PHYSICO-CHEMICAL CHARACTERIZATION OF MANGANESE-BEARING PARTICLES IN AN URBAN AREA LOCATED CLOSE TO A MANGANESE ALLOY PRODUCTION PLANT

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Introduction

In recent years, numerous studies in relation with ambient air manganese exposure health effects, mainly associated with neurotoxic disorders, have been developed, not only focused on occupational, but also in non-occupational exposure (Roels et al., 2012). Despite there is still no agreement about the effects of non-occupational manganese exposure and there is not a specific European regulation that establishes limit values for manganese in air, institutions such as the World Health Organization (WHO) has proposed an annual average guideline value of 150 ng/m^3.

Manganese is a transition metal, which can occur in various oxidation states (primarily Mn^{+2}, Mn^{+3}, Mn^{+4}). Despite more efforts should be done in establishing its bioaccesibility and toxicity mechanisms, it is generally agreed that it is strongly linked to particle size and morphology, chemical composition and oxidation state. In this respect, the use of scanning electron microscopy-energy dispersive X ray (SEM-EDX) and X ray diffraction (XRD) can be valuable tools, leading to an improvement in the assessment of manganese potential hazardous effects in both environment and human health. Since only a few studies deal with manganese-bearing particles emitted from ferroalloy plants (Marris et al., 2013), the present study aims to deepen the understanding of the physico-chemical characteristics of particulate matter and atmospheric deposition in the nearby of a manganese alloy plant located in an industrial-urban area.

Methods

Sampling locations. Two sampling points were chosen in the proximity of a ferroalloy plant, which specializes in silicomanganese and ferromanganese alloy production, located in Cantabria (northern Spain), in a industrial-urban area where previous studies have shown high concentrations of manganese in ambient air (Moreno et al., 2011).

Sample collection. Aerosol samples have been collected by means of low and high volume samplers (2.3 m^3/h and 30 m^3/h respectively) onto quartz fiber, cellulose and polycarbonate filters. The most suitable sampling time and substrate were chosen for each technique. Atmospheric deposition samples have been collected monthly based on EN 15841:2009 and then filtered onto nitrocellulose filters.

Analysis. The Mn level in the studied samples was determined by ICP-MS after a microwave-assisted acid digestion. The size, morphology and chemical composition of the individual particles present in each matrix were studied by SEM-EDX. XRD was used to determine the composition of the major crystallographic phases.

Results

The Mn levels in the studied samples ranged from 22 to 1279 ng/m^3 in PM_{10} and from 2000 to 4000 µg/m^2day in bulk deposition. Different particle groups were identified by SEM-EDX in bulk deposition samples, most of them containing Mn. The three most abundant groups were: (i) 13 to 28% of particles containing mainly Si, Ca, Mn, Al and Mg and attributed to vitrified silico-manganese slag; (ii) 12 to 27% of particles with Mn, Fe and Si as main elements corresponding to Mn alloys products; (iii) 11 to 18% of particles composed of Mn, Si, Fe, Al and Ca attributed to manganese ore. These groups were found in lower amount in PM samples where spherical particles were significantly evidenced and ascribed to condensates from the Mn alloy smelting process. Since silico-manganese slags are mainly vitreous, few manganese species associated to these slags were identified in deposition samples by XRD: e.g. alabandite (MnS). Rhodochrosite ($MnCO_3$) was also identified in deposition and PM samples; it is assumed that this phase is present in fugitive emissions from Mn ore piles. Hausmannite (Mn_3O_4), manganosite (MnO) and bixbyite $(Fe,Mn)_2O_3$ were also identified in deposition samples, probably from emissions originated at the Mn ore storage and the ferroalloys milling process.

Conclusion

Manganese-bearing particles are mostly present in PM and bulk deposition samples collected in an urban area in the vicinity of a manganese alloy plant, most of them consisting of silico-manganese slags, Mn alloys and Mn ores together with spherical particles coming from condensation processes at the smelter.

References

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