

# Spatial distribution of manganese concentration and load in street dust in Mexico City

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## Abstract

**Objective.** To obtain a first indication of the distribution and extent of manganese (Mn) contamination in Mexico City. Mn concentration and load in street dust were analyzed in order to reveal the most contaminated areas. **Materials and methods.** 482 samples of street dust were analyzed through inductively coupled plasma-optical emission spectroscopy. The contamination factor (CF), the geoaccumulation index (Igeo) and the spatial interpolations of the kriging indicator were calculated. **Results.** A slight influence of anthropogenic activities is detected on the Mn content of street dust. The highest levels of pollution by concentration (Igeo=*uncontaminated* to *moderately contaminated*) are grouped towards the city's north (industrial) and center (commercial and high traffic) areas. The areas with the highest Mn load were located towards the east and northwest areas (Igeo=*moderately contaminated*). **Conclusions.** These findings will serve as a baseline to assess future variations in Mn content in Mexico City's environment.

Keywords: manganese; environmental pollution; dust

## Resumen

**Objetivo.** Obtener una primera aproximación sobre la distribución espacial de la contaminación por manganeso (Mn) en la Ciudad de México. Se analizó la concentración y carga de Mn en el polvo de la calle para identificar las áreas más contaminadas. **Material y métodos.** 482 muestras de polvo de la calle fueron analizadas con espectroscopía de emisión por plasma de acoplamiento inductivo. Se calculó el factor de contaminación, índice de geoacumulación, y las interpolaciones espaciales del indicador kriging. **Resultados.** Existe una ligera influencia de actividades antropogénicas en el contenido de Mn del polvo de la calle. Los niveles más altos de contaminación por concentración (Igeo=*no contaminado* a *moderadamente contaminado*) se agruparon en el norte (industrial) y centro (comercial y de alto tráfico) de la ciudad. Las áreas con las cargas de Mn más altas estuvieron al este y noroeste (Igeo=*moderadamente contaminado*), donde había más polvo. **Conclusiones.** Estos resultados servirán como punto de referencia para evaluar variaciones futuras en el contenido de Mn en la Ciudad de México.

Palabras clave: manganeso; contaminación ambiental; polvo

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## Chemical analysis

Mn total concentration was determined in street dust by inductively coupled plasma-optical emission spectroscopy (ICP-OES). 0.4 g of dried and sieved dust was digested with 20 mL HNO<sub>3</sub> concentrated in an ETHOS EASY Microwave Digestion Platform (Milestone INC). The heating program was as follows: each sample's temperature should rise to 175±5°C in approximately 5 min and remain at 175±5°C for 4.5 min. After cooling, samples were filtered with a Whatman No. 42 filter paper, transferred into a 50 mL flask and brought to volume with Type A water.

Quality controls included reagent blanks, duplicate samples, and spiked samples. The quality assurance and quality control (QA/QC) results showed no sign of contamination or losses in any of the analyses. The digests and the quality controls were triply analyzed with an ICP-OES spectrometer (Agilent Technologies 5100) using the USEPA method 6010C. Curve multi-element QCS-26R (High Purity) solutions were used for calibration preparations. The Radio Frequency potency (RF power) was 1.2 kW. Nebulization flow was 0.7 L/min and argon plasma flow was 12.0 L/min. Detection limit was 0.04 mg/L (5 mg/kg). Quantification limit was 0.12 mg/L (15 mg/kg). All samples were above the detection limit.

## Contamination degree, spatial analysis, and human health risk assessment

Descriptive statistical analysis of both Mn concentration (mg/kg<sup>2</sup>) and Mn load (mg/m<sup>2</sup>) on street dust were carried out, as well as Spearman correlation coefficients for non-normal distribution. Mn load in street dust (mg/m<sup>2</sup>) was calculated by multiplying Mn concentration (mg/kg) and street dust load in kg/m<sup>2</sup>.

Furthermore, the contamination level could be estimated as the quotient of Mn concentration in each sample over the background value, which is known as the contamination factor):

$$CF = \frac{C_n}{B_n}$$

Where  $C_n$  is Mn concentration in each sample point and  $B_n$  is background value. CF less than 1 indicates *insignificant contamination*, 1-3 is *moderate contamination*, 3-6 is *considerable contamination* and more than 6 indicates *high contamination*.<sup>13</sup>

Usually, background value indicates an average concentration of natural values in a site. When there are no background values available, as in the case of Mexico

City, the world background values for soils<sup>14</sup> or even the minimum value of the study data have been used.<sup>15</sup> To obtain the background value, we decided to normalize the data through log transformation and removal of outliers using Tukey Inner Fences (TIF=Q3+1.5 IQR or Q1-1.5 IQR), and use the first decile as the background value (170 mg/kg for concentration, and 4.5 mg/m<sup>2</sup> for load). Since Mexico City is a historic area, it is possible that all samples are impacted by anthropogenic Mn, however using the first decile instead of the minimum value, some variation is allowed.

The world background value of Mn in soils is very high (488 mg/kg);<sup>14</sup> we consider it is not suited to be used in this study due to the fact that soils are analyzed in the particle size below 2 000 μm, while we studied the street dust of Mexico City in the particle size below 250 μm, leaving a huge quantity of Mn contained in bigger particles outside the scope of this analysis.

In order to obtain another contamination index to produce a more robust contamination degree analysis, geoaccumulation index (Igeo) was also calculated. Igeo considers small variations in the background value using a 1.5 factor.

$$I_{geo} = \log_2 \left( \frac{C_n}{1.5 \times B_n} \right)$$

Igeo can be interpreted as follows:  $I_{geo} < 0$  (*uncontaminated*), 0-1 (*uncontaminated to moderately contaminated*), 1-2 (*moderately contaminated*), 2-3 (*moderately to highly contaminated*), 3-4 (*highly contaminated*), 4-5 (*highly to very highly contaminated*), >5 (*very highly contaminated*).

The Kruskal-Wallis and Dunn nonparametric tests were used for variance analysis by township. The null hypothesis is stochastic homogeneity, which is equivalent to equality of expected values of rank sample means. Kruskal-Wallis test examines if there is an observed tendency to be larger (or smaller) in at least one population than all the remaining populations together. The analyses were done with the R Project software, version 3.52.

CF and Igeo spatial distribution maps for Mn concentration and load were designed from a geo-statistical analysis using GS+ software. The interpolation method was kriging, equations can be found elsewhere.<sup>13</sup> To determine the spatial autocorrelation, the data semivariogram was calculated and adjusted to a theoretical model in order to estimate CF and Igeo at unsampled sites, using the kriging indicator method. It accepts data non-normality and converts the estimated values into indicator values that rank from 0 to 1. The output is the probabilities range of exceeding a cut-off value.

Different levels of contamination indexes were used as cut-off values to obtain several interpolations that were then overlapped in order to get a final map for each index. For the CF map, the cut-off values were: 1 (probability <50% meaning *insignificant contamination*, >50% meaning *moderate contamination*), 3 (probability >50% meaning *considerable contamination*) and 6 (probability >50% meaning *high contamination*).

For the Igeo map, cut-off values were 0 (probability <50% meaning *uncontaminated*, >50% meaning *uncontaminated to moderately contaminated*), and 1 (probability >50% meaning *moderately contaminated*). We did not find Igeo values greater than 2, which is why the last cut-off value used was 1. For a study of this scale, we used the UTM projection, zone 14, horizontal datum ellipsoid and the World Geodetic System 84 (WGS84).

The non-carcinogenic hazard index (HI) developed by the USEPA was calculated for Mn exposure from street dust, both for children and adults (supplementary material). The estimated daily intake (EDI) in mg/kg per day by ingestion ( $EDI_{ing}$ ), inhalation ( $EDI_{inh}$ ), dermal contact ( $EDI_{dermal}$ ) were obtained and divided into their corresponding reference dose (RfD) to obtain the hazard quotients for each exposure pathway ( $HQ_{ing/inh/derm}$ ), and finally HI was found summing all those  $HQ_{ing/inh/derm}$ .

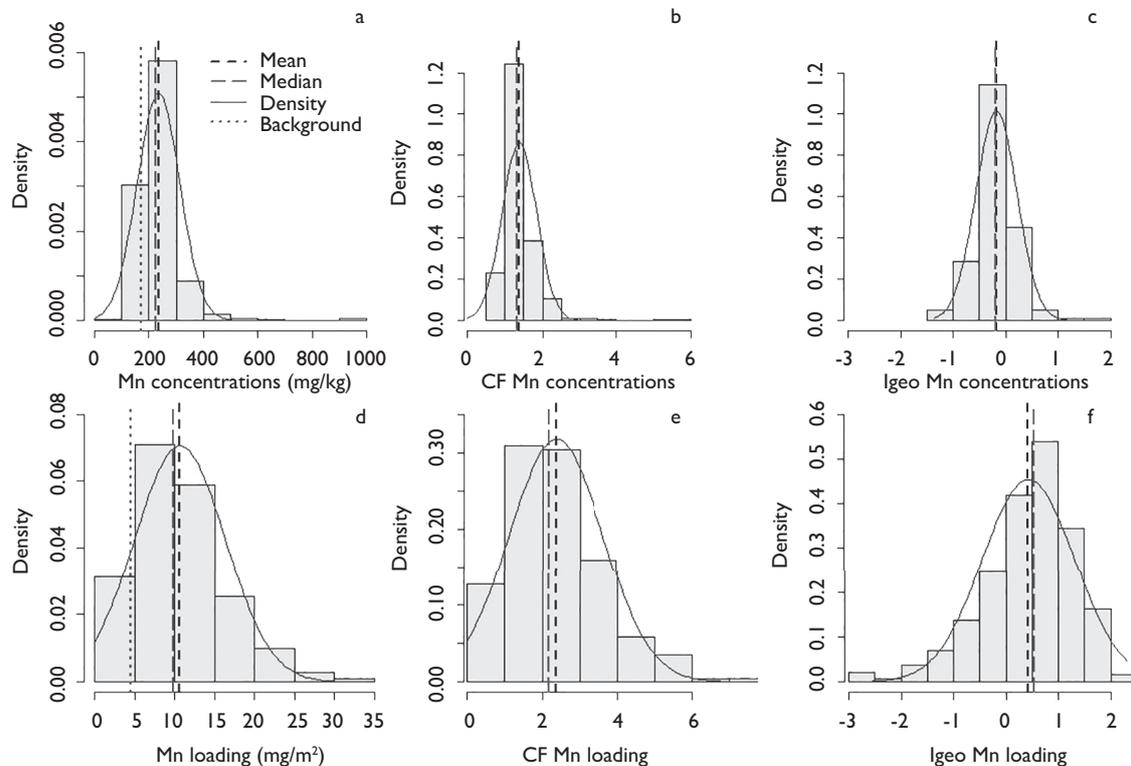
derm. HI higher than 1 indicates that possible adverse effects to human health may occur.

## Results

### Contamination degree

Mn concentration and load have been altered by human activities since their frequency's distributions are positively skewed (figure 2a and d). Average contamination degree for Mn concentrations was *moderate* (CF=1.38), according to CF, which had an interval from *insignificant contamination* (min=0.59) to *considerable contamination* (max=5.83) (figure 2b). On the other hand, if Igeo, which considers small natural variations in the background value, is considered, average pollution degree was *uncontaminated* (Igeo=-0.17); while the interval stood from *uncontaminated to moderately contaminated* (min=-1.35, max=1.96) (figure 2c).

For Mn load, contamination average level was *moderate* (CF=2.38), according to CF, which varied from *insignificant contamination* (min=0.2) to *high contamination* (max=7.46) (figure 2e). If Igeo was considered, contamination average degree was *uncontaminated to moderately contaminated* (Igeo=0.43); while the interval went from



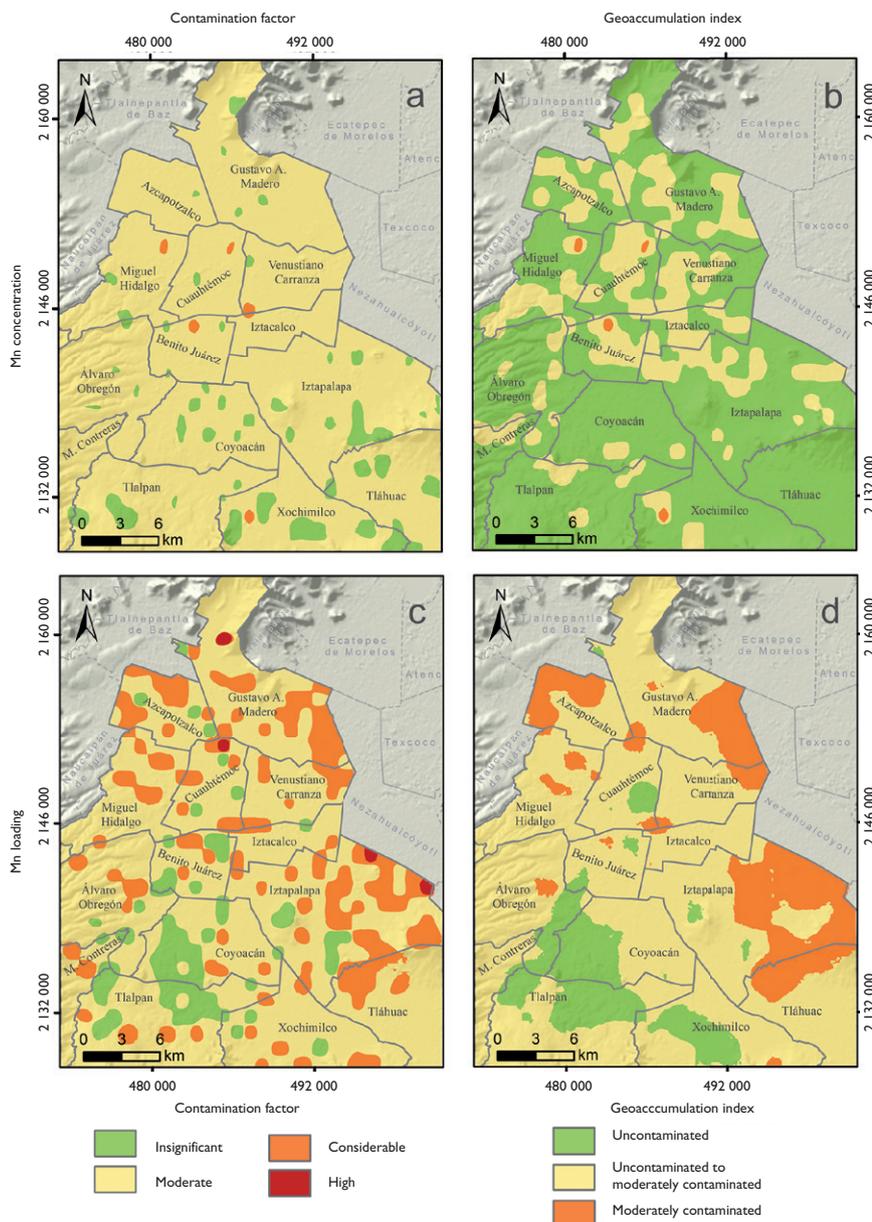
**FIGURE 2. FREQUENCY DISTRIBUTION FOR MANGANESE (Mn) CONCENTRATION AND LOAD (A AND D), FOR THEIR CONTAMINATION FACTORS (CF) (B AND E) AND GEOACCUMULATION INDEX (IGEO) (C AND F)**

uncontaminated to moderately to highly contaminated (min=-2.88, max=2.31) (figure 2f).

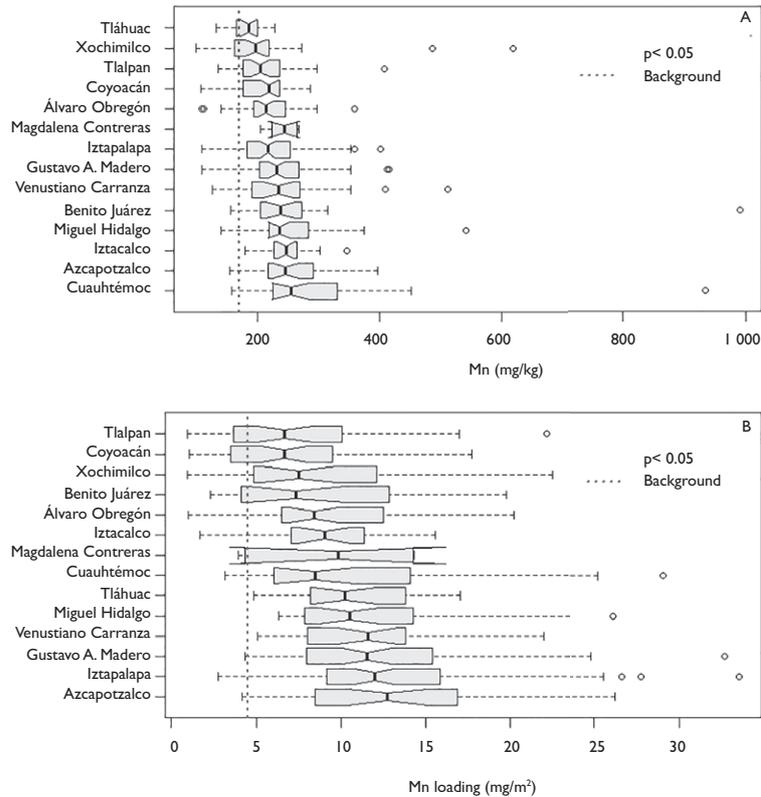
On the other hand, street dust load had a greater impact than Mn concentration over Mn load, as the Spearman correlation coefficient between Mn load and street dust load was positive ( $r=0.87$ ), while the correlation coefficient between Mn load and Mn concentration was weak ( $r=0.32$ ). Street dust load averaged  $46 \text{ g/m}^2$  with an interval from  $5\text{-}173 \text{ g/m}^2$  and a variation coefficient of 50%.

### Spatial distribution, municipal analysis, and human health risk assessment

CF showed a moderate degree of contamination by Mn concentration in virtually all of Mexico City (figure 3a). Some small areas, mainly towards the south, showed insignificant contamination. Only five isolated areas had a considerable level, in the municipalities of Miguel Hidalgo, Cuauhtémoc, Benito Juárez, Xochimilco and one between Iztacalco and Venustiano Carranza.



**FIGURE 3. SPATIAL DISTRIBUTION OF THE CONTAMINATION FACTOR AND GEOACCUMULATION INDEX FOR MANGANESE (Mn) CONCENTRATION AND LOAD**



**FIGURE 4. BOX AND WHISKER PLOT FOR MANGANESE (Mn) CONCENTRATIONS (A) AND Mn LOAD (B) BY MUNICIPALITY, ORDERED FROM LOWER TO HIGHER ACCORDING TO DUNN'S NON-PARAMETRIC TEST**

Using Igeo, most of the city remains *uncontaminated* (figure 3b) by Mn concentration, especially towards the south. *Uncontaminated to moderately contaminated* levels were found in the center and north areas in the municipalities of Azcapotzalco, Gustavo A. Madero, Miguel Hidalgo, Cuauhtémoc, Venustiano Carranza, Benito Juárez, Iztacalco and the north of Iztapalapa. Only four areas are *moderately contaminated*.

In terms of contamination by Mn load in street dust, more extensive areas were found compared to those of Mn concentration, with varying degrees of pollution. CF showed *moderate contamination* in most parts of the city (figure 3c). The most extensive areas with *insignificant contamination* were located between the municipalities of Coyoacán and Tlalpan, while the most extensive areas with *considerable contamination* surrounded the city, mainly in the municipalities of Iztapalapa, Gustavo A. Madero and Azcapotzalco. Three hotspots with *high contamination* were located: two east of Iztapalapa and one north of Cuauhtémoc.

If Igeo is considered, the pattern remains practically the same as for the CF by Mn load, only much more defined (figure 3d). The *uncontaminated areas* were located to

the southwest, between the municipalities of Coyoacán, Álvaro Obregón, Tlalpan and Xochimilco. *Moderately contaminated* areas were located in the periphery, mainly in the municipalities of Iztapalapa, Gustavo A. Madero and Azcapotzalco. As for Igeo, hotspots were not differentiated.

The municipalities of Cuauhtémoc, Azcapotzalco, and Iztacalco had the highest concentrations (figure 4a). North municipalities showed the highest Mn concentrations, specially found in Cuauhtémoc. On the other hand, south municipalities had lower Mn concentrations. Furthermore, Tláhuac, Tlalpan, and Xochimilco in the south have the lowest concentrations of other potentially toxic elements also reported.<sup>13,16</sup> Azcapotzalco and Iztapalapa were the municipalities with greater Mn load (figure 4b). Tlalpan and Coyoacán had the lowest Mn load.

No human health risk due to Mn exposure in street dust was found, neither for children nor for adults. Average HI (summing ingestion, inhalation and dermal contact) was 0.4 for children, and 0.005 for adults. The maximum value obtained was 0.6 for children and 0.08 for adults. All of them were below the safe level. The main exposure pathway was ingestion, which represented 86% of the HI for children, and 71% for adults.

## Discussion

### Contamination degree

Our results showed that there is a slight influence of human activities on the Mn concentration and load in Mexico City's street dust, since frequency distributions were positively skewed and average CF showed *moderate contamination*. This type of distribution is common for anthropogenic elements because concentration depends on the distance to the source: the closer a sample is to the source, the higher the concentrations are.<sup>13,17,18</sup>

Contamination level undoubtedly is based on the background value selected. In this case, we used as background value of 170 mg/kg for Mn concentration, as was explained in the methods section. Other studies have used a background value for soils, for example Chinese background is 557 mg/kg.<sup>19,20</sup> Only three street dust samples in Mexico City surpassed this value. However, Mn may be retained in soils or absorbed by plants, while Mn particles in street dust are intemperized, until they become breathable particles smaller than 10 microns, and can be resuspended in the air. Thus, considering a background value for soil could lead us to underestimate the level of street dust contamination. Furthermore, soil background value depends on each study site and it has not yet been estimated for Mexico City.

In order to get a very clear idea of the contamination degree and its possible effects, this work's results are compared with those found in other international studies (table I).

Mn concentrations in Mexico City's street dust (100-990.5 mg/kg) were found within the range of the concentrations of an area widely using MMT gasoline (17-959 mg/kg). Furthermore, those concentrations were associated with Mn levels in children's blood.<sup>6</sup> This background information makes it advisable to analyze Mn bioavailability in street dust as well as a biomarker to Mn exposure, such as toenails or hair,<sup>2</sup> in Mexico City's children. Children are most vulnerable because they have higher absorption rates and have not fully developed Mn excretion mechanisms.<sup>4,6</sup>

Compared to a site with wide use of Mn pesticides, average Mn concentration and load in Mexico City's street dust were higher (235.2 mg/kg and 10.7 mg/m<sup>2</sup>) than those of Salinas Valley, California intramural dust (171 mg/kg and 1.9 mg/m<sup>2</sup>).<sup>5</sup> Although it is expected that street dust has higher amounts of Mn, this antecedent is an reminder to pay more attention to Mn contamination.

Compared to a site adjacent to a Mn alloy production plant (less than 2 km), main Mn load in Mexico City was very close to main Mn load rate in Simões Filho, Brazil (12 mg/m<sup>2</sup>/30 days).<sup>2</sup> However, in Brazil,

**Table I**  
**COMPARISON OF MANGANESE CONCENTRATION AND LOAD IN SEVERAL INTERNATIONAL STUDIES**

Study site	Characteristic	Sample type	Concentration or load	Mean	Median	Range	Reference
Johannesburg, Africa	MMT gasolines	School dust		404	314	17-959	6
Cape Town, Africa	No MMT gasoline	School dust		73	76	38-99	6
Salinas, USA	Fungicides Maneb and Mancozeb	House dust		171		2-414	5
Xi'an, China	No contamination (Chinese background 557 mg/kg)	Road dust	Concentration (mg/kg)	339.4		282-430	19
Dhaka, Bangladesh	No contamination (Chinese background 557 mg/kg)	Road dust		262	266	194-415	20
Mexico City	Atmospheric contamination	Street dust		235	224	100-990	This study
Simões Filho, Brazil	Ferromanganese alloy plant	Street dust	Load rate (mg/m <sup>2</sup> /30 day)	12*		9.0-38	2
Salinas, USA	Fungicides maneab and mancozeb	House dust		1.9		0.001-25	5
Mexico City	Atmospheric contamination	Street dust	Load (mg/m <sup>2</sup> )	10	11	0.9-34	This study

\* Geometric mean

MMT: methylcyclopentadienyl manganese tricarbonyl

authors analyzed a 30-day rate, while in Mexico City we do not know how much accumulation is produced in that amount of time.

### **Spatial distribution, municipal analysis, and human health risk assessment**

Maps showed that Igeo was more precise while demarcating contamination spatial distribution by Mn concentration and load in Mexico City's street dust (figure 3). Igeo spatial distribution for Mn concentration corroborated human activities increase Mn levels in the city, as the most contaminated areas were concentrated towards the north and center of the city. These are areas where industrial and commercial activities predominate, and there is a lot of car traffic. Furthermore, it has been reported that residents from the north area have been exposed to higher PM<sub>10</sub> and PM<sub>2.5</sub> concentrations with high levels of the following metals: Mn, Zn, Cu, Pb, Ti, Sn, V and Ba.<sup>10</sup>

On the other hand, if Mn distribution was dominated by natural sources, it would be expected that the highest concentrations were located around the city, near the less urbanized sites or towards the southeast because of the active Popocatepetl volcano, as the volcanic activity is one of Mn main natural sources.<sup>4</sup>

By estimating the spatial distribution of Mn load contamination, a strong influence of street dust load was observed, as the areas with the highest Mn load were located towards the east and northwest of the city, where there was more dust. This influence was also exhibited by the high Spearman correlation coefficient between street dust load and Mn load ( $r=0.87$ ). Other authors have also observed this.<sup>5</sup>

This shows the need to maintain cleaning plans in order to reduce exposure to Mn load and other potentially toxic elements. Street dust load can work as an indicator of the cleaning plans, the higher the street dust load, the lower the success of the cleaning plans. Gunier and colleagues<sup>5</sup> have reported that Mn load can be reduced by keeping the house clean and using rugs at the entrance. Indoor Mn concentrations can also be reduced by keeping the windows closed.<sup>1</sup>

Although spatial analysis allows us to distinguish areas with greater pollution, municipal variance analysis allows us to identify municipalities with higher Mn concentration and load. Thanks to the Kruskal-Wallis test, it was possible to identify Azcapotzalco as the municipality with the worst contamination by Mn concentration and load. Nevertheless, this could not be distinguished in the Mn concentration pollution maps,

so it is important to use different kinds of analyses to complement results.

On the other hand, it was possible to corroborate the spatial distribution patterns observed in Igeo Mn concentration and load maps. In the case of concentration, center and northern municipalities had higher values than those on the south, with statistically significant differences. As for the Mn load, periphery municipalities had higher values than those inside the city.

Even when no human health risk due to Mn exposure in street dust was found, it is important to keep monitoring this element since the maximum HI of the data for children ( $HI_{\text{children}}=0.61$ ) was close to the safe limit of 1. As this study demonstrated, street dust loading has an important influence on the Mn loading (total quantity of Mn in the street dust), therefore, local exposure factors (ingestion rate, particle emission factor, etc.) should be considered to obtain a more accurate human health risk assessment.

## **Conclusions**

This study is the first to report the concentration and load of manganese in urban dust in Mexico City. There is a slight influence of human activities in Mn concentration and load in street dust. Mn concentration was 235.2 mg/kg and load average, 10.7 mg/m<sup>2</sup>. Although this is not a serious situation, caution is recommended due to lack of reference values. These findings can serve as a background to assess future potential changes in Mexico City's Mn concentration in the environment.

Geoaccumulation index showed better resolution that the contamination factor in order to limit Mn pollution. The most contaminated areas by Mn concentration were found in central and northern Mexico City. As the Mn load is concerned, a strong influence of street dust load was observed, since a strong correlation was found between both, and the most contaminated areas were located towards the east and northwest of the city, where there was more dust.

Because the most contaminated areas by Mn concentration and Mn load were different, it is important to consider both variables in pollution and exposure studies of potentially toxic elements. The only municipality both with high Mn concentration and load was Azcapotzalco, which implies a double risk. An efficient street and house cleaning system may reduce exposure to a dust load of potentially toxic elements.

*Declaration of conflict of interests.* The authors declare that they have no conflict of interests.

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