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Geochemical anomalies of toxic elements and arsenic speciation in airborne particles from Cu mining and smelting activities: Influence on air quality

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HIGHLIGHTS

- Geochemical anomalies of toxic elements in PM_{10} related to mining have been studied.
- High concentrations of Cu and As have been detected in rural and background stations.
- As speciation explains the low impact of the mining area on the rural surrounding.
- Pyrometallurgic activity produces fine particles which are transported long-distance.

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ABSTRACT

A characterization of chemical composition and source contribution of PM_{10} in three representative environments of southwest Spain related to mining activities (mineral extraction, mining waste and Cu-smelting) has been performed. A study of geochemical anomalies was conducted in the samples collected at the three stations between July 2012 and October 2013. The influence of Cu-smelting processes was compared to other mining activities, where common tracers were identified. The Cu and As concentrations in the study area are higher than in other rural and urban stations of Spain, in which geochemical anomalies of As, Se, Bi, Cd, and Pb have been reported.

The results of source contribution showed similar geochemical signatures in the industrial and mining factors. However, the contribution to PM_{10} is different according to the type of industrial activity. These results have been confirmed performing an arsenic speciation analysis of the PM_{10} samples, in which the mean extraction efficiency of arsenic depended on the origin of the samples. These finding indicate that the atmospheric particulate matter emitted from Cu-smelting has a high residence time in the atmosphere. This indicates that the Cu-smelter can impact areas of high ecological interest and considered as clean air.

1. Introduction

Atmospheric particulate matter (APM) presents a complex geochemical composition with a multiple origin [1]. Anthropogenic emissions of APM are generally less relevant than the natural sources [2], but they can represent the input of high concentrations of toxic elements (e.g., Cu, Zn, Cd, Pb, As and Se) in the air. This is especially important in the case of industrial activities, such as mining and smelting [3,4].

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The search for mineral raw materials containing strategic elements has increased in recent years. One of the most relevant elements is Cu, associated to massive and hydrothermal sulphides. Operations related to mining activities can affect the air quality. Exploration, extraction [5] and transport of mineral ore by trucks [6] generate elevated concentrations of coarse particles enriched in toxic elements and may impact negatively on human settlements near mining centers.

Abandonment of mining operations generates large of uncontrolled solid or liquid mining waste (several thousand million tons per year worldwide) [7]. Fine particles from tailing suffer resuspension and are dispersed around mining abandoned zones. In this case, the impact of deposition particles [8,9] is more important than respirable particles [10–12]. Particles derived from mining operations can be incorporated in household dust, affecting children [13]. Moreover, the transport of mining wastes during reclamation after accident of mining tailings dams, incorporate high concentrations of toxic elements in coarse particles (e.g., Aznalcollar Mine accident in 1998) [14].

Cu-smelters based on pyrometallurgic processes are the most important emissions sources of fine and ultrafine size APM, with high concentration of Cu, As, Zn, Cd and Pb, among others [15–18]. These pollutants can impact on soils, plants and animals, and affect the human health. Several epidemiological studies have evaluated the exposure to ambient air pollution near smelters for cancer risk [19].

In most mining centers all the operations are concentrated in the same place, being difficult to quantify the apportionment of every source of impact in the APM. In the present work we have the opportunity to quantify the contribution of three main sources mining activity, separated by around 100 km distance between them. Therefore, we present the results of a chemical characterization in PM_{10} in three relevant localities of southwest of Spain and the Riotinto Mining District, related to Cu mineral extraction (Las Cruces Mine), Cu-smelting (Huelva city) and historic abandonment of mining waste (Nerva), from July 2012 to October 2013. The main objective is to characterize geochemical anomalies in toxic elements and As speciation in APM, and its influence areas.

2. Material and methods

2.1. The study area

The Iberian Pyrite Belt (IPB) is a mineralized Late Paleozoic mega-belt composed by volcanogenic massive sulphides, located in southwest Spain [20]. Containing around 250 Mt of pollimetalic sulphides, is considered as one of the most important deposits in the World [21].

In the northern sector of IPB, the Riotinto Mining District is composed by several bodies of massive sulphide deposits, exploited since Roman times. Today is relevant the negative environmental heritage and degradation resulting of several centuries of exploitation. Several open pits have generated an important volume of mining waste with toxic elements, draining low-pH water to streams and Tinto and Odiel Rivers [22].

Las Cruces Mine is located in the eastern part of IBP, where the mineralization is covered by Neogene sediments of the Guadalquivir Valley [21]. This open pit mine is near the city of Seville (around 10 km), where the main ore extracted contains covelline with an average of 6.2% of Cu. The mineral ore is submitted to the typical mechanical operations (mining transport, crushing and grinding), that are responsible for the emission of particulate matter, mainly in the coarse fraction. Hydrometallurgy technology is used for transformation of ore into Cu-cathodes, involving some advantages compared to pyrometallurgical processes: (a) inhibits the generation of SO_2; and (b) provides a better recuperation metal (over 90%) with respect to conventional technology of flotation, producing Cu cathodes of high quality (grade A″: 99,9935% Cu). Recently, supergene enrichment has been studied in order to characterize Au–Ag–Hg [23], originated by subsurface microbial activity [24].

Today, metallic mining is considered as a major shake-economic area due to the opening of some mines in the southwest of Spain (e.g., Aguas Teñidas and Las Cruces Mines). However, mining activities produce a deep environmental impact on the ecosystems and on the human health of the population living near the mines.

The city of Huelva has maintained a relation with mining activities for more than one hundred years. Mineral ore from the Riotinto mining district was exported through its harbor. Also, since de 1960s a Cu-smelter was placed in one of the industrial estates that surround the city. Polymetallic sulphides coming by ship from Asia and South America are transformed using pyrometallurgic smelting methods. Actually, it is the second Cu-smelter in Europe, with a total production of 247,000 t of Cu cathodes (comm. per. Atlantic Copper SLU, 2012). Another relevant industry in Huelva was based on the production of phosphoric acid by the attack of sulphuric acid with phosphorite transported by ship from Western Sahara. Both factories are localized near the city (around 2 km) in a main wind direction (Fig. 1). The sea breeze is considered representative of summertime conditions in the area of Huelva, in which can be linked to the transport of the pollution plume to Huelva and nearby areas [25].

Since 1999, the Autonomous Government of Andalusia develops an Environmental Plan for the city of Huelva, jointly with the National Research Council (CSIC). Several studies have quantified the source contribution of deposition particles [26], TSP (Total Suspended Particles [27], PM_{10}–$PM_{2.5}$ [28–31] and ultrafine particles (<0.1 μm) [18], highlighting as several elements (As, Se, Bi, Cd, Zn, Cu) correspond to the representative geochemical anomalies near the Cu-smelter. Recently, the emission factor of Cu-smelter by size has been characterized [32], demonstrating that toxic elements are emitted in the fine and quasi-ultrafine particles (<0.33 μm). The term quasi-ultrafine has been defined by Minguillón et al. [33] (Dp < 0.25 μm; $PM_{0.25}$).

Several epidemiological works have related environmental factors derived of industrial plumes and mining wastes with high cancer risk [34,35], conforming the so-called "triangle of cancer" between the provinces of Huelva, Seville and Cádiz. Recently, it has been demonstrated as the cognitive behavior of children in primary schools of Huelva is related to a high concentration of Cd [36].

2.2. Experimental methods

One-year strategy sampling period was designed to assess the presence of toxic elements in atmospheric aerosol in the SW of Spain. The selected period was between July 2012 and October 2013, during which one daily sample per week was collected using Munktell® quartz fiber filters. High volume samplers (CAV-A-PM1025, 30 $m^3\ h^{-1}$) equipped with PM_{10} inlets were used in the sampling of APM. Three monitoring stations were selected (Fig. 1):

- Urban background site under the influence of industrial emissions (University Campus monitoring station, CAM). This station belongs to the Air Quality Network of the Department of the Environment of the Autonomous Government of Andalusia. A total of 64 filters were sampled during the study period of July 2012 to July 2013.
- Rural area in the municipality of Nerva (NER) in the Riotinto Mining District. Nerva is localized around of the largest historic mining tailing of the IPB. The high volume sampler was placed on