2009-2017 TRENDS OF PM10 ~~AIR QUALITY~~ IN THE LEGENDARY RIOTINTO MINING DISTRICT OF SW SPAIN

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ABSTRACT

This study is the first to perform a chemical characterization and source contribution of particulate matter (PM_{10}) occurring through the abandonment and reopening of a historical sulphide mine. This long-range analysis covers the period 2009–2017 in the Riotinto mining district (Iberian Pyrite Belt, Southwestern Spain), which is a mining district of world-class importance. This mine represents a susceptible anthropogenic emission source of toxic sulphide-associated elements in atmospheric particulate matter, which affects the air quality of the nearby areas. A total of 567 samples of 24 h were collected from 2009 to 2017 in a rural station. The filters were analysed to determined Organic and elemental carbon, mayor and trace elements and water soluble compounds of PM_{10}.

The trends of PM_{10} and geochemical characterisation were studied considering the following periods: mine abandonment (2009–2014) and the mine's state during (2015–2016) and after (2017) implementation of new emission abatement technology at this mine. The results revealed relatively high concentrations of Cu, Zn, Pb, As, Sb, and Bi during 2015–2016. A reduction of 42–59% was observed after 2017 for the same elements in PM_{10}. Five sources were identified: regional, mining, aged sea salt, combustion + traffic and crustal, using Positive Matrix Factorization Model (PMF5). The contribution of the mining factor was higher in the reopening period (4.2 μg m^{-3}, 16%). These results have been confirmed by As speciation analysis, in which the low extraction percentage obtained is related to the origin of the metalloids associated with sulphide ores.

The reduction of emissions of atmospheric particulate matter in the mining processes is the main objective in the implementation of measures considering the technological progress for cleaner and sustainable mining. In the case of reopening of historical mines, with low ore grade and greater extraction of ore and rock, a major effort must be made in order to avoid a negative influence on the environment and human health.

Keywords: Air quality, PM_{10}, arsenic, metals, mine

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1. Introduction

Mining activity and mainly open pit operations are considered the major sources of particulate emission to atmosphere (Nriagu and Pacyna, 1988), highlighting the operations of exploitation, transport, abandonment of mining and waste accident in coal, and metallic and no metallic ore (Table S1). Fugitive atmospheric particles matter (APM) exert a considerable influence on the concentration, toxicity (Bell et al., 2001; Plumlee and Morman, 2011) and the human health (Magas et al., 2007; Wild et al., 2009; WHO, 2013, Patra et al., 2016) (Table S1). These APM inside open mine regions show high levels of heavy metals and metalloids (Tsai and Cheng, 2004; Park and Kim, 2005) that can be transported to near areas, which affects the quality of air and human health Recently, Csavina et al. (2012) considered the transport of heavy metals and metalloids by APM to be an important pathway for their redistribution in the environment. Hence, these pollutants can reach long distances before being finally deposited on the ground or inhaled (Rasmussen, 1998; Zota et al., 2009; Wai et al., 2016). However, studies on the dispersion of metals and metalloids in APM with mining activities are scarce, although the associated environmental and health risks are known (Brotons et al., 2010; Taylor et al., 2010; Csavina et al., 2011, Table S1).

Mining of Cu resources are taking high relevance in the current world due to the depletion of mineral resources and economic growth (Valenta et al., 2019). The reopening of metallic historical mining with low ore grade implies a greater extraction, movement and treatment of ore and rock (Lagos et al. 2018), and in consequence, a negative influence on the environment (Valenta et al. 2019).

~~In this work, we study a chemical characterization and source contribution of PM_{10} occurring through the abandonment and reopening of the Riotinto historical sulphide mine, one of the more important open pit Cu mines of Europe.~~

In the last decade, in the Iberian Pyrite Belt (SW Iberian Peninsula), a resurgence of metallic mining has occurred owing to increases in prices, especially for Cu, which favours the opening of new mines (e.g. Cobre las Cruces Mine) or reopening of other legendary ones such as the Riotinto mining district.

Relevant geochemical anomalies of APM related to mining processes in Las Cruces Mine, Seville province, has been interpreted in Sánchez de la Campa et al. (2015). They found higher concentrations of Cu and As than those in other urban and rural Spanish areas in which high concentrations of As, Se, Bi, Cd, and Pb have been described. However, arsenic speciation studies in PM_{10} have established differences in its contribution, in which the average extraction efficiency of As in PM_{10} samples depends on the origin of the APM.

In Riotinto, past mining, mineral processing, and smelting industries have generated great amounts of hazardous mining residues from its exploitation since pre-Roman times. Recently, the levels and chemical compositions of PM_{10} (particles with aerodynamic diameter below or equal to 10 μm) and depositional particles in this area have been defined by Sánchez de la Campa et al. (2011) and Castillo et al. (2013), respectively.

In this work, we study a chemical characterization and source contribution of PM_{10} occurring through the abandonment and reopening of the Riotinto historical mine, one of the more important open pit Cu mines of Europe. Our study focuses on the trend evolution of PM_{10} and sulphide-associated elements concentrations regarding the monitoring of fugitive emission implemented at a Cu mine in the Riotinto mining district, SW Spain. The concentration of tracer elements such as As, Pb, and Zn occurring through mining activity has been determined in PM_{10} during the period 2009–2017 in Nerva town, a rural zone located near the open pit. For trend analyses, three periods have been distinguished: mine abandonment (2009–2014) and during (2015–2016) and after (2017) the implementation of emission abatement technology at the Cu mine. The As speciation analysis as well as the extraction percentage obtained will permit knowledge the origin of As associate sulphide ores in PM_{10}. The toxicity of As is dependent on its chemical form, oxidation state, and physical state of gas versus in solution (Pershagen et al., 1982; Viraraghavan et al., 1992). The reduction of emissions of APM in the mining processes is a main objective in the application of measures considering the technological progress for cleaner and sustainable mining.

2. Material and methods

2.1. The study area

The Riotinto mining district is one of the world's principal sulphide geochemical anomalies (Fig. 1) (Leistel et al., 1998). This region is of great historic interest and is considered as one of the largest volcanogenic massive sulphide outcrops worldwide, which has been exploited dating back to pre-Roman times (Davis et al., 2000). Its intense activity has been reflected in the notable environmental degradation of the area (Galán et al., 2003; Lottermoser, 2010). Mining operation in this district ceased in 2001 owing to low Cu prices. In 2015, a new mining project began with an initial production of 5 Mt per year in the pre-activity stage, evolving to 9.5 Mt per year in the full operational stage. During the mining inactivity period, the impacts of the fugitive particles and emissions in the air were minimal but were clearly identified (Sánchez de la Campa et al., 2011; Sánchez de la Campa et al., 2015).

The location of the sample monitoring station for PM_{10} and a panoramic view of the waste mining area during the inactive and operational mining periods are shown in Fig. 1. The predominant wind directions for the study period 2009–2017 was NNE and W~~SW~~. These results are indicated in the wind rose diagram inset in Fig. 1.

2.2. Cu concentrate production at Atalaya mining project

In 2015, the historic mine of Riotinto has returned to activity through the Atalaya Mining Project in the Cerro Colorado area (Fig. 1). During mining activity, the extracted mineral is processed by crushing, grinding, and flotation to obtain Cu concentrate as the final product. During the primary crushing process, the ore is reduced to a size of 165 mm. This mineral is then stored in the 'coarse warehouse' and is later transported to the secondary and tertiary crushing circuit. During the first phase of this process, the material is screened to a size of approximately 16 mm and is later transferred to the 'fine warehouse'. Here, a primary mill reduces the mineral to its final size up to 1.5 mm. The mineral is later subjected to a series of cyclones that classifies the material by gravity in which the finer sizes overflow and pass to the flotation area, and the coarser sizes are moved to additional stages of grinding. From this process a fine dust of less than 160 µm is obtained, which is mixed with water and pumped to the flotation area, where physical–chemical processes are used to recover the metallic content.

The Atalaya mining project reached a production capacity of 9.5 Mt of ore per year at the end of 2016, aided by an important process of modernisation of the metallurgical facilities, particularly in the construction of new grinding and flotation areas. The operation of the mining–metallurgical Atalaya project is estimated to be about 16 years.

The main control operations on air quality are related to the implementation of emission abatement technology of fugitive particles into the atmosphere. These consist of implementing irrigation, adaptation, and regeneration of tailings and planning of operations using atmospheric dispersion models to minimise the impact of APM on the surrounding population (personal communication, Atalaya mining).

2.3. Experimental methods

The period considered in this study was from 2009 to 2017. PM_{10} samples were collected by using a high-volume sampler (MCV CAV-PM1025 model, 30 m^3 h^{-1}, UNE-EN 12341:2015) equipped with PM_{10} inlets installed on the roof of the Nerva town hall building, located about 1 km from the mine. Quartz filters (Munktell) were used for the collection of PM_{10}. Samples were collected for 24 h with a frequency of one filter every four days during the sampling period from 2009 to 2010. From 2011 to 2017, the frequency was one sample per week. Five samples collected in the La Dehesa site (see Fig. 1) during intensive campaign of one month (from 29 August to 29 September 2016) has been included in this study in order to comparison to As speciation results with the obtains in Nerva station.

The mass concentrations of PM_{10} were obtained by weighing the filters, using a Sartorius LA130 S-F balance with 0.1 mg sensitivity and using standard procedures of at 50% and 20 °C relative humidity and temperature, respectively. Afterwards, the half fraction of each of filter was digested in an acid solution with 2.5 ml HNO_3: 5 ml HF: 2.5 ml $HClO_4$, which was modified after the methodology reported by Querol et al. (2001). Analytical techniques such as Inductively coupled plasma optical emission spectrometry (ICP-OES; Jobin Yvon model ULTIMA2) was used for determination of major elements (Al,

Ca, K, Na, Mg, Fe, Ti, and Mn), and ICP-mass spectrometry (MS; Hewlett-Packard HP4500 and Agilent model 7700) was used to determination trace elements (Li, Be, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Cd, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ta, W, Tl, Pb, Bi, Th, and U). The mean precision and the accuracy for most of the studied elements were in the range of 5–10% and were controlled by repeated analysis of NBS-1663a and NBS-1663b (fly ash) reference materials. The detection limit (DL) for most of elements in solution was 0.01 ppb.

The soluble fraction of a one-quarter part of each filter was extracted with Milli-Q grade deionised water at 60 °C. After leaching, the content of major anions (SO_4^{2-}, NO_3^-, and Cl^-) and NH_4^+ in the leachates was determined by ion chromatography (Dionex DX-120; Methrom 883 Basic IC Plus) (Querol et al., 2002). Finally, during the period 2009–2013, a circular section punch 25 mm in diameter for each filter was employed to determine the total carbon (C_{total}) content using an elemental analyser (LECO SC-144 DR equipment). From 2014 to 2017, a section of 1.5 cm^2 punch of each filter was analysed to determine the concentration of organic carbon (OC) and elemental carbon (EC) by a using thermal–optical transmission (TOT) technique employing an OC–EC analyser (Sunset Laboratory) with EUSAAR_2 temperature protocol.

The detection limit for C_{total}, calculated on repetitive analysis of 10 blanks, was 0.4 µg cm^{-2} per section of filter. The accuracy and precision of the TOT technique were below 5% and were determined after repeated analyses of standards of known concentration (sucrose 99.9% reagent grade; 42.1 µg cm^{-2}).

Speciation analysis of As (arsenite As(III) and arsenate As(V)) was performed by high performance liquid chromatography coupled with hydride generation and atomic fluorescence spectrometry (HPLC–HG–AFS) according to a methodology proposed for As speciation in APM (Oliveira et al., 2005; Sánchez-Rodas et al., 2007; Sánchez de la Campa et al., 2008). The detection limits obtained were 0.1 ng m^{-3} for As(III) and 0.4 ng m^{-3} for As(V).

To determine the temporal trend in the pollutant concentrations during the period 2009–2017, the Theil–Sen function included in the R programming language and its openair package for statistical analysis (Carslaw and Ropkins , 2012a; 2012b) was used considering the concentrations and chemical composition of PM_{10} per day. A nonparametric Mann–Kendall test for the trend was applied by characterisation of the temporal trend analysis. The significance is represented by p. The symbols shown next to each trend estimated its statistical significance such that $p < 0.001$ = ***, $p < 0.01$ = **, $p < 0.05$ = *, and $p < 0.1$ = +.

3. Results and discussion

The mean concentrations and chemical composition of PM_{10} from 2009 to 2017 are shown in Table 1 considering the three periods established in this study: prior to abandonment and during and after the implementation of emission abatement technology. To describe and evaluate the statistically significant trends of all periods, the

long-terms trend of PM_{10} and its components were assessed by using the Theil–Sen approach (Table 1).

3.1. Mean PM_{10} and chemical composition

The mean concentrations of PM_{10} for the three study periods were highly similar, between 26 and 27 μg m^{-3} (Table 1). These values are lower than the annual limit of 40 μg m^{-3} established in the European Air Quality Directive (2008/50/EC) but are above the 19–21 μg m^{-3} range reported for PM_{10} at rural monitoring stations in Spain (Querol et al., 2004; Querol et al., 2008). However, no exceedance of the daily limit value, at 50 μg m^{-3} (2008/50/EC) has been reported.

The concentrations of sulphide-associated elements such as Ti, Cu, Zn, As, Sn, Sb, Pb, and Bi as well as those of other elements and compounds are also summarised in Table 1 for the three periods established in this study. Overall, our results reveal that the highest mean concentrations for sulphide-associated elements were found during the initiation of mining activities, more specifically in 2016, at 62.4 ng m^{-3}, 25.3 ng m^{-3}, 49.1 ng m^{-3}, 4.47 ng m^{-3}, 0.78 ng m^{-3}, 1.31 ng m^{-3}, 11.5 ng m^{-3}, 0,39 ng m^{-3} for Ti, Cu, Zn, As, Sn, Sb, Pb, and Bi, respectively. It should be noted that the mean concentrations for this period do not exceed the 2008/50/EC target values of 6 ng m^{-3} for As and 500 ng m^{-3} for Pb. A concentration reduction of 13–57% was obtained in 2017 for these sulphide-associated elements after implementation of the current emission controls. The abetment techniques consist of irrigation, adaptation, and regeneration of tailings as well as planning of operations using atmospheric dispersion models. The concentration reductions, calculated from the data in Table 1, are Bi: 59%; Zn: 57%; As: 56%; Pb: 47%; Sb: 46%; and Cu: 42%. The lowest percentages were found for Sn and Ti, at 19% and 13%, respectively. Sánchez de la Campa et al. (2015) reported that the annual mean concentrations of these elements in Gerena, a town near the mining areas of the Iberian Pyrite Belt, were higher than in Nerva, highlighting the case of Cu, at 49.8 ng m^{-3}. Similar concentrations were found for Ti: 43.9 ng m^{-3}; Zn: 29.9 ng m^{-3}; As: 1.52 ng m^{-3}; Sn: 1.06 ng m^{-3}; Sb: 0.61 ng m^{-3}; Pb: 7.02 ng m^{-3}; and Bi: 0.26 ng m^{-3}.

The relatively high and similar concentrations found for C_{total}, K, and Cl^- during the three study periods are comparable to the values described by Sánchez de la Campa et al. (2011). This similar distribution can be associated to the influence of additional biomass burning sources.

3.2. Inter-annual variations

The analysed data were studied by using the Mann-Kendall test and the Theil–Sen algorithm. The trend estimate and statistical significance are shown in Table 1. The results show a representative rising trend in the annual average concentrations of sulphide-associated elements such as Ti, Mn, Cu, Zn, Mo Ba, Zr, and Pb. In addition, a representative increasing trend in the annual mean concentrations of SiO_2 and Al_2O_3 was observed. The rest of the elements and compounds did not present a clear trend estimate. High statistical significance ($p < 0.001$) was found for K, Fe, PO_4^{3-}, Li, Be, Sc,

As, Y, Zr, Sb, Hf, Tl, and Th, and lower statistical significance values ($p < 0.01$ and $p < 0.05$) were obtained for SiO_2, Al_2O_3, Mn, Co, Cu, Mo, Cs, U, Mg, NH_4^+, Ti, Cr, Ga, Ge, Se, Rb, Nb, La, Ce, and Pb. The lowest significance ($p < 0.1$) corresponds to Sr. No statistical significance was observed for the remaining elements and compounds.

Seasonal variation was observed for the concentration of some sulphide-associated elements in PM_{10}. A smooth trend with a 96% confidence interval was performed, as shown in Fig. 2. The maximum concentrations of Cu, As, Bi, Pb, and Sb were always found in summer during the 2015–2016 period. In addition, high concentrations of these elements were found in autumn during the same period. These maximum concentrations are related to the reopening of the Atalaya mine in 2015–2016, which is coincident with this same period. In winter, increases in the sulphide-associated elements were not observed owing to the high frequency of Atlantic mass and precipitation registered during this season of the year.

3.3. Source contribution of PM_{10}

Positive matrix factorisation was performed on the dataset recorded from 2009 to 2017 in Nerva. The results obtained during the three periods considered in this study were also included, with the following five factors identified (Fig. 3).

- F1 (regional) is characterised by NH_4^+, SO_4^{2-}, and NO_3^-. V, Ni, and Zn have also been identified in this source. The ions are associated with secondary aerosols. The presence of Ni, V, and Zn was affected by industrial combustion of fossil fuel (Viana et al., 2008). The annual maximum contributions were 4.7 μg m^{-3} 2009 and 2010 and 4.4 μg m^{-3} in 2016 (Fig. 4). A seasonal variation was observed, highlighting the maximum concentration of this source during summer (Fig. 3). The highest levels of solar radiation were relevant during this period. The F1 source accounted for 15% of the PM_{10} mass, at 3.7 μg m^{-3}.

- F2 (mining) has a chemical profile similar to that of raw material extracted from Atalaya mine, which is defined mainly by Bi, Cu, As, Sb, Pb, and Zn. This chemical profile is similar to that described in the industrial estate located near the city of Huelva (Pb, As, Cu, Cd, Sn, Zn and PO_4^{3-}, Alastuey et al., 2006), as well as the Riotinto mine Sánchez de la Campa et al., 2011) and the Cobre las Cruces mine (Sánchez de la Campa et al., 2015). The contribution of the F2 source was less than 1 μg m^{-3} between 2009 and 2014, which is related to inactivity of the mining–metallurgical operation of Atalaya mine. The maximum contribution, at 4.2 μg m^{-3}, was observed in 2016 related to the start of the extraction activity followed by a decrease to 2.6 μg m^{-3} in 2017 related to the implementation of emission abatement technology (Fig. 4). The F2 source accounted for 7% of the PM_{10} mass, at 1.7 μg m^{-3}.

- F3 (aged sea salt) is characterised by elements related to the mixing of marine aerosols such as Na, Cl^-, and Mg with elements of ship emission affinity such as NO_3^- and SO_4^{2-} (Viana et al., 2014). The maximum contribution of F3 was 5.4 μg

m^{-3} in 2013 and, and the value was constant at 3.4–4.5 μg m^{-3} during the rest of the study period (Fig. 4). The minimum contribution of 2.2 μg m^{-3} was obtained in 2011. The marine aerosol did not show a clear seasonal pattern (Fig. 3). This source accounted for 16% of the PM_{10} mass, at 4.0 μg m^{-3}.

- F4 (combustion + traffic) contains K, C_{total}, and NH_4^+ as well as NO_3^- Cr, Zn, and Pb. Major elements and compounds such as C_{total}, K, and NO_3^- are associated with both sources, whereas the presence of trace metals such as Cr, Zn, and Pb are representative of traffic emissions. The temporal variation of this factor displayed high concentrations during winter (Fig. 3). It should be noted that in Nerva and its nearby areas, wood burning in fireplaces is the main biomass burning source. The annual distribution of this source was constant during the entire period at 7.5–8.5 μg m^{-3}. However, a peak concentration of 10.5 μg m^{-3} was characterised in 2011 (Fig. 4). The F4 source accounted for 32% of the PM_{10} mass, at 8.1 μg m^{-3}.

- F5 (crustal) is constituted by elements related to the resuspension of crustal material and soil dust such as Al, Ca, K, Mg, Fe, Rb, Sr, Li, and La. The highest contributions of this source were recorded in summer, a period characterised by the minimum rainfall levels along the year and by the increase in the frequency of Saharan dust outbreaks (Rodríguez et al., 2001) (Fig. 3). In February 2016, a relevant episode of Saharan dust outbreak was registered. Two major trends were found: one between 2009 and 2015, at 4.4–8.8 μgm^3, and another between 2016 and 2017, at 9.9–10.1 μg m^{-3} (Fig. 4). The increases in this source during the last period are clearly related to fugitive particle emissions from mining activities. The F5 source accounted for 31% of the PM_{10} mass, at 7.7 μg m^{-3}.

3.4. Speciation of As in particulate matter during 2015–2017

~~The toxicity of As is dependent on its chemical form, oxidation state, and physical state of gas versus in solution (Pershagen et al., 1982; Viraraghavan et al., 1992).~~ Therefore, a speciation study considering inorganic As species was performed using selected samples of PM_{10} from Nerva and La Dehesa containing high As concentrations of more than 4 ng m^{-3}. Previous results obtained from 2016 at La Dehesa, located in the vicinity of the Atalaya mine (Fig. 1), prior to implementation of emission abatement technology are included for comparison in Table 2.

To clarify the industrial origin and mining sources of As, the results of inorganic As(III) and As(V) identified by Sánchez-Rodas et al. (2007) and Sánchez de la Campa et al. (2015) were also considered in this study (Table 2). The results show that As(V) was always the main As species at all sampling sites, accounting for >90% of the total As content of the samples. However, the percentages of the extraction differed, at 30% in Cobre las Cruces Mine, 11–12% in this study, and 95% in Huelva. Similar values obtained in La Dehesa, at 12%, and Nerva, at 11%, indicate that the As originated from the same emission source. The low percentage of extraction obtained from Nerva and

La Dehesa rural sites is related to the insoluble nature of the ore extracted in the mine, as a sulphide of Cu–Fe. However, the mean extraction efficiency of the samples obtained from Cobre las Cruces Mine was higher, at about 30%. This difference in extraction efficiency between Nerva and La Dehesa and the Las Cruces mine indicates different mineralogical compositions of the extraction ore of both mines, specifically sulphide of primary origin in pyrite, chalcopyrite, sphalerite, and arsenopyrite in the Atalaya mine and that of secondary origin in covelline in the Las Cruces mine (Sánchez de la Campa et al. (2015). On the contrary, the high extraction percentage in Huelva is related to the oxidation of sulphides in the pyrometallurgy process of the Cu smelter (Sánchez de la Campa et al., 2018; Sánchez-Rodas et al., 2007).

4. Conclusions

Geochemical anomalies in toxic sulphide-associated elements in PM_{10} have been identified in the case of the historical Riotinto mine (Iberian Pyrite Belt, Spain) during 2009–2017. In the abandoned mine period (2009–2014), low concentrations of sulphide-associated elements and PM_{10} were found (abandoned period: Cu: ng/m3, Zn ng/m3 ,Pb ng/m3 y As ng/m3; active mining: Cu ng/m3 Zn ng/m3 Pb ng/m3 y As ng/m3) . In the periods of reopening and prior to implementation of emission abatement technology, a twofold increase in the concentrations of these elements was observed in 2016, followed by a decrease of 42–59% in 2017.

A seasonal trend was observed for sulphide-associated elements concentrations, with maximum levels occurring mainly in summer associated with sea breezes and North African dust outbreaks, which were more frequent along this period. The minimum concentrations were registered in winter in association with high rainfall and greater frequency of Atlantic front input.

The source contribution analysis using PMF5 has revealed as the mining factor was higher in the reopening period (4.2 μg m^{-3}, 16%) compared with the abandoned period (1 μg m^{-3}). Finally, the As speciation analysis in the study area indicated that As is mostly present as As(V), at >90% compared with As(III). The low percentage of the extraction obtained during speciation analysis, at 11–12% clearly denotes the association of As and sulphides.

The emission abatement technology of fugitive particles into the atmosphere were effectives in order to minimise the impact of APM on the surrounding population. They consist of implementing irrigation, adaptation, and regeneration of tailings and planning of operations using atmospheric dispersion models.

This study has documented as the implementation of the best abatement technologies in historical mines with low ore grade and greater treatment of ore and rock, need a major effort in order to avoid a negative influence on the air quality.

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Figure captions

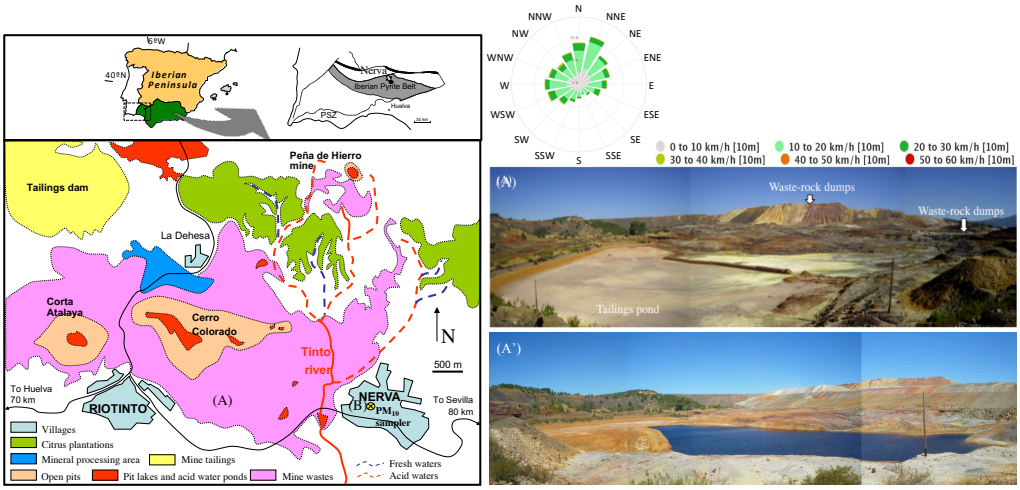

Fig. 1. Map of the Riotinto Mining District and location of the PM_{10} sampler in Nerva. (A–A′) Panoramic view of the Riotinto mining area showing tailings and waste-rock dumps prior to and during the mine reopening.

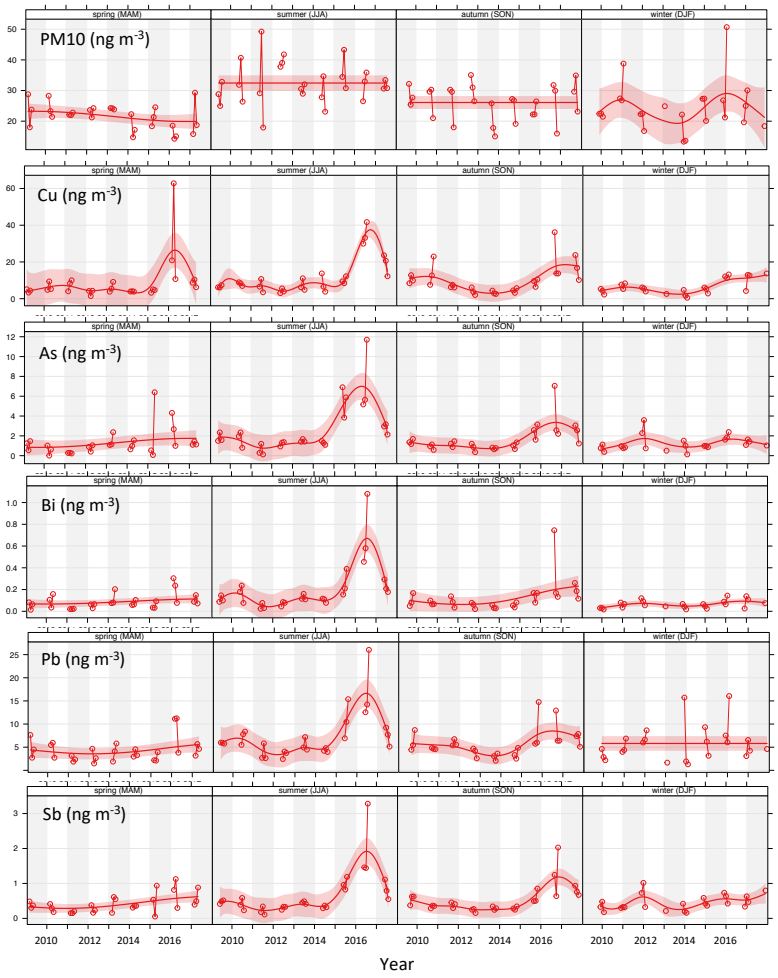

Fig. 2. Seasonal variation of PM_{10} and sulphide-associated elements (Cu, As, Bi, Pb and Sb) for the period 2009–2017. Dots correspond to monthly mean concentrations. The solid lines and bands stand for the smooth trend with a 95% confidence interval. Spring (MAM): March, April, May; Summer (JJA): June, July, August; Autumn (SON): September, October, November.

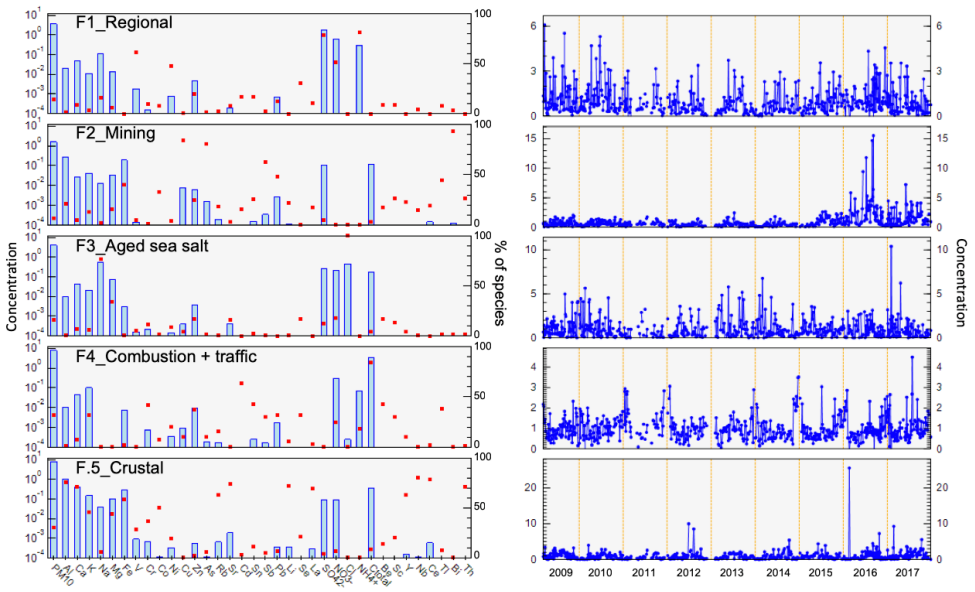

Fig. 3. Source profiles (left panels) and temporal evolutions (right panels) of contributions of primary factors.

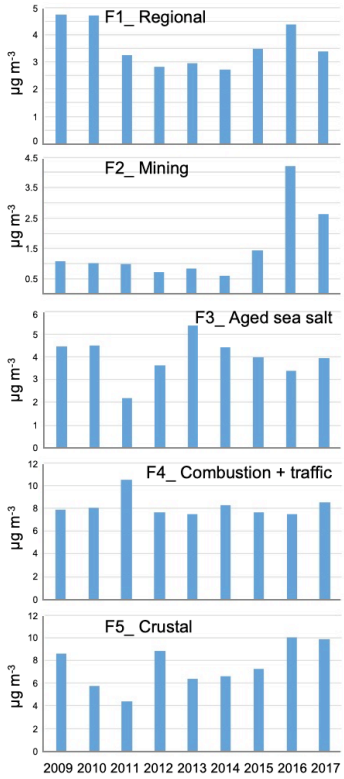

Fig. 4. Source contribution registered in each year at Nerva station.

Table 1.

Mean concentrations of PM (μg m^{-3}) and sulphide-associated elements (ng m^{-3}) in PM_{10}, showing differences in three periods of mine abandonment and during and after emission abatement technology implementation at the Cu mine in 2009–2017. The trend estimate and statistical significance are p < 0.001 = ***, p < 0.01 = **, p < 0.05 = *, and p < 0.1 = +.

Sampling period	Abandonment mine **2009-2014**	During **2015**	**2016**	After **2017**	**Trend estimate (μg m-3 • year-1)**	**Statistical Significance**
μg m^{-3}	mean	mean	mean	mean		
nº filters	348	59	80	80		
PM_{10}	26	27	27	27	-0,15	
C_{total}	4,12	3,67	4,27	4,60	0,1	
C org*	3,82	2,15	3,85	4,28		
Cnm*	3,92	1,93	0,43	0,40		
$CO_3^=$	1,32	1,56	1,96	1,68	0,04	
SiO_2	3,19	4,56	6,41	5,55	0,26	**
Al_2O_3	1,06	1,51	2,14	1,85	0,09	**
Ca	0,56	0,64	0,79	0,66	0,01	
K	0,31	0,33	0,45	0,46	0,02	***
Na	0,75	0,69	0,66	0,71	-0,01	
Mg	0,19	0,24	0,31	0,27	0,01	*
Fe	0,37	0,44	0,88	0,74	0,03	***
PO_4^{3-}	0,06	0,06	0,09	0,14	0,01	***
SO_4^{2-}	2,21	2,09	2,92	2,32	0,02	
SO_4^{2-}anthrop.	2,02	1,92	2,76	2,14	0,02	
SO_4^{2-} marine	0,19	0,17	0,17	0,18	0	
NO_3^-	1,34	1,34	2,74	1,39	0	
Cl	0,56	0,50	0,48	0,52	0	
NH_4^+	0,47	0,43	0,48	0,37	-0,01	*
ng/m^3						
Li	0,40	0,47	0,76	0,69	0,04	***
Be	0,01	0,02	0,03	0,03	0	***
Sc	0,09	0,12	0,21	0,22	0,01	***
Ti	35,6	48,4	62,4	54,1	1,87	*
V	2,78	2,85	3,82	3,14	0,06	
Cr	1,83	2,42	2,53	2,03	0,11	*
Mn	8,66	70,0	14,1	14,7	0,71	**
Co	0,19	0,19	0,36	0,32	0,01	**
Ni	1,81	1,32	1,79	3,44	0,04	
Cu	6,10	7,65	25,3	14,8	0,69	**
Zn	23,2	21,7	49,1	21,1	0,34	
Ga	0,47	0,17	0,35	0,30	-0,02	*
Ge	0,05	0,03	0,06	0,16	0	*
As	1,12	2,98	4,47	1,97	0,13	***
Se	0,34	0,22	0,13	0,13	-0,01	*
Rb	0,95	0,99	1,53	1,33	0,04	*
Sr	2,27	2,39	3,33	2,82	0,08	+
Y	0,20	0,19	0,41	0,40	0,02	***
Zr	1,56	2,11	4,19	7,44	0,31	***
Nb	0,11	0,10	0,20	0,22	0,01	*
Mo	3,27	4,83	5,54	5,80	0,34	**
Cd	0,14	0,13	0,15	0,23	0	
Sn	0,59	0,60	0,78	0,63	0	
Sb	0,36	0,67	1,31	0,70	0,05	***
Cs	0,05	0,05	0,09	0,08	0	**
Ba	13,0	11,9	24,1	12,4	0,33	
La	0,35	0,37	0,65	0,52	0,02	*
Ce	0,62	0,66	1,19	1,02	0,04	*
Lu	0,01	0,01	0,01	0,01	0	
Hf	0,07	0,08	0,19	0,29	0,01	***
Ta	0,01	0,01	0,01	0,02	0	
W	0,03	0,07	0,04	0,11	0	
Tl	0,03	0,03	0,06	0,03	0	***
Pb	4,75	7,20	11,5	6,12	0,22	*
Bi	0,08	0,13	0,39	0,16	0,01	***
Th	0,09	0,10	0,17	0,17	0,01	***
U	0,04	0,04	0,08	0,08	0	**

C org* and Cnm* in NERVA 2014, 2015, 2016 and 2017 are replaced by the OC and EC analyses.

Table 2.

Total As concentration, As species, and percentage of As extraction in PM_{10} samples collected in 2016 from Nerva and La Dehesa. Data of Huelva, Gerena, and Cobre las Cruces Mine are included for comparison. The results expressed as ng m^{-3} (mean ± standard deviation). N indicates the number of samples.

Sampling site	*N*	Astotal[a]	As(III)[b]	As(V)[b]	% Extraction	Reference
Huelva	22	16.4 ± 11.7	0.4 ± 0.3	14.9 ± 13.1	94 ± 19	Sánchez Rodas et al. (2007)
Cobre las Cruces Mine	23	36.2 ± 25.6	0.3 ± 4.3	8.5 ± 4.3	30 ± 15	Sánchez de la Campa et al. (2015)
La Dehesa	5	25.3 ± 10.7	0.3 ± 0.1	2.5 ± 1.1	12 ± 4.5	This study
Nerva	1	43.4	0.4	4.2	11	

[a] As_{total} calculated after acid digestion and determination by ICP-MS.
[b] As(III) and As(V) calculated after liquid extraction and determination by HPLC-HG-AFS.

SUPPLEMENTARY DATA

Article title:
2009-2017 TRENDS OF AIR QUALITY IN THE LEGENDARY RIOTINTO MINING DISTRICT OF SW SPAIN

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Table S1. Case studies according to mineral exploitation, transport, abandoned mine, mining waste accidents and bioaccesibility and health risk, related to air quality and coal, metallic and no-metallic ore mining.

	Coal	Metallic ore	no metallic ore
Exploitation	India (Ghose and Majee, 2000) Wales (Jones et al., 2002) India (Chaulya 2004., 2005) Turkey (Onder and Yigit., 2009) Colombia (Huertas et al., 2012a; 2012b) Australia (Richardson et al., 2019)	Ni-Cu, Bostwana (Ekosse., 2004 Cu, Marocco (El Khalil et al., 2008) Sb, China (Zhang et al., 2008) Cu, Mexico (Meza-Figueroa et al., 2009) As, China (Zhao et al., 2019) Au-Ag-Pb-Zn-Cu, Australia (Schneider et al. 2019)	Hg-Sb, China (Ao et al. 2019., 2020) Diamand, Canada (Liberda et al., 2015) Limestone, China (Peng et al., 2016)
Transport	Appalachia, USA (Aneja et al., 2012)	Fe, India (Sinha et al., 1997) Au, Nevada, USA (McDonald et al., 2003) Fe, Australia (Hinwood et al., 2014)	---
Abandonment of mining	S Africa (Bell et al., 2001)	Au, Canada (Wong et al., 1999) Pb-Cu-Zn, Germany (Kempter and Frenzel., 2000) Au, Spain (Moreno et al., 2007) Pb-Zn, Oklaoma (Zota et al., 2009) Cu, Spain (Sánchez de la Campa et al., 2011) Ag-Sn, Bolivia (Fontúrbel et al., 2011) Fe-Cu-Pb-Zn-Ag, Italy (Comero et al., 2012) Au, Australia (Martín et al., 2017) Pb-Zn-Fe, Spain (Sánchez Bisquert et al., 2017) Pollimetalic, Spain (Blondet et al., 2019)	Hg, Spain (Moreno et al., 2005) Hg, Spain (Loredo et al., 2007)
Mining waste accidents	---	Cu, Spain (Querol et al., 1999, 2000)	---
Bioaccessibility and Health risk	England, Pless-Mulloli et al., (2000) China (Jia., 2015)	Cu, Korea (Kim et al., 2008) Ni, China (Li and Hu., 2018) Pb-Zn-Mn, China (Du et al., 2019) Pb-Cu-Zn-Ag-V, Namibia (Ettler et al., 2019) U, France (Husson et al., 2019) REE, China (Tian et al., 2019)	---

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