Geochemical anomalies in aerosol induced by mining and metallurgical activities in SW Spain

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SW Spain, and more specifically the Iberian Pyrite Belt, has been an area of intense mining and metallurgy since Roman times to the present. In the nineteenth century, mineral extraction coexisted with a rudimentary smelters based on so-called "teleras": wood furnaces with polymetallic sulfides burning for weeks.

Anthropogenic emissions can influence negatively on air quality due to SO_2 "clouds" and toxic elements. Subsequently, large smelters were installed, implying an improvement compared to the "teleras", although affecting adversely the air quality of mining towns. In 1970, the 2nd Industrial Development Plan of Spain was developed in the city of Huelva, favoring the placement of a Cu smelter near the town. Today, this Cu smelter is the second most important of Europe, with a total production in 2011 of 247,000 tons of Cu cathodes.

Mining-industrial activity has been referred to explain the high cancer mortality suffered by this region of Spain (Abente Lopez et al., 2006), conforming a "cancer triangle" between the provinces of Cadiz, Seville and Huelva, with extensions towards Extremadura (Benach et al., 2003).

In this work, we present a geochemical study in PM10 during the years 2009 to 2011 in three sampling monitoring stations representative of the **mining area** (Nerva, Rio Tinto Mining District), **urban area with industrial influence** (Campus Universitario del Carmen, Huelva) and **rural background** (Matalascañas, near the Doñana National Park), in order to characterize: 1) the main geochemical anomalies of toxic elements, 2) seasonality, and 3) source contribution.

Normally, mining and smelting operations occur in the same place, and therefore, this study is a good opportunity to quantify the impact from and extension of mining waste resuspension (Sánchez de la Campa et al., 2011a), and compare them with those derived from the smelter (Alastuey et al., 2006; Sánchez de la Campa et al., 2011b) strategy of PM10 implies high volume captors at intervals between 1-2 times every week. The number of filters obtained in each sampling station was 208 at University Campus, 220 and 189 in Nerva (Riotinto Mining District) and Matalascañas (Doñana) respectively. Filters were weighing under standard conditions (T and RH), and they were digested with strong acid according Querol et al. (1996). Furthermore, part of the filter was used to obtain a lixiviated with degree MQ H2O. Subsequently, the samples were analyzed by ICP-MS, ICP-OES, IC and Ctotal Analyzer. The total mass analyzed is between 70-80%.

The results of this study confirm the geochemical anomalies in As, Se, Bi, Cd, and Pb at a Spanish point of view (Querol et al., 2008) and Andalusia (de la Rosa et al., 2010).

Chemical analysis of PM10 near Cu-smelter near Huelva city, demonstrate the important contribution of Cu + Zn + As + Cd + Pb + Sn + Bi in air (Fernández-Camacho et al. 2012). The main emission sources of As are the flash furnace (144 $\mu g/m^3$) and refining furnace (18.75 $\mu g/m^3$). The peak concentration corresponds to a grain size of these particles in the fine (<1 micron) and ultrafine fraction (<0.1 microns) in the flash furnace and the refining furnace, respectively.

We conclude that high temperatures of smelting processes can produce particles of toxic elements (eg As, Se, Bi, Cd and Pb) in the ultra-fine fraction, with high residence-time, allowing long-distance transport, compared with coarse particles derived from mining waste. Therefore, they can impact in ecological zones of high interest (eg Doñana National Park), away Industrial States.

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