Environment International 119 (2018) 455–465

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Use of CALPUFF to predict airborne Mn levels at schools in an urban area impacted by a nearby manganese alloy plant

Daniel Otero-Pregigueiro, Ignacio Fernández-Olmo*

Chemical and Biomolecular Engineering Department, University of Cantabria, Avda. Los Castros s/n, 39005 Santander, Cantabria, Spain

ARTICLE INFO

Handling Editor: Guan Zhu

Keywords:
Atmospheric manganese
Children
School
Dispersion modelling
CALPUFF

ABSTRACT

Children are susceptible to the health effects derived from elevated manganese (Mn) environmental exposure; residents living in urban areas where ferromanganese alloy plants are located are usually exposed to high Mn levels. In this work, a dispersion model developed by the USEPA, CALPUFF, has been used to estimate the airborne Mn levels near educational centers located in Santander bay, Northern Spain, an urban area where high Mn levels have been measured in the last decade. The CALPUFF model was validated in a previous work from a multi-site one-year observation dataset. Air manganese levels in 96 primary, secondary and high schools located in Santander bay were estimated using the CALPUFF model for two months corresponding to warm and cold periods using real meteorological data and Mn emission rates corresponding to different emission scenarios. Results show that when the emission scenario that best represented the observations dataset is used, the air Mn levels exceed the WHO guideline (i.e. 150 ng Mn/m^3) in 24% and 11% of the studied schools in the cold and warm periods respectively. These exceedances depend on the distance from the FeMn alloy plant and the direction of the prevailing winds. Additional emission scenarios based on the implementation of preventive and corrective measures are simulated and analysed in terms of the number of exceedances of the WHO guideline. The age range of children has been also considered in the analysis.

1. Introduction

The exposure to moderate/high levels of the metal(loid)s present in the atmosphere is of concern due to adverse health effects derived from their character (e.g. carcinogen, neurotoxic, etc.). Although a considerable contribution to the total metal(loid) emission is from natural origin, the anthropogenic emission of these pollutants is much higher in urban and industrial areas (Snyder et al., 2009). Iron and steel industry and the nonferrous metallurgy are reported to be the most intensive airborne and land pollution sources of the metal(loid)s (Hagelstein, 2009). For example, in 2003, the metals industry was the largest source of metal air toxics in the US followed by the electric power industry (Hagelstein, 2009). An environmental assessment of the iron and steel production performed by Strezov and Chaudhary (2017) revealed most significant contribution of manganese (Mn), followed by titanium (Ti), zinc (Zn), chromium (Cr) and lead (Pb). Moreover, Mn alloy production plants are the major source of air Mn (US EPA, 1984).

Although Mn is an essential and abundant micronutrient required for normal development and growth (Erikson and Aschner, 2003; Erikson et al., 2005; Nielsen, 1999), excessive and prolonged inhalation of Mn particulates results in its accumulation in selected brain regions that causes central nervous system (CNS) dysfunctions and an extrapyramidal motor disorder, referred to as manganism (Martin, 2006). Prolonged and chronic exposure to Mn represents a risk factor Parkinson's disease (Gorell et al., 1999). Different studies reported that inhalation is the most hazardous route of Mn exposure; airborne Mn directly enters the organism being absorbed very effectively (Andersen et al., 1999; Krachler et al., 1999; Mergler et al., 1999).

Since Mn is neurotoxic and considering that the brain and central nervous system are developed in the early years of life, the exposure to Mn may cause neurotoxic effects of particular concern in infants and children (Menezes-Filho et al., 2011; Rodríguez-Barranco et al., 2013). Exposure to environmental Mn in utero has also been associated with decreased neurocognitive and neuro-motor functions (Takser et al., 2004). Recent studies on children and infants have shown the association of Mn exposure with neurotoxic disorders, including motor, behavioral and cognitive deficits (Carvalho et al., 2014; Crossgrove and Zheng, 2004; Mora et al., 2015; Riojas-Rodríguez et al., 2010; Rodríguez-Barranco et al., 2013). Exposure to airborne Mn in children has been found to be associated with cognitive impairment measured as reduced Intelligence Quotient (IQ) (Menezes-Filho et al., 2011; Riojas-Rodríguez et al., 2010). Since Mn neurotoxicity is known for pyramidal

* Corresponding author.
E-mail address: fernandi@unican.es (I. Fernández-Olmo).

https://doi.org/10.1016/j.envint.2018.07.005
Received 4 April 2018; Received in revised form 2 July 2018; Accepted 3 July 2018

effects in adults and has been related to early Parkinsonism (Lucchini et al., 2007, 2012; Roels et al., 2012), control of motor function may be impaired also in younger individuals after early life exposure.

In the face of the evidence of unhealthy effects as a consequence of environment Mn overexposure, a reference concentration (RfC) of 50 ng/m^3 in the respirable fraction has been established by the U.S. Environmental Protection Agency for chronic exposure (US EPA, 1993). The Agency for Toxic Substances and Disease Registry (ATSDR) established a chronic-duration inhalation minimal risk level for Mn of 300 ng/m^3 (ATSDR, 2012). An annual average guideline value of 150 ng/m^3 has also been proposed by the World Health Organization (WHO, 2000). Nevertheless, the Air Quality European Directives (2004/107/EC and 2008/50/EC) only regulate the levels of other metal (loid)s such as As, Cd, Ni and Pb.

Air Mn levels in urban areas have been reported in the literature. Querol et al. (2007) reported air Mn concentrations of 4–23 ng/m^3 in numerous urban background sites in Spain. Datasets from 15 major cities in Korea over a 16-year time span (1991–2006) were evaluated by Myeong et al. (2009). The mean Mn concentration measured from all the major cities in Korea throughout the entire study period was 71 ng/m^3, while the annual mean values of different cities ranged from 10.5 ng/m^3 in Yeosu (2003) to 615 ng/m^3 in Wonju (2006). The Mn levels were considerably larger in industrialized areas than in other land-use types. The highest Mn concentrations reported in the literature are usually found in the vicinities of ferromanganese alloy plants. For instance, a 24-h Mn concentration of 1130 ng/m^3 has been reported by Colledge et al. (2015) in the Marietta community (Ohio, USA); Haynes et al. (2010) also reported an annual average concentration of 203 ng/m^3 in the same area. Close to Salvador (Brazil), a 24-h Mn concentration in $PM_{2.5}$ of 151 ng/m^3 was reported by Menezes-Filho et al. (2009). Ledoux et al. (2006) also reported a 12-h average air Mn concentration of 7560 ng/m^3 near a ferromanganese alloy plant located in Boulogne-Sur-Mer agglomeration (120,000 inhabitants, France). In addition, several studies have recently reported high levels of air Mn in the vicinity of a manganese alloy plant in the Region of Cantabria, northern Spain: Moreno et al. (2011) reported an annual average value of 166 ng/m^3 in the capital of this region, Santander, in the year 2007. Moreover, in Maliaño, a small town where the ferroalloy plant is placed, annual average levels of 781 and 1072 ng/m^3 were reported in 2005 and 2009 respectively (CIMA, 2006; CIMA, 2010). A maximum monthly value of 713.9 ng/m^3 was still measured in the same town in 2015 (Hernández-Pellón and Fernández-Olmo, 2016).

A useful way for assessing the exposure to metal(loid)s in the atmosphere is the use of dispersion models in order to provide an integrated understanding of the phenomena that take place (Chen et al., 2012). Furthermore, dispersion models are an essential instrument to develop abatement strategies that can help effectively reduce the levels of the metal(loid)s. Only a few studies have modelled the concentrations of air Mn: Haynes et al. (2010), Colledge et al. (2015) and Fulk et al. (2016) modelled the exposure to air Mn levels through the AERMOD model while Carter et al. (2015) simulated atmospheric Mn deposition using the SCIPUFF model. Industrial emission data for particulate-bound metals required to run these models have low confidence ratings since metal emissions are usually estimated on worst-case emission factors, and sometimes not reported (Hagelstein, 2009). The metal industry database quality is uncertain since most of the emission inventories are not representative of site conditions and operations (Hagelstein, 2009). In a recent study, a day-by-day Mn emission inventory depending on the operating conditions of a ferromanganese plant was developed to run the CALPUFF model to estimate the Mn levels in Santander bay (Otero-Pregigueiro et al., 2018). This model showed a reasonable agreement between observations and Mn modelled values in four sites close to the ferroalloy plant. Unlike AERMOD, CALPUFF is a non-steady-state puff model, and it is recommended for certain near-field applications involving complex terrain and meteorological conditions (Scire et al., 2000). For example, CALPUFF is capable of tracking the puff emitted before, during and after wind shifts and reversals (Burger, 2004), allowing to take into account the wind direction changes that typically occur in the summertime in Santander bay.

Taking into account that children are the most sensitive group to Mn environmental exposure, the large time they spend at school, and the high levels of Mn measured in the last years in Santander bay, the aim of this study is to evaluate the outdoor air Mn concentration in the educational centers existing along this bay using the CALPUFF dispersion model that was previously validated with a large experimental dataset (Otero-Pregigueiro et al., 2018). In addition, alternative emission scenarios corresponding to the potential application of preventive and corrective measures in the main Mn industrial source (i.e. the manganese alloy plant), and also considering the Mn emissions from other minor industrial sources, are evaluated using CALPUFF modelling, as a preliminary approach to estimate the exposure to one of the most susceptible population groups, corresponding to infants, children and adolescents.

2. Methodology

2.1. Site description

The study is focused on the Region of Cantabria, northern Spain, more precisely in Santander bay (Fig. 1). Main land uses are residential, industrial and commercial. SW and NE are the prevailing wind directions. The main industrial activities taking place in the bay are sources of air Mn, such as a steel plant, two iron foundries and a ferromanganese alloy production plant (see Fig. 1). The later one is located in Maliaño, a 10,000 inhabitants town, where high concentrations of Mn in ambient air have been previously reported (Hernández-Pellón and Fernández-Olmo, 2016; Hernández-Pellón et al., 2017). This town is 7 km away from Santander (172,656 inhabitants in 2016), which is the capital of Cantabria and the most populated city of the region.

The ferromanganese alloy production plant produces high carbon ferromanganese (FeMn HC), refined ferromanganese (FeMn MC) and silicomanganese (SiMn) in electrical furnaces with a maximum capacity of 225,000 t/year. Last reported production rate was 131,000 t in 2015 (Ferroatlántica, 2016). A total of 96 educational centers are located alongside the Santander bay inside a circle of 11 km radius centered at the ferroalloy plant. These schools account for 37,002 students: 23.2% are infants from 3 to 5 years old; 41.4% are children from 6 to 11 years old; 26.1% are teenagers from 12 to 15 years old and 9.3% are youths from 16 to 17 years old. A detailed list of these educational centers is shown in Table S1. The location of each center, the distance from the manganese alloy plant, and the number of students by age range are also shown in Table S1.

2.2. Model characteristics and setup

In a previous work, we used the CALPUFF model to estimate the PM_{10}-bound Mn concentration alongside the Santander bay; it was validated by comparing the modelled results with a multi-site one-year observation dataset (Otero-Pregigueiro et al., 2018). A detailed description of the Mn emission rate estimation and model characteristics and setup can be found in Otero-Pregigueiro et al. (2018). A brief summary is shown below; the Mn emission rates from the Mn industrial sources identified in the studied area (i.e. the manganese alloy plant, the steel plant and the iron foundries) were estimated from emission factors obtained from US EPA (1984); the required information about production rates, energy and raw material consumption, efficiency, and plant characteristics were taken from Environmental Declarations of the companies (Ferroatlántica, 2016; Global Steel Wire S.A., 2015) and Integrated Prevention and Pollution Control (IPPC) permits (BOC, 2008a, 2008b, 2008c, 2008d). A detailed description of the Mn sources and their emissions was only conducted for the ferromanganese alloy