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Characterization of manganese-bearing particles in the vicinities of a manganese alloy plant

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HIGHLIGHTS

- Most of the particles collected in an urban area near a Mn alloy plant contain Mn.
- PM_{10} is mainly composed of Si-Mn particles with spherical shapes and small sizes.
- Mn-bearing particles in deposition samples are mostly attributed to alloys and slags.
- Mn solubility is expected to be higher in PM_{10} compared to deposition samples.

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ABSTRACT

Numerous studies have associated air manganese (Mn) exposure with negative health effects, primarily neurotoxic disorders. Despite there is not a specific European regulation, institutions such as the World Health Organization (WHO) have proposed an annual average guideline value of 150 ng/m^3. Bioaccessibility and toxicity mechanisms of Mn remain unclear, however it is generally agreed that adverse health effects are strongly linked to particle size and morphology, chemical composition and oxidation state. This study aims to deepen the understanding of the physico-chemical characteristics of PM_{10} and deposition samples collected in an urban area in the proximities of a ferromanganese alloy plant. Total Mn content was determined by ICP-MS after a microwave-assisted acid digestion. The size, morphology and chemical composition of individual particles were studied by SEM-EDX. XRD was used to identify the major crystalline phases. Most of the particles observed by SEM-EDX contain Mn. 60% of Mn-PM_{10} particles were spheres of small size and were attributed to condensation processes at the smelting unit. Mn-bearing particles present in deposition were characterized by irregular shapes and bigger sizes, most of them consisting of SiMn slags and Mn ores and alloys, and attributed to diffuse emissions from raw material and product handling and processing. Due to the differences in the characteristics of Mn-bearing particles found in the different matrices, further studies on the potential toxicity and health effects of these particles should be done, especially in relation with the small and spherical particles present in PM_{10}, which are expected to be more problematic.

1. Introduction

Manganese (Mn) is a trace element considered essential to human health. Due to its catalytic and regulatory function, it plays an important role in several enzyme systems, being therefore required for a wide variety of physiological processes. It is necessary for the metabolic activity, skeletal development, as well as for the maintenance of the nervous and immune systems (Santamaria, 2008). In addition, it contributes to a normal reproductive hormone function and to the prevention of cellular oxidative stress (Freeland-Graves et al., 2015; Keen et al., 2000). Although Mn, as a nutrient, is vital for the human body, it can be toxic as a result of overexposure.

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Mn toxicity to humans by inhalation has been widely reported in comparison with other routes of exposure (ATSDR, 2012; WHO, 2000), mainly linked to neurological problems. Chronical occupational exposure can lead to the development of manganism, with some general resemblance to Parkinson's disease (Flynn and Susi, 2009; Kwakye et al., 2015; Park, 2013). Whereas the impacts of Mn exposure in human health have been extensively established in relation with workplaces (Crossgrove and Zheng, 2004), there has only been a growing interest in the last decade about the consequences of Mn chronic exposure in the overall population, especially in susceptible groups like children (Carvalho et al., 2014; Riojas-Rodríguez et al., 2010; Rodríguez-Barranco et al., 2013). In this regard, recent studies suggest that ambient air Mn exposure may also be associated with neurotoxic disorders, including motor and cognitive deficits (Chen et al., 2016; Lucchini et al., 2012; Menezes-Filho et al., 2011; Rodríguez-Agudelo et al., 2006; Roels et al., 2012). Even though negative health effects as a consequence of airborne Mn overexposure have been pointed out, there is no specific European regulation that establishes limit values for Mn in air. Nevertheless, the World Health Organization (WHO) has proposed an annual average guideline value of 150 ng Mn/m^3.

Mn is an element present in several environmental matrices, however, high concentrations in air are due to anthropogenic sources, one of the most important being the ferromanganese alloy production. According to the WHO criteria, exceedances of Mn concentrations in air have been widely reported in areas close to Mn alloy plants, pointing out that even when PM_{10} levels fulfil the European regulatory limits, Mn should be a cause of concern in locations influenced by the emission from this activity. For instance, Haynes et al. (2010) have reported an annual average concentration of Mn of 203 ng/m^3 at approximately 4.5 miles to the north/northeast of a ferromanganese refinery located in the Marietta community (14,515 inhabitants, USA). Also, an average Mn concentration of 7560 ng/m^3 in dust collected by global filtration have been reported by Ledoux et al. (2006) in the vicinities of a ferromanganese metallurgy plant located in Boulogne-sur-Mer agglomeration (120,000 inhabitants, France).

Mn levels in air reach 4–23 ng/m^3 in several urban background areas in Spain (Querol et al., 2007), nevertheless annual average concentrations above the WHO guideline have been repeatedly reported in the Region of Cantabria, northern Spain. In Santander, capital of the region (174,000 inhabitants), located 7 km-NE of a ferromanganese alloy plant, an annual average value of 166 ng Mn/m^3 was reported in 2007 (Moreno et al., 2011). Also in 2005 and 2009, annual average levels of 781 ng Mn/m^3 (CIMA, 2006) and 1072 ng Mn/m^3 (CIMA, 2010) respectively, were obtained in the area of Maliaño, a small town with around 10,000 inhabitants where the ferroalloy plant is located. Even though the application of corrective measures in the plant in 2008 led to an improvement of Mn air concentrations in Santander, where mean values of 49.1 ng Mn/m^3 (Arruti et al., 2010) and 31.5 ng Mn/m^3 (Ruiz et al., 2014) were reported in 2008 and 2009, respectively, Mn levels in 2015 still exceeded the WHO recommendation in some areas of Maliaño town, with monthly mean values up to 713.9 ng/m^3 and reaching 3200 ng/m^3 daily Mn concentrations (Hernández-Pellón and Fernández-Olmo, 2016).

Mn emissions to the atmosphere sourcing from ferroalloy plants can exist as aerosols or suspended particulate matter (ATSDR, 2012). Smallest particles will remain suspended for long periods and then, together with bigger particles, will be deposited by dry or wet deposition. Particulate matter is generated from several activities during ferroalloy production, including raw material handling, sintering, smelting and tapping, casting and product handling (Davourie et al., 2016). Mn ores can be directly introduced into the electrical furnaces or agglomerated with other raw materials such as fluxes and coal in a sintering unit. Fig. 1 shows the most common point and fugitive sources of particulate matter (PM) and therefore, potential sources of Mn, in a typical Mn ferroalloy production plant without sintering process. The variety of point and diffuse Mn sources in a ferroalloy plant shown in Fig. 1 may lead to the emission of a mixture of Mn-bearing particles with different physico-chemical characteristics.

Even though more efforts should be done in establishing Mn bioaccessibility and toxicity mechanisms (Santamaria, 2008), it is generally agreed that they are strongly linked to particle size and morphology, chemical composition and oxidation state (Majestic et al., 2007). The size distribution of Mn-bearing particles will determine their capability of passing the larynx (thoracic fraction) and ciliated airways (respirable fraction) during inhalation, and therefore could determine their potential health effects. Also, the particle size distribution within the respirable aerosol fraction may have large consequences for the pulmonary Mn absorption (Ellingsen et al., 2013). The predominant oxidation states of Mn found in the inhalable aerosol fraction in FeMn and SiMn plants are Mn^0 and Mn^{2+}; however, Mn^{3+} and Mn^{4+} have also been previously identified (Thomassen et al., 2001). In addition, particle solubility is important for the systemic uptake of Mn after inhalation. In this regard, a greater association has been found between the more soluble Mn compounds and their presence in biological samples, with respect to insoluble Mn compounds (Ellingsen et al., 2003). Thus, taking into account the variety of emission sources from ferroalloy plants, the study of the physico-chemical characteristics of Mn-bearing particles is essential to better assess their potential health effects.

In the last years, some studies have focused on the assessment of PM toxicity based on its physico-chemical characteristics (Dieme et al., 2012; Megido et al., 2016; Perrone et al., 2010; Rosas Pérez et al., 2007), but only a few studies dealt with the characterization of Mn-bearing particles collected inside or in the vicinities of ferromanganese alloy plants. According to the literature, dust samples collected in different locations inside ferromanganese alloy plants have been already studied (Fig. 1). In particular, PM emissions from the chimneys, e.g., downstream of the industrial filters (Arndt et al., 2016; Marris et al., 2012, 2013), Mn ores (Arndt et al., 2016), as well as samples collected directly from air pollution control devices such as wet scrubbers (Shen et al., 2005) or other industrial filters (Arndt et al., 2016) have been evaluated. In addition, indoor air samplings have been carried out in the factories at different locations: raw materials area (Gunst et al., 2000) and smelting, tapping, ladle and casting area (Gjønnes et al., 2011; Gunst et al., 2000; Kero et al., 2015). Only a few studies focused on the characterization of Mn-bearing particles sampled in residential areas in the vicinities of these plants (Ledoux et al., 2006; Marris et al., 2012, 2013; Moreno et al., 2011).

In the present study, inductively coupled plasma mass spectrometry (ICP-MS), scanning electron microscopy-energy dispersive X ray (SEM-EDX) and X ray diffraction (XRD) have been applied to deepen the understanding of the physico-chemical characteristics of particulate matter and atmospheric deposition in the nearby of a Mn alloy plant located in an industrial-urban area in the Region of Cantabria (northern Spain).

2. Materials and methods

2.1. Area of study

The area of study of this work is located in the north of Spain, in the Region of Cantabria (585,179 inhabitants, 2015), specifically along the Santander Bay. This study has been focused in Maliaño, a town with around 10,000 inhabitants located in the southern part