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Impact of ferromanganese alloy plants on household dust manganese levels: Implications for childhood exposure

E.L. Lucas [a], P. Bertrand [a], S. Guazzetti [b], F. Donna [c], M. Peli [c], T.P. Jursa [a], R. Lucchini [a,c,d], D.R. Smith [a,*]

[a] University of California, Santa Cruz, CA 95064, USA
[b] Public Health Service, Reggio Emilia, Italy
[c] University of Brescia, Brescia, Italy
[d] Ichan School of Medicine at Mount Sinai, New York, NY, USA

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ABSTRACT

Adolescents living in communities with ferromanganese alloy plant activity have been shown to exhibit deficits in olfactory and fine motor function. Household dust may serve as an important manganese (Mn) exposure pathway to children, though dust Mn concentrations have not previously been measured to assess household contamination from ferromanganese alloy plant emissions. Here we determined the association between dust concentrations and surface loadings of Mn and other metals (Al, Cd, Cr, Cu, Fe, Pb, and Zn) in indoor and outdoor household dust from three Italian communities that differ by history of ferromanganese alloy plant activity: Bagnolo Mella, with an active ferromanganese alloy plant ($n=178$ households); Valcamonica, with historically active plants ($n=166$); and Garda Lake, with no history of ferromanganese plant activity ($n=99$). We also evaluated Mn levels in other environmental (soil, airborne particulates) and candidate biomarker (blood, hair, saliva, fingernails) samples from children within the households. Household dust Mn concentrations and surface loadings were significantly different between the three sites, with levels highest in Bagnolo Mella (outdoor median Mn concentration=4620, range 487–183,000 μg/g), intermediate in Valcamonica (median=876, range 407–8240 μg/g), and lowest in Garda Lake (median=407, range 258–7240 μg/g). Outdoor dust Mn concentrations in Bagnolo Mella, but not the other communities, were significantly inversely related with distance from the plant ($R^2=0.6630$, $P<0.0001$). Moreover, outdoor dust Mn concentrations and loadings were highly predictive of but significantly higher than indoor dust Mn concentrations and loadings by ~2 to ~7-fold (Mn concentrations) and ~7 to ~20-fold (Mn loadings). Finally, both indoor and outdoor dust Mn concentrations and outdoor dust Mn loading values were highly significantly correlated with both soil and air Mn concentrations, and with children's hair and fingernail Mn concentrations, but weakly or not associated with saliva or blood Mn levels. Given the evidence associating elevated Mn exposure with neurological impairments in children, these data support that dust Mn levels should be reduced in contaminated environments to protect the health of resident children.

1. Introduction

Manganese (Mn) is an essential nutrient, although elevated Mn exposures have been associated with neurotoxicity in adults and children (ATSDR, 2012; WHO, 2000; Aschner et al., 2005; Lucchini et al., 2007). Children are considered particularly susceptible to the health impacts of elevated Mn exposure, with studies reporting reduced birth weight, IQ deficits, increased oppositional and attention problems, and fine motor and sensory deficits associated with elevated Mn exposure (ATSDR, 2012; Bouchard et al., 2011; Wasserman et al., 2006; Bouchard et al., 2007; Lucchini et al., 2012; Zota et al., 2009; Claus Henn et al., 2010, 2012). There are a number of natural and anthropogenic sources of Mn in the environment that may contribute to elevated exposures over the life span, including contaminated groundwater, combustion of the gasoline additive methylcyclopentadienyl manganese tricarbonyl (MMT), the fungicides maneb and mancozeb, and ferromanganese alloy facilities (ATSDR, 2012; Bouchard et al., 2011; Wasserman et al., 2006; Lucchini et al., 2012; Gunier et al., 2013; Menezes-Filho et al., 2009; Borgese et al., 2013).

The iron and steel industry consumes ~90% of the worldwide Mn produced (Bouaziz et al., 2011), and it represents one of the

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* Correspondence to: Microbiology and Environmental Toxicology, Physical and Biological Sciences Bldg., University of California, Santa Cruz, CA 95064, USA.

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most regionally significant anthropogenic sources of Mn to the environment-contributing up to 80% of industrial Mn emissions (ATSDR, 2012; EPA, 2008). Manganese is used as an alloying element in the metal industry, where it is alloyed with silicon and iron forming silicomanganese and ferromanganese (Pearson et al., 2005). In steel production, addition of Mn to ferromanganese alloys imparts unique physical properties of tensile strength and flexibility compared to ferroalloy steels with lower Mn levels (ATSDR, 2012; Pearson et al., 2005; Bouaziz et al., 2011). While the Mn content in steel is generally in the range of 0.05%–12%, standard ferromanganese alloys may contain substantially greater levels of Mn.

Soil naturally contains between 500 and 900 μg Mn/g, and airborne Mn concentrations in areas without anthropogenic sources range from 0.01 to 0.07 $\mu g/m^3$ (WHO, 2000; Gerber et al., 2002). In areas adjacent to ferro- or silico-Mn industries Mn levels can exceed 0.5 $\mu g/m^3$, which is well above the world health organization's (WHO) annual average air guideline value for long-term Mn exposure of 0.15 $\mu g/m^3$ (WHO, 2000). Coarse Mn particles (defined by WHO as $> PM_{2.5}$) originating from ferromanganese alloy plant emissions settle within meters to kilometers of the plant, while finer particles ($< PM_{2.5}$) can be transported larger distances through the air (WHO, 2000).

The Province of Brescia, Italy contains both historic (Valcamonica valley) and currently active (Bagnolo Mella) ferromanganese alloy industries, and studies have reported associations between environmental Mn exposures and health deficits in children and elderly adults in the impacted communities (Lucchini et al., 2007, 2012, 2014; Borgese et al., 2013). In addition, a higher prevalence of Parkinsonian disturbances in aged adults associated with environmental Mn exposure has also been reported (Lucchini et al., 2007). Environmental Mn associated with airborne particulates and settled dust has been implicated as the exposure source/pathway to children and adults in these areas. Household dust is a well-known exposure pathway for metals, particularly in children, through ingestion and inhalation of particles (Lanphear et al., 1998, 2002; Lioy et al., 2002; Zota et al., 2011). This exposure pathway is especially well-described for household dust lead (Pb) exposure to children, resulting in elevated blood Pb levels and health problems (Taylor et al., 2013; Lanphear et al., 1998, 2002; Wilson et al., 2006). Analysis of soil samples in Valcamonica and Garda Lake (control region) demonstrated higher levels of Mn in Valcamonica in the readily extractable fractions, suggesting a higher level of environmental Mn exposure in regions with historic ferromanganese alloy plant activity (Borgese et al., 2013). In addition, the Mn concentration in air particulates was previously determined to be approximately two to three-times higher in Valcamonica than Garda Lake (Borgese et al., 2011). An initial screening of household dust samples in Brescia using XRF showed higher concentrations of Mn in samples located nearby municipalities with historic or active ferromanganese alloy plants in comparison to regions without these plants (Zacco et al., 2009).

In light of the above, indoor and outdoor settled dust from the houses of children in the province of Brescia, Italy were analyzed for Mn and other metals (aluminum, cadmium, chromium, copper, iron, lead, and zinc) to determine whether dust metal levels were significantly elevated in association with local ferromanganese alloy plant activity. We hypothesized that (1) Mn levels in household dust from Bagnolo Mella will be significantly higher than levels in dust from Valcamonica or the Garda Lake reference area; (2) Mn dust concentrations will have an inverse relationship with distance from the active and historic ferromanganese alloy plants in Bagnolo Mella and Valcamonica, respectively; (3) Mn concentrations in indoor household dust will be associated with, but lower than corresponding levels in outdoor house dust; and (4) household dust Mn levels will be associated with Mn levels in other environmental media (e.g., soil, airborne Mn) and candidate biomarkers of Mn exposure in resident children (e.g., hair, fingernails, saliva), evidencing that dust may pose an important Mn exposure pathway for adolescents.

2. Methods

2.1. Study sites

The study focused on households within three areas in the Province of Brescia, Italy: Bagnolo Mella, Valcamonica, and Garda Lake (Fig. 1). Bagnolo Mella (population 12,700) is a municipality with an active ferromanganese alloy plant that has produced ferromanganese since 1973, and is situated in a flat plains region. Valcamonica is a valley of the pre-Alps with an average width of approximately 3 km and mountains of about 3000 m on either side. Winds average 5 km/h in the valley, primarily southwest to northeast in the day and northeast to southwest at night. Three ferromanganese alloy plants have operated in the valley in the municipalities of Sellero (population 1500) from 1973 to 1987, Breno (population 5000) from 1921 to 2001, and Darfo (population 13,200) from 1902 to 1995 (Lucchini et al., 2012). Communities within the Garda Lake region of the Province have had no history of ferromanganese alloy plant activity so were used as the reference group.

2.2. Sample collection

Indoor and outdoor dust samples were collected for each household from various horizontal surfaces between December 2010 and October 2013. Dust samples were collected by sweeping a measured area (60–35,000 cm^2, median 1230 cm^2) with a plastic brush (cleaned between samplings) into a plastic bag, or using a cyclone vacuum that deposited collected dust into a plastic sample jar. The two methods of sample collection were balanced across the three study sites. The total mass of collected dust ranged from 0.7 to 2673 mg (median 90.8 mg). Indoor and outdoor dust samples were analyzed from 153 households from Bagnolo Mella, 88 households from Valcamonica (Sellero: 50, Breno: 37, Darfo: 1), and 72 households from Garda Lake. The total number of households for each study site for which paired indoor and outdoor dust samples were analyzed were 135 (Bagnolo Mella), 78 (Valcamonica) and 64 (Garda Lake).

2.3. Sample preparation

All laboratory reagents (e.g., HNO_3) were trace metal grade. Ultrapure Milli-Q water with resistivity of 18.2 $M\Omega\ cm^2$ was used for all dilutions. Deionized water (DI) was used to rinse plasticware where stated.

Dust samples were dried in a 60 °C oven for at least 2 days, and non-dust debris was manually removed. For dust samples less than 100 mg, the entire sample was transferred to a polypropylene test tube (polytube) to obtain the sample weight. For samples greater than 100 mg, the sample was thoroughly mixed to homogeneity and approximately 100 mg was used. The mass of dust processed for analyses ranged from ~1 to 100 mg. Dust samples were leached in 7.5 N HNO_3 at 80 °C for 4 h with vortexing every hour. The resultant leachate was diluted in the polytube with Milli-Q, centrifuged at 3000*g* for 20 min, and the supernatant decanted into polyethylene scintillation vials for analyses.

2.4. Analysis

Dust metal concentrations were determined using inductively