An estimation of mercury concentrations in the local atmosphere of Almadén (Ciudad Real Province, South Central Spain) during the twentieth century

José Tejero, Pablo L. Higueras, Ignacio Garrido, José M. Esbrí, Roberto Oyarzun & Santiago Español

Environmental Science and Pollution Research

ISSN 0944-1344

Environ Sci Pollut Res
DOI 10.1007/s11356-014-2860-5

Environ Sci Pollut Res
DOI 10.1007/s11356-014-2860-5

ATMOSPHERIC POLLUTANTS IN A CHANGING ENVIRONMENT

An estimation of mercury concentrations in the local atmosphere of Almadén (Ciudad Real Province, South Central Spain) during the twentieth century

José Tejero · Pablo L. Higueras · Ignacio Garrido · José M. Esbrí · Roberto Oyarzun · Santiago Español

Received: 3 February 2014 / Accepted: 31 March 2014

Abstract We show the first estimations of long-term (100 years, 1900 to 2000) total gaseous mercury concentrations (TGM) in the urban area of Almadén. The estimation was carried out by comparing data on known metallic mercury production with measured TGM concentrations. The estimated diurnal background level ranges from 60 to 120 ng m^{-3} and corresponds to periods when the metallurgical complex (cinnabar roasting plant) was shut down. The average TGM concentration during the period from 1900 to 2000 was about 600 ng m^{-3} (with peaks above 1,200 ng m^{-3}). Additionally, a 24-h-based TGM monitoring program has highlighted significant differences between the diurnal and nocturnal concentrations, particularly during the warmer months. In this regard, given that the average nocturnal to diurnal ratio is 2.12, we suggest that the average nocturnal concentrations must have exceeded 1,200 ng m^{-3}, and peak nocturnal concentrations could have reached levels up to 2,400 ng m^{-3}. Our estimations indicate that most parts of the town of Almadén were generally exposed to TGM concentrations in air that exceed the World Health Organization air quality guideline for Hg (1,000 ng m^{-3}) for countryside and urban areas.

Keywords Almadén · Metallurgy · Atmospheric mercury estimations · Total gaseous mercury · TGM

Introduction

Mercury (Hg) is a transition metal that belongs to group IIB of the periodic table, and it is the only metal that is liquid at room temperature, besides mercury is highly volatile due to its high-vapor pressure. This latter characteristic is also the cause of toxicological concerns, both directly (chronic exposure to Hg vapor produces a disease called hydrargyrism) and indirectly (atmospheric mercury, Hg^0, can be transformed into ionic mercury, Hg^{2+}, and then undergo dry and/or wet deposition onto soils and freshwater). In turn, Hg^{2+} can be converted into toxic methylmercury, $[CH_3Hg]^+$, which bioaccumulates in fish. Metallic Hg is obtained by roasting cinnabar (HgS), which is by large the main ore mineral of this metal.

Almadén is a small town (about 6,000 inhabitants) (INE 2013) located in the SW of the Ciudad Real Province (Spain) (Fig. 1), and it is also the center of the Almadén Hg mining district, which has produced almost one third of the total industrial production of this metal (about 7 million tons) during approximately 2,000 years of almost continuous activity (Hernández et al. 1999; Hylander and Meili 2003).

Descriptions of the geology, mining history and environmental concerns regarding the district can be found in the following references: Saupé (1990), Hernández et al. (1999), Higueras et al. (2013a) (geology and mining history), Lindberg et al. (1979), Ferrara et al. (1998), Higueras et al.

Responsible editor: Gerhard Lammel

J. Tejero (✉) · I. Garrido
Departamento de Mecánica Aplicada e Ingeniería de Proyectos, Universidad de Castilla-La Mancha, E.I.M.I. Almadén, 13400 Almadén, Ciudad Real, Spain
e-mail: jose.tejero@uclm.es

P. L. Higueras · J. M. Esbrí
Departamento de Ingeniería Geológica y Minera, Universidad de Castilla-La Mancha, E.I.M.I. Almadén, 13400 Almadén, Ciudad Real, Spain

R. Oyarzun
Departamento de Cristalografía y Mineralogía, Universidad Complutense de Madrid, Av. Complutense s/n, 28071 Madrid, Spain

S. Español
Fundación Almadén–Francisco Javier de Villegas, C/José Luis Rodríguez López de Haro 1, 13400 Almadén, Ciudad Real, Spain

J. Tejero · P. L. Higueras · I. Garrido · J. M. Esbrí · R. Oyarzun
Instituto de Geología Aplicada, Universidad de Castilla-La Mancha, E.I.M.I. Almadén, 13400 Almadén, Ciudad Real, Spain

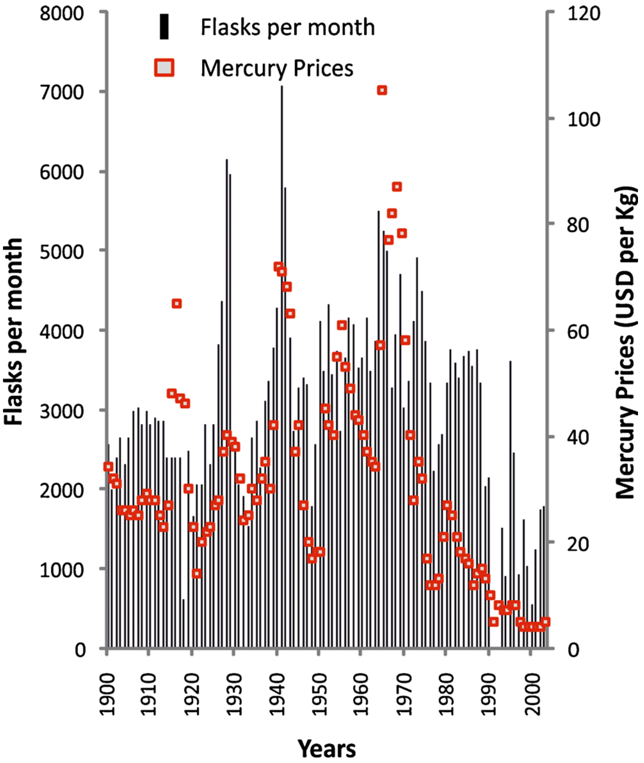

Fig. 1 Evolution of production and mercury prices during the twentieth century. Production data are from local historical museum. Prices are from Swain et al. (2007)

(2003, 2005, 2013b), Gray et al. (2004, 2010), Moreno et al. (2005), Millán et al. (2006), Molina et al. (2006), Sierra et al. (2008, 2011, 2012), Díez et al. (2011), and Martínez-Coronado et al. (2011) among others.

The history of Almadén cannot be understood without considering the history of its mines and vice versa. Intensive exploitation of the mines did not begin until the second century BC when the Roman occupation was consolidated in the region. Given that vermilion (the red dye obtained from cinnabar) (Escosura 1878) was a luxury product, the profitability of the mines must have been enormous. The site became important once again during the Arab domination from the eight to the twelfth centuries. From the sixteenth century onwards, Hg became a highly valuable commodity due to its use in the amalgamation of the South American gold and silver, which made the metal a strategic product that brought incalculable economic benefits for Spain. It was during this period that Almadén developed as an important mining center, decisively contributing to the exploitation of silver and gold from the American colonies. From the 1900s onward, one of the main Hg consumers in industrialized countries was the chlor–alkali industry, e.g. in 1996, 40 % of the Hg produced worldwide was consumed by chlorine producers (Sznopek and Goonan 2000). Other industrial uses of Hg were as catalysts in organic reactions, cosmetic creams, metal shields, barometers, thermometers, lubricants, batteries, laser beams, Hg vapor lamps and water sterilizers. Besides, Hg was a component in alkyl compounds that were used in agriculture as fungicides in order to avoid the proliferation of slime in paper pulp, as pesticides in fruit trees and in the treatment of grains and seeds (Tejero 2011).

After a turning point in 1901, the level of Hg production remained below 3,300 flasks per month (Fig. 1). From 1925 onwards, Almadén experienced a major production increase of up to 6,167 flasks per month, which coincided with the installation and use of the new Cermak and Spirek furnaces (Tejero et al. 2014); however, civil unrest in Northern Spain (1934) resulted in a decrease in production. Production increased again with the onset of the Spanish Civil War and the Second World War, reaching an historic peak in the year 1941 (7,083 flasks per month). However, by the end of the 1940s, production declined once again. The installation of the so-called Pacific furnaces in the 1950s coincided with an increase in production and levels between 4,200 and 5,800 flasks per month were reached until the end of the century. In this regard, highs and lows in production were linked to supply and demand rather than the methods and metallurgical techniques used in these years. On the other hand, ecological and public health concerns caused by the so-called Minamata incident in Japan in 1956 (e.g. Harada 1995) and the poisoning in Iraq by Hg compounds used as grain fungicides (Bakir et al. 1973) resulted in a serious decline in Hg prices and the closure of most Hg mines worldwide. In this regard, the United Nations Environment Program (UNEP) implemented its Hg plan as an instrument to achieve international control over the industrial activities in which Hg was used. As part of this program, a series of norms have been established since 2001 and these include prevention, minimization, Hg waste management, disposal and long-term storage (UNEP 2002). These actions led to the establishment of international regulations for the Hg trade. For example, in January 2005, the European Commission adopted a Hg strategy (EURLex 2005) with the aim of phasing out this toxic metal and banning the export of all kinds of Hg compounds, including Hg alloys with a Hg concentration of at least 95 % by weight (DEFRA 2010). The strategic planning also indicated that surplus Hg should be safely stored. Furthermore, the USA joined the European Union in setting a date to ban Hg exports, thus reducing the supply of commodity Hg into the world market (Mercury Policy Project 2008). In 2013, the Minamata Convention (UNEP 2013) provided the framework for a new treaty to control and reduce the use of a variety of Hg containing products; production, exports and imports will be banned by 2020.

Significant variations in Hg price (Fig. 1) occur for two main reasons: major wars and predatory dumping practices by the producing countries. Particularly noteworthy is the 1962–1970 period, with a production peak in 1965 induced by the massive demand for the metal from the chlor–alkali industry and a drastic fall starting in 1969 triggered by the aforementioned environmental and toxicological concerns. During the rest of the twentieth century, prices progressively declined to US$5 kg^{-1}, and it was only in the early twenty-first century that Hg prices recovered and even surpassed those prior to the 1960s–1970s crisis.

All of the events outlined above led to significant changes in Almadén. For example, the number of inhabitants has fluctuated markedly in response to the discontinuities in Hg production (Fig. 2). Mining activity, after hundreds of years of providing work to almost all of the inhabitants in the area, made Almadén a prosperous city and the main industrial center of the entire region, with a population peak of over 13,500 inhabitants in the 1960s. However, from the 1970s onward, the town has undergone a gradual decline in the population down to the present 6,000 inhabitants. The mine and the metallurgical complex closed in 2003.

The evolution of mining and metallurgical techniques in Almadén was important during the twentieth century. As a result of the extensive exploitation of the mine throughout history, cinnabar roasting evolved from primitive and inefficient processes (with the release of high levels of Hg vapor) to an industrial era involving sealed furnaces systems, which nevertheless did not fully prevent the escape of gases from the chimney. The first methods for the production of Hg were rudimentary, gave low yields and resulted in severe health problems for the operators. For example, Guillermo Sánchez Martín reported in 1923 (Tejero and Montes 2011) that about 36 % of the mine workers were affected to some degree by Hg poisoning. In this regard, technological improvements led to production increases and an improvement in sanitary conditions in the 1980s and 1990s (Tejero et al. 2011, 2013). The sanitary technology developed by the company's Occupational Health Department is currently applied in the context of cooperation with developing countries and, in particular, in artisanal gold mining with the aim of improving the quality of life and working conditions of miners.

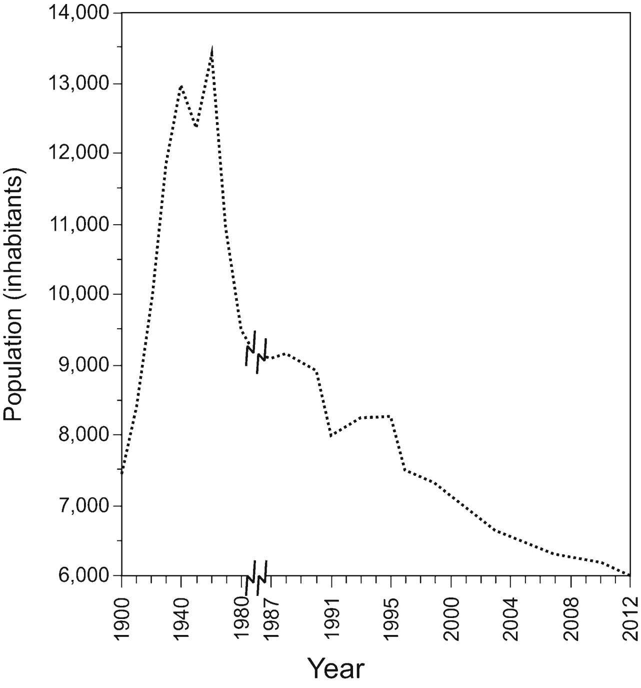

Fig. 2 Population evolution of Almadén town (Spain) in the 1900s and 2000s. Source: Spanish 'Instituto Nacional de Estadística' (INE 2013)

Despite the technological advances that were made over the years, the main consequence of Hg production has always been local atmospheric pollution with extremely toxic vapors of the element. Clinical studies have not been performed on the general population, but studies on exposed workers (García-Gómez et al. 2007 and references therein) describe high Hg levels in blood and urine and detrimental effects on the central nervous and urinary systems. In this regard, the presence of these vapors at the site was documented during the late twentieth (Ferrara et al. 1998) and early twenty-first centuries (Higueras et al. 2006, 2013b), and we used these data to estimate the historic levels of this pollutant in the Almadén urban area.

Methodology

The data from Ferrara et al. (1998) and Higueras et al. (2013b) were compared with known historic metallic Hg production figures obtained from the local historic archive (managed by 'Fundación Almaden Francisco de Villegas'). Data used for this study were as follows:

- Diurnal atmospheric Hg concentrations gathered by Ferrara et al. (1998) during September 1993 and February 1994 using remote sensing LIDAR technologies and handcraft point monitors.
- Some discrete measurements of Hg concentrations during the last 10 years were published by Higueras et al. (2013b). All of these data are diurnal and refer to the Almadén urban area and its surroundings. These data were collected using portable LUMEX RA-915 instruments.
- For the continuous (24 h) measurements of atmospheric Hg concentrations, we used a TEKRAN 2537 instrument during the period October 2007 to October 2009 at the Las Cuevas mine site and from November 2011 to the present day at the Almadén School of Mines about 900 m to the SE of the mining and metallurgical complex.
- Annual metallic Hg production data for the period 1900 to 2003.
- Detailed monthly metallic Hg production data for the period 1990 to 2003.

Ferrara et al. (1998) used two different methodologies: (a) LIDAR Remote Sensing technology for the determination of

Hg concentrations above the town (these results were not used in this work) and (b) discrete measurements. Sampling sites used by these authors are shown in Fig. 3.

Higueras et al. (2013b) used a LUMEX RA-915+ analyzer (Sholupov et al. 2004) in car-driven surveys covering the town area and its surroundings. Measurements were continuous (every second). During the first survey, a GPS device was used to record the geographic position of selected points, and the rest of the positions were interpolated based on the known positions. During the second survey, a GPS device was used to track the itinerary; thus, an integration of the GPS and the analytical files provided the exact location of every analytical site every second.

Unpublished data for the continuous (24 h) measurements were obtained using a TEKRAN 2537B (Tekran 2012). This is an automated ambient air analyzer that performs continuous long-term, unattended analysis of total gaseous mercury (TGM). The chosen sites were (a) Las Cuevas mine (Llanos et al. 2010) located approximately 8 km NE of Almadén (geographic coordinates: 38° 49′ 20″ N, 4° 45′ 32″ W), where the measurements were taken during the period November 2007 to December 2009 and (b) the Almadén School of Mines located approximately 900 m SE from the main mining and metallurgical complex (*Cerco de San Teodoro*) (geographic coordinates for this measuring site: 38° 46′ 18″ N, 4° 50′ 05″ W), where measurements were started in November 2011 and are still being recorded (January 2014).

During the TGM surveys, the accuracy of the Lumex RA-915M system was checked prior to each measurement, and a baseline correction was made every 15 min to avoid lamp intensity drift effects (<1 ng m^{-3} in 15 min). GEM measurements were obtained using a TEKRAN instrument in accordance with the European standard CSN EN 15852 (European Standards 2013) developed by Working Group 25 of the European Committee for Standardizations (CEN) Technical Committee 264 'Air Quality' (Brown et al. 2010a, b). This equipment was periodically calibrated with an external spike of Hg vapor using a calibrated Hamilton Digital Syringe and a Tekran Model 2505 Hg vapor calibration unit. The sensitivity of this equipment was <0.1 ng m^{-3} over the sampling period used in this work. Besides, Fernández-Patier and Ramos-Díaz (2012) carried out an intercomparison exercise with Lumex RA-915M and Tekran 2537B devices belonging to Spanish institutions IGeA-UCLM and 'Instituto de Salud Carlos III' (Madrid). The results yielded a compatibility index (after ISO/IEC Guide 43-1 1997) of less than 1 for all experiments.

Mercury production at the Cerco de San Teodoro complex was recorded by the mining company until the closure of the metallurgical plant in 2003. The production profile for the twentieth century and for many years was recorded on a monthly basis (although, unfortunately, not for every year). The older production can be tracked from old production data from which the annual production from the year 1500 onwards can be estimated. The monthly production during the time span (1990–2003) was used to find a mathematical relationship of the type Y=aX+b, where Y is total gaseous mercury and X is the production of metallic mercury. Based on this function, monthly productions for the whole century (calculated on the basis of the annual data) were used to estimate the TGM concentrations.

The next step involved the calculation of estimated values, which was carried out on the assumption that the TGM concentrations are correlated with the metal production, although they are also affected by the local meteorological conditions and even differences in the type of furnaces used in the metallurgy of mercury. We interpolated data from the urban area of Almadén using the Local Polynomial method of SURFER 11 (Fig. 3). The method uses the neighboring data within an ellipse for each grid node (Golden Software Surfer 2011). One of the surfaces obtained from the process (corresponding to the June 2002 survey) is shown in Fig. 4.

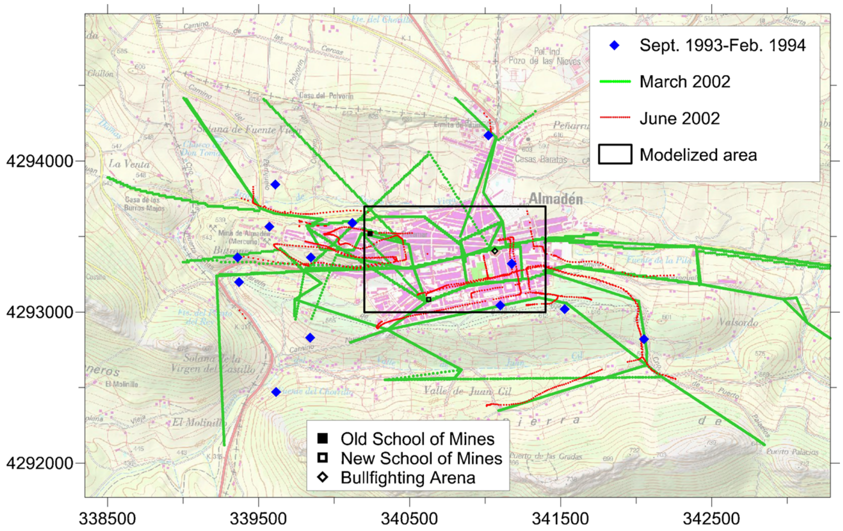

Fig. 3 Sampling sites from Ferrara et al. (1998) (*blue rhombs*) and sampling tracks from Higueras et al. (2013b) (*coloured lines*). The *inner rectangle* has been used for the concentration estimations

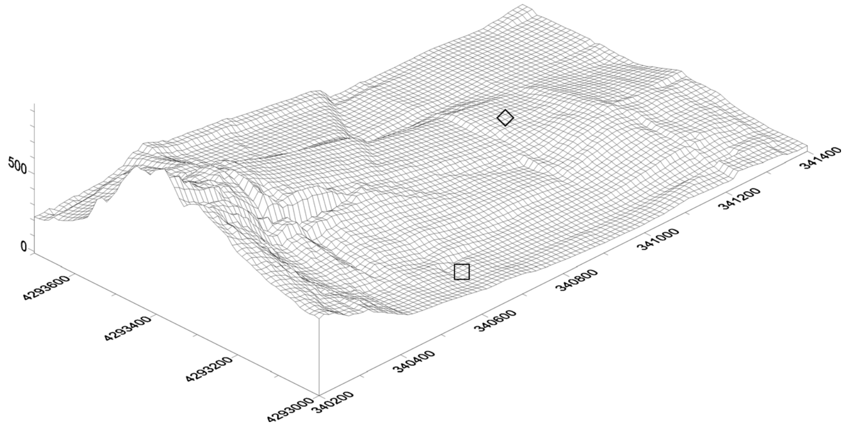

Fig. 4 3D view of the results of gridding corresponding to the June 2002 survey. Estimations correspond to all the nodes shown in the surface. The *open rhomb* corresponds to the location of the bullfighting plaza, the *open square* to the modern Almadén School of mines, and the *solid square* (not visible in this figure due to elevations) to the old Almadén School of Mines

Results

The correlation between production data (in flasks per month) and the average value of the atmospheric Hg concentration for the gridded area is very high (R^2=0.98) (Fig. 5) and the fitting equation is:

$$\mathrm{TGM} = 0.17\mathrm{P} + 67.88 \tag{1}$$

where TGM is the concentration in nanogram per cubic meter and P is the production in flasks per month. This equation was used to estimate atmospheric total gaseous Hg concentrations for the whole twentieth century in yearly averages on the basis of the declared Hg production (Fig. 6). It can be seen from the figure that the concentrations are well above the maxima levels recommended by international organizations (WHO 2000; USEPA 2007). The average monthly production was 3,062 flasks and the corresponding estimated TGM was 583 ng m^{-3}. Peak production (7,800 flasks per month), corresponding to the year 1941, could have caused an average concentration of about 1,260 ng m^{-3}. One should also take into account the TGM concentrations corresponding to degasification of the mine dump (which did not undergo reclamation until a few years ago). The first dataset analyzed in this study (from Ferrara et al. 1998) corresponds to one of these periods, and the average TGM concentration was 112 ng m^{-3}. This value is not far from the ordinate in the origin of Eq. 1 (at 68 ng m^{-3}) and could be taken as a proxy for the range of values expected as a background for non-production periods.

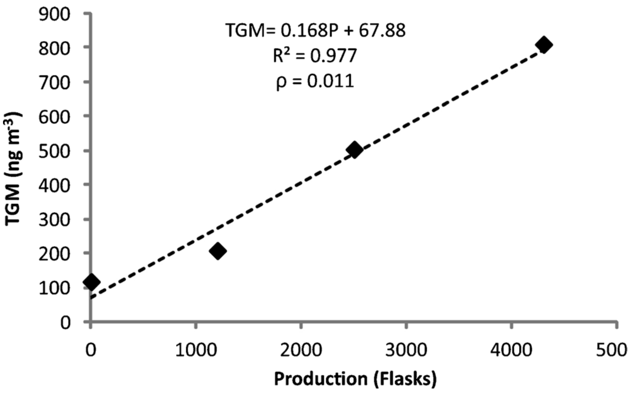

Fig. 5 Plot of metallic mercury production vs average calculated value of atmospheric mercury concentration for the gridded area and for each of the four data sets considered (data from Table 1)

The contour maps obtained by the gridding process, corresponding to the surveys carried out by Higueras et al. (2013b) (Fig. 7), raise considerable concerns: large sectors of the town area must have been constantly affected by TGM concentrations above the WHO (2000) air quality guideline (at 1,000 ng m^{-3}) and the USEPA (2007) reference level for air concentration (at 300 ng m^{-3}) (Table 1). In this regard, the

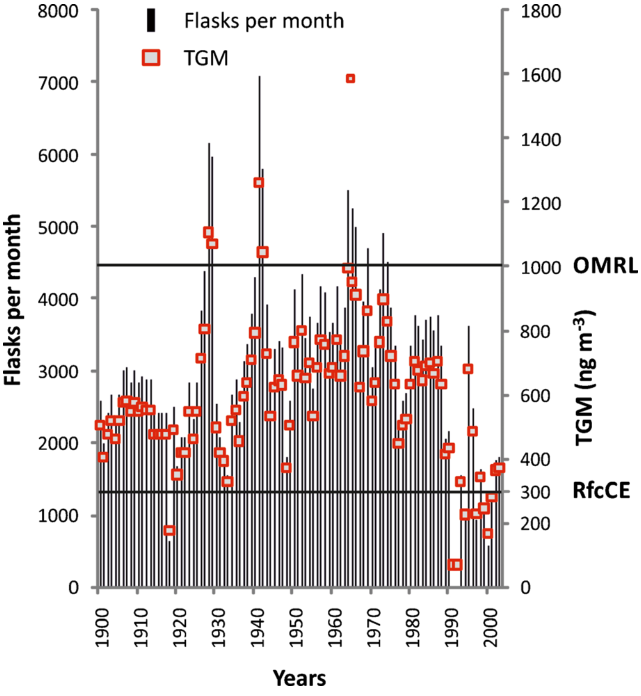

Fig. 6 Historic production of metallic mercury (*bars*) and estimation of yearly averages of TGM affecting the town area (*rectangle* shown in Fig. 3) (*squares*). OMRL: WHO (2000) maximum recommended level; RfcCE: USEPA (2007) reference concentration for chronic exposure

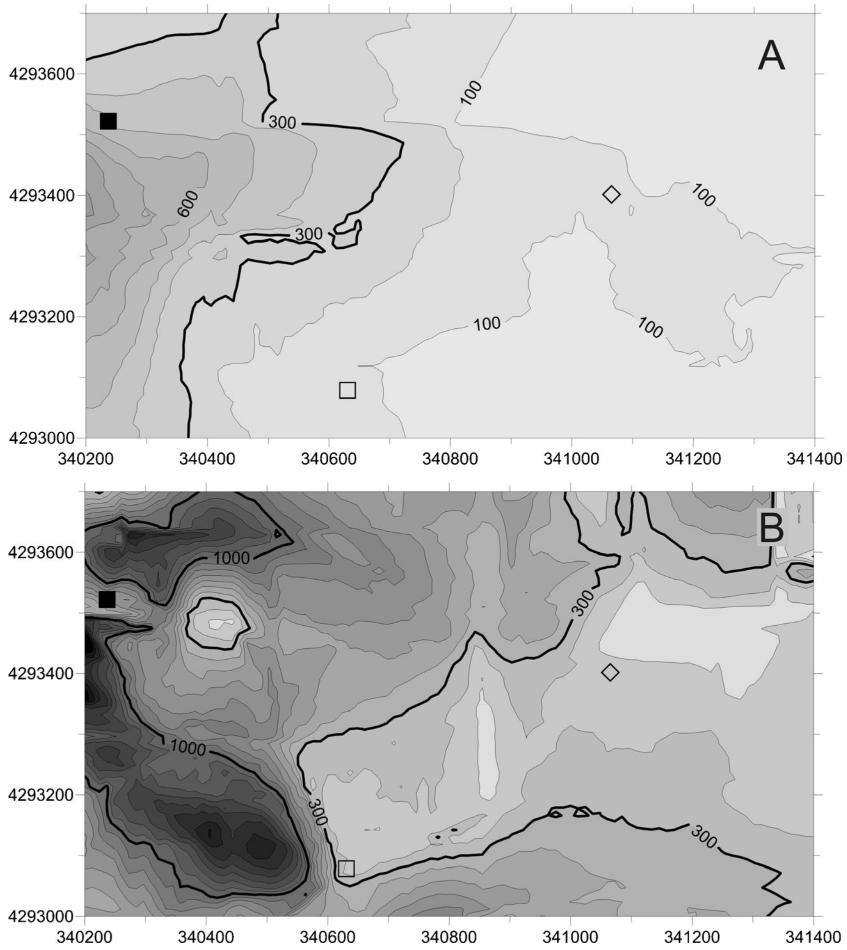

Fig. 7 Contour maps obtained from the gridding process with the March 2002 (**a**) and June 2002 (**b**) surveys (Higueras et al. 2013b). References as in Figs. 3 and 4

correlation between Hg production and the area affected by these concentrations shows a good linear relationship (Fig. 8), which can also be used to estimate TGM concentrations in the urban area as TGM = *f*(P). In our estimation, a production above 4,300 flasks per month may have caused 100 % of the town to be exposed to concentrations above 300 ng m^{-3}, whereas a figure above 7,000 flasks per month could have resulted in 50 % of the town being exposed to levels above 1,000 ng m^{-3}. For the average production over the century (3,062 flasks per month), 72.4 and 17.3 % of the town could have been affected by TGM concentrations above 300 and 1,000 ng m^{-3}, respectively (Fig. 9). In terms of monthly or daily production, the production has undoubtedly been proportionally higher, and TGM concentrations may well have been even higher than the estimated values.

Measurements carried out continuously during 24 h at the Las Cuevas (2007–2009) and Almadén (2011–2012) sites (Table 2) highlighted the effects of TGM concentrations during the diurnal–nocturnal and the winter–summer seasonal cycles. During the warmer periods, a diurnal mixing layer is formed in the lower atmospheric levels, which favors the dilution of atmospheric pollutants. Conversely, during the night, the atmosphere remains static which results in increased concentration of the pollutants due to gas entrapment at lower altitude. Given that the average night/day ratio is 2.12, an estimation of nocturnal concentrations can be obtained by

Table 1 Flasks per month (FpM) produced and total gaseous mercury (TGM) during measurement days considered in this study. All Hg data in ng m^{-3}

Date	FpM	N	TGM	Area >300 Hg (%)	Area >1,000 Hg (%)
Feb-94	0	13	110	2	0
Jun-02	1,200	1,214	200	24	0
Mar-02	2,500	9,038	500	66	13
Sep-93	4,300	13	800	99	28

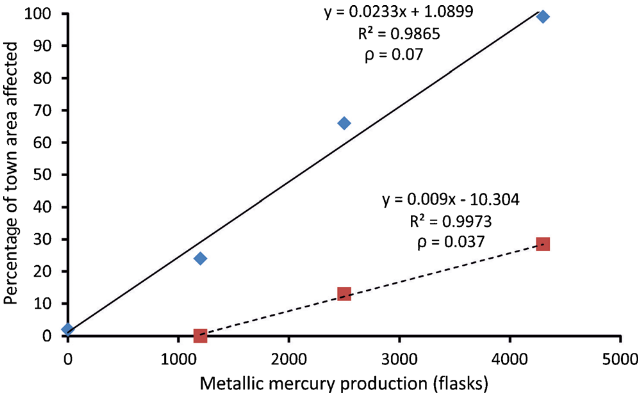

Fig. 8 Plot of metallic mercury production vs percentage of the town area affected by concentrations higher than USEPA (2007) reference concentration for chronic exposure (300 ng m^{-3}) (*blue rhombs* and *continuous line*) and higher than WHO (2000) maximum recommended level (1,000 ng m^{-3}) (*red squares* and *broken line*)

multiplying the estimated data by this figure. On this basis and taking into account that the average TGM concentration for the complete century could be in the order of 580 ng m^{-3}, the nocturnal values for the TGM concentrations in the town area are estimated to be close to 1,240 ng m^{-3}. Thus, considering the estimated diurnal peak average concentration (at 1,261 ng m^{-3}), the average nocturnal concentration could have been 2,673 ng m^{-3} in the year 1941.

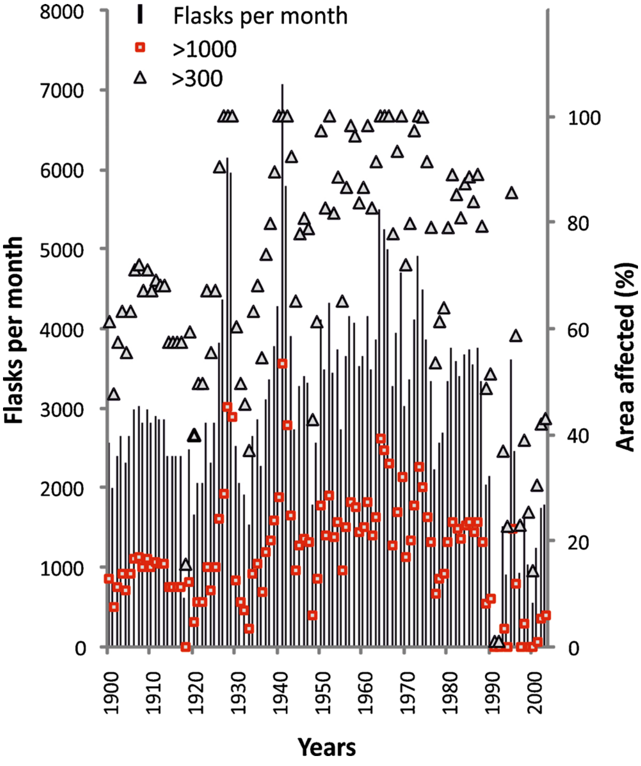

Fig. 9 Evolution of metallic mercury production (*bars*) and of average percent of town affected by TGM concentrations above the USEPA (2007) reference concentration for chronic exposure (300 ng m^{-3}) (*gray triangles*) and above the OMS (2000) maximum recommended level (1,000 ng m^{-3}) (*red squares*)

Table 2 Average gaseous mercury concentrations in Almadén and Las Cuevas mine during night and day hours. All Hg data in ng m^{-3}

	Night	Day	Night/day ratio
Almadén			
Autumn	20	12	1.7
Winter	13	14	0.9
Spring	31	16	1.9
Summer	73	28	2.6
Total	42	20	2.1
Las Cuevas			
Total	251	200	1.2

Conclusions

The main conclusions drawn from this study are the following:

- Atmospheric Hg concentrations in the urban area of Almadén show significant variations in TGM concentrations, and these can be related to Hg production.
- The high correlation between Hg production and TGM concentration allows estimations for this pollutant during the twentieth century.
- The concentrations of Hg were often higher than those allowed under present day regulations, including the WHO (2000) air quality guideline and the USEPA (2007) reference level for air concentration. The daily average Hg concentration during the twentieth century could have been in the order of 580 ng m^{-3}, which is well above the USEPA (2007) reference level.
- Concentrations above these thresholds have frequently affected the whole urban area.
- During the night, the atmospheric Hg concentrations are more than two times higher than those during the day. On this basis, the average night time concentrations during the twentieth century could also have been above the WHO (2000) quality guideline.
- All of the TGM concentration figures would have affected most of the local population (>10,000 inhabitants) during the years of higher Hg production.
- Unfortunately, studies on the potential effects on the health of the local population as a consequence of such high TGM concentrations have not been performed to date.

Acknowledgments This work was funded by the Spanish Ministry of Economy and Competitiveness (Project CTM2012-33918). The local mining company (MAYASA) and the Historic Museum 'Fundación Almadén Francisco de Villegas' provided the production data needed for our calculations. We thank Dr. Neil Thompson for revising the manuscript.

References

Bakir F, Damluji SF, Amin-Zaki I et al (1973) Methylmercury poisoning in Iraq: an interuniversity report. Science 181:230–241

Brown RJC, Pirrone N, van Hoek C, Horvat M, Kotnik J, Wangberg I et al (2010a) Standardisation of a European measurement method for the determination of mercury in deposition: results of the field trial campaign and determination of a measurement uncertainty and working range. Accred Qual Assur 15:359–366

Brown RJC, Pirrone N, Van Hoek C, Sprovieri F, Fernández R, Toté K (2010b) Standardisation of a European measurement method for the determination of total gaseous mercury: results of the field trial campaign and determination of a measurement uncertainty and working range. J Environ Monitor 12(3):689–695

DEFRA (2010) The mercury export and data (enforcement) regulations 2010: guidance notes. Department for Environment, Food and Rural Affairs, UK. http://archive.defra.gov.uk/environment/quality/chemicals/documents/mercury-export-data-regs.pdf. Accessed 25 Feb 2013

Díez S, Esbrí JM, Tobias A, Higueras P, Martínez-Coronado A (2011) Determinants of exposure to mercury in hair from inhabitants of the largest mercury mine in the world. Chemosphere 84:571–577

Escosura L (1878) Metallurgic treatment history of quicksilver in Spain. Imprenta y Fundición del M. Tello, Madrid (in Spanish)

EURLex (2005) Community Strategy Concerning Mercury, Commission of the European Communities. Brussels. http://eur-lex.europa.eu/LexUriServ/site/en/com/2005/com2005_0020en01.pdf. Accessed 22 Jan 2014

European Standards (2013) CSN EN 15852—Ambient air quality—standard method for the determination of total gaseous mercury. http://www.en-standard.eu/en-15852-ambientair-quality-standard-method-for-the-determination-of-totalgaseous-mercury. Accessed 25 Feb 2014

Fernández-Patier R, Ramos-Díaz MC (2012) Informe del Ejercicio de lntercomparación de Mercurio Gaseoso total en aire ambiente "IN SITU" (año 2011). Ined. Repport, Instituto de Salud Carlos III, Centro Nacional de Sanidad Ambiental, Área de Contaminación Atmosférica. Ministerio de Economía y Competitividad, España, 7 pp. In Spanish

Ferrara R, Maserti BE, Anderson M, Edner H, Ragnarson P, Svanberg S, Hernández A (1998) Atmospheric mercury concentrations and fluxes in the Almadén district (Spain). Atmos Environ 32:3897–3904

García-Gómez M, Caballero-Klink JD, Boffetta P, Español S, Sällsten G, Gómez-Quintana J (2007) Exposure to mercury in the mine of Almadén. Occup Environ Med 64(6):389–395

Golden Software Surfer (2011) User's guide. Golden Software Inc., Colorado

Gray JE, Hines ME, Higueras PL, Adatto I, Lasorsa BK (2004) Mercury speciation and microbial transformations in mine wastes, stream sediments, and surface waters at the Almadén Mining District, Spain. Environ Sci Technol 38:4285–4292

Gray JE, Plumlee GS, Morman S, Higueras PL, Crock JG, Lowers H, Witten ML (2010) In vitro studies evaluating leaching of mercury in mine waste calcine using simulated human body fluids. Environ Sci Technol 44:4782–4788

Harada M (1995) Minamata disease: methylmercury poisoning in Japan caused by environmental pollution. CRC Crit Rev Toxicol 25:1–24

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

Higueras P, Oyarzun R, Biester H, Lillo J, Lorenzo S (2003) A first insight into mercury distribution and speciation in soils from the Almadén mining district, Spain. J Geochem Explor 80:95–104

Higueras P, Munhá J, Oyarzun R, Tassinari CCG, Ruiz IR (2005) First lead isotopic data for cinnabar in the Almadén district (Spain): implications for the genesis of the mercury deposits. Miner Deposita 40:115–122

Higueras P, Oyarzun R, Lillo J, Sánchez-Hernández JC, Molina JA, Esbrí JM, 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, Lillo J, Morata D (2013a) Intraplate mafic magmatism, degasification, and deposition of mercury: the giant Almadén Hg deposit (Spain) revisited. Ore Geol Rev 51:93–102

Higueras P, Esbrí JM, Oyarzun R, Llanos W, Martínez-Coronado A, Lillo J, López-Berdonces MA, García-Noguero EM (2013b) Industrial and natural sources of gaseous elemental mercury in the Almadén District (Spain): an updated report on this issue after the cease of mining and metallurgical activities in 2003 and major land reclamation works. Environ Res 125:197–208

Hylander D, Meili M (2003) 500 years of mercury production: global annual inventory by region until 2000 and associated emissions. Sci Total Environ 304:13–27

INE (2013) National Statistical Institute, http://ine.es. Accessed 30 Jan 2014

ISO/IEC 43-1 (1997) Proficiency testing by interlaboratory comparisons—Part 1: development and operation of proficiency testing schemes

Lindberg SE, Jackson DR, Huckabee JW, Janzen SA, Levin MJ, Lund JR (1979) Atmospheric emission and plant uptake of mercury from agricultural soils near the Almaden mercury mine. J Environ Qual 8:572–578

Llanos W, Higueras P, Oyarzun R, Esbrí JM, López-Berdonces MA, García-Noguero EM, 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

Martínez-Coronado A, Oyarzun R, Esbrí JM, Llanos W, Higueras P (2011) Sampling high to extremely high Hg concentrations at the Cerco de Almadenejos, Almadén mining district (Spain): the old metallurgical precinct (1794 to 1861 AD) and surrounding areas. J Geochem Explor 109:70–77

Mercury Policy Project (2008) U.S. joins EU in banning mercury exports; environmentalists applaud bi-partisan effort. Published on line: October 15th, 2008, http://mercurypolicy.org/?p=489. Accessed 25 Feb 2013

Millán R, Gamarra R, Schmid T, Sierra MJ, Quejido AJ, Sánchez DM, Cardona AI, Fernández M, Vera R (2006) Mercury content in vegetation and soils of the Almadén mining area (Spain). Sci Total Environ 368:79–87

Molina JA, Oyarzun R, Esbrí JM, Higueras P (2006) Mercury accumulation in soils and plants in the Almadén mining district, Spain: one of the most contaminated sites on Earth. Environ Geochem Health 28:487–498

Moreno T, Higueras P, Jones T, McDonald I, Gibbons W (2005) Size fractionation in mercury-bearing airborne particles (HgPM10) at Almadén, Spain: implications for inhalation hazards around old mines. Atmos Environ 39:6409–6419

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

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

Sierra MJ, Millán R, Esteban E, Cardona AI, Schmid T (2008) Evaluation of mercury uptake and distribution in Vicia sativa L. applying two different study scales: greenhouse conditions and lysimeter experiments. J Geochem Explor 96:203–209

Sierra MJ, Millán R, Cardona AI, Schmid T (2011) Potential cultivation of *Hordeum vulgare* L. in soils with high mercury background concentrations. Int J Phytoremediation 13:765–778

Sierra MJ, Rodríguez-Alonso J, Millán R (2012) Impact of the lavender rhizosphere on the mercury uptake in field conditions. Chemosphere 89:1457–1466

Sznopek JL and Goonan TG (2000) The materials flow of mercury in the economies of the United States and the world. USA Geological Survey Circular 1197, vers. 1.0, USA Geological Survey, Nov. 2000, http://pubs.usgs.gov/circ/2000/c1197/c1197.pdf. Accessed 23 Jan 2014

Swain EB, Jakus PM, Rice G, Lupi F, Maxson PA, Pacyna JM, Penn A, Spiegel SJ, Veiga MM (2007) Socioeconomic consequences of mercury use and pollution. Ambio 36:45–61

Tejero J (2011) Historic and technological evolution of metallurgical furnaces on mercury metallurgy in Almadén mines: start of Cermak-Spirek and Spirek furnaces. (Evolución histórico-tecnológica de los hornos en la metalurgia del mercurio en las Minas de Almadén: implantación de los hornos Cermak-Spirek y Spirek). Ph.D. dissertation, University of Cordoba, Cordoba, Spain (in Spanish)

Tejero J, Montes F (2011) The Mines of Almadén seen by a doctor. Salud Trab 19:79–83 (in Spanish)

Tejero J, Español S, Serrano JJ, Montes F (2011) Mercury levels on the environment and in biological fluids. Case of the metallurgy in Almadén, Spain (1986-2001). Salud Trab 19(1):77–83 (in Spanish)

Tejero J, Español S, Montes F (2013) Detection criteria and preventive measures for occupational disease in the Mines of Almaden (Spain). Environ Monit Assess 185:9125–9138

Tejero J, Garrido I, Mata F, Rubio ML (2014) Metallurgy of mercury in Almadén: from aludel furnaces until Pacific furnaces. Rev Metal. doi:10.3989/revmetalm

Tekran (2012) Tekran 2537 CVAFS automated ambient air analyzer. Tekran Products, Ambient Air. http://www.tekran.com/products/ambient-air/tekran-model-2537-cvafs-automated-mercury-analyzer/. Accessed 28 Jan 2014

UNEP (2002) Global mercury assessment. UNEP, Geneva. http://www.chem.unep.ch/MERCURY/Report/GMA-report-TOC.htm. Accessed 30 Jan 2014

UNEP (2013) Minamata Convention Agreed by Nations. Global Mercury Agreement to Lift Health Threats from Lives of Millions World-Wide Global Mercury Assessment. Geneva, Switzerland

USEPA (2007) Mercury, elemental reference concentration for chronic inhalation exposure (RfC). http://www.epa.gov/teach/chem_summ/mercury_elem_summary.pdf. Accessed 30 Jan 2014

WHO (2000) Air quality guidelines for Europe. Second edition. European Series, vol. 91. WHO Regional Publications. 9 pp. http://www.euro.who.int/__data/assets/pdf_file/0005/74732/E71922.pdf. Accessed 30 Jan 2014