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Time and space variations in mercury and other trace element contents in olive tree leaves from the Almadén Hg-mining district

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ABSTRACT

Olive trees (*Olea europaea*, L.) are a very important agricultural resource for Spain in general and for the Castilla-La Mancha region in particular. These trees provide significant amounts of olive oil and olives for direct consumption. In this paper we discuss analytical constraints regarding the uptake of metallic trace elements from soils and other sources for olive-trees growing in the Almadén mercury mining district, the world's largest producer of this element, which is currently inactive. The study was based on the analysis of these metals in soils and sets of olive trees of different ages from seven sites located at different distances from the main mercury sources. The results show good correlations between soil and leaf contents for major elements from the soils (Fe, Al, Mg and Ca), but very little or no relationship between metallic trace elements in soils and leaves. However, bioavailable mercury in the soil does correlate well with leaf contents, indicating a significant uptake of this fraction. Furthermore, detailed analysis of the temporal evolution of mercury contents in leaves compared with the temporal evolution of local atmospheric mercury contents, which decreased dramatically in recent years due to the reclamation of the main dump of the mine, indicates some influence of this parameter on the incorporation of mercury in the leaves and suggests a possible mechanism of atmospheric uptake of the element. Mercury contents in local olive oil and olives are slightly higher for samples taken from areas with also higher mercury concentrations in soils, but levels are well below maximum recommended levels for human food.

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1. Introduction

1.1. The study area

The Almadén mercury mining district is located in the Castilla-La Mancha region in South-Central Spain (Fig. 1). This area corresponds to the biggest mercury geochemical anomaly in the world and has yielded almost one third of the total global production of this element (Hernández et al., 1999). Descriptions of the geological characteristics of the area can be found in reports by Saupé (1990) and Hernández et al. (1999), among others, while 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), Martínez-Coronado et al. (2011) have described environmental concerns regarding mercury in the area and include local soil/plant relationships. In particular, Molina et al. (2006) reported mercury contents in olive tree leaves, which is the main aspect discussed in this paper. Gray et al. (2004), Higuera et al. (2003, 2006) and Conde et al. (2008)

describe high to very high mercury contents in soils at the regional scale; in particular, Conde et al. (2008) study a transect of mercury contents in soils from the Almadén periurban area and find mercury concentrations that point out to the element as a pollutant agent for drainage waters. Díez et al. (2011) studied mercury contents in the hair from inhabitants of the area and found slightly higher values for inhabitants of Almadén compared to those in surrounding areas, thus indicating a certain health risk.

From the physiographic point of view, the Almadén area is characterised by an Appalachian relief, meaning a landscape dominated by long 'sierras' and narrow valleys that follow approximately the E–W geologic structural trends; the 'sierras' correspond to quartzite outcrops and the valleys to shale-dominated geological formations (Fig. 1). As a semiarid area, with precipitation in the range 550–700 mm/year, dry farming agriculture and livestock dominate the activities in the valleys and the 'dehesa' (Spanish term for the regionally characteristic landscape of smooth plains and hills with tree vegetation dominated by oak trees, *Quercus ilex*), is the predominant landscape. Olive trees (*Olea europaea*, L.) are also quite common and these correspond to 'sierra' varieties and, in particular, to the 'Cornicabra' variety. Local soils have been classified as Cambisols (Leptic or Chromic) (Conde et al., 2008).

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Fig. 1. Location of the study area. The Castilla-La Mancha region is shadowed. Locations mentioned in Table 1 are all shown in this scheme.

1.2. Olive trees, soils and heavy metals

The olive is a perennial leaf tree that has been cultivated for centuries. Nowadays, there are more than 8 million ha producing olives in the world and most of these are located around the Mediterranean Basin. In Spain there are more than 2 million ha with more than 300 million trees. Moreover, Castilla-La Mancha is the second largest region in Spain (below Andalucía) in terms of hectares dedicated to olive culture, with 300,000 ha approximately (Barranco et al., 2004).

It is well known that leaf analysis must be based on standardised sampling methods and that results must be compared only with standard values obtained by those procedures. Standard values for olives have been compiled by Fernández-Escobar et al. (1999) based on data reported by Bould (1966).

Several studies have been carried out in Mediterranean regions and areas of influence to investigate soil origins, parent materials and their characteristics (Amorós et al., 2010; Carlevalis et al., 1992). Indeed, recently published studies have focused on the area under consideration in this paper (Conde et al., 2009; De la Horra et al., 2008). 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 (Lanyon et al., 2004; White, 2009; Wild, 1992). On the other hand, contents of trace elements give an insight into the geochemical origin (García-Navarro et al., 2009) and potential toxicity (Conde et al., 2009; García-Navarro et al., 2009; Patra and Sharma, 2000) of the soil.

The metabolism of trace elements in plants has been widely studied (Kabata-Pendias, 2001; Wild, 1992). 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 of the cultivation environment (Bargagli, 1995; Kabata-Pendias, 2001; Vavoulidou et al., 2004; Zeiner et al., 2005).

It is widely accepted that 17 major and 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 these are necessary only for certain species, whereas others only have stimulating effects for plant growth, but their functions have not yet been identified (Wild, 1992). Other elements seem to be not needed at all and are toxic to plants: Hg, Cu, Ni, Pb, Co and Cd and also possibly Ag, Be and Sn.

The olive tree is a pluriannual leaf tree and bears leaves from three different years. Some previous data on metallic element contents in these leaves have been reported (Bargagli, 1995; Gascó and Lobo, 2007; Madejón et al., 2006) and data for fertilisation programmes has been published (Bould, 1966; Fernández-Escobar et al., 1999; Vavoulidou et al., 2004). In general terms, the behaviour of these elements in leaves with time corresponds to three different models:

- Accumulation with time. This behaviour corresponds to structural elements (Bould, 1966; Fernández-Escobar et al., 1999) and to elements that are difficult for the plant to excrete. This behaviour has been previously described for Ca (Bould, 1966; Fernández-Escobar et al., 1999) and Ni (Madejón et al., 2006).
- Decay in content with time. This model corresponds to essential elements that are necessary for the plant metabolism. Contents are therefore higher in young leaves and decay with time (Bould, 1966; Fernández-Escobar et al., 1999). Some potentially toxic elements such as Pb, Zn and As show this behaviour (Madejón et al., 2006).
- Constant elements. This behaviour corresponds to elements that have approximately constant concentrations in leaves. Mn and Cu correspond to this model (Madejón et al., 2006).

This work describes and discusses the distribution of mercury in olive tree leaves in the heavily contaminated area and surroundings outlined above, in order to assess the particular behaviour of this element in this plant, both in terms of time and space. Besides, we have analysed mercury contents in the edible fruits (olives) and in olive oil from the area, in order to eventually recognise risks for human consumption of these olive-tree derivate foods. Moreover, we compared

Fig. 2. Plot of linear correlations between soil and leaf contents for Ce, Cr (low correlation observed), Sr, Cs (positive correlation but not significant) and for Fe and Al (positive and significant correlation at 95%). All data in mg kg^{-1} .

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 moved progressively away from them, up to a location situated some 74 km to the North of Almadén (see Table 1 for details). Sampling was carried out in one survey for soils and two surveys for leaves. The first survey was carried out in May 2010 and included soils and leaves. Soil samples were taken from the A Horizon, up to 10–50 cm depth, using peak

and spade and a weight of 2.5 kg was removed in each case. The samples were stored and transported to the laboratory in plastic bags. Olive tree leaves were also taken during this survey and these were obtained from four different trees from each site, with leaves characterised as being from the present year, the previous year and the year before that as suggested by Barranco et al. (2004). In this way three sets of leaves were taken from each site with ages of 2, 14 and 26 months, respectively.

The second survey was carried out in January 2011 and included only olive tree leaves, from the same sites sampled in the first survey; in this case leaves from that year had not grown yet, so two sets of leaves were collected from each of the seven sites (aged 8 and 20 months). Each set of leaves included at least 100 leaves. In

Table 1

Description of the sampling sites used for the present study. Distances to source correspond to distances to Almadén mine (*) or to Almadenejos decommissioned metallurgical precinct (**).

Site	Short description	X coord.	Y coord.	Distance to source (km)
1	Almadén urban area, south of the main dump	340054	4293486	0.433 (*)
2	Almadén surroundings, close to a decommissioned metallurgical plant	340075	4293871	0.380 (*)
3	Near Chillón, a locality 3 km NW from Almadén	337813	4294755	2.050 (*)
4	Almadenejos, near an smelting facility with heavily Hg-contaminated soils	351507	4289240	0.340 (**)
5	Fontanosas, supposed non-contaminated site	366656	4291811	15.290 (**)
6	Almódovar del Campo, supposed non-contaminated site	390909	4285415	40.300 (**)
7	Picón, supposed non-contaminated site	407999	4324209	74.770 (*)

summary, five different sets of leaves were obtained, aged 2, 8, 14, 20 and 26 months, but these had different histories. Fruits (olives) were taken also from four different trees at sites 1, 2 and 3 (Table 1) as well as from a blank area (Brazatortas) located some 50 km to the East of Almadén (Fig. 1). Olive oil was collected from two “almazaras” (the local name for the factories where the olive oil is extracted from olives), one located in Chillón (see Table 1 and Fig. 1) and processing olives from the whole Almadén area, and the second in Guadalmez, a village located some 13 km to the SW of Almadén (Fig. 1), and processing olives from an area with minor mercury presence in soils. Olive oil was of the “virgen extra” quality, so just extracted from olives by pressure, implying no chemical treatment at all.

Pre-treatment of soil samples included air-drying, homogenisation, sieving below 2 mm, and taking an aliquot and grinding in an agate mortar to a grain size of 0.10–0.15 mm; leaf samples were rinsed with deionised water, air-dried, ground and homogenised before chemical analysis.

Total mercury in soils was determined using a Lumex RA-915+ device, an Atomic Absorption Spectrometer with a pyrolysis unit (RP-91c) in which the sample matrix was destroyed and mercury atoms were counted by Atomic Absorption Spectroscopy with Zeeman effect to avoid any matrix effect on quantification (Molina et al., 2006; Sholupov et al., 2004). Bioavailable mercury was determined according to the methodology reported by Pérez et al. (2008). Briefly, this methodology involves 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 3500 r.p.m. for 10 min, the extracts were filtered through a 0.22 µm filter (Millex-GS, Millipore) and analysed by AAS (AMA 254).

Total mercury in olive samples was determined using an Atomic Absorption Spectrometer (AMA254) fitted with a catalyser to dry and decompose the sample and then trap the mercury released in an amalgamator before quantification by Atomic Absorption Spectrophotometry. Quality control was achieved with equipment blanks, analysis of duplicates and certified reference material (SRM 2710). The detection limit for this matrix was 10 ng·g⁻¹, while precision and accuracy were 0.2% and 96.4%, respectively. Determination of total mercury contents in olive oil and olives was carried out in the same way as for olive leaves, but using aluminium oxide to avoid explosions on the catalyser caused by combustible volatile compounds released during pyrolysis of these samples.

Multielemental analysis of solid samples was performed at the I.R.I.C.A. Laboratories (University of Castilla-La Mancha), by means of a sequential spectrometer Philips, mod. 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 fundamentals parameters for plants. Quality control was achieved with analysis of duplicate samples and certified reference material (NIST-2710a for soils and BCR-62 for plants), obtaining quantitative recoveries of (87%–124%) in soil certified elements (Co, Cu, Zn, As, Sr, Ba, La, Pb), and (76%–153%) in plant certified elements (Cu, Zn, Pb). The rest of analysed elements are below detection limits or not certified at the corresponding reference materials, therefore their values may be considered as estimations.

Statistical data treatment was performed with STATGRAPHICS Plus 5.1 (Copyright© 1994–2000 Statistical Graphics Corp.).

3. Results and discussion

3.1. Metal contents in soils

The analytical results for metal contents in the analysed soils are shown in Table 2 along with average and reference levels for Castilla-La

Table 2
Elemental contents in soils for the seven sampled sites. CLM AM: average values for soils from Castilla-La Mancha region (Jiménez-Ballesta et al., 2010); CLM RL: reference levels for soils calculated after Spanish legislation for Castilla-La Mancha region (Jiménez-Ballesta et al., 2010). All values in µg g⁻¹.

Site	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	As	Rb	Sr	Y	Zr	Nb	Mo	Sn	Cs	Ba	La	Ce	Hf	Ta	W	Pb	Th	U	Nd
1	23.7	234.1	302.7	43.3	181.7	44.0	98.5	17.9	14.0	31.9	166.0	25.9	242.5	27.4	0.8	2.0	3.8	320.9	46.6	103.8	5.5	1.0	1.3	17.6	8.3	1.8	46.3
2	25.0	242.2	291.1	44.2	177.1	43.3	99.6	18.9	13.5	36.3	199.2	27.2	239.9	29.3	1.2	0.6	1.9	443.9	53.5	115.8	5.3	1.3	0.9	17.8	9.6	2.1	49.1
3	16.3	170.0	139.0	23.3	62.8	45.1	137.0	14.8	5.0	54.8	112.5	23.0	309.4	27.3	1.8	4.8	6.1	427.2	47.4	103.9	7.7	0.6	1.7	66.2	11.3	1.2	44.3
4	12.8	110.5	60.0	12.8	30.8	39.5	148.8	11.9	n.d.	67.0	140.0	22.8	285.9	17.1	0.9	6.7	2.5	448.7	49.4	94.3	9.0	0.9	0.7	122.9	11.5	n.d.	39.2
5	12.6	124.0	86.9	12.4	29.2	20.8	58.4	13.7	10.8	71.0	69.1	25.1	349.7	19.9	0.9	0.6	4.9	398.2	53.8	107.9	9.9	n.d.	2.1	49.3	14.6	3.6	45.8
6	6.8	72.9	56.9	9.4	16.9	19.4	22.4	8.4	5.7	43.6	34.0	20.1	311.1	14.1	0.8	0.6	3.9	258.8	39.9	99.0	9.7	1.2	2.2	22.4	12.4	3.3	34.9
7	9.2	72.3	82.9	11.1	25.2	14.7	31.9	8.2	7.3	59.4	64.9	22.2	440.9	15.7	0.5	n.d.	1.2	368.4	42.6	91.9	12.9	0.0	2.2	38.5	13.4	3.5	37.7
CLM AM	23.6	49.9	54.8	5.8	16.9	10.3	35.7	11.1	7.4	86.2	380.0	17.9	167.6	8.0	0.9	4.0	7.7	389.9	23.6	57.7	4.9	2.2	3.2	19.3	9.6	3.8	21.6
CLM RL	50.8	123.2	113.4	20.8	42.6	27.0	85.6	26.7	16.1	234.7	1846.4	38.3	413.1	18.7	2.0	8.7	14.2	1049.3	48.4	97.9	10.0	4.0	5.5	44.2	21.6	10.3	40.1

Mancha region (data from Jiménez-Ballesta et al., 2010). Most of the measured concentrations can be considered as normal contents for non-contaminated rural areas, with values close to or below those reported by Jiménez-Ballesta et al. (2010). On the other hand, some elements show concentrations well above these reference values; calcophilic elements such as V, Cr, Co, Ni, Cu, Zn and Pb have concentrations above their Reference Levels for some of the analysed soils, particularly in proximity to urban areas: sites 1 and 2 are close to Almadén, site 3 is close to Chillón, and site 4 is close to Almadenejos. Besides, these sites are located in areas characterised by the presence of mafic magmatic rocks (García-Sansegundo et al., 1987), a situation that could explain these higher values—in particular for V, Cr, Co and Ni. Cu and Zn are elements that are usually linked to periurban pollution (see Martínez-Coronado et al., 2011 for an example in Almadenejos). Pb shows maximum values in sites 3, 4 and 5, and this can be related to the regionally common galena (PbS) mineralisations exploited historically in the area. 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. García-Navarro et al. (2011) also stated that Rare Earth Elements are closely related to clay content in similar soils. It can be seen from Table 2 that relatively high contents were determined for La, Ce and Nd.

Furthermore, other elements, including Rb, Sr and U, show concentrations well below normal values for the region, a finding that can be explained in terms of regional geology variations. Sr is usually linked to carbonate rocks, which are very scarce in the Almadén area but are common in other geological domains in Castilla-La Mancha. Rb and U are usually linked to granites and gneisses, which are common in other areas of the region (Amorós et al., 2011; Conde et al., 2009) but not in the area under investigation. Mercury is, as expected (see Conde et al., 2008; Gray et al., 2004; Higuera et al., 2003, 2006), extremely high in the proximity of the mercury mining areas (Almadén and Almadenejos, sites 1, 2 and 4 in Table 1) and contents clearly decrease with distance from these pollution sources. In particular, Conde et al. (2008) study a transect of mercury contents in soils from the Almadén periurban area and find mercury concentrations that point out to the element as a pollutant agent for drainage waters.

3.2. Metal contents in leaves

Average leaf contents for some major and trace elements are shown in Table 3 along with some reference values (Fernández-Escobar et al., 1999; Kabata-Pendias, 2001; Wild, 1992). Values in Table 3 correspond to averages of the values measured for the five leaf sets, with different ages, taken from each site; the complete measured concentrations can be found in Appendix 1 (Excel Table for additional material).

Measured values for V, Cr and Co are above average world contents but are below toxicity levels. The Pb content is below world normal values but above contents reported for Calabria (Italy) by [Bargagli \(1995\)](#) ($<1 \text{ mg kg}^{-1}$). Ni values (3.4 mg kg^{-1}) can also be considered as normal and below toxicity levels (10 mg kg^{-1}) and this is consistent with data reported by [Madejón et al. \(2006\)](#) and [Gascó and Lobo \(2007\)](#); lower levels ($<1 \text{ mg kg}^{-1}$) were reported by [Bargagli \(1995\)](#) for Calabria (Italy). Zn levels (21.1 mg kg^{-1}) are close to the world average and below values reported by [Vavoulidou et al. \(2004\)](#) for Greece (68 mg kg^{-1}), and also below values measured by [Madejón et al. \(2006\)](#) in wild olive trees at Azalcóllar (Seville, Spain) after the 1998 mining spill event (60 mg kg^{-1}). Values for Rb, Sr, Nb, Cs, La, Ce and Nd are reported here for the first time for olive tree leaves and references for these elements were not found in the literature.

The mercury content in leaves ranges from 0.2 mg kg⁻¹ in the youngest leaves collected from the uncontaminated sites to 6.6 mg kg⁻¹ for the oldest leaves from the area in proximity to the

Table 3
Elemental contents in olive tree for some major (Mg-Fe, %) and trace elements (Cl- Nd, $\mu\text{g g}^{-1}$) in the 7 sampled sites. For each element the value is the average of 3 year leaves. Reference values from Kabata-Pendias (2001), *Barranco et al. (2004) and ** Wild (1992).

Site	Mg	Al	Si	P	K	Ca	Fe	Cl	V	Cr	Co	Ni	Zn	Pb	Ba	Rb	Sr	Nb	Cs	La	Ce	Nd
1	0.151	0.117	0.178	0.354	1.382	0.669	0.010	0.092	3.9	4.8	2.8	2.7	21.9	4.1	35.9	2.9	66.9	3.1	5.4	4.2	9.3	4.5
2	0.165	0.049	0.093	0.409	1.349	1.117	0.012	0.109	3.8	4.5	2.5	2.7	31.1	4.1	47.8	2.8	75.9	3.1	4.4	1.1	10.0	6.0
3	0.151	0.119	0.222	0.255	0.952	1.005	0.014	0.093	4.1	5.4	2.9	2.1	18.4	3.5	29.8	2.4	32.6	3.5	4.7	3.3	10.0	2.5
4	0.168	0.026	0.073	0.365	1.300	1.221	0.010	0.118	3.3	4.5	3.0	1.6	13.3	4.2	33.0	2.0	45.2	3.3	4.8	nd	8.2	3.5
5	0.139	0.033	0.129	0.361	1.212	0.830	0.011	0.070	3.6	4.4	3.0	5.1	21.2	3.9	57.3	2.7	48.7	3.3	8.1	1.7	14.7	5.0
6	0.153	0.020	0.047	0.411	1.153	1.150	0.011	0.092	5.0	4.4	2.9	4.8	19.3	3.4	51.7	3.4	56.3	4.1	7.1	nd	13.5	4.3
7	0.125	0.018	0.062	0.361	0.899	1.134	0.009	0.089	3.73	4.57	2.87	4.57	22.87	3.37	35.23	3.97	57.37	3.27	4.50	2.65	10.77	6.50
Average	0.150	0.055	0.115	0.359	1.178	1.018	0.011	0.095	3.9	4.6	2.8	3.4	21.1	3.8	41.5	2.9	54.7	3.4	5.6	2.6	10.9	4.6
W-normal	>0.1*			0.1–0.3*	>0.8*	>1*	0.05–0.025**	>0.5*	0.2–1.5	0.1–0.5	0.02–1	0.1–5	>10*	0.1–50	30–300							
W-toxic									5.0–10	5.0–30	15–50	10–100	100–400	30–300	>500							

[illegible]

Fig. 3. Plot of linear dependence between total mercury in soil and mercury in leaves (left) and bioavailable mercury in soil and mercury in leaves (right). $R = 0.133$ (not significant) in the first case and $R = 0.82$ (significant at 95%) for bioavailable mercury. All data in mg kg^{-1} .

uncontaminated areas; on the other hand, there is no European regulations concerning mercury contents in edible oil: [Codex Alimentarius Commission \(2003\)](#) states maximum contents of 0.1 mg kg^{-1} for As and Pb in olive oil, but makes no reference to mercury. Assuming a

similar toxicity for these elements, the analysed olive oil from the Almadén area does not suppose a risk for local population, although it possibly contributes to the also slightly higher mercury concentrations in hair from the local inhabitants ([Díez et al., 2011](#)).

Fig. 4. Plot of trace metals contained in leaves versus their age in years. Point 1 corresponds to the youngest leaves taken during the 2010 survey; point 2 to the average contents of 1 year old leaves taken in 2010 and 2011; and point 3 to the older leaves (aged 2 years) taken during the two surveys. All concentrations in mg kg^{-1} .

Fig. 5. Plot of mercury concentrations in leaves versus their age in months. Leaves aged 2, 14 and 25 months correspond to the first survey, carried out in May 2010, while leaves aged 8 and 21 months correspond to the second survey, carried out in January 2011. Hg concentrations in mg kg⁻¹.

4. Conclusions

The main conclusions of this study are outlined below:

1. Soils from the study area, centred in the Almadén mercury mining district, contain normal contents in metallic trace elements and these are conditioned by the local geology or urban locations of the area. 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.
2. Elemental concentrations in olive tree leaves are also normal, although our data are the first detailed data in this context for leaf samples. Apart from the major elements (Al, Ca, Fe, K, Mg), metallic 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 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.
3. The temporal evolution of metallic contents in the studied leaves showed that some elements became more concentrated with time (Sr and Hg), some elements decayed with time (Zn, Cr and Rb) and some elements remained constant (Ni). Especially interesting was the study of the temporal evolution of mercury, which seems to have some correlation with changes in atmospheric mercury concentrations. The mercury concentrations reached maximum values in the leaves while those atmospheric concentrations were higher.
4. Based on the results of this study, the uptake of bioavailable mercury from the soils appears to be the main factor that explains the concentration of mercury in olive tree leaves. Furthermore, the temporal evolution of mercury contents in the leaves, with peaks during periods of higher atmospheric mercury concentrations, suggest aerial intake by leaves as an additional mechanism of mercury uptake.

Further studies involving a detailed investigation of this process are needed in order to confirm or modify this interpretation.

5. The usage as food of local olive oil and olives does not represent a risk for human health, although probably is a contribution for the higher levels of mercury in hair recognised for local population in previous studies.

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Appendix 1. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jgexplo.2012.04.012>.

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Table 5

Mercury contents ($\pm$ standard deviation) in olive oil and olives from the Almadén area. See Table 1 for description of sites, and Fig. 1 for locations.

Sample type and location	Hg mg kg ⁻¹
Olives, site 1	0.162 $\pm$ 0.010
Olives, site 2	0.077 $\pm$ 0.007
Olives, site 3	0.018 $\pm$ 0.002
Olives, Brazatortas	0.045 $\pm$ 0.007
Olive oil, Chillón	0.049 $\pm$ 0.011
Olive oil, Guadalmez	0.011 $\pm$ 0.001

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