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Characterisation of trace metals in atmospheric particles in the vicinity of iron and steelmaking industries in Australia

K. Mohiuddin [a,*], V. Strezov [a], P.F. Nelson [a], E. Stelcer [b]

[a] Graduate School of the Environment, Department of Environment and Geography, Faculty of Science, Macquarie University, NSW, Australia
[b] Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW, Australia

HIGHLIGHTS

- PM_1 to the PM_{10} mass at all sampling sites varies from 20 to 46%.
- Fe and Co in industrial coarse particles were correlated very strongly.
- Fe (0.20–12.2%) and Zn (0.05–2.0%) were the leading contributing metals.
- Mass concentration of industrial particles is about 0.5–2.5 times higher.
- Metal enrichment in industrial particles was found about 3.4–14 times higher.

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ABSTRACT

The aims of this work are to provide a detailed physicochemical assessment of atmospheric particles collected in the vicinity of three iron and steelmaking plants and to indicate the importance of chemical characterisation of the particles, in addition to the assessment of the particle size and concentrations. In this study, atmospheric sampling sites were selected downstream of three iron and steel processing operations in Australia and one background site in an urban area with little industrial activity. The collected particles were analysed for a range of particle size mass concentrations and detailed chemical analysis of the trace metals Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn in the corresponding particle size ranges was carried out. The $PM_{2.5}$ fractions in the PM_{10} particles at all sampling sites ranged from 35 to 62% indicating fine particles made a significant contribution to this size fraction at these sampling sites. Similarly, PM_1 to the total PM_{10} at all sites varied from 20 to 46% and contributed significantly to the PM_{10} mass loading. When compared to the background sampling site, all detected metals in the particles collected near the iron and steelmaking operations had 3.4–14 times higher concentrations of PM_{10}, $PM_{2.5}$ and PM_1. Iron (Fe) was found to be the dominant metal in the particles collected in vicinity of the iron and steel processing industries contributing up to 12% of the total particle mass loading. This study suggests that the metal composition of PM_{10}, $PM_{2.5}$ and PM_1 varies significantly between sites and the associated metal exposure value is considerably higher in the vicinity of iron and steel processing industries than in the urban area for the same particle concentration level.

1. Introduction

Steel has a significant role in modern society with continued demand due to diverse applications of steel products. Production of iron and steel is associated with a number of significant environmental challenges, one of which is emission of particles to the atmosphere. Iron and steel industries generate a significant amount of coarse particles mainly originating from mechanical processes such as moving piles of iron ore, coal and iron ore loading, and release of and reactions of fine particles in high temperature processes such as cokemaking, sinter plants, blast furnaces and basic oxygen furnaces. Atmospheric particles can have potential adverse impacts on human health through inhalation and respiratory deposition, with children, the elderly and people with respiratory problems being especially vulnerable groups of the population. Metals associated with atmospheric particles can cause harmful effects on human health (Lippmann et al., 2006; Lippmann and Chen, 2009; Bollati et al., 2010) and ecosystems (Berggren et al., 1990; de Vries et al., 2007).

* Corresponding author.
E-mail addresses: kazi.mohiuddin@mq.edu.au, ammohiuddin@yahoo.com (K. Mohiuddin).

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The impact of atmospheric particles on human health and environment depends on their physical and chemical properties. In the atmosphere, particles can change their size, adsorb gaseous molecules onto their surface, coalesce with each other and can be removed by deposition processes. Epidemiological investigations strongly suggest that human mortality and morbidity is increased due to higher concentration of inhalable particles (Pope, 2000; Lin and Lee, 2004; Querol et al., 2004; Arditsoglou and Samara, 2005; Dominici et al., 2005; Namdeo and Bell, 2005; Ning and Sioutas, 2010), but respirable particles in the size range of $PM_{2.5}$ and PM_1 are particularly hazardous as they can be transported deep into the alveolar region of the lungs and the bloodstream (Krombach et al., 1997; Park and Wexler, 2008; Valiulis et al., 2008).

Apart from the particle size distribution, the chemical composition of particles is particularly important for environmental assessment of specific emissions. Inhalation of iron dust has been linked to chronic bronchitis, breathlessness, chronic cough (Xu et al., 1992), chronic phlegm (Chen et al., 2006), pneumoconiosis (Kuo et al., 1998), reduced lung function (Banks et al., 1999), and can lead to chronic obstructive pulmonary disease (COPD) (Driscoll et al., 2005). Previous studies showed the chemical properties of atmospheric particles were related to iron emissions with different industrial processes including iron and steel industries (Querol et al., 2004; Garimella and Deo, 2008). Atmospheric particulates generated from iron and steel industries have high concentrations of Cd, Cr, Fe, Mn, Ni and Zn (Machemer, 2004; Querol et al., 2007). Pope et al. (1992); Pope (1996) described how the closure of a Utah Valley steel mill resulted in an overall decrease in PM_{10} concentrations and associated Fe, Cu and Zn content. Hutchison et al. (2005) found increasing inflammation of rat's lungs with increasing metal content in atmospheric particles released from steelworks. In addition, the Fe-bearing particles in total suspended particles and PM_{10} are found in higher concentrations nearby steel plants (Ledoux et al., 2006; Mazzei et al., 2006; Choël et al., 2007), however there are uncertainties in trace metals, including iron associated with size resolved air particles, especially fine and submicron size particles, in the vicinity of iron and steel industries in Australia.

The objective of this study was to investigate the metals associated with atmospheric PM_{10}, $PM_{2.5}$ and PM_1 particles and to reveal the dominant particle size and marker elements in the vicinity of iron and steel industries in Australia. To achieve this, the concentration of selected trace metals Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn in atmospheric PM_{10}, $PM_{2.5}$ and PM_1 collected near three iron-steel plants and an urban background sites in Australia were analysed. This work aims to improve the understanding of the dominant size and trace metals, physicochemical characteristics, and human exposure levels of air particles in the vicinity of different iron and steel processing plants in Australia when compared to the results from a non-industrial urban background site.

2. Methods

2.1. Sampling sites

Four sampling sites were selected from different areas in Australia to investigate concentration of metals in atmospheric particles collected near different iron and steelmaking plants. These sites were Cringila (CR), Rooty Hill (RT) and Macquarie Park (MQ) located in New South Wales and Whyalla (WH) site located in South Australia. CR and WH sampling sites were located in the vicinity of integrated iron and steel processing industries. The processing route of these industries is blast furnace (BF) - basic oxygen furnace (BOF). RT sampling site was located near an electric arc furnace (EAF) steelmaking process. MQ site was located in an urban area near to the sports field at Macquarie University, about 20 kms from the Sydney CBD. This sampling location was selected for comparison as there should be little very near field influence by industrial activity as the closest significant industrial site is more than 5 km from this location. The CR and WH are described as urban-industrial sites, RT as an industrial site and MQ as an urban-background site. Meteorological conditions especially wind speed and direction at all sampling sites are important influential factors for particle deposition and for their transportation range. Fig. 1 shows the windroses at CR, RT, WH and MQ sites during PM sampling campaign which indicates the multi directional wind gust at the sampling sites in addition to the downwind direction from Wollongong steelworks (WOS), Rooty Hill steelworks (ROS) and Whyalla steelworks (WHS) as an important parameter for short and long term air particle transportation from multiple sources.

2.2. Sampling equipment

An eight staged Micro Orifice Uniform Deposit Impactor (MOUDI) model M100-R was deployed at the sampling sites to collect the atmospheric particles from April 2011 to November 2011. The range of aerodynamic diameter of atmospheric particle (Dp) was used to present the size distribution of particle population as coarse ($10 < Dp < 2.5$ μm), intermodal ($2.5 < Dp < 1$ μm) and submicron ($Dp < 1$ μm) particles. The 50% cut off diameters (D_{50}) of the MOUDI stages were 10.0, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32 and 0.18 μm including an inlet (18 μm) and exit stage (<0.18 μm) (Marple et al., 1991). The sampling flow rate of 30 l min^{-1} was used for the entire sampling campaign. The inlet level of MOUDI sampler was at 1.5 m height from the ground. Stretched Teflon filters (PTFE membrane, 2 μm pores, 47 mm diameter, Pall Corporation) were used as substrate in all stages of the MOUDI sampler. Seven sets (10 samples per set from inlet and exit stage in addition to eight stages of MOUDI sampler) of air particulate samples of different size fractions were collected from each sampling site for at least 24 h particle loading.

2.3. Sample analysis

Teflon substrates were weighed before and after the atmospheric sampling at the Australian Nuclear Science and Technology Organisation (ANSTO) using Mettler Toledo MX5 microbalance with repeatability of 1.0 μg. Both blank and loaded Teflon substrates were conditioned for 24 h by maintaining humidity of 45 ± 5% and temperature of 22 ± 1.5 °C to reach equilibrium. Laboratory standard weights of 50 and 20 mg were measured before, during and after each weighing session to ensure accuracy of the weight measurements. The mass and elemental concentrations of PM_{10}, $PM_{2.5}$ and PM_1 were calculated by summing the concentrations of the corresponding stages.

The collected aerosol samples were analysed at ANSTO using multi-elemental accelerator based Proton Induced X-ray Emission (PIXE) technique. This technique can measure the following most commonly occurring elements in atmospheric particles: Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn and have been described in detail elsewhere (Cohen, 1993, 1998; Cohen et al., 1996). The trace metals of particular interest related to iron and steel processing industries such as Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn are analysed and discussed in this study. The total particle deposition area was measured using a dot grid method assuming the particle deposition under each nozzle is uniform. After acquiring the digital images of particles on Teflon substrates, the total surface area was calculated using transparent plastic sheet with imprinted dot grid lines.