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Monitoring the levels of particle matter-bound manganese: An intensive campaign in an urban/industrial area

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Abstract

The aim of this work is to monitor the manganese levels in the particulate matter throughout the Santander Bay, an urban/industrial area located in the region of Cantabria (northern Spain). Previous studies developed in the region have shown high concentrations of manganese in ambient air according to the World Health Organization (WHO) criteria, most likely due to the presence of a ferromanganese alloy plant in the area. An intensive PM_{10} sampling campaign has been carried out for a year in nine monitoring sites (one per month) by means of a low volume sequential sampling device (2.3 m^3/h) equipped with a 15 filter cartridge. 28 samples have been collected in each location onto 47 mm quartz fiber filters. The filters were subjected to microwave assisted acid digestion (HNO_3:H_2O_2 with a mixture of 8:2 ml) based on UNE-EN 14902:2006. Inductively coupled plasma mass spectrometry (ICP-MS) was then used for metal analysis. In addition to Mn, also Ti, V, Fe, Ni, Cu, Zn, As, Mo, Cd, Sb and Pb were analyzed. According to the results obtained in the present sampling campaign, the highest daily manganese level at Santander Bay reached 3200 ng/m^3 with a monthly average higher than the 150 ng/m^3 established by the WHO as an annual average guideline value in six monitoring sites (up to 713.9 ng/m^3). The highest manganese levels were found at N-NE of the ferroalloy plant, which agrees with the prevailing winds (S/SW). Although monthly samplings have been carried out in each location, these results suggest that manganese concentrations in ambient air in some sites of the Santander Bay would exceed the WHO recommendation. In addition, the strong linear relationship found between Mn and V, Fe, As, Cd and Pb in the vicinities of the plant suggests that the presence of some of these metals in the area may be also related to this activity.

Keywords: Manganese; Particulate matter; Ferromanganese alloy industry

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1. Introduction

Manganese is an element present in nature in different environmental matrices: soils, rocks, water, etc. Although in some areas, the presence of manganese in air is a consequence of natural phenomena, high manganese concentrations come from anthropogenic sources. Manganese emissions to the atmosphere are mainly as particles. Smallest particles will remain suspended, while bigger particles and the soluble fraction of small particles will be deposited on the surface by dry and wet deposition. The main sources of anthropogenic manganese emissions are: ferromanganese alloy production, battery production, fuel consumption and to a minor extent the used of anti-detonating additives in gasoline in some countries. There is a growing interest in ambient air manganese exposure, especially in susceptible groups like children and infants. Occupational exposure effects to high/moderate levels of manganese in ambient air have been widely reported mainly linked to neurological problems. However, recent studies suggest that health effects due to non-occupational manganese exposure may be also associated with neurotoxic disorders, including motor and cognitive deficits (Carvalho et al., 2014; Lucchini et al., 2012). Since manganese is not considered as a carcinogenic element, there is not a specific European regulation that establishes limit values for manganese in air. However, the World Health Organization (WHO) has proposed as a guideline an annual average limit value of 150 ng/m^3.

The aim of this work is to monitor the levels of manganese in the particulate matter in an urban/industrial area in the region of Cantabria (northern Spain), where previous studies have shown high concentrations of manganese in ambient air according to the WHO criteria. The location of a ferroalloy plant in the area, which specialises in silicomanganese and ferromanganese alloy production, has been identified as the most likely source of manganese. As Table 1 shows, in 2007 manganese levels in air exceeded the WHO guideline in Santander (Moreno et al., 2011), capital of the region (7 km NE of the plant). After 2008 the implementation of corrective measures in the ferroalloy plant, due to the application of the integrated pollution prevention and control (IPPC) permit led to an improvement of the manganese air concentrations in Santander. Mean annual values of 49.1 ng/m^3 (Arruti et al., 2010) and 31.5 ng/m^3 (Ruiz et al., 2014), were obtained in 2008 and 2009, respectively. Also, the environmental research center of the region (CIMA) has reported manganese levels above the WHO guideline in 2005 and 2009 (781 ng/m^3 (CIMA, 2006) and 1072 ng/m^3 (CIMA, 2010), respectively) in Maliaño, a small town where the ferroalloy plant is located. In accordance with this, the present study also aims to verify the improvement in the manganese levels nearby the ferromanganese alloy plant.

Table 1. Previous manganese levels in PM_{10} along the Santander Bay.

Site	Year	Mean (ng Mn/m^3)	Maximum (ng Mn/m^3)	Reference
Santander, Tetuán	2007	166	1041	Moreno et al., (2011)
Santander, ETSII y T	2008	49.1	242	Arruti et al., (2010)
Santander, ETSII y T	2009	31.5	201	Ruiz et al., (2014)
Alto Maliaño	2005	781	19440	CIMA, (2006)
Alto Maliaño	2009	1072	8860	CIMA, (2010)
Guarnizo, CIMA	2009	118	587	Ruiz et al., (2014)

2. Methodology

2.1 Area of study

The area of study of this work is located in the north of Spain, in the region of Cantabria, specifically along the Santander Bay an urban/industrial area with a population of around 250000 inhabitants located at less than 10 km from a ferromanganese alloy plant. To perform this study nine monitoring sites were selected trying to cover as many angles from the likely manganese source as possible, in order to contemplate all possible wind direction scenarios. Whenever possible, closed locations from the source were selected, distances ranging from 0.3 to 2.5 km. Among the selected sampling locations there are schools, high schools, cultural centres, etc. Figure 1 shows the location of the nine monitoring sites with respect to the placement of the ferromanganese alloy plant.

Fig. 1. Sampling points selected to perform the intensive PM_{10} sampling campaign: 1. CROS: Official monitoring site (CIMA), 2. GUAR: Official monitoring site (CIMA), 3. VALLEC: Valle de Camargo Secondary School, 4. CULTJH: Juan de Herrera Cultural Center, 5.CPPV: Pedro Velarde Public School, 6.CPJH: Juan de Herrera Public School, 7.CCV: La Vidriera Cultural Center, 8.CMFC: Cros Municipal Center for training, 9. GUARCRC: Private house in Guarnizo town

2.2 Sampling and analysis

The 24-h PM sampling campaign has been performed for 1 year, from January 2015 to January 2016 by a low volume sequential sampling device (PM_{10}, 2.3 m^3/h) equipped with a 15 filter cartridge. This sampler was moved once a month to a different location in order to collect 28 daily samples per location and a total of 252 samples during the whole sampling campaign. PM_{10} has been collected onto 47 mm quartz fiber filters (Sartorius).

Once the gravimetric determination was performed, the filters were subjected to microwave assisted acid digestion (HNO_3:H_2O_2 with a mixture of 8:2 ml, up to 220ºC) based on UNE-EN 14902:2006. Inductively coupled plasma mass spectrometry (ICP-MS) was then used for metal analysis. In addition to manganese, Ti, V, Fe, Ni, Cu, Zn, As, Mo, Cd, Sb, Pb were also analyzed in order to look for correlations between them.

3. Results and discussion

Table 2 summarizes the position of the sampling locations with respect to the manganese source, the sampling periods, maximum and mean manganese levels and the standard deviations obtained in all the monitoring sites during the intensive sampling campaign. It should be noted that although monthly samplings have been carried out at each location, these results suggest that manganese levels would exceed the 150 ng/m^3 established by the WHO as an annual average in 6 of the 9 monitoring sites. This was corroborated from an extensive annual sampling campaign carried out in CROS site in 2015 (one sample per week, 52 samples), where an annual mean manganese level of 231.8 ng/m^3 was obtained, similar to the monthly mean value obtained in February (266.7 ng/m^3). The maximum monthly mean value was found at CPJH site (713.9 ng/m^3), reaching a maximum daily value of 3204 ng/m^3.

Table 2. Location of the monitoring sites in relation with the ferromanganese alloy plant. Sampling period, maximum and mean manganese level in air (ng/m^3) and standard deviation obtained in the nine monitoring sites

Site	**Distance (m)**	**Position**	**Sampling period (2015)**	**Maximum (ng Mn/m^3)**	**Mean (ng Mn/m^3)**	**Standard deviation (ng Mn/m^3)**
CROS	850	NNW	30/01-27/02	1670.5	266.7	450.7
GUAR	790	S	04/03-01/04	917.2	156.3	226.6
VALLEC	1380	W	22/04-20/05	155.1	36.9	43.5
CULTJH	800	NE	22/05-19/06	1068.9	208.0	319.1
CPPV	730	WNW	23/06-21/07	657.9	130.0	146.9
CPJH	400	NNE	23/07-21/08	**3204.0**	**713.9**	653.8
CCV	350	NNW	02/09-30/09	2061.6	670.4	652.0
CMFC	1130	N	02/10-30/10	1859.5	589.2	575.2
GUARCRC	2450	SSW	14/11-13/12	126.8	25.4	29.9

As Figure 2(a) shows, during the sampling period in CPJH site the most frequent winds were from S-SW with low speeds (0.28-2 m/s) and NE with low, but also medium speeds (2-4 m/s). This wind pattern is frequent in this area in summer. As it is shown in the manganese rose plotted over the map in Figure 3, the highest manganese concentrations (>1000 ng/m^3) come mainly from WSW and SWS, in accordance with the ferromanganese alloy plant location, and not from NE, even though it is the most frequent wind sector. The second highest monthly and daily values were found at CCV site (670.4 ng/m^3 and 2061.6 ng/m^3, respectively). The third and fourth highest monthly and daily values were found at CMFC site (589.2 ng/m^3 and 1859.5 ng/m^3, respectively) and at CROS site (266.7 ng/m^3 and 1670.5 ng/m^3, respectively). Although CMFC and CROS sites are located very close, significant differences between manganese levels have been found probably due to the meteorological conditions. In particular, the sampling at CMFC site coincided with a period of low rainfall (42 mm), while precipitation at CROS site during the sampling period was much higher (300 mm).

In Figure 2(b), the wind rose at CROS site shows that during the sampling period the most frequent winds came from S-SW with low speeds (0.28-2 m/s). This wind pattern is frequent in this area in winter. In Figure 3 manganese rose also shows that even though the most frequent winds came from WSW direction, higher manganese levels sourced from S and SWS, in accordance with the ferroalloy plant location.

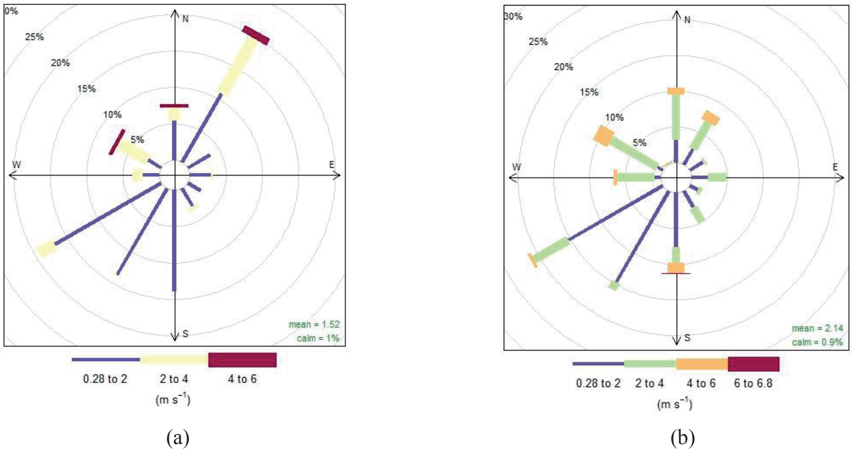

Fig. 2: Wind roses calculated at the studied area: (a) CPJH site (23/07/15 to 21/08/15). (b) CROS site (30/01/15 to 27/02/15). Wind roses developed with Openair tools. According to Beaufort scale, calm criteria: 0.28 m/s

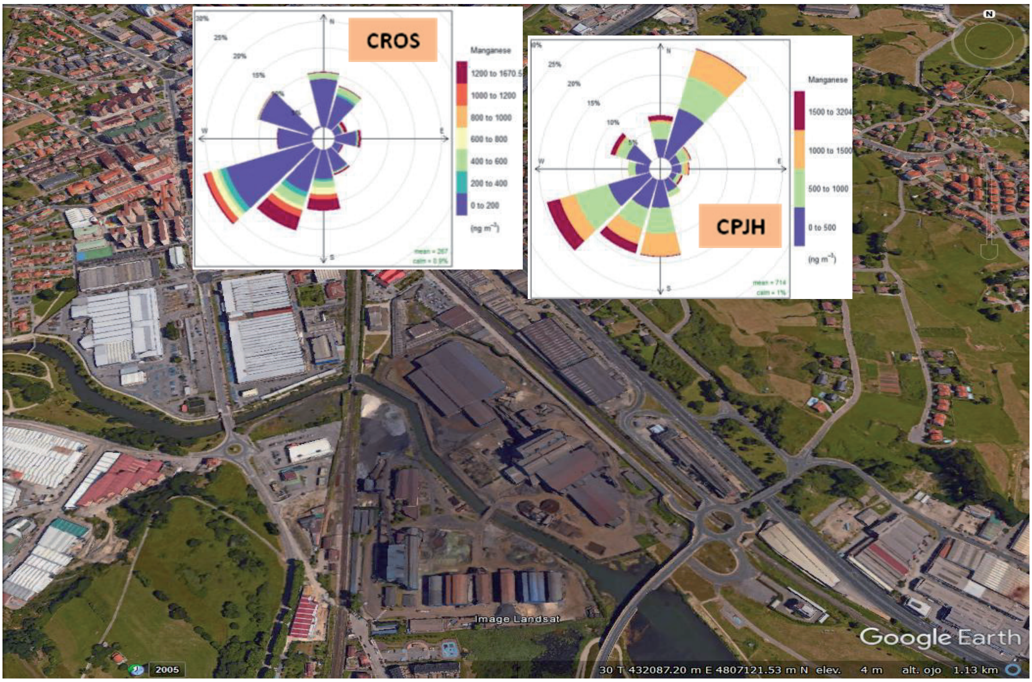

Fig. 3: Manganese roses at CPJH (23/07/15 to 21/08/15) and CROS (30/01/15 to 27/02/15) sites. Manganese roses developed with Openair tools. According to Beaufort scale, calm criteria: 0.28 m/s

As Table 3 shows, strong linear relationship between Mn and V, Fe, As, Cd and Pb was found at CROS and CCV sites, located in the N direction in the vicinities of the ferroalloy plant. The high correlation between Fe and Mn can be attributed to the presence of both metals as major components of the alloys. Since Pb has been previously identified as an impurity contained in the manganese ores, the presence of this metal in air in the area may be related with the ferroalloy plant production; however further work should be done in order to explain the high correlations between Mn and V, Cd and As.

Table 3. Pearson coefficient between manganese and V, Fe, As, Cd and Pb ($p<0.01$)

Site	**V**	**Fe**	**As**	**Cd**	**Pb**
CROS	0.85	0.76	0.64	0.85	0.76
CCV	0.67	0.74	0.72	0.68	0.77

4. Conclusions

Although manganese air concentrations have improved with respect to 2007-2008, still exceed the value of 150 ng/m^3 established by WHO as an annual average guideline value in some sites of the Santander Bay. The highest manganese levels are found at sites located at N-NE of the ferroalloy plant, which agrees with the prevailing winds (S/SW). Therefore, further corrective measures should be applied to reduce the air manganese levels in the area closed to the ferroalloy plant. Furthermore, the development of a manganese air concentrations data base in the area will be a useful tool for the regional administration and for future modeling and epidemiological studies.

5. Acknowledgements

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