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Size distribution and chemical composition of particulate matter stack emissions in and around a copper smelter

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HIGHLIGHTS

- Particle size characterization of Cu-smelter stack emissions has been reported.
- Smelting and refining are the main source of toxic elements in the quasi ultrafine fraction.
- Fugitive emissions represent a significant metal and metalloid contribution.
- Cu-smelter emissions cause increase in ultrafine PN and SO_2 in Huelva city.

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ABSTRACT

This paper reports on results from a multi-sampling campaign (stack, fugitive emissions and ambient air measurements) to characterise the geochemical signature of metal and metalloid particles emitted from one of the largest Cu-smelters in the world (in Huelva, SW Spain). Exceptionally high concentrations of very fine particles (<0.33 μm) bearing As, Cd, Pb, Cu, Bi, Zn ($\sum>100$ μg m^{-3}) are emitted from the Flash Smelting Furnaces, but high levels are also emitted by the other main chimney stacks, namely Refining Furnaces, Sulphuric Plant, Converters Unit, and Crushing Plant. Enhanced concentrations of the same elements are also observed in ground measurements near the industrial complex. During the sampling campaign, the presence of plumes from the Cu-smelter over the nearby city of Huelva was identified based on increased concentrations of gaseous pollutants, particulate metals and ultrafine particle numbers (PN). The results demonstrate that the Cu-smelter is an important source of inhalable toxic elements carried by fine airborne particles. The pollution abatement systems applied so far appear to be relatively ineffective in preventing metalliferous air pollution events, potentially increasing health risks to local and regional populations.

1. Introduction

Copper smelters refine ore to produce the metal to satisfy demands worldwide (Jaunky, 2013). The industry can have significant impact on the environment (e.g. soils, water, vegetation, air) (Savard et al., 2006) due to the high toxicity of the raw material, which is mainly concentrate ore. Smelter emissions are potential sources of airborne metal and metalloid contaminants (Csavina et al., 2011). Smelting uses heat and chemical reducing agents to decompose the ore, driving off other elements as gasses or slag. The primary metal and metalloid constituents of the particulate matter emitted by the smelter are Cu and Fe oxides, although other elements, such as As, Sb, Pb, and Zn may also be emitted into the atmosphere.

Numerous studies around the world have focused on the impact of airborne smelter emissions of metals on the environment (e.g. Martley et al., 2004; Williamson et al., 2004; Pope et al., 2005; Tye et al., 2006; Wong et al., 2006; Zdanowicz et al., 2006; Boyd et al., 2009; Gawel et al., 2014). The enrichment in metals and metalloids (e.g. As, Cd and Pb) of aerosols in smelter plumes represents a risk to human health (Csavina et al., 2011; Kovaĉević et al., 2010;

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Fernández-Camacho et al., 2012). Arsenic in particular is one of the most highly toxic elements released by Cu-smelters (Hedberg et al., 2005). This metalloid is recognized to be carcinogenic by the International Agency for Research on Cancer (2004), causing a variety of cancers (e.g. skin, lung) and other adverse human health effects (Mandal and Suzuki, 2002, Yoshikawa et al., 2008; Ciarroca et al., 2012). Epidemiological studies have focused on the association between environmental exposure to air pollution (emissions of inorganic arsenic, sulphur dioxide and various heavy metals) and lung cancer risk, with indications of an increased risk of lung cancer of population living close to a Cu-smelter (Bessö et al., 2003). Other studies based on occupational exposure have also revealed an increase in relative risk of respiratory cancer for smelter workers in close contact with airborne As (Viren and Silvers, 1999; Lubin et al., 2000). Besides this relationship that exists, we must also take into account the exposure time, as it has been argued that short exposures to high concentrations are more harmful than more prolonged exposures at lower concentrations (Lubin et al., 2008).

This paper focuses on a well documented industrial air pollution region (Huelva, SW Spain) (Querol et al., 2001; Alastuey et al., 2006) where Cu smelting is a significant source of airborne metal and metalloids (e.g. As, Cd, Cu, Zn, Pb, Bi) (Sánchez de la Campa et al., 2011a), with As being the main tracer for its emission plumes (Sanchez-Rodas et al., 2007; Sánchez de la Campa et al., 2008; de la Rosa et al., 2010). Since 2001, when the first chemical speciation of particulate matter was performed in the study area, the mean As concentration in PM_{10} (particles with an aerodynamic diameter of 10 μm or smaller) was higher than the 6 ng m^{-3} target value proposed by the EU as a recommended average value (EU, 2004) during some years (e.g. 10 ng m^{-3} in 2005, 9.9 ng m^{-3} 2006 and 6.6 ng m^{-3} in 2007). The most affected population is the inhabitants of Huelva, a city which lies very close (3 km) to the industry (Fernández-Camacho et al., 2010). However, the smelter emissions may also affect more distant areas (Chen et al., 2012). The probability of significant airborne transport is further enhanced by the high concentration of fine (<2.5 μm) and ultrafine particles (UFP; <0.1 μm) (Fernández-Camacho et al., 2012).

Industrial emissions are the main source of UFP in Huelva city (Fernández-Camacho et al., 2012). The industrial contribution is higher than vehicle exhausts one, the typical UFP source in urban areas (Reche et al., 2011; Rodríguez et al., 2007). An increasing number of studies are showing that industrial sources (e.g. power and steel plants, refineries, smelters) and shipping emissions that release large amounts of gaseous precursors such as SO_2, are potential sources of UFP (Csavina et al., 2011; Silva et al., 2010; González and Rodríguez, 2013; Liu et al., 2013; Martinello et al., 2014). In the case of smelting operations, ultrafine and fine particles result by condensation of high temperature vapours and subsequent diffusion and coagulation (Zdanowicz et al., 2006; Banic et al., 2006). Moreover, UFP have also important implications for human health effects (Sioutas et al., 2005; Knibbs et al., 2011; Araujo, 2011; Kelly and Fussell, 2012; Reche et al., 2014).

In this study a multi-sampling campaign was designed to characterize the size distribution and chemical composition of PM emitted by the different chimney stacks in a Cu-smelter, and to assess the occurrence of potential fugitive emissions around the industry. Additionally, the transport of these emissions to the adjacent city of Huelva and rural areas was studied based on ambient air measurements. A major objective of this study was to determine the geochemical signature of the fine and quasi-ultrafine particles (<0.33 μm) emitted, as a means to identify the most polluting Cu-smelter process and better understand particle transport patterns. Given the make-up of industrial activity in the Huelva area, our campaign offered a unique opportunity to study the influence on air quality of the Cu smelting process without the interference of PM contributions from typical mining operations such as grinding, millings and mine tailings. In order to do this, we obtained size-fractionated chemical compositions (in the 0.33–37 μm range) of particles collected from the main atmospheric stacks emission sources in the largest industrial complex located in Huelva. To our knowledge, this is the first size-resolved characterisation of metal and metalloid stack emissions of step-by-step copper smelting process (e.g. crushing, smelting and refining) ever reported.

2. Methodology

2.1. Cu-smelting process

The Cu-smelter industry is located in the Punta del Sebo estate, in an estuary just 2 km southwest from the city of Huelva. The smelter is the largest producer of Cu in Spain, the second in Europe and the seventh largest in the world, producing $3.2*10^6$ tons of Cu per year (Khokhar et al., 2008). The main activity of the industry is the production of Cu anodes and cathodes using different mineral concentrates as raw material. The facilities are divided into several different production units, each producing their own point source for emissions. In Figs. 1 and 2, main Cu-smelter processes (ore crushing, flash furnace slag extraction, sulphuric acid production, matte conversion, and refining) are represented.

The crushing plant is one of the preliminary steps, together with the drying process, after the Cu concentrate is received from the exterior port. The next step involves the flash smelting furnace unit where emissions from the matte (intermediate product with a high Cu content) and slag (molten waste material) extraction from the furnace are produced during the Cu concentrate melting process. The hot gas stream is directed into a recovery boiler, and once particles are cleaned, is conducted to the sulphuric acid plant where gas scrubbing and production of sulphuric acid take place. The next process is the conversion of the matte obtained from the flash furnace or electric furnace. The Cu matte is separated from the other residual metals which did not remain with the slag in the flash furnace. The products obtained in the converters are slag, which is sent to the electric furnace, and blister Cu. The blister Cu is refined in three furnaces through oxidation processes until the oxygen content is acceptable. These gases are then released to the atmosphere via the emission stack.

All chimney stacks have an air pollution control process (APC) consisting of baghouse filters in the crushing plant and the flash furnace, a washing plant and gas filter candles in the sulphuric plant, and a baghouse filter with SO_2 abatement by dry method in the converters unit. Finally, each refining furnace APC includes wet electrostatic filters.

2.2. Sampling strategies

An aerosol sampling campaign using multidisciplinary techniques was performed between 29 August and 7 September 2011. Fig. 1 shows a map of the sampling sites and the location of the Cu-smelter. Detailed locations of the stacks and fugitive emissions sampling are also included. Table 1 summarises the industrial emissions and ambient PM samples obtained during the campaign. The data available have been linked to the table or figure results included in this study.

2.2.1. Industrial emissions sampling

Individual total PM samples from the chimney stacks in the Cu-smelter industry were isokinetically obtained using a NAPP 31-200TC particulate sampling probe with the standard EPA Reference Method (U.S. EPA., 2000a,b), for particles being retained in a