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Manganese and lead levels in settled dust in elementary schools are correlated with biomarkers of exposure in school-aged children☆

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ABSTRACT

Previously, we showed that manganese (Mn) levels in settled dust in elementary schools increased at a rate of 34.1% per km closer to a ferro-manganese alloy plant in the rainy season. In this study, we investigated how this environmental pollution indicator varied in the dry season and if there was an association with Mn biomarker levels in school-aged children. Dust samples were collected with passive samplers (disposable Petri dishes) placed in interior and exterior environments of 14 elementary schools. Occipital hair, toenails and blood samples were collected from 173 students aged 7–12 years from three of these schools, with varying distance from the industrial plant. Mn and lead (Pb) levels were measured by graphite furnace atomic absorption spectrometry. Mn concentration geometric means (GM) in dust fall accumulation in interior environments of schools located at 2, 4, 6 and > 6 km-radii from the plant were 2212, 584, 625 and 224 μg Mn/m^2/30 days, respectively. The modelled rate of change of dust Mn levels decreases by 59.8% for each km further from the plant. Pb levels in settled dust varied between 18 and 81 μg/m^2/30 days with no association with distance from the plant. Blood lead levels median (range) were 1.2 μg/dL (0.2–15.6), of which 97.8% were <5 μg/dL. Mn in hair and toenails were 0.66 μg/g (0.16–8.79) and 0.86 μg/g (0.15–13.30), respectively. Mn loading rates were positively associated with log MnH ($\beta = 1.42 \times 10^{-5}$, $p < 0.001$) after adjusting for children's age; and also with log MnTn ($\beta = 2.31 \times 10^{-5}$, $p < 0.001$) independent of age. Mn loading rates explained 18.5% and 28.5% of the variance in MnH and MnTn levels, respectively. School-aged children exposure to Mn, independently of age, increases significantly with school proximity to the ferro-manganese alloy plant.

1. Introduction

Manganese (Mn) is an important microelement, present in enzymes involved in growth and metabolism regulation in humans and other living beings. However, the homeostatic mechanisms that control Mn concentrations in the various organs can be overwhelmed by excessive exposure from sources other than diet, particularly airborne Mn (ATSDR, 2012). Environmental respiratory exposure to Mn originates from various anthropogenic activities, which emit gross and ultrafine particles formed by Mn ore exploitation (Rodriguez-Agudelo et al., 2006), manganese alloy production (Haynes et al., 2015; Lucchini et al., 2012a, b; Menezes-Filho et al., 2009a; 2011; Bowler et al., 2007; Baldwin et al., 1999), mancozeb application by aerial spraying (van Wendel de Joode et al., 2014; Mora et al., 2015), use of MMT as gasoline additive (Röllin et al., 2005; Zayed, 2001) and welding fume (Keane et al., 2010).

Airborne Mn, present in the ultrafine fraction of particulate

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matter, eventually settles down as dust. Recent studies have evaluated Mn levels in dust as a source of exposure to children (Menezes-Filho et al., 2016; Gulson et al., 2014; Lucas et al., 2015; Gunier et al., 2014). Mn content in dust can be estimated in three ways: (i) as concentration, when the amount of dust sample collected is weighed and Mn concentration is expressed as μg Mn per gram of dust; (ii) as loading, when Mn content is measured in the dust sampled per unit of area (μg Mn/m^2) and (iii) as loading rate, when loading is a measure of dust fall accumulation over time. In the latter, loading is adjusted for a defined period of sampling time and expressed as a rate of accumulation (μg Mn/m^2/30 days for example). All approaches are very informative; more detailed information on their respective advantages and disadvantages, as well as several sampling techniques are published elsewhere (Menezes-Filho et al., 2016).

Settled dust as a source of exposure, especially for children, has been extensively studied for lead (Pb) exposure (Fillion et al., 2014; Taylor et al., 2013; Lanphear et al., 1998; Gulson et al., 1995). Pb is a ubiquitous environmental contaminant with no known physiological role in humans or other organisms. Neurotoxic effects on children is very well described in the scientific literature (Skerfving et al., 2015; ATSDR, 2007; Lidsky and Schneider, 2003). Airborne Pb and dust are among the main predictors of children exposure to lead (Zota et al., 2015; Glorennec et al., 2012; Gulson et al., 2006; Meyer et al., 1999; Lanphear et al., 1998; Clark et al., 1991). In a series of investigations carried out in Australia, Gulson et al. measured Pb content as loading rates, using polyethylene disposable petri dishes as passive samplers and demonstrated that Pb dust loading rates represent an important pathway of Pb to children total exposure (Gulson et al., 2014).

Biomonitoring of blood lead levels is very much needed in Low and Medium-income Countries (LMIC) in addition to the biomonitoring of other metals, such as Mn. Due to the fact of being a micronutrient with tight homeostatic control, its biological monitoring still is an issue. Mn blood levels are rarely associated with Mn environmental levels as observed by Baker et al. (2014) and Smith et al. (2007). This biomarker is even less useful detecting association with neuropsychological endpoints in children, as observed in a review by Zoni and Lucchini (2013) and by Menezes-Filho et al. (2009a, b). On the other hand, the keratinized tissues like hair and nails have being used extensively to assess exposure to Mn from varied sources (Lucas et al., 2015; Rodrigues et al., 2015; Oulhote et al., 2014; Laohaudomchok et al., 2011; Menezes-Filho et al., 2009b; Bouchard et al., 2007).

Our studies of hair manganese (MnH) levels in children living in the vicinity of a Mn transformation plant showed that MnH concentration was associated with residence location with respect to the plant, sex and length of time their mothers had lived in this region prior to their birth (Menezes-Filho et al., 2009a). Later, in the same community, we reported that hair, but not blood, Mn levels were significantly associated with deficits in intellectual performance, when adjusted for nutritional status and maternal education (Menezes-Filho et al., 2011). Similar results were observed with Mexican children exposed to airborne Mn from mining and transformation (Riojas-Rodríguez et al., 2010). Several other studies have found significant associations between MnH levels and cognitive and behavioral effects in children (Bouchard et al., 2007; Lucchini et al., 2012a, b; Menezes-Filho et al., 2013; Carvalho et al., 2014; Oulhote et al., 2014; Haynes et al., 2015).

Mn levels in nails or toenails as a biomarker has recently been used to assess exposure and effect in children (Rodrigues, et al. 2015; Lucas et al., 2015). Due to their lower growth rates, metal levels measured in these matrices generally reflect six months to one-year of exposure window, respectively. In the adult population living near a Mn transformation plant in Brazil, we measured fingernail Mn levels and found that they were significantly associated with decrement in dexterity and increased processing speed (Viana et al., 2014).

We previously assessed Mn and Pb levels in dust fall accumulation during the raining season in fifteen elementary schools near a Mn transformation plant in Bahia, Brazil (Menezes-Filho et al., 2016). Mn loading rates were much higher than those reported by Gulson et al. (2014), using the same technique, in daycare centers in Sydney, Australia. School proximity to the main emission source was the major determinant of the Mn loading rates. The present study, which is part of wider ongoing project (PIECES - Industrial pollution and effect on children's behavior in Simões Filho, Brazil) assesses children's exposure in the same schools during the dry season, Mn concentrations in occipital hair and toenails and examines the association between Mn loading rates in dust fall accumulation and these Mn biomarkers of exposure.

2. Material and methods

2.1. Study area

The municipality of Simões Filho is located approximately 30 km from Salvador, the capital city of the State of Bahia, Brazil. The weather is tropical, with average annual pluviometry of 1579 mm, varying from 67 mm in December (dry season) to 240 mm in May (wet season); mean temperature is 24.9 °C. The predominant winds generally blow from Northeast, East and Southeast, from the sea to land (Bahia, 2013).

The estimated population for 2016 was 135,000 (IBGE, 2017). There are 67 elementary schools in 11 sub-regions, attended by approximately 18,000 six to fourteen-year-old children (personal communication provided by the Education Department coordinator). A ferro-manganese alloy plant, located approximately 2 km from downtown, has been in operation since the early 1970's with an annual production of ferro-manganese alloys of 280,000 tons (Brazil, 2003).

We selected 18 elementary schools spatially distributed around the manganese transformation plant, with a minimum of 100 students in the age range of 7–12 years. After a first inspection visit, three schools were excluded: two were under renovation and one was situated near a quarry with a high volume of trucking. Settled dust samplers were installed in 15 elementary schools (22.4% of all schools) with at least one in each sub-region. In one of the schools, the samplers were contaminated with wall scrapings and painting. These samplers were discarded. The locations of the remaining 14 schools, which were monitored, are presented in Fig. 1.

Approval and support was provided by the Simões Filho Municipality Secretary of Education and agreement was obtained from each school principal. The Ethics Committee of the Federal University of Bahia approved the investigation protocol (N. 874.463/2014).

2.2. Dust sampling protocol

The dust collection period was performed during the dry season from mid-February thru mid-March, for 37–41 days. In each school, 10 metal-free disposable polyethylene Petri dishes, used as dust samplers, were installed in interior (classrooms) and exterior environments (recreational area, outer walls, etc.). Because of the high loss rates in our previous study (Menezes-Filho et al., 2016) we developed a low-cost, simple method to install using a cardboard support (Fig. 1S, Supplemental material). Dust samplers were fixed with silicon glue and placed at least 2.5 m from the floor, out of children's reach. The samplers were labeled and their exact position recorded. At the end of sampling period, we were able to