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Metal(loid) bioaccessibility and inhalation risk assessment: A comparison between an urban and an industrial area

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ABSTRACT

The content of metal(loid)s in particulate matter (PM) is of special concern due to their contribution to overall (PM) toxicity. In this study, the bioaccessibility and human health risk of potentially toxic metal(loid)s associated with PM_{10} were investigated in two areas of the Cantabrian region (northern Spain) with different levels of exposure: an industrial area mainly influenced by a ferromanganese alloy plant; and an urban area consisting mainly of residential and commercial activities, but also affected, albeit to a lesser extent by the ferroalloy plant. Total content and bioaccessible fractions in simulated lung fluids (SLFs) of Fe, Mn, Zn, Ni, Cu, Sb, Mo, Cd and Pb were determined by ICP-MS. Gamble's solution and artificial lysosomal fluid (ALF) were used to mimic different conditions inside the human respiratory system. A health risk assessment was performed based on the United States Environmental Protection Agency's (USEPA) methodology. Most metal(loid)s showed moderate and high bioaccessibility in Gamble's solution and ALF, respectively. Despite the high variability between the samples, metal(loid) bioaccessibility was found to be higher on average at the industrial site, suggesting a greater hazard to human health in the proximity of the main metal(loid) sources. Based on the results of the risk assessment, the non-carcinogenic risk associated with Mn exposure was above the safe limit (HQ > 1) under all the studied scenarios at the industrial site and under some specific scenarios at the urban location. The estimated carcinogenic inhalation risk for Cd exposure at the industrial site was found to be within the range between 1.0×10^{-6} to 1.0×10^{-4} (uncertainty range) under some scenarios. The results obtained in this study indicate that Mn and Cd inhalation exposure occurring in the vicinities of the studied areas may pose a human health risk.

1. Introduction

Atmospheric particulate pollution is an increasing cause of concern for human health, especially in urban and industrialized areas. It is implicated in a wide variety of cardiovascular (Brook et al., 2010; Fiordelisi et al., 2017; Hoek et al., 2013) and respiratory diseases (Noh et al., 2016; Taj et al., 2017), including lung cancer (Raaschou-Nielsen et al., 2013). Additionally, numerous epidemiological studies have associated particulate matter (PM) exposure with reproductive problems (Carré et al., 2017) and neurodevelopmental and neurodegenerative diseases (Wang et al., 2017).

The potentially adverse health effects from the inhalation of PM depend on its physico-chemical characteristics (Kelly and Fussell, 2012), which vary significantly in urban, industrial and rural areas around the world (Mukherjee and Agrawal, 2017). Transition metals are of particular interest for the assessment of PM toxicity, due to the fact that they are capable of generating reactive oxygen species (ROS) (Verma et al., 2010), which induce inflammatory responses, DNA damage and oxidative stress (Peixoto et al., 2017; Van Den Heuvel et al., 2016). Many of these metals are emitted by industrial activities such as Al, Fe, Zn, Mn and Pb by the integrated steel industry (Hleis et al., 2013; Sylvestre et al., 2017; Yatkin and Bayram, 2008), Mn by the ferroalloy industry (Haynes et al., 2010; Lucas et al., 2015; Mbengue et al., 2015; Menezes-Filho et al., 2016), As and Cu by Cu smelters (Chen et al., 2012; Sánchez de la Campa et al., 2011) and Zn, Cd and Pb by Zn smelters (MacIntosh et al., 2010). An evaluation in terms of exposure and potential health risks for local residents is vital when these activities are located close to urban areas.

The identification of the true harmful components of PM, i.e. those potentially able to cause adverse health effects via inhalation, is a critical goal for toxicological studies (Kelly and Fussell, 2012). The toxicity of metal(loid)s in PM or dust upon uptake into the human lung is usually evaluated using one of three main approaches: 1) In-vivo methods using lab animals 2) In-vitro methods using cultured cells and 3) In-vitro methods using simulated lung fluids (SLF)s. Both in-vivo animal studies and in-vitro exposure to culture cells are complex and

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expensive. Therefore, in-vitro methods using SLFs are considered to be a streamlined and inexpensive alternative for toxicological studies (Kastury et al., 2017).

In this approach, the soluble metal(loid) fraction extracted with the SLFs is used as an estimation of the metal(loid) bioaccessible fraction, i.e. the amount of metal(loid) that actually interacts with the organism's contact surface and is potentially available for absorption by the organism (U.S. Environmental Protection Agency EPA, 2007). Although this approach has been applied in many works, the lack of standardized methods hinders interstudy comparisons (Guney et al., 2016; Wiseman, 2015). Significant methodological differences exist in the leaching agents employed, as well as in particle size and assay parameters, namely extraction time, liquid to solid (L/S) ratio, temperature and agitation (Caboche et al., 2011; Mukhtar and Limbeck, 2013; Wiseman, 2015). One-step or sequential extraction methods using water or simple chemicals as leaching agents have been widely applied to in-vitro metal (loid) dissolution studies (da Silva et al., 2015; Heal et al., 2005; Majestic et al., 2007; Mugica-Álvarez et al., 2012; Niu et al., 2010; Tessier et al., 1979; Voutsa and Samara, 2002). However, in the last decade, there has been a shift to physiologically based extraction techniques using SLFs as leaching agents (Boisa et al., 2014; Caboche et al., 2011; Henderson et al., 2014; Pelfrêne et al., 2017). The most commonly used SLFs are Gamble's solution and artificial lysosomal fluid (ALF). Gamble's solution (pH = 7.4) is representative of the interstitial fluid in the deep lung, whereas ALF (pH = 4.5) represents the more acidic intracellular conditions found in the lysosomes of alveolar macrophages (Mukhtar and Limbeck, 2013). Most of these studies focused on assessing the bioaccessibility of metal(loid)s in certified reference materials or commercial products (Caboche et al., 2011; Colombo et al., 2008; Midander et al., 2007; Pelfrêne et al., 2017) or the comparison between metal(loid) bioaccessibility in different SLFs or PM size fractions (Coufalík et al., 2016; Mukhtar et al., 2015; Potgieter-Vermaak et al., 2012; Wiseman and Zereini, 2014), with most of them being conducted in urban areas. Only a few of these studies evaluate the influence of specific industrial activities (Huang et al., 2018; Mbengue et al., 2015). Additionally, the methodology for the selection of the appropriate extraction fluid type in combination with the particle size is rarely discussed in the literature. According to Mukhtar and Limbeck (2013), particles in the range of 2.5–10 μm are in most cases deposited in the pharyngeal and tracheal region, and transported by the mucociliary clearance adoral and swallowed, thus reaching the gastrointestinal tract; while particles less than 1 μm can reach the alveolar lung regions and interact with the lung fluid. In contrast, Wiseman (2015) considers that particles smaller than 5 μm reach the pulmonary region of the respiratory tract where they are more likely to dissolve in lung fluids or be phagocytized by resident macrophages. In this regard, as Wiseman (2015) notes, more attention should be paid to the implications of the particle size and to the appropriate selection of the SLF.

The health risk assessment associated with the inhalation route has been traditionally based on the total metal(loid) content. As a result of this and according to Huang et al. (2018), the exposure risk of metal (loid)s in PM may be overestimated. In this regard, the current trend in exposure assessment and risk calculation methods is shifting towards determining the bioaccessibility fraction of the studied metals(loids) in SLFs (Huang et al., 2018, 2016, 2014; Kastury et al., 2017).

The aim of this work is to assess the bioaccessibility of potentially toxic metal(loid)s (i.e. Fe, Mn, Zn, Ni, Cu, Sb, Mo, Cd and Pb) associated with PM_{10} collected in the Cantabrian region (northern Spain), whose presence in the air has been mainly attributed to local industries and other anthropogenic activities. In this regard, a ferroalloy plant has been identified as the main metal(loid) source in the area (mainly Mn, Fe, Zn, Cd and Pb), followed by vehicular traffic (main tracers Cu, Fe, Sb and Mo) and to a minor extent oil combustion processes (main tracers Ni and V) (Hernández-Pellón and Fernández-Olmo, 2017). Additionally, a steel plant has been found to contribute to Zn, Cu, Cd and Pb levels (Arruti et al., 2011). The differences in metal(loid) bioaccessibility at different distances from the main metal(loid) sources will be evaluated by studying two different sites: an urban-industrial area mainly influenced by the presence of a ferromanganese alloy plant; and an urban area with a lower impact from local industrial emissions, which is mostly comprised of residential and commercial activities, but also affected to a lesser extent by the ferroalloy plant. The health risk via the inhalation route will be calculated based on both the total and the bioaccessible concentrations of the studied metal(loid)s, and the limitations of these calculations will be addressed.

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 (580,140 inhabitants, 2017), specifically along the Santander Bay. This study has been conducted in two locations:

1) Santander (172,656 inhabitants, 2016), which is located in the northern part of the Bay, is the most populated city of the Region, being mainly commercial and residential. The sampling site (ETSIIT, UTM, 30T, X = 435450, Y = 4813651, 7 m a.s.l.) is situated on the campus of the University of Cantabria, on the rooftop of the "E.T.S de Ingenieros Industriales y de Telecomunicaciones" building (30 m above ground) and represents an urban background site.
2) Maliaño (9440 inhabitants, 2016), is a town located alongside the southern part of the Bay. It is highly impacted by nearby industrial activities, such as steel, ferromanganese and silicomanganese production. The sampling site (Vidriera, UTM, 30T, X = 431899, Y = 4807290, 5 m a.s.l.) is located on the rooftop of the "Cultural Center of La Vidriera" (8 m above ground) some 350 m north of a manganese alloy production plant, and therefore represents an urban-industrial site. The presence of this plant in Maliaño has been previously associated with high concentrations of Mn in the air (Moreno et al., 2011; Ruiz et al., 2014). The location of the monitoring sites and the main metal(loid) sources is shown in Fig. S1.

2.2. Sampling and filter preparation

A PM_{10} sampling campaign was carried out at the two selected monitoring sites. A previous study showed that most of the particle types identified in PM_{10} filters collected at the Vidriera site had mean diameters of less than 2.5 μm (Hernández-Pellón et al., 2017). PM_{10} samples were collected by means of a low volume sampler device (2.3 m^3/h), equipped with a 15 filter cartridge, on 47 mm Teflon filters (PALL). This substrate was selected in order to minimize possible sample loss due to sorption of particles in the filters (Zereini et al., 2012) and because of the lower amount of metal(loid) impurities (Karanasiou et al., 2005). Twenty daily samples were collected at the Vidriera site from January to February 2017. Later, 20 additional daily PM_{10} samples were collected from February to March 2017 at the ETSIIT site.

Once the gravimetric determination was performed, the filters were cut into three pieces using ceramic scissors: one quarter of the filter was used for the total metal(loid) content analysis, while the remaining portion of the filter was cut into two equal pieces in order to assess the bioaccessible levels of the metal(loid)s.

2.3. Total metal(loid) content digestion procedure

The digestion was carried out in a 24 slot heating plate equipped with 10 ml closed PFA vessels. One quarter of each filter was treated for 60 min at 90 °C with a mixture of 3 ml of 65% HNO_3, 1.5 ml of 30% H_2O_2 and 50 μl of HF. The reagents used were of analytical grade or higher purity. The concentrated HNO_3, H_2O_2 and HF were sourced from Merck. After sample digestion, the non-dissolved sample constituents