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Personal inhalation exposure to manganese and other trace metals in an environmentally exposed population: Bioaccessibility in size-segregated particulate matter samples

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ABSTRACT

Exposure to environmental airborne manganese (Mn) can lead to neurotoxic disorders and cognitive deficits. The degree of exposure can be assessed by personal sampling of particulate matter (PM) or through biomarkers of exposure. The aim of this work was to characterise the personal exposure to airborne Mn and other trace metals by measuring their bioaccessibility in PM filters taken from personal samplers in an environmentally exposed adult population living in the vicinity of a ferromanganese alloy plant in Santander Bay (northern Spain). Concentrations of bioaccessible and non-bioaccessible Mn and other metals associated with coarse ($PM_{10\text{-}2.5}$) and fine ($PM_{2.5}$) modes were quantified from 24 h personal samplers in 130 participants divided into two groups according to their Mn exposure: highly ($n = 65$) and moderately ($n = 65$) exposed. Gastric fluid and artificial lysosomal fluid (ALF) were used in the bioaccessibility tests as surrogate agents for the body fluids that can come into contact with coarse and fine particles, respectively. The mean air Mn levels in $PM_{10\text{-}2.5}$ and $PM_{2.5}$ were 127.2 and 126.2 ng/m^3, respectively, in the highly exposed group, and 18.6 and 31.7 ng/m^3 in the moderately exposed group. The bioaccessibility (%) of Mn in gastric fluid and ALF was also found to be greater in the highly exposed group. The results indicate that people living near Mn alloy plants have an increased potential health risk for Mn exposure due to higher total air Mn concentrations and bioaccessibility.

1. Introduction

Chronic exposure to ambient air manganese (Mn) can induce neurotoxic effects (Lucchini et al., 2009; Fernández-Olmo et al., 2020). One of the most significant anthropogenic sources of airborne Mn is the production of ferromanganese alloys, besides battery manufacturing and road traffic due to fuel consumption in countries where methylcyclopentadienyl Mn tricarbonyl (MMT) is permitted for use as an anti-knocking agent in fuels (US EPA, 1984). Although, Mn is not regulated by a specific European air quality directive, the World Health Organization (WHO) has proposed an annual average guideline value of 150 ng/m^3 (WHO, 2000).

The exposure to air Mn in residential areas near Mn industrial sources may be assessed by measuring its concentration in particulate matter (PM) filters from stationary and personal sampling campaigns, or by using biomarkers of exposure to Mn. Traditionally, stationary samplers have been used to monitor metals in ambient PM. However, such samplers only provide information about the specific site where the monitoring is taking place (Fulk et al., 2016); another option is the use of PM personal samplers.

Relatively few studies have measured the personal concentration of trace metals (Graney et al., 2004; Pollitt et al., 2016). Most of them focused on one specific metal; for example, epidemiological studies in population groups exposed to Mn that analysed the total content in airborne PM collected from Personal Environmental Monitors (PEMs) (Solís-Vivanco et al., 2009; Haynes et al., 2012; Lucchini et al., 2012). However, the metal (loid)s bioaccessibility (i.e., the fraction of an element that is solubilised in a simulated biological solution), rather than its total content, may provide a more accurate picture of the risk of inhalation exposure (Mukhtar and Limbeck, 2013; Wiseman, 2015). While several studies have been conducted into the bioaccessibility of trace elements in PM filters from stationary samplers (Wiseman and

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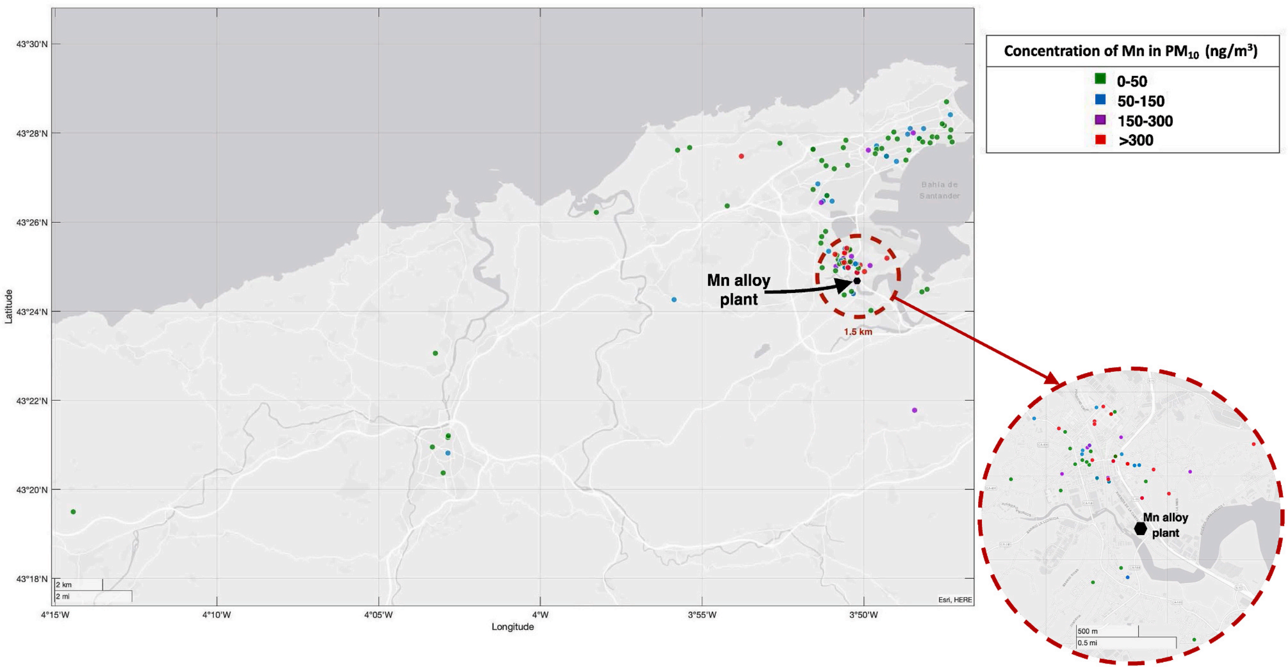

Fig. 1. Location of participants' residence and the Mn alloy plant. Total Mn concentration in PM_{10} (ng/m^3) for each participant is also shown.

Zereini, 2014; Hernández-Pellón et al., 2018), the concentration of bioaccessible metals from PEMs remains to be investigated. This is a critical goal because trace elements solubilised in biological fluids may reach the systemic blood circulation, thus posing a greater risk to humans. Only a few authors have measured the water-soluble fraction of trace metals on personal filters (Graney et al., 2004; Yang et al., 2018). However, the use of water as a leaching agent is not as suitable as that of biological fluids to simulate the conditions inside the human body (Caboche et al., 2011; Wiseman, 2015). In this regard, Graney et al. (2004) highlighted that biological fluids should be used in extraction/leaching procedures applied to PEMs. The synthetic body fluid should be selected according to the fate of the PM in the human body, which depends on its particle size. Coarse particles in the range 2.5–10 μm ($PM_{10\text{-}2.5}$) are mostly deposited in the pharyngeal and tracheal region, at which point they are swallowed and transported towards the digestive system where they come into contact with the gastric juice (Falta et al., 2008; Alpofead et al., 2016; Gao et al., 2018; Corona-Sánchez et al., 2021). Whereas fine particles of less than 2.5 μm ($PM_{2.5}$) can be transported to the alveolar region, where they may dissolve inside phagolysosomes (Mukhtar and Limbeck, 2013; Kastury et al., 2018b; Corona-Sánchez et al., 2021; Expósito et al., 2021).

The aim of this work was to characterise adult personal exposure to airborne Mn and other metals collected in the Cantabria region (northern Spain), whose presence in ambient air has been mainly attributed to a Mn alloy plant (Hernández-Pellón and Fernández-Olmo, 2019a,b). We determined the contents of bioaccessible and non-bioaccessible Mn (i.e., the fraction of non-solubilised metal in the chosen simulated fluid) and other metals (Fe and Pb) in coarse ($PM_{10\text{-}2.5}$) and fine ($PM_{2.5}$) modes and studied the correlation between Mn exposure and the distance from the participant's residence to the Mn alloy plant.

The results presented in this paper are part of a cross-sectional study intended to describe the environmental personal exposure to Mn and other metals using PEMs and certain biomarkers of exposure, and to determine the association between environmental Mn exposure and motor and cognitive function in an adult population.

2. Materials and methods

The study was carried out in Santander Bay (Cantabria, northern Spain) where there is a ferromanganese alloy plant. A personal PM sampling campaign was carried out from November 2019 to November 2020 using PEMs. One hundred and thirty volunteers were recruited and the population divided into two groups: (1) highly exposed ($n = 65$): participants living ≤1.5 km from the Mn alloy plant, and (2) moderately exposed ($n = 65$): participants living >1.5 km from the plant. Fig. 1 shows the location of the participants' residence and the Mn alloy plant.

A two-stage personal modular impactor (SKC PMI coarse) connected to a personal pump (SKC Airckeck XR5000) operating at a flow rate of 3 L per minute (lpm) was used to collect 24-h $PM_{2.5}$ and $PM_{10\text{-}2.5}$ samples. The $PM_{2.5}$ and $PM_{10\text{-}2.5}$ samples were collected on 37 and 25 mm polytetrafluoroethylene (PTFE) membrane filters, respectively.

Filters were analysed in a two-step procedure. First, the in vitro bioaccessibility test was carried out by extracting each filter with 10 ml of each leaching agent in an end-over-end rotation incubator system at 30 rpm and 37 °C. After the leaching test, samples were centrifuged and the supernatants filtered. The experimental procedure is described in detail in Expósito et al. (2021). According to this procedure, gastric fluid, using the composition given by the US EPA (2007), was selected as the surrogate agent to represent the body fluids that can come into contact with coarse particles. A limitation of this procedure is the assumption that all the coarse particles are cleared by mucociliary activity and swallowed towards the digestive system. According to Kastury et al. (2018a), approximately 90% of these particles are cleared via this mechanism. On the other hand, simulated lung fluids (SLFs) are recommended as surrogate agents for fine particles (Kastury et al., 2018b; Corona-Sánchez et al., 2021). Gamble's solution and artificial lysosomal fluid (ALF) are the most commonly used SLFs. However, as the PM mass collected by the PEMs was very low, we only used one SLF: ALF was selected as the lung fluid to extract $PM_{2.5}$ filters because of its higher bioaccessibility with respect to Gamble's solution (Hernández-Pellón et al., 2018), and because ALF-based bioaccessibility is independent of the L/S ratio, unlike that based on Gamble's solution (Expósito et al., 2021). The composition of ALF was based on the one used by Colombo et al. (2008). Different extraction times were used according to previous studies; thus, 24 h was chosen for ALF (Caboche et al., 2011; Kastury

Table 1
Detection limits for the studied metal (loid)s, number and percentage of samples with metal (loid)s concentrations below the detection limit ($n = 130$).

		V	Mn	Fe	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
Coarse, bioaccessible	DL	5.47	0.76	14.39	7.39	0.86	58.33	0.04	0.55	0.11	0.20	5.74
	n < LD	130	2	28	125	92	120	107	122	112	119	127
	% < LD	100.0	1.5	21.5	96.2	70.8	92.3	82.3	93.8	86.2	91.5	97.7
Coarse, Non-bioaccessible	DL	0.14	2.52	64.00	25.16	15.15	41.03	0.07	1.24	0.32	2.32	1.84
	n < LD	58	53	86	129	123	112	124	129	125	130	126
	% < LD	44.6	40.8	66.2	99.2	94.6	86.2	95.4	99.2	96.2	100.0	96.9
Fine, bioaccessible	DL	0.51	0.59	31.42	8.13	3.48	13.00	0.24	0.12	0.27	0.20	0.42
	n < LD	127	6	88	124	88	72	113	107	90	100	16
	% < LD	97.7	4.6	67.7	95.4	67.7	55.4	86.9	82.3	69.2	76.9	12.3
Fine, Non-bioaccessible	DL	0.16	0.99	36.56	5.39	6.07	17.37	0.06	0.14	0.03	0.10	0.73
	n < LD	29	9	40	110	100	84	122	100	0	3	69
	% < LD	22.3	6.9	30.8	84.6	76.9	64.6	93.8	76.9	0.0	2.3	53.1

Table 2
Characteristics of the study population by exposed group.

Characteristics		Moderately exposed (>1.5 km) $n = 65$	Highly exposed (≤1.5 km) $n = 65$	Total $n = 130$	*p*-value[a]
Distance from the main metal source [km]	Mean (SD)	7.30 (5.29)	0.80 (0.30)	4.05 (4.94)	<0.001
	Range	2.04–33.98	0.27–1.50	0.27–33.98	
Age	Mean (SD)	39.77 (13.45)	43.66 (14.31)	41.72 (13.97)	0.092
	Range	20–71	20–71	20–71	
Sex	Female, n (%)	46 (70.8%)	49 (75.4%)	95 (73.1%)	0.553
	Male, n (%)	19 (29.2%)	16 (24.6%)	35 (26.9%)	
Years residing	Mean (SD)	11.60 (12.42)	18.97 (14.04)	15.26 (13.71)	<0.001
	Range	1–60	1–71	1–71	

[a] From Chi-squared (sex) or U Mann Whitney test (rest of variables).

Table 3
Bioaccessible and non-bioaccessible concentrations (ng/m^3) in $PM_{10-2.5}$ and $PM_{2.5}$ modes by exposed group.

	Highly exposed (n = 65)		Moderately exposed (n = 65)		Total (n = 130)		
	Mean (SD)	Median	Mean (SD)	Median	Mean (SD)	Median	p-value[a]
Concentration of Mn in PM_{10} (ng/m^3)	253.40 (440.66)	105.67	50.38 (81.23)	19.97	151.89 (331.66)	43.87	<0.001
Concentration of Mn in $PM_{10-2.5}$ (ng/m^3)	127.24 (292.37)	53.49	18.63 (43.92)	7.86	72.93 (215.26)	16.47	<0.001
Concentration of Mn in $PM_{2.5}$ (ng/m^3)	126.16 (190.10)	44.58	31.74 (48.43)	12.78	78.95 (146.07)	25.00	<0.001
Bioaccessible concentration of Mn in $PM_{10-2.5}$ (ng/m^3)	107.62 (242.15)	45.91	14.61 (38.46)	5.62	61.11 (178.90)	13.61	<0.001
Non-bioaccessible concentration of Mn in $PM_{10-2.5}$ (ng/m^3)	19.62 (51.31)	8.19	4.022 (7.23)	1.26	11.82 (37.33)	3.38	<0.001
Bioaccessible concentration of Mn in $PM_{2.5}$ (ng/m^3)	109.20 (178.30)	34.24	23.42 (40.46)	8.07	66.31 (135.79)	17.05	<0.001
Non-bioaccessible concentration of Mn in $PM_{2.5}$ (ng/m^3)	16.96 (22.85)	7.50	8.32 (17.27)	4.33	12.64 (20.64)	5.80	<0.001
Bioaccessible concentration of Fe in $PM_{10-2.5}$ (ng/m^3)	72.64 (98.51)	41.32	36.69 (74.19)	18.83	54.66 (88.72)	31.61	<0.001
Bioaccessible concentration of Pb in $PM_{2.5}$ (ng/m^3)	15.46 (20.69)	6.81	10.28 (17.68)	4.53	12.87 (19.34)	5.27	0.067
Non-bioaccessible concentration of Fe in $PM_{2.5}$ (ng/m^3)	119.89 (250.44)	69.27	95.73 (170.10)	60.23	107.81 (213.59)	65.08	0.106

[a] U Mann-Whitney test (two-sided).

et al., 2018b) and 1 h for the gastric fluid (US EPA, 2007; Deshommes et al., 2012).

Secondly, the insoluble fraction (non-bioaccessible fraction) was digested based on European standard UNE EN 14902:2006, which comprises acid digestion of the filter in a microwave system (Milestone Ethos One) using closed PTFE vessels (HNO_3:H_2O_2, 4:1, up to 220 °C).

The bioaccessible and non-bioaccessible concentrations of 11 elements (V, Mn, Fe, Ni, Cu, Zn, As, Mo, Cd, Sb and Pb) from the PEMs was measured by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500 CE). The results focused on elements with at least 50% of samples above the detection limit (DL): bioaccessible and non-bioaccessible Mn concentration in both modes, bioaccessible Pb and Fe concentration in $PM_{2.5}$ and $PM_{10-2.5}$ modes, respectively, and non-bioaccessible Fe concentration in the $PM_{2.5}$ fraction. Values below the DL were replaced with DL/2 for statistical calculations. The detection limits and percentage of samples below the DL are shown in Table 1.

Statistical analysis of the data was performed using SPSS, version 22. The Kolmogorov–Smirnov test was used for testing if the variables followed a normal distribution. The Mann–Whitney *U* test was used to determine differences in exposure indices across the study populations in the two groups (highly and moderately exposed) because the data were not normal distributed. In addition, we studied the association between metal concentrations and the distance of each home from the Mn alloy plant by determining the Spearman correlation coefficients. Statistical significance was set as a p-value of <0.05, and all tests were two-sided.

3. Results and discussion

The main participant characteristics are summarised in Table 2. The mean distance to the Mn industrial source was 0.8 km in the highly exposed group compared to 7.3 km in the moderately exposed group. The mean age of the volunteers was 41.7 years, with no significant differences between the two groups.

Concentrations of bioaccessible and non-bioaccessible metals (Mn, Pb and Fe) associated with $PM_{2.5}$ and $PM_{10-2.5}$ modes by exposed group are given in Table 3. Moreover, Fig. 2 presents the variability of bioaccessible concentrations in each group; the variability can be explained by the different time spent outdoors and indoors during personal sampling (Haynes et al., 2012; Du et al., 2017), distances from the main source (Mbengue et al., 2015; Hernández-Pellón et al., 2018), meteorological conditions (Hernández-Pellón and Fernández-Olmo, 2019b)

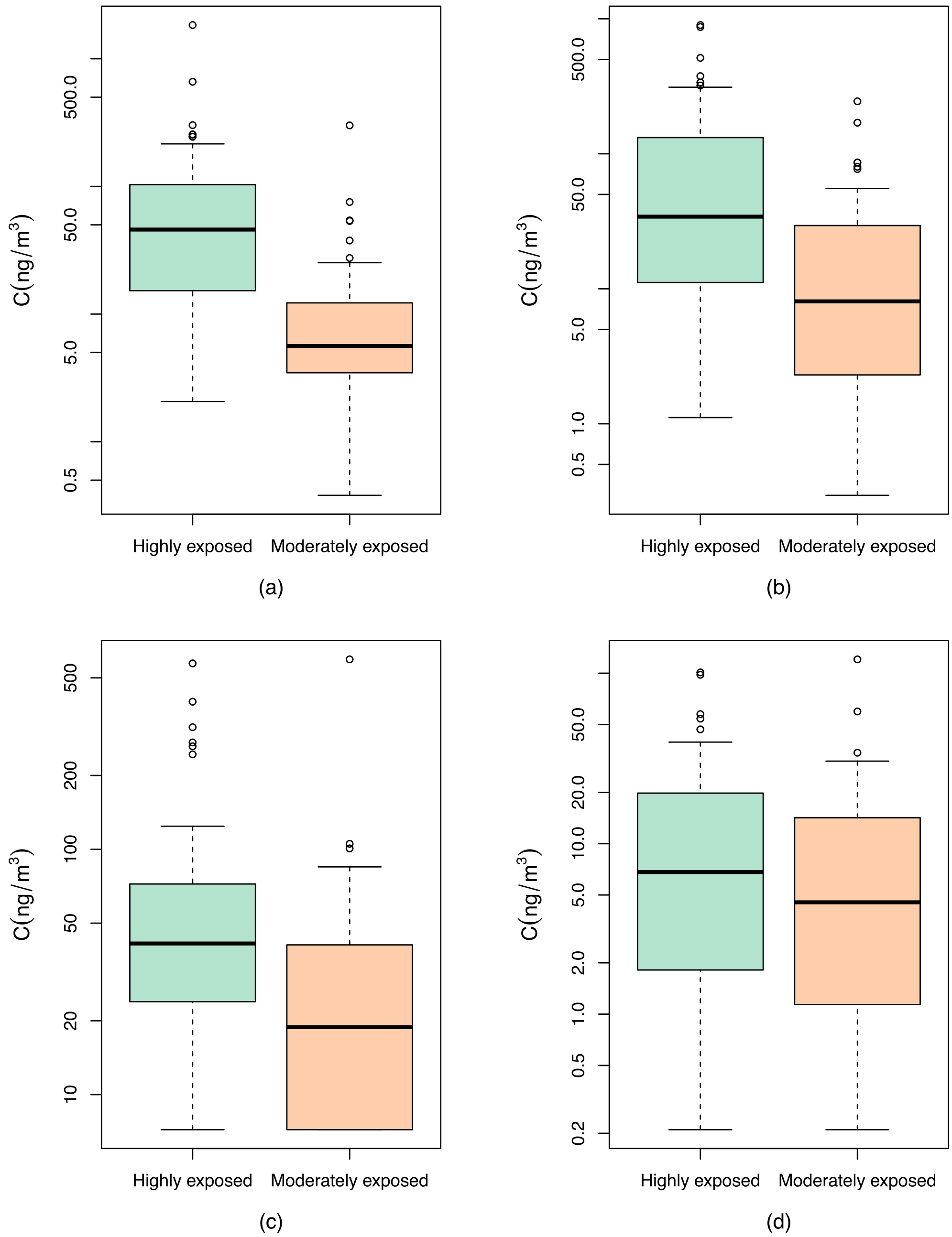

Fig. 2. Bioaccessible concentrations of Mn, Fe and Pb in gastric fluid ($PM_{10\text{-}2.5}$) and ALF ($PM_{2.5}$) by exposed group: (a) Mn in $PM_{10\text{-}2.5}$; (b) Mn in $PM_{2.5}$; (c) Fe in $PM_{10\text{-}2.5}$; (d) Pb in $PM_{2.5}$.

and Mn emission patterns (Mbengue et al., 2015; Davourie et al., 2017). Bioaccessible Mn levels in the two size fractions and Fe bioaccessible values in the coarse fraction were consistently and significantly ($p < 0.01$) higher in the highly exposed group in line with the greater proximity to the Mn alloy industry. Bioaccessible Pb concentrations in the $PM_{2.5}$ fraction were lower in the moderately exposed group but without reaching statistical significance. Furthermore, there were no significant differences between groups in terms of non-bioaccessible Fe content in the fine mode.

Table 3 also shows that Mn was equally distributed between the coarse and fine modes, both in the bioaccessible and non-bioaccessible fractions. The contribution of the fine fraction to total Mn was slightly higher in the moderately exposed group ($PM_{2.5}/PM_{10}$ ratio of 0.63) than in the highly exposed group ($PM_{2.5}/PM_{10}$ ratio of 0.52). Bowler et al. (2015) reported a lower mean modelled $PM_{2.5}/PM_{10}$ ratio for Mn (0.28) near a ferromanganese plant in Marietta (Ohio, USA). Studies on the size distribution of pollutants contained in PM are mainly based on stationary sampling (Wiseman and Zereini, 2014; Kastury et al., 2017; Du et al., 2018). Few studies have analysed the size distribution of PM-bound pollutants collected from PM personal samplers. For example, Rasmussen et al. (2018) characterised element concentrations in $PM_{2.5}$ and $PM_{10\text{-}2.5}$ modes in personal microenvironments of Windsor, Ontario (Canada) and found similar $PM_{2.5}/PM_{10}$ ratios for Mn with respect to indoor sampling (0.62 vs 0.63) and much higher with respect to outdoor sampling (0.32). In the vicinity of Mn ferroalloy plants, Mn bearing coarse particles were mainly attributed to fugitive emissions from slag, tapping, casting, crushing and screening (Davourie et al., 2017; Hernández-Pellón, 2017). These particles have a low buoyancy (Fulk et al., 2016), so their concentration is higher near to ferromanganese alloy plants; whereas, fine particles, which were mainly attributed to condensation processes in the plants' smelting units (Hernández-Pellón et al., 2017), are transported over longer distances.

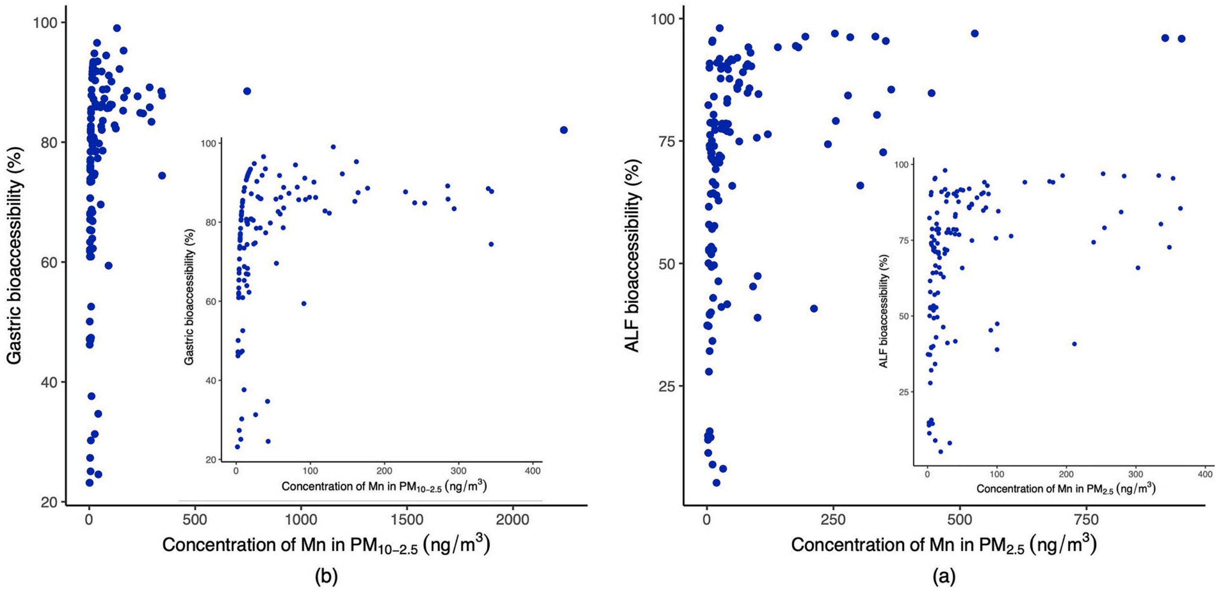

Fig. 3. Variation of Mn bioaccessibility (%) in gastric fluid and ALF with the total concentration of Mn.

The total PM_{10}-bound Mn concentration was calculated by summing the bioaccessible and non-bioaccessible concentrations obtained in fine and coarse modes. The arithmetic mean (n = 130) was 151.9 ng/m^3; in the highly exposed group, the mean was 253.4 ng/m^3, which is similar to the annual average of 231.8 ng/m^3 measured in 2015 in Maliaño (the town where most of the highly exposed participants lived) (Hernández-Pellón and Fernández-Olmo, 2019a). The highest value of 3145.3 ng/m^3 was measured in one participant living in this area and was higher than the maximum stationary value measured in a site located 350 m from the Mn alloy plant (2061.6 ng/m^3 in 2015). Anyway, on average the total air Mn value recommended by WHO was exceeded by the population living in the vicinity of the Mn industrial source.

In contrast to other studies using PEMs, Mn levels in this work were generally much higher (Graney et al., 2004; Pollitt et al., 2016). Our levels were even higher than those reported in studies done in residential areas close to Mn industrial sources; e.g., Lucchini et al. (2012) reported a mean value of 49.5 ng/m^3 in $PM_{2.5}$ in an exposed population in northern Italy, and Haynes et al. (2012) a geometric mean of 8.1 ng/m^3 in PM_{10} in Marietta (Ohio, USA). Higher Mn levels in PEMs were only reported near Mn ore mines in Molango (Mexico) with a mean of 420 ng/m^3 in PM_{10} (Solís-Vivanco et al., 2009).

Table 4
Spearman correlation matrix for metal concentrations and distance from source.

	Bioaccessible concentration of Mn in $PM_{10-2.5}$ (ng/m^3)	Non-bioaccessible concentration of Mn in $PM_{10-2.5}$ (ng/m^3)	Bioaccessible concentration of Mn in $PM_{2.5}$ (ng/m^3)	Non-bioaccessible concentration of Mn in $PM_{2.5}$ (ng/m^3)	Bioaccessible concentration of Pb in $PM_{2.5}$ (ng/m^3)	Bioaccessible concentration of Fe in $PM_{10-2.5}$ (ng/m^3)	Non-bioaccessible concentration of Fe in $PM_{2.5}$ (ng/m^3)
Non-bioaccessible concentration of Mn in $PM_{10-2.5}$ (ng/m^3)	0.75[b]						
Bioaccessible concentration of Mn in $PM_{2.5}$ (ng/m^3)	0.83[b]	0.60[b]					
Non-bioaccessible concentration of Mn in $PM_{2.5}$ (ng/m^3)	0.63[b]	0.49[b]	0.70[b]				
Bioaccessible concentration of Pb in $PM_{2.5}$ (ng/m^3)	0.53[b]	0.40[b]	0.68[b]	0.56[b]			
Bioaccessible concentration of Fe in $PM_{10-2.5}$ (ng/m^3)	0.49[b]	0.33[b]	0.29[b]	0.25[b]	0.21[a]		
Non-bioaccessible concentration of Fe in $PM_{2.5}$ (ng/m^3)	0.22[a]	0.13	0.22[a]	0.43[b]	0.14	0.16	
Distance from main source (km)	−0.60[b]	−0.45[b]	−0.41[b]	−0.30[b]	−0.10	−0.32[b]	−0.12

[a] p-value<0.05.
[b] p-value<0.01.

Lead was mainly detected in the fine mode (88% and 47% of measurements were above the DL for the bioaccessible and non-bioaccessible fractions, respectively, as shown in Table 1). The mean bioaccessible Pb concentration in the fine fraction (12.87 ng/m^3) was well below the annual limit value in PM_{10} established by Directive (2008)/50/EC (500 ng/m^3); as Pb levels in the coarse fraction were typically below the DL, the total PM_{10}-bound Pb concentration was also below this limit value.

The bioaccessibility of Mn was significantly higher ($p < 0.01$) in the highly exposed group (mean of 81.8% in gastric fluid/coarse mode and 77.1% in ALF/fine mode) than in the moderately exposed group (69.8% and 61.6%, respectively). As shown in Fig. 3, the bioaccessibility of Mn associated with coarse (gastric fluid) and fine (ALF) modes increased with the corresponding total Mn concentration, which was greater for participants living closer to the industrial source of Mn. Similarly, Hernández-Pellón et al. (2018) reported a decrease of Mn solubility in Gamble's solution and ALF with distance from a Mn alloy plant in PM_{10} samples. Similar results were also observed by Mbengue et al. (2015) regarding the bioaccessibility of metals in Gamble's solution for PM_1 samples influenced by metallurgical activities.

The Spearman correlation coefficients between the measured metals were evaluated in each fraction (Table 4). The table also presents the coefficients between the metals and the distance from the participants' residence to the plant. Overall, the correlations were stronger when the bioaccessible fraction was considered. A high correlation coefficient was returned for bioaccessible Mn in coarse and fine modes ($r = 0.83$). Furthermore, relatively high correlation coefficients were observed between bioaccessible Pb and Mn in the fine mode ($r = 0.68$), and between bioaccessible Fe and Mn in the coarse mode ($r = 0.49$), see Table 4.

We obtained significant negative correlation coefficients for the distance from the Mn source with bioaccessible Mn concentrations in $PM_{10\text{-}2.5}$ and $PM_{2.5}$, and with Fe in $PM_{10\text{-}2.5}$ ($r = -0.6$, -0.41 and -0.32, respectively). Negative, but not significant correlation was observed between distance and bioaccessible Pb levels. Iron, Mn and Pb were previously identified as tracers of the ferromanganese alloy plant located in the study area, although Fe was also emitted by road and rail traffic (Hernández-Pellón and Fernández-Olmo, 2019b).

Recent studies have highlighted the potential risk associated with the environmental exposure to airborne Mn, primarily neurotoxic disorders and cognitive deficits (Lucchini et al., 2012; Fernández-Olmo et al., 2020). Although most of these studies have been conducted near industrial sources of Mn, the total airborne concentration is lower than in our study. Moreover, the bioaccessible fraction was not determined. Therefore, considering that, according to our results, higher Mn bioaccessibility (%) is related to higher total Mn concentrations, people living in the vicinity of the ferromanganese alloy industry are exposed to higher concentrations of bioaccessible Mn, posing a greater potential risk to their health. In this context, further studies should investigate whether impaired cognitive and motor function has a stronger correlation with bioaccessible Mn concentration than with total Mn content.

Furthermore, a debate should be opened on the appropriateness of the WHO annual reference value for Mn and even on the lack of a limit/threshold value in the European Union. Although some authors have pointed out the need to increase the WHO reference guideline value and the US EPA reference concentration (i.e., 50 ng/m^3), such debate was focused on the airborne total concentration of Mn (Winder et al., 2010; Gentry et al., 2017). However, its bioaccessible concentration, which may better reflect the risks derived from the exposure to airborne Mn, has not been considered in the literature until now.

4. Conclusions

Bioaccessible and non-bioaccessible concentrations of Mn and other metals were measured in $PM_{10\text{-}2.5}$ and $PM_{2.5}$ samples from 130 participants living in Santander Bay. The participants were divided into two groups according to their Mn exposure, highly and moderately exposed, based on the distance between the volunteer's residence and the main Mn source, a ferromanganese alloy plant. The highest levels of bioaccessible and non-bioaccessible Mn in both size fractions and bioaccessible Fe in $PM_{10\text{-}2.5}$ were obtained in the population group living within 1.5 km of the Mn alloy plant, with significant negative correlations found between airborne metal levels and distance to the Mn source. The variability in metal levels noted in both groups was attributed to different patterns occurring during the sampling period, such as time spent outdoors and indoors, meteorological conditions and Mn emission rates. In addition, the results showed that higher Mn bioaccessibility (%) was found at higher total Mn concentrations. Therefore, the population living in the vicinity of the ferromanganese alloy industry is exposed to higher concentrations of bioaccessible Mn, posing a greater potential hazard to their health.

Author contribution

A. Expósito: Investigation, Writing – original draft, Formal analysis; B. Markiv: Investigation, samples collection; L. Ruiz-Azcona: Investigation, samples collection. M. Santibáñez: Supervision, Funding acquisition; I. Fernández-Olmo: Conceptualization, Methodology, Reviewing and Editing, Supervision, Funding acquisition

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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