Variations in mercury and other trace elements contents in soil and in vine leaves from the Almadén Hg-mining district

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Abstract

Purpose Vines (*Vitis vinifera*, L.) are a very important agricultural resource for Spain in general and for the Castilla-La Mancha region in particular, providing important productions of wines. Grapes and raisins are used for direct consumption too. In this work, we study analytical constraints regarding metallic trace elements uptake, focusing on Hg, from vines growing in the Almadén mercury mining district, the world's largest producer of this element, inactive nowadays.

Materials and methods The study started with the analysis of these metals in soils and sets of vines leaves from seven sites located at different distances from the Almadén Hg mine. The samples of soils were dried at ambient temperature for 1 week. They were then sifted (<2 mm) and were stored for subsequent analysis. The leaves were dried and the leaf blade and petiole were separated. About 2 g of each sample were hand milled and analyzed using the same fluorescence spectrometer. Total mercury in soils and vine leaves were determined using a Lumex RA-915+ device, an atomic absorption spectrometer with a pyrolysis unit (RP-91c).

Results and discussion Results show significant correlations between soil and leaves contents for total and organic mercury ($R=0.934$ and 0.984 , respectively). Hg contents range in soil from 2,376 to 0.04 mg/kg in non-polluted places. For the

organic fraction, the range varies between 197.49 and 3.15 mg/kg. Total Hg contents measured in leaves were from 5.14 mg/kg (close to dump zone of the mine) to 0.03 mg/kg in the proximity of Carrión de Calatrava, located some 100 km away from Almadén. Mercury reaches maximum in the proximity of known sources of the element: the mining and/or metallurgical areas of Almadén and Almadenejos.

Conclusions Soils from the study area contain normal contents in trace metals, and these are conditioned by the local geology or urban locations of the area. Trace metals contents in leaves do not show a relationship with soil contents, possibly due to the low bioavailability of these elements in the soils investigated. Mercury is, as expected for this area, an exception to this trend, with very high concentrations that reach maximum values in the proximity of the known sources of the element: the proximity of mining and/or metallurgical areas in Almadén and Almadenejos.

Keywords Bioaccumulation · Metallic trace element · Pollution

1 Introduction

The Almadén mercury mining district, located in South-Central Spain, Castilla-La Mancha region (Fig. 1), corresponds to the biggest mercury geochemical anomaly in the world, having yielded almost one-third of total production of the element (Hernández et al. 1999). Description of the geological characters of the area can be found in Saupé (1990) and Hernández et al. (1999), among others, meanwhile Lindberg et al. (1979), Huckabee et al. (1983), Higuera et al. (2003), Millán et al. (2004, 2006, 2011), Molina et al. (2006), Moreno-Jiménez et al. (2006) and Martínez-Coronado et al. (2011) describe environmental concerns for mercury in the area including local soil/plant relationships.

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Fig. 1 Location of plots M1 to M6 in Almadén mining district and M7 in Carrión de Calatrava (non contaminated zone)

The cultivation of the grapevine in Castilla-La Mancha is of great national and global importance due to the large area in question (467.690 ha according to official data, Ministry of agriculture, feeding and environmental). This importance is reflected in the traditions and in the economic impact that the wine sector has on the regional economy (Pillet 2007). Eleven appellations of origin and other quality control requirements for the wine serve to increase the added value of the product. The factors outlined above demonstrate the importance of the ‘terroir’ in the valuation of the wines (Hugget 2006). The soil is one of the most important components of the ‘terroir’ (together with the climate and the cultural practises). It is therefore of interest to ascertain the influence of the soil and to obtain analytical evidence.

Several studies have been carried out on Mediterranean regions and areas of influence to investigate soil origins, parent materials and their characteristics (Carlevalis et al. 1992; Amorós et al. 2010). The study of geochemical soil composition provides information, along with other complementary data, about fertility and the availability of nutrients

for plants. Major elements provide information about total structural components and potential nutrients (Wild 1992; Lanyon et al. 2004; White 2009). On the other hand, contents of trace elements give an insight into the geochemical origin (García-Navarro et al. 2011) and potential toxicities (Patra and Sharma 2000; Conde et al. 2009) of the soil.

The metabolism of trace elements in plants has been widely studied (Wild 1992; Kabata-Pendias 2001). However, every plant–soil system has to be specifically studied, since the behaviour could differ depending on the elements present in a particular system (Kabata-Pendias 2001; Molina et al. 2006), as well as on the particular chemical form of the element in the soil. In all previously studied cases, plant composition (leaves, fruits, juices, tubers, etc.) always reflected the chemical properties from the cultivation environment (Bargagli 1995; Kabata-Pendias 2001; Vavoulidou et al. 2004; Zeiner et al. 2005; Higuera et al. 2011).

At present, it is well known that 17 trace elements (Al, B, Br, Cl, Co, Cu, F, Fe, I, Mn, Mo, Ni, Rb, Si, Ti, V and Zn) are essential for plants; it has been proved that some of them are

Table 1 Metals contents in soils studied (Fe in g/kg and Cu, Zn and Pb in mg/kg) (M1 to M7 are the name of samples; CLM, Castilla La Mancha)

	M1	M2	M3	M4	M5	M6	M7	$\bar{x}$	Levels of CLM (¹) (Amorós et al. 2011) (²) (Jiménez-Ballesta et al. 2010)	Levels in olive leaf (Higuera et al. 2011)
Fe	48.50	43.28	45.83	44.35	56.16	47.49	21.53	43.88	38.69 ⁽¹⁾	–
Cu	27.10	35.30	27.50	20.60	39.50	10.60	14.70	25.04	27.00 ⁽²⁾	32.40
Zn	92.30	120.80	103.80	85.80	148.80	51.60	33.80	90.99	86.50 ⁽²⁾	85.23
Pb	67.80	30.60	34.40	35.60	122.90	17.20	16.70	46.46	44.20 ⁽²⁾	47.81

Table 2 Metals contents in vine leaves studied (Fe in g/kg and Cu, Zn and Pb in mg/kg) (M1 to M7 are the name of samples)

	M1	M2	M3	M4	M5	M6	M7	$\bar{x}$	Levels in olive leaf (Higueras et al. 2011)
Fe	0.18	0.14	0.25	0.22	0.16	0.14	0.11	0.17	0.01
Cu	0.00	0.70	0.50	1.10	12.95	7.47	14.27	5.28	–
Zn	19.20	18.20	17.80	18.20	46.75	47.00	22.77	27.13	21.10
Pb	3.40	2.80	2.70	3.20	3.65	12.17	4.90	4.69	3.80

necessary only for some species, and others have just stimulating effects for plant growing, but their functions have not been yet identified (Wild 1992). Some elements seem to be not needed at all, and can be toxic to plants: Hg, Ni, Pb, Co and Cd, mainly.

In this paper, we study the distribution of mercury and some metals (Fe, Cu, Zn and Pb in soil and leaf) in vine leaves of contaminated area and surroundings and in an area 100 km from the mine, and their soils, in order to assess the particular behaviour of these elements in this plant. Moreover, we compare the Hg uptake with the uptake of other trace elements in order to better explain the absorption behaviour for this element in this plant.

2 Materials and methods

Sampling sites for this study were selected as a transect from the main mercury pollution sources and progressively away from them, up to a locality sited some 100 km away from Almadén (Fig. 1).

The samples of soils were described and collected according with FAO guidelines (2006) from surface horizons, under the plant. Each sample was dried at ambient temperature for 1 week. They were then sieved (<2 mm) and were stored for subsequent analysis. The leaves were collected after harvest and from the middle part of the shoot. After, the samples were dried at 105 °C and the leaf blade and petiole were separated. About 2 g of each sample were hand milled and analyzed using the same fluorescence spectrometer.

Total mercury in soils and vine leaves were determined using a Lumex RA-915+ device, an atomic absorption spectrometer with a pyrolysis unit (RP-91c), where sample matrix is destructed and mercury atoms are counted on an atomic absorption spectroscopy with Zeeman effect to avoid matrix effect on quantification (Molina et al. 2006). Bioavailable mercury was performed according to the methodology reported by Perez et al. (2008). Briefly, this methodology consists on lixiviate extraction with 0.5 M HCl for 1 h with magnetic stirring. The solid/water ratio was 1 g:20 ml. After centrifugation at 3,500 rpm for 10 min, the extracts were filtered with a 0.22 µm filter (Millex-GS, Millipore) and analyzed by AAS (AMA 254).

The other metals were determined by X-ray fluorescence, using a calibration for trace elements in a sequential spectrometer (Philips, model Magix Pro) with a 4 kW light element super sharp RH target end window X-ray tube, a set of analyzer crystals of LiF220, LiF200, Ge, PE y PX1 and with a flow and a sealed proportional detector in tandem, plus a scintillation detector in parallel. The analysis of the samples was carried out as fused glass discs and using a specific calibration for soils and one adapted from fundamental parameters for plants. The quality control was evaluated by duplicate analysis of certified reference samples (BCR 62, SMR 1573, SMR 1515).

3 Results and discussion

3.1 Metal contents in soils

The analytical results for metal contents in the analyzed soils are shown in Table 1, along with average reference levels for Castilla-La Mancha region (Jiménez-Ballesta et al. 2010) and results of other study about Almadén (Higueras et al. 2011). Average of the measured concentrations can be considered as normal contents for non-contaminated rural areas, with values close to those reported by Jiménez-Ballesta (2010) and Higueras et al. (2011). However, some samples show concentrations above these reference values; Cu and Zn have concentrations above their reference levels for some of the analyzed soils, particularly in proximity to the mine (sites 1, 2 and 3) and site 5 close to Almadenejos. And Pb is above their

Table 3 Total mercury contents in soils and vine leaves studied (mg/kg) and Bioavailable (Bioav.) Hg in soils (ng/g) (M1 to M7 are the name of samples)

	Total Hg in soil	Bioav. Hg in soil	Hg in leaves
M1	162.33	23.52	0.80
M2	2376.67	197.49	5.14
M3	544.00	80.91	2.19
M4	162.00	18.92	1.17
M5	105.33	53.05	2.03
M6	0.04	4.89	0.06
M7	0.04	3.15	0.03

Fig. 2 Soil/leaf relationship for total and organic mercury

references for sites 1 and 5 too. Fe is above levels of Sparks (2003), except in sample 7.

Cu and Zn are elements that are usually linked to periurban pollution (Martínez-Coronado et al. 2011). Similar soils have been studied in nearby areas by Amorós et al. (2010, 2011), and they often show a slightly acidic pH and relatively high clay content; these studies showed that many metallic elements are straightly linked to the clay fraction: Fe, Al, V, Cr, Co, Ni, Cu, Zn and Pb.

3.2 Metal contents in leaves

Average leaf contents for trace metals are shown in Table 2 along with reference values by Higuera et al. (2011). The Pb content (4.69 mg/kg) is below world normal values (Kabata-Pendias 2001) but above contents reported by Higuera et al. (2011). Fe values (0.17 mg/kg) are above world normal values (Wild 1992) and levels in Almadén by Higuera et al. (2011). Zn levels (27.13 mg/kg) are above the world average (Barranco et al. 2004) and values reported by Higuera et al. (2011). Values for Cu were not found in the literature.

3.3 Soil–leaf relationships

The values obtained for correlation between soil and leaf contents did not indicate significant correlations in any element. The biological absorption coefficient is calculated as the ratio between the concentration of any studied element in the plant and the concentration found in the corresponding soil ($BAC = [\text{leaf blade}]/[\text{soil}]$). For our data, all BAC is well lower than the general level for the world (Kabata-Pendias 2001).

3.4 Mercury

Table 3 displays the mercury contents obtained from the soils and vines from contaminated and uncontaminated areas.

Results in the samples from the evidently contaminated areas are higher than in the samples from uncontaminated areas.

Total mercury contents in soil from 2,376 mg/kg in contaminated areas to 0.04 mg/kg in non-polluted places. In the case of organic fraction, the range varies between 197.49 and 3.15 mg/kg.

The mercury content in leaves ranges from 0.03 mg/kg in leaves collected from the uncontaminated sites to 5.14 mg/kg for leaves from the area in proximity to the Almadén mine. Despite the fact that levels in some cases are above the 3 mg/kg value suggested as toxic by Kabata-Pendias (2001), visual symptoms of toxicity were not observed.

The soil/leaf relationship for mercury was of particular interest in this study. Mercury uptake from the soil depends to a large degree on the chemical species available in the soil, particularly in mining areas, where cinnabar is the main mercury form present in the soil (Llanos et al. 2011). As mentioned before, correlation between leaf contents and total mercury in the soil is high ($R=0.934$), but if we take into account the bioavailable mercury contents, the correlation is higher ($R=0.984$) than in the previous case (Fig. 2).

4 Conclusions

The following main conclusions of this study are outlined below:

1. Soils from the study area, centred in the Almadén mercury mining district, shown normal contents in trace metals, and these are conditioned by the local geology or urban locations of the area. Nevertheless, some samples show concentrations above these reference values, mainly in proximity to the mine (sites 1, 2 and 3) and site 5 close to Almadenejos.
2. In leaves, the Fe, Zn and Pb content is over the values by Higuera et al. (2011). Values for Cu were not found in the literature and it is highly influenced by pesticide treatments.

3. Trace metals contents in leaves do not show a relationship with soil contents, possibly due to the low bioavailability of these elements in the soils investigated. In fact, all BAC is lower than the general level for the world (Kabata-Pendias 2001).
4. Mercury is, as expected for this area, an exception to this trend, with very high concentrations that reach maximum values in the proximity of the known sources of the element: the proximity of mining and/or metallurgical areas in Almadén and Almadenejos. Mercury is also an exception and has high contents, well above published toxic levels, which do not correlate with total Hg contents in the soil but do show a strong correlation with bioavailable mercury. The soil/leaf relationship for total mercury was high ($R=0.934$) and higher ($R=0.984$) for bioavailable mercury.

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