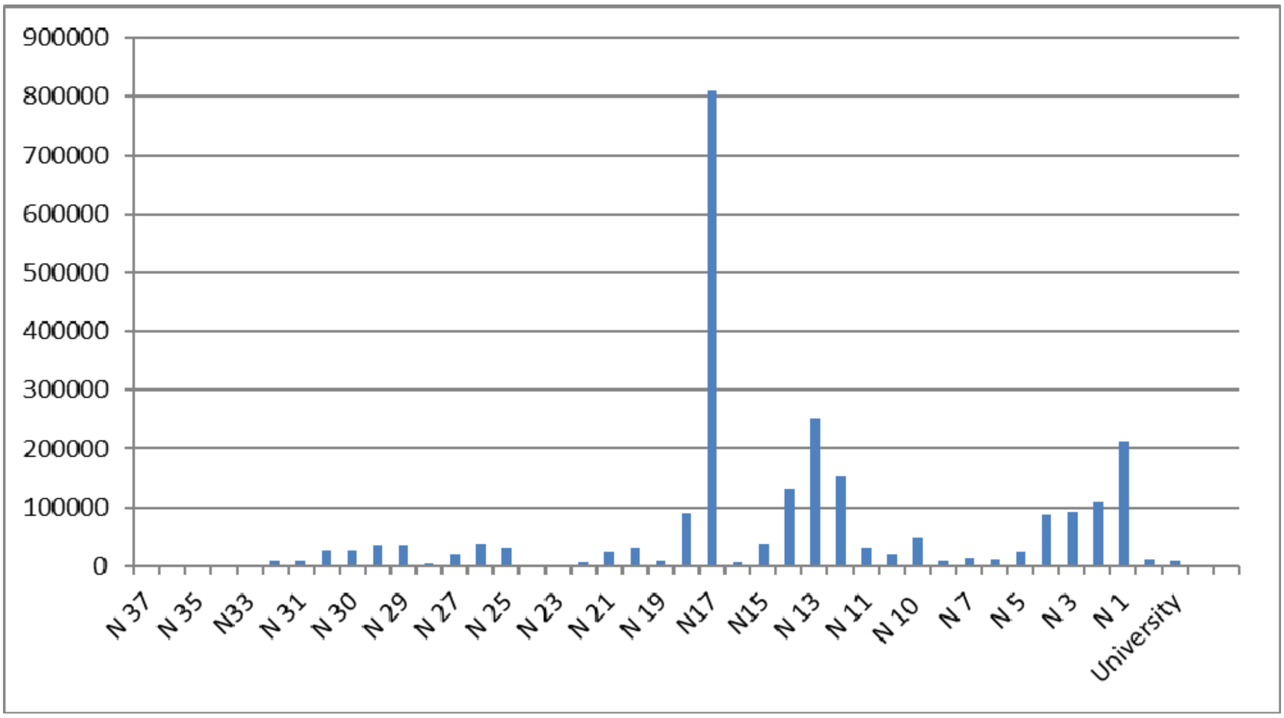

Fig. 2. Average mercury concentration in TGM (ng m^{-3})

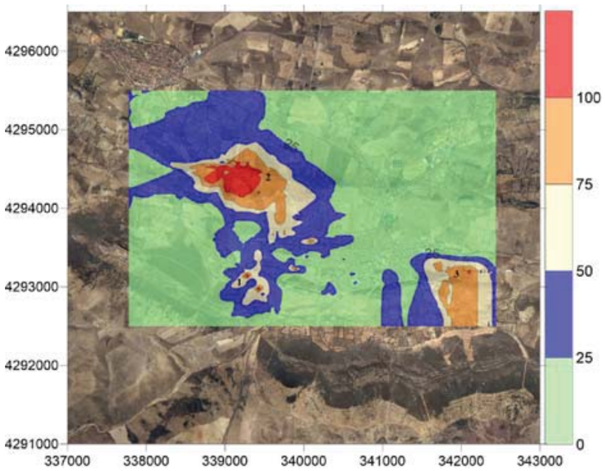

Fig. 3. Total gaseous mercury concentration measured with Lumex R - 915+ equipment

Conclusion

It seems that mosses are more appropriate for monitoring gaseous mercury over a longer period than direct measurements. These organisms provide information of where the main mercury source is and of the preferential dispersion pattern in the studied area.

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This article was reviewed by Prof. Dr. Irena Kostova and Assoc. Prof. Dr. Anatoliy Angelov.