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P r e s e n t e

Me permito informar a usted que, en la reunión ordinaria del Subcomité de Ecología y Manejo Integral de Ecosistemas del Posgrado en Ciencias Biológicas, celebrada el día **17 de enero de 2022,** se aprobó el siguiente jurado para el examen de grado de **DOCTORA EN CIENCIAS,** de la estudiante **AGUILERA PANTOJA ANAHÍ,** con número de cuenta **412023332** con la tesis titulada**, "CONTAMINACIÓN POR ELEMENTOS POTENCIALMENTE TÓXICOS EN CIUDADES MEXICANAS CON AMBIENTES CONTRASTANTES",** realizada bajo la dirección del **DR. FRANCISCO BAUTISTA ZÚÑIGA**, quedando integrado de la siguiente manera:

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Sin otro particular, me es grato enviarle un cordial saludo.

A T E N T A M E N T E
"POR MI RAZA HABLARÁ EL ESPÍRITU"
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A mis papás, Lupita y Javier,

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ÍNDICE

RESUMEN

En las ciudades, toneladas de partículas que contienen metales pesados se liberan al medio ambiente y se acumulan en las superficies de las calles. Los metales pesados son tóxicos, persistentes y bioacumulables. Sin embargo, existe una falta de información sobre los niveles y posibles riesgos de los metales pesados en el polvo urbano de las ciudades mexicanas. Tampoco está claro si la forma urbana tiene un papel en su acumulación, principalmente en los casos en que no existe una fuente única dominante, como probablemente sea el caso de la Ciudad de México. Por tanto, el objetivo general de esta tesis fue evaluar la contaminación por metales pesados en el polvo urbano y sus posibles riesgos ecológico y a la salud humana en las ciudades mexicanas de Toluca, San Luis Potosí, Morelia, Mérida, Ensenada y Ciudad de México.

Se recolectaron alrededor de 100 muestras de polvo urbano durante la temporada de secas en la Ciudad de México en 2011, Ensenada en 2012, San Luis Potosí en 2017, Morelia en 2014, Mérida en 2016 y Toluca en 2013. Las concentraciones de Cu, Pb, Zn, Mn y Fe se midieron por dispersión de energía de fluorescencia de rayos X (XRF-ED). Solo en el caso de Morelia se utilizó espectroscopia de emisión óptica de plasma acoplado inductivamente (ICP-OES). Para evaluar el nivel de contaminación de cada metal pesado, se utilizó el factor de contaminación (CF) y el índice de carga de contaminación (PLI) con dos valores de fondo diferentes: el primer decil de la distribución de frecuencias como valor de fondo local y el establecido para suelos a nivel mundial. También se evaluaron los posibles riesgos ecológicos y para la salud humana. Posteriormente, recolectamos 482 muestras de polvo urbano en la Ciudad de México, determinamos las concentraciones de cinco metales pesados (Cr, Cu, Pb, Zn y Ni) utilizando ICP-OES, y calculamos el PLI. Analizamos el origen de los elementos con base en niveles de referencia globales, la correlación espacial con el índice Global Moran's I y se identificaron los principales factores que influyeron en las concentraciones de metales pesados aplicando mínimos cuadrados ordinarios (MCO) y modelos de regresión espacial. La distribución espacial de Mn en la Ciudad de México se analizó mediante el indicador de kriging.

Como producto de este doctorado se publicaron cinco artículos de los cuales se concluyó que dependiendo del valor de fondo variaron las ciudades más contaminadas; cuando se tomó como referencia el valor de fondo mundial del suelo, todas las ciudades estudiadas estuvieron contaminadas, excepto Mérida. Por el contrario, cuando se utilizó un valor de fondo local (decil 1), Mérida y Morelia fueron las más contaminadas. El índice de riesgo ecológico indicó que no hay riesgo por Cu, Pb, Zn y Mn en el polvo urbano de las ciudades estudiadas. Sin embargo, el Pb fue el metal que más contribuyó al riesgo ecológico potencial en todas las ciudades. El Pb también puede ser un riesgo potencial para la salud de los niños y la exposición crónica a Fe y Mn podría desencadenar muchos malestares. Por otro lado, en la Ciudad de México se encontraron bajos niveles de autocorrelación espacial para Cr, Cu, Pb, Zn y Ni, con base en el muestreo de 482 muestras de polvo de la calle. La mayoría de las covariables no detectaron ninguna relación con los metales pesados. El área de los camellones tuvo una relación positiva débil (nivel de significancia del 90%) pero consistente con el Cr, Cu, Ni, Pb y el PLI. La distancia al aeropuerto tuvo una relación débil (nivel de significancia del 90%) e inversa con Pb. Las unidades de fabricación se asociaron con un aumento de Cu (nivel de significancia del 95%), mientras que el índice de entropía se asoció con un aumento de Ni (nivel de significancia del 95%). Se detectó una leve influencia de las actividades antropogénicas en el contenido de Mn del polvo de la calle. Los niveles más altos de contaminación (Igeo = no contaminado a moderadamente contaminado) se agruparon hacia las áreas norte (industrial) y centro (comercial y de alto tráfico) de la ciudad. Las áreas con mayor carga de Mn se ubicaron hacia las áreas este y noroeste (Igeo = moderadamente contaminadas).

ABSTRACT

In cities, tons of particles containing heavy metals are released into the environment and accumulate on street surfaces. Heavy metals are toxic, persistent and bioaccumulative. However, there is a lack of information on the levels and possible risks of heavy metals in urban dust in Mexican cities. It is also unclear whether urban form plays a role in its accumulation, mainly in cases where there is not a single dominant source, as is probably the case in Mexico City. Therefore, the general objective of this thesis was to evaluate heavy metal contamination in urban dust and its possible ecological and human health risks in the Mexican cities of Toluca, San Luis Potosí, Morelia, Mérida, Ensenada and Mexico City.

About 100 urban dust samples were collected, during the dry season, in Mexico City in 2011, Ensenada in 2012, San Luis Potosí in 2017, Morelia in 2014, Mérida in 2016 and Toluca in 2013. The concentrations of Cu, Pb, Zn, Mn and Fe were measured by X-ray fluorescence energy dispersive (XRF-ED). Only in the case of Morelia inductively coupled plasma optical emission spectroscopy (ICP-OES) was used. To assess the contamination level of each heavy metal, the contamination factor (CF) and the contamination load index (PLI) were used with two different background values: the first decile of the distribution of frequencies as the local background value and the one established for soils worldwide. Potential ecological and human health risks were also assessed. Subsequently, we collected 482 urban dust samples in Mexico City, we determined the concentrations of five heavy metals (Cr, Cu, Pb, Zn, and Ni) using ICP-OES, and calculated the PLI. We analyzed the origin of the elements based on global reference levels, the spatial correlation with the Global Moran's I index, and the main factors that influenced heavy metal concentrations were identified by applying ordinary least squares (OLS) and spatial regression models. The spatial distribution of Mn in Mexico City was analyzed using kriging indicator.

As a result of this doctorate thesis, five articles were published from which it was concluded that depending on the background value, the most polluted cities varied; When the global background value of soils was taken as a reference, all the cities studied were contaminated, except Mérida. On the contrary, when a local background value (decile 1) was used, Mérida and Morelia were the most contaminated. The ecological risk index indicated that there is no risk due to Cu, Pb, Zn and Mn in the urban dust of the cities studied. However, Pb was the metal that contributed the most to potential ecological risk in all cities. Pb can also be a potential health risk for children, and chronic exposure to Fe and Mn could trigger many ailments. On the other hand, in Mexico City, low levels of spatial autocorrelation were found for Cr, Cu, Pb, Zn and Ni, based on the sampling of 482 street dust samples. Most of the covariates did not detect any relationship with heavy metals. Median strip area had a weak (90% significance level) but consistent positive relationship with Cr, Cu, Ni, Pb, and PLI. Distance to the airport had a weak (90% significance level) and inverse relationship with Pb. Manufacturing units were associated with an increase in Cu (95% significance level), while entropy index was associated with an increase in Ni (95% significance level). A slight influence of anthropogenic activities on the Mn content of street dust was detected. The highest levels of pollution (Igeo = not polluted to moderately polluted) were clustered toward the northern (industrial) and central (commercial and high-traffic) areas of the city. The areas with the highest Mn load were located towards the east and northwest areas (Igeo = moderately contaminated).

INTRODUCCIÓN

Los polvos urbanos son portadores y el medio de reacción de muchos contaminantes, que impactan el ambiente, el clima y la salud humana (Xu et al., 2019). Los polvos urbanos son un sumidero de las partículas contaminantes del aire y, al mismo tiempo, son una fuente de contaminación para el mismo aire, los suelos cercanos y los cuerpos de agua que reciben estas partículas por depósito seco (resuspensión y sedimentación), y húmedo (escorrentía del agua de lluvia).

Los polvos urbanos funcionan como un indicador de la contaminación atmosférica, son fáciles de muestrear y analizar. La alta movilidad de los polvos permite identificar la contaminación de corto a mediano plazo. Los polvos son un subproducto directo de las emisiones vehiculares e industriales y, por su menor tamaño, tienen una gran área superficial a la que se pueden adherir los elementos potencialmente tóxicos (Jiang et al., 2018).

Los elementos potencialmente tóxicos son más comúnmente conocidos como metales pesados, como se podrá corroborar en el capítulo I de esta tesis; por tanto, se les denominará metales pesados a lo largo del documento. Los metales pesados pueden ser tóxicos o dañinos para el ambiente y los seres vivos, incluso a bajas concentraciones. Generalmente se les asocia con densidades relativamente altas (> 5 g/cm^3), ya que se asume que la densidad está relacionada con la toxicidad. Además, los metales pesados son persistentes en el ambiente y se bioacumulan, por lo cual se han ganado la atención pública (Lin et al., 2017). El mecanismo de toxicidad de los metales pesados se puede explicar por su habilidad para interactuar con las proteínas nucleares y el ADN, causando un deterioro de las macromoléculas biológicas (Helaluddin et al., 2016).

Los efectos de la urbanización en la calidad ambiental son distintos entre regiones con diferente grado de desarrollo, topografía, recursos naturales y políticas públicas (Liang et al., 2019). Ensenada, San Luis Potosí, Ciudad de México, Toluca, Morelia y Mérida son ciudades mexicanas localizadas a distintas latitudes, con ambientes geológicos y actividades económicas distintas. Estas ciudades, se encuentran dentro de las 20 Zonas Metropolitanas con mayor número total de habitantes, con excepción de Ensenada que es un área urbana media (SEDATU, 2018), por tanto, podrían poner de manifiesto la situación actual en términos de contaminación por metales pesados en la que se encuentran las ciudades mexicanas.

La definición de contaminación como el incremento de una sustancia con respecto a un nivel natural y que puede ocasionar daños para la vida de un ecosistema presenta muchas problemáticas prácticas. Por un lado, ha sido muy complicado encontrar el nivel de referencia "natural" en ambientes urbanos para el polvo urbano que es una matriz compuesta por una mezcla de materiales antrópicos y naturales. Por otro lado, parece apropiado establecer un nivel de referencia natural, al que comúnmente se le denomina valor de fondo (*background value*, en inglés), para cada ciudad, considerando las características locales de cada sitio. Sin embargo, esto dificulta hacer comparaciones entre ciudades, en términos absolutos de las cantidades de los contaminantes (Hakanson, 1980).

Determinar si un contaminante ocasiona daños a la vida de un ecosistema también es una labor difícil que se debe tomar en cuenta al identificar si una ciudad está contaminada. Por tanto, se han utilizado índices de riesgo ecológico y a la salud humana, como una primera aproximación para evaluar posibles riesgos para la vida en las ciudades (Jiang et al., 2018; Lin et al., 2017; Xu et al., 2019).

En esta investigación, propusimos evaluar la contaminación por metales pesados en el polvo urbano de seis ciudades mexicanas, elegidas de acuerdo con la disponibilidad de las bases de datos del equipo de trabajo, así como por su variedad en términos de latitud, geología, tamaño y actividades económicas. Para esta evaluación utilizamos dos niveles de fondo, uno local y otro global, para identificar las ciudades más contaminadas y analizar el efecto que tiene el valor de referencia empleado. También evaluamos algunos índices de riesgo ecológico y a la salud humana para complementar el análisis de la contaminación.

Otro asunto importante relacionado con la contaminación por metales pesados en el polvo urbano es identificar los factores de la forma urbana que se relacionan con la contaminación, incrementando o disminuyendo las concentraciones de los metales pesados. Previamente se ha encontrado que algunos factores como el uso de la tierra, el desarrollo industrial y la construcción de edificios empeoran la contaminación en las áreas urbanas (Jung et al., 2019; Liang et al., 2019). Desde el punto de vista social, aspectos como la recaudación tributaria y el nivel educativo se han asociado con una disminución de la contaminación urbana (Liang et al., 2019). En ciudades con una economía mayoritariamente relacionada con el sector servicios, como la Ciudad de México, existen múltiples fuentes pequeñas y dispersas que dificulta la identificación de los principales factores relacionados con la contaminación. Por este motivo, utilizamos el caso de la Ciudad de México para evaluar la posible asociación entre la forma urbana (densidad de población, superficie de rodamiento, entre otras y los metales pesados en el polvo urbano; por medio de regresiones múltiples.

La resiliencia es un término clave en el estudio de la contaminación urbana y se define como la habilidad de un sistema para absorber los cambios de estado de alguna variable o parámetro y seguir persistiendo. En la literatura se reconocen varios tipos de resiliencia: 1) Resiliencia técnica, se refiere a la capacidad física de una organización para seguir trabajando cuando ocurre una crisis. 2) Resiliencia organizacional, está relacionada con la habilidad de los manejadores de crisis de tomar decisiones e implementar medidas que evitan que empeore la crisis y reduzcan los impactos. 3) Resiliencia económica, engloba la habilidad de una organización para enfrentar costos adicionales después de una crisis, y 4) resiliencia social, habilidad de una sociedad para minimizar los impactos con ayuda de un equipo de emergencia o con la participación de voluntarios (Bueno et al., 2021).

Debido a que la resiliencia urbana es el resultado de una interacción compleja de muchos factores, la resiliencia cambia, no permanece estática. Si bien la resiliencia se basa en la evaluación, tratamiento, monitoreo y comunicación de riesgos; se distingue del enfoque tradicional de preparación de riesgos porque la resiliencia implica adaptación a las situaciones inesperadas. El concepto de resiliencia se ha adoptado en el área de manejo de riesgos y en el de la salud pública como la capacidad social, económica y ambiental de un sistema para responder a un evento peligroso y seguir existiendo (Kapucu et al., 2021).

SITIOS DE ESTUDIO

Las ciudades se eligieron con base en los datos disponibles en el grupo de trabajo. Se procuró tener ciudades diversas, con distintos tamaños en extensión y cantidad de habitantes, diferentes ambientes geológicos (provincias fisiográficas) y distintas actividades económicas. La Ciudad de México es la más poblada de todo el país, San Luis Potosí se caracteriza por ser una ciudad metalúrgica, Ensenada es una ciudad mediana dedicada principalmente a actividades costeras, Mérida es la ciudad principal de la península de Yucatán, dedicada principalmente al turismo. Morelia es una ciudad mediana con actividades secundarias y terciarias. Toluca es una ciudad con actividades industriales (CONAPO & SEDESOL, 2012).

Ensenada

Las provincias fisiográficas son regiones resultantes de la acción de un mismo conjunto de agentes modeladores del terreno, mismo origen geológico, semejante tipo de suelo y de vegetación. Ensenada se localiza en la Península de Baja California, al norte del país (Fig.1). La ciudad de Ensenada se ubica entre los paralelos 27° 59' y 32° 24' N; y los meridianos 112° 44' y 116° 54' W; con una altitud de 20 msnm, ocupa el 73.13% de la superficie del estado. Posee un clima mediterráneo seco subhúmedo, con precipitaciones escasas que se concentran en los meses más fríos, (de noviembre a febrero). Por su ubicación costera la ciudad tiene un clima especialmente afectado por la corriente fría de California, y por el hecho de que la temperatura oceánica alcanza sus máximos niveles estivales en agosto y septiembre, no en junio y julio como acontece en el interior de los continentes.

Ensenada tiene una población total de alrededor de medio millón de habitantes, con un crecimiento anual del 1.6% (SEDATU, 2018). Es una ciudad con actividad turística y es el paso hacia el sur de la península por la carretera transpeninsular. La principal actividad económica es la pesca, otras actividades económicas son el turismo y la agricultura (Cortés et al., 2015).

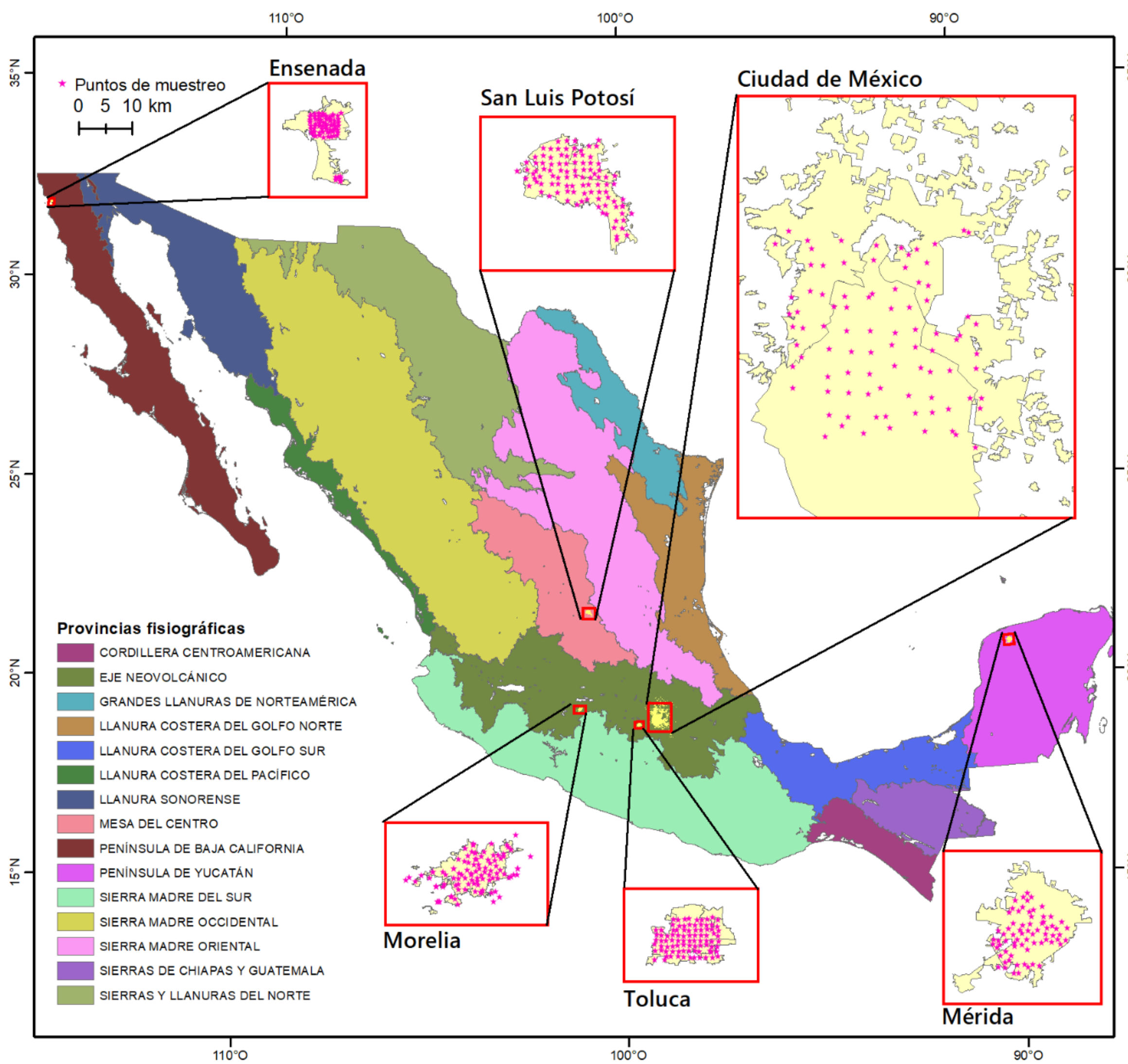

Fig. 1 Mapa de ubicación de las zonas urbanas estudiadas

San Luis Potosí

San Luis Potosí se ubica en la Mesa del Centro, la cual es una provincia formada por amplias llanuras interrumpidas por sierras dispersas de origen volcánico. La ciudad de San Luis Potosí se localiza a los 22.15° N y 100.98° W, en el centro de México, dentro del valle de San Luis Potosí, a una altitud media de 1860 msnm (Fig. 1). El clima es seco templado y semiseco templado al Sur, seco semicálido al Norte y muy seco templado al centro. La precipitación pluvial anual es de 372.9 mm, con una temperatura media de 16.8 °C. La ciudad está formada básicamente por aluvión, mientras que la Sierra de San Miguelito, localizada del lado oeste está formada por rocas ígneas intrusivas.

La Ciudad de San Luis Potosí, junto con su zona conurbana, cuenta con 1,040,443 habitantes (772,604 en San Luis Potosí y 267,839 en Soledad de Graciano Sánchez), lo que la convierte en la undécima zona metropolitana de México, debido a su población total, y en la décima zona, en cuanto a producción económica total, de acuerdo con el Instituto Nacional de Estadística y Geografía y (INEGI (Instituto Nacional de Estadística y Geografía), 2014). La superficie urbana de esta zona metropolitana se reportó en 188.63 km^2 (152.45 de San Luis Potosí y 36.18 km^2 de Soledad de Graciano Sánchez).

En cuanto a producción bruta, las principales actividades económicas en el estado son: manufacturas, servicios privados no financieros, comercio, transporte/correo/ almacenamiento y minería. San Luis Potosí genera el 77% de la producción bruta del Estado y emplea al 69% de las personas ocupadas en actividades secundarias y terciarias. Desde 1890, existe un complejo minero metalúrgico, al noroeste de la ciudad. Además, desde 1963 cuenta con un parque industrial, al sureste de la ciudad, con más de 253 empresas, destacando 35 fundidoras, 50 empresas en la industria básica del hierro, acero y metales no ferrosos, 34 en la producción de auto partes y 91 dedicadas a la industria química (hule, plásticos y productos farmacéuticos) (Aragón-Piña et al., 2006).

Morelia

La Ciudad de México, Toluca y Morelia se localizan dentro de la zona fisiográfica llamada Eje Neovolcánico, la cual se considera como una enorme masa de rocas volcánicas, lavas y otras manifestaciones ígneas (Fig. 1).

La ciudad de Morelia está localizada a 19°46′06″N, 101°11′22″W al centro-norte del estado de Michoacán, a una altitud de 1920 msnm. Se presenta un clima subhúmedo con temperatura media anual de 17.5 y precipitación pluvial de 773 mm. Los vientos dominantes proceden del suroeste y noreste, son variables en julio y agosto con intensidades de 2.0 a 14.5 km/h (Fig. 1). El basamento de roca de la ciudad se compone de riolita (cantera), así como de materiales volcánicos no consolidados (tepetate) (Delgado Carranza et al., 2015).

El área urbana abarca alrededor de 85 km^2, con una población de 597511 habitantes, junto con su área metropolitana consta de 806 822 habitantes y existen más de 300 mil vehículos automotores. Las principales actividades económicas del municipio de Morelia son el comercio, turismo y servicios (63.7%); la industria de la construcción y la manufacturera (25.9%); y la agricultura (10.4%). El sector industrial incorpora los siguientes giros: elaboración de aceite comestible, productos químicos, resinas, harina, fundición, industria del plástico, calderas, los dulces en conservas, embotellamiento de agua y refrescos, fabricación de generadores eléctricos, turbinas hidráulicas y de vapor y productos de celulosa y papel (Delgado Carranza et al., 2015).

Ciudad de México

La mancha urbana de la Ciudad de México, capital del país, está ubicada en la cuenca del Valle de México, a una altitud de 2240 metros sobre el nivel del mar, principalmente dentro de la zona lacustre que antes ocupaba el lago de Texcoco, con una superficie de 1485 km^2. Habitan 8.9 millones de personas y su densidad de población es de 5966 habitantes/km^2 (Fig. 1). En la ciudad y zona conurbada habitan 23 500 000 habitantes, circulan 4 000 000 vehículos, y funcionan 40 000 industrias pequeñas y medianas.

En la Ciudad de México hay dos épocas climáticas durante el año: la estación invernal seca de noviembre a abril y la lluviosa de mayo a octubre. Durante el invierno son frecuentes las inversiones térmicas. Hasta que el sol calienta el aire frío, alrededor de las 9 o 10 am, los contaminantes se dispersan. Los vientos predominantes tienen una dirección noreste a suroeste, en donde se topan con la Sierra del Ajusto que impiden el paso del viento, dificultando también la dispersión de los contaminantes. (Vallejo et al., 2003).

La parte norte del sitio de estudio corresponde a un centro industrial importante con una alta densidad de población. La parte centro comprende el centro histórico y socioeconómico de la ciudad, con una alta actividad urbana y comercial. El área sur ha estado dominada por actividades residenciales y comerciales (Rodríguez-Salazar et al., 2011).

Toluca

Toluca está localizada en la parte central del Estado de México, sus coordenadas son 19° 17' 29 N y a los 99° 39' 38 O. Se sitúa en la cima de una meseta elevada, con una altitud máxima de 4340 msnm en el volcán "Nevado de Toluca" y una altitud promedio de 2640 msnm en la región central del valle. Hay dos tipos de clima en la región: subhúmedo templado y subhúmedo semifrío, con una temperatura anual de -3°C y 14°C. La lluvia anual varía entre 800 y 1200 mm (Fig. 1). Los vientos predominantes tienen una dirección sur - norte. Toluca es el segundo centro urbano más importante del Estado de México, presenta un acelerado crecimiento anual (Ávila-Pérez et al., 2019).

La mayor parte de las actividades económicas (57%) son del sector terciario, mientras que el 36% son del sector secundario: industria metalúrgica, química, petroquímica, del vidrio y sus derivados, plásticos y caucho, generación de electricidad, minería y construcción (Ávila-Pérez et al., 2019).

Mérida

Mérida se localiza en la Península de Yucatán, el terreno de esta provincia es predominantemente plano. Su altitud promedio es menor a 50 msnm. Es la provincia más joven de México y está formada por rocas calcáreas marinas. Los suelos dominantes son del grupo Leptosol, con fracturas de la roca caliza superficial. La ciudad de Mérida, Yucatán se ubica en las coordenadas 20°58′04″N y 89°37′18″O, en una planicie kárstica con una altitud promedio de 9 msnm (Fig. 1). Tiene un clima definido como el más seco de los cálidos subhúmedos, de acuerdo con el sistema de Köppen modificado por la República Mexicana (García, 2014), con régimen de lluvias de verano y presencia de canícula; presenta poca oscilación térmica (entre 5 y 7°C).

Mérida es la ciudad más importante del estado de Yucatán ya que es el centro de las actividades políticas, comerciales, educativas, industriales, financieras y de salud tanto del estado como de toda la Península de Yucatán. También es la ciudad con mayor densidad de población del sureste mexicano, con actividades industriales, de comercio y tránsito vehicular (Chan Te, 2017).

JUSTIFICACIÓN

En el último siglo la mayor parte de la población mundial ha pasado de vivir en sitios rurales a sitios urbanos (Lawrence, 2003) y las tendencias indican que el mundo se está volviendo cada vez más urbano (Steiner, 2008). En México, al comienzo del siglo XXI, el 72% de la población habita en zonas metropolitanas, conurbaciones y centros urbanos (CONAPO & SEDESOL, 2012). La alta densidad de población implica un consumo sustancial de recursos y la consiguiente producción masiva de residuos. Más aún, los ambientes naturales son reemplazados por otros artificiales disminuyendo la autorregulación de los ecosistemas urbanos. Por lo tanto, las concentraciones de los contaminantes tienden a exceder los valores de fondo de muchas ciudades, causando distintos grados de contaminación (Men et al., 2018).

Diversos estudios reportan que la contaminación ambiental en las grandes urbanizaciones de muchos países se ha convertido en un problema grave. Tanto fuentes naturales como antrópicas liberan polvo al ambiente, que contiene metales pesados asociados (Ali et al., 2017; Chen et al., 2014; García-Rico et al., 2016). El polvo se puede movilizar a través de distintos mecanismos y entrar en el cuerpo humano por medio de tres rutas de exposición: inhalación, ingestión o dérmica.

Dependiendo de factores como la toxicidad del elemento, biodisponibilidad, concentración, así como de cuestiones socioeconómicas y del estado de salud de la persona, los metales pesados pueden generar efectos adversos en la salud de la población expuesta (Calderón et al., 2001; Carrizales et al., 2006; Salustri et al., 2010).

Esto ha hecho necesario el estudio de la contaminación urbana por metales pesados. En diversas ciudades de México se han llevado a cabo diagnósticos de contaminación por metales pesados (Bautista et al., 2017; Cejudo-Ruíz et al., 2015; Cortés et al., 2015; Delgado Carranza et al., 2015). Sin embargo, no se ha realizado una comparación entre estas que nos permita tener un panorama general del grado de contaminación de las grandes ciudades mexicanas.

IMPORTANCIA DEL PROYECTO

Los beneficios de la generación de conocimiento en relación con la contaminación por metales pesados en los polvos urbanos en estas ciudades mexicanas son, principalmente, para los millones de personas que en ellas habitan, ya que con los resultados obtenidos se pone de manifiesto el grado de contaminación, se identifican a los metales que representan un riesgo para la salud humana, se distinguen algunas probables fuentes y mecanismos de movilidad de los metales en el polvo urbano. Esta información es útil para la toma de decisiones por lo que se espera que mejore la calidad de vida de la población. El análisis integral con los modelos de regresión podría tener importantes implicaciones de planeación urbana y también abre espacio a nuevas investigaciones sobre la movilidad y destino de los metales pesados del polvo dentro del sistema urbano.

PREGUNTA DE INVESTIGACIÓN

¿Existe contaminación por metales pesados en el polvo urbano de seis ciudades mexicanas, esta contaminación puede representar un riesgo potencial ecológico y a la salud humana?

¿Existe una asociación positiva entre la densidad poblacional e industrialización con la contaminación por metales pesados?

OBJETIVO GENERAL

Evaluar la contaminación por metales pesados en el polvo urbano y los riesgos ecológico y a la salud humana en las ciudades mexicanas de Toluca, San Luis Potosí, Morelia, Mérida, Ensenada y Ciudad de México.

OBJETIVOS PARTICULARES

1) Identificar la(s) ciudad(es) más contaminada(s) por metales pesados mediante análisis de varianza. Analizar visualmente la relación entre la contaminación, el tamaño de la población y el ambiente geológico (provincia fisiográfica).
2) Evaluar la contaminación por metales pesados en el polvo urbano de la Ciudad de México, utilizando índices de contaminación con un nivel de fondo global y otro local. Encontrar la

asociación entre la contaminación y el posible riesgo a la salud humana utilizando la metodología de la USEPA.

3) Evaluar la posible asociación entre la forma urbana (densidad de población, densidad de empleos, superficie de rodamiento, distancia al aeropuerto, distancia al zócalo, unidades de manufactura, unidades contaminantes, índice de entropía, cobertura de vegetación, área de los camellones e índice de marginación) y los metales pesados en el polvo urbano de la Ciudad de México; por medio de regresiones múltiples.

ESTRUCTURA DE LA TESIS

La estructura de la tesis se divide en cinco capítulos:

Capítulo I, se enfocó en hacer una revisión del estado del arte y las futuras líneas de investigación en el tema de la contaminación y riesgo a la salud por metales pesados en el polvo urbano. Ya que se requiere una visión general del tema y dentro de los estudios del que abordan esta problemática existen muchas diferencias estructurales y metodológicas.

Capítulo II, se plantearon las preguntas ¿Existe contaminación por metales pesados en el polvo urbano de seis ciudades mexicanas seleccionadas de acuerdo con las bases de datos disponibles y procurando diversidad tamaños, ambientes geológicos y actividades económicas, esta contaminación puede representar un riesgo potencial ecológico y a la salud humana?, ¿Cuál es la ciudad más contaminada, es la ciudad más grande e industrializada? Esto debido a que los efectos de la urbanización sobre la calidad ambiental varían entre regiones con diferentes grados de desarrollo, topografía, recursos naturales y políticas públicas. Se espera que las ciudades más grandes e industrializadas tengan las mayores concentraciones de metales pesados, sin embargo, no sabemos si esto sucede de manera proporcional al tamaño.

Capítulo III ¿Existe contaminación por metales pesados en el polvo urbano de la Ciudad de México? ¿esa contaminación representa un riesgo para la salud humana? Debido a que los metales pesados se utilizan ampliamente en la Ciudad de México y en exceso pueden ser tóxicos. Este análisis se hizo a partir de un muestreo intensivo de 482 muestras y una técnica analítica más precisa, con la intención de mejorar la evaluación a la salud. Además se incluyeron más elementos en el análisis, respecto a los que se analizaron en el capítulo anterior, y la evaluación del nivel de contaminación se complementó con otro índice.

Capítulo IV, se analizó de manera particular el manganeso ya que existe una preocupación médica por la presencia de marcas del Parkinson en gente joven de CDMX. El Mn podría ser una causa, pero no existe información sobre sus concentraciones en el ambiente urbano. En los capítulos anteriores se demostró la importancia de incluir al Mn y el Fe en los estudios de contaminación por metales pesados en el polvo urbano. El análisis realizado en este capítulo fue principalmente espacial.

Capítulo V, en el último capítulo se abordó la pregunta de investigación ¿Cuáles son los elementos de la forma urbana asociados a la concentración y carga de los metales pesados en el polvo urbano de la Ciudad de México? Ya que, en el ambiente construido, la distribución espacial de las concentraciones y cargas de los metales pesados tienen causas múltiples. Por tanto, el estudio de la forma urbana permite identificar aquellos elementos de mayor relevancia asociados con los metales pesados.

CAPÍTULO I

“Health risk of heavy metals in street dust”

En este capítulo hicimos una revisión sistemática del estado del arte del tema de contaminación por metales pesados en el polvo urbano y su asociación con los posibles riesgos a la salud que pueda generar la contaminación. Los estudios que se consideraron para la revisión estuvieron basados en la metodología de estimación de riesgos a la salud humana desarrollada por la Agencia de los Estados Unidos de América para la Protección del Ambiente (USEPA, por sus siglas en inglés).

Esta investigación se hizo para establecer los antecedentes de la tesis doctoral. Los pasos que se siguieron fueron los siguientes:

1. Selección de bases de datos: se seleccionó la *Web of Science* como la base de datos más adecuada porque considera artículos de diferentes editoriales y cuartiles del indicador de ranking de revistas. De esta manera, disminuimos el sesgo de seleccionar solo un tipo de artículo.
2. Búsqueda con palabras clave: “*street dust*”, “*heavy metals*” y “*human health*” fueron utilizadas como palabras clave en la búsqueda de los artículos. Se exploraron los títulos y los resúmenes y se seleccionaron los artículos según los criterios de inclusión (Fig. 1).
3. Selección de estudios: los artículos descargados fueron leídos en su totalidad para determinar si debían ser excluidos de acuerdo con los criterios de exclusión. Para que un estudio se considerara elegible, tuvo que cumplir con todos los criterios de inclusión y no tuvo que cumplir con ningún criterio de exclusión.
4. Extracción y síntesis de datos: extrajimos el nombre del primer autor, año de publicación, ciudad de estudio, país, el nombre que se le dio al material analizado (polvo de la calle) y a los elementos de interés, el número de muestras, la metodología utilizada, el tamaño de las partículas, los habitantes, las concentraciones de los metales pesados y los índices de riesgo no carcinogénico (HI) y riesgo carcinogénico (RI). También extrajimos las principales fuentes identificadas.

La búsqueda se realizó en abril de 2019. Después de buscar en la Web of Science, encontramos 197 artículos con las palabras clave: polvo de la calle (*street dust*), metales pesados (*heavy metals*) y salud humana (*human health*). Entre esos artículos, solo 46 cumplieron con los criterios de inclusión, y después de leer el texto completo, 8 artículos fueron excluidos de acuerdo con los criterios de exclusión. Por lo tanto, en total 38 artículos cumplieron los criterios de inclusión y no cumplieron los criterios de exclusión; en un artículo los autores analizaron dos ciudades diferentes, para este artículo cada ciudad fue considerada como una observación independiente. La ubicación de las 39 ciudades seleccionadas se puede ver en la Figura 2.

Durante la búsqueda y evaluación de los estudios, se identificaron diferentes términos para referirse a las partículas sólidas que se depositan en las superficies impermeables de los ambientes urbanos: *street dust* (polvo de la calle, 42%), *road dust* (polvo de la carretera, 32%), *dust* (polvo, 8%), *urban dust* (polvo urbano, 5%), *outdoor dust* (polvo exterior, 5%), *atmospheric dry deposition* (depósito atmosférico seco, 3%), *settled dust* (polvo sedimentado, 3%), y *surface dust* (polvo superficial, 3%); entre paréntesis se expresa el porcentaje de los artículos que utilizaron cada término. Polvo de la calle (*street dust*) y polvo de la carretera (*road dust*) fueron los términos más utilizados; por lo tanto, *street dust* se usó en este artículo para referirse a este material, y alentamos a nuestros lectores a usar también este término para estandarizar el concepto y facilitar la búsqueda y el análisis en el tema.

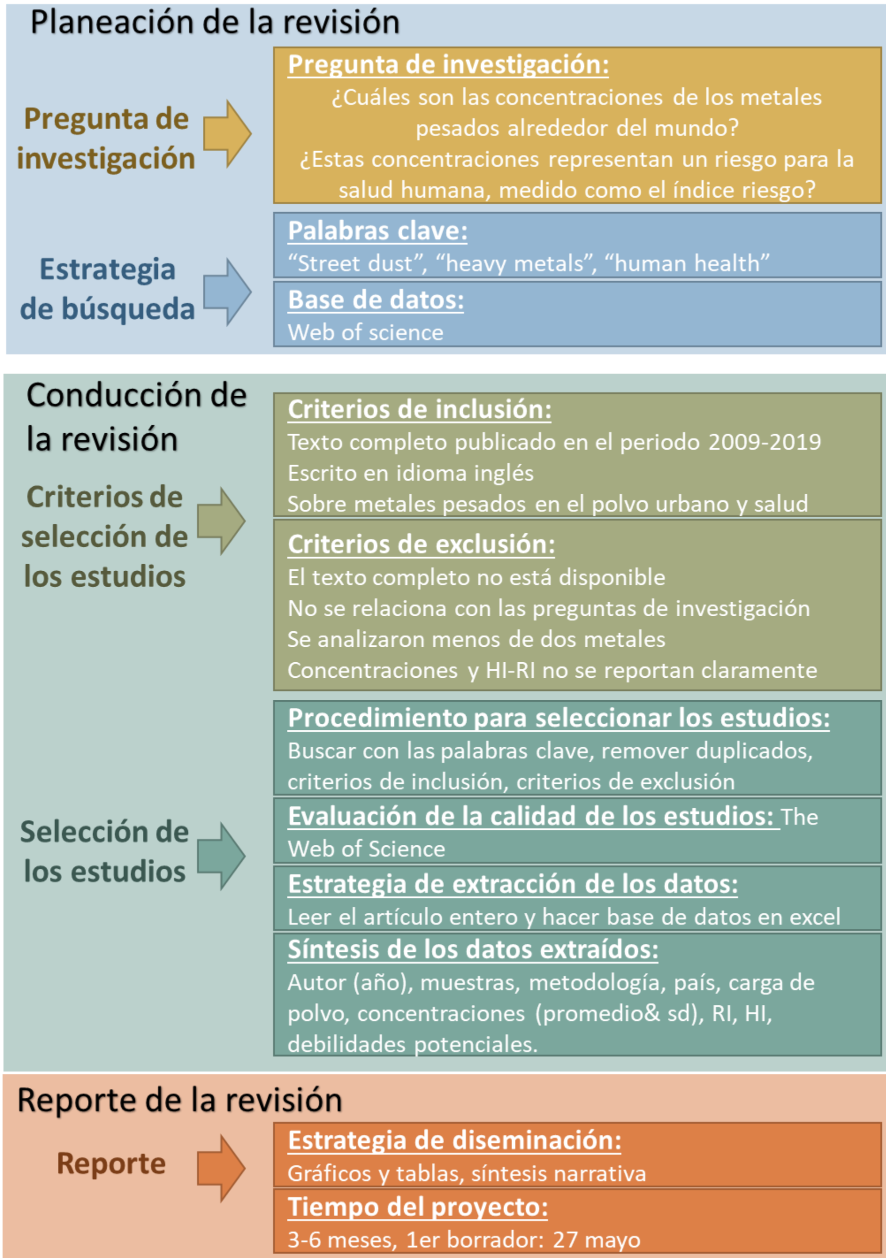

Fig. 1 Protocolo para hacer la revisión sistemática.

Otros sinónimos de "metales pesados" (55%) que se encontraron fueron: metales (18%), elementos potencialmente tóxicos (5%), metales tóxicos (5%), metales traza (5%), metales pesados tóxicos (3%), metales potencialmente tóxicos (3%), elementos pesados (3%) y elementos (3%). El término "metales pesados" ha sido definido de manera ambigua a lo largo del tiempo, ninguno de los artículos seleccionados ofrece una definición para este concepto, sin embargo, es utilizado en más de la mitad de los estudios. Como es el término más común y reconocido, sugerimos seguir usándolo en los estudios de polvo de la calle.

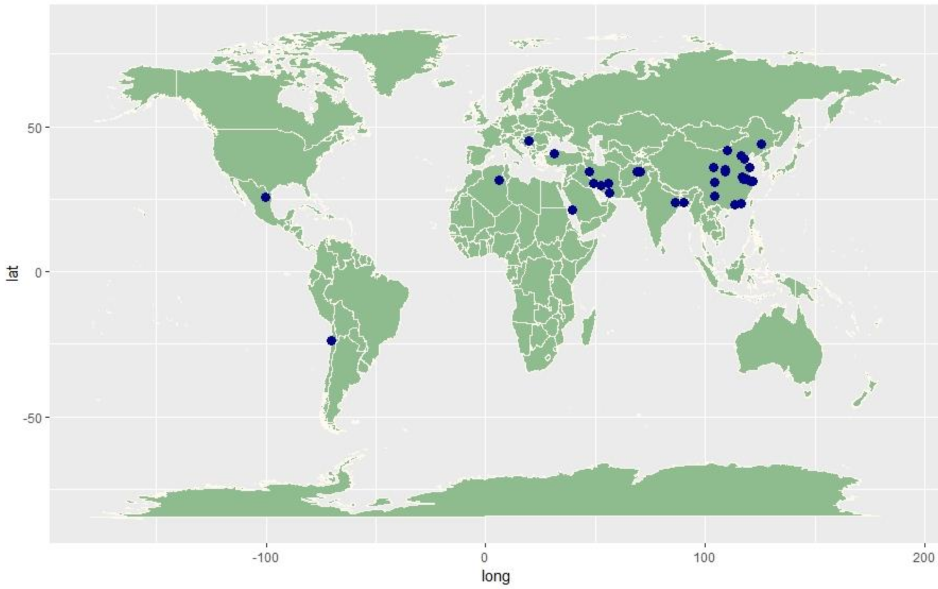

Fig. 2 Ubicación de los sitios de estudio seleccionados (círculos azules).

En cuanto al año de publicación, existe una tendencia ascendente a lo largo del tiempo (Fig. 3). Especialmente en 2018, hubo un auge en las publicaciones. El proceso de búsqueda para esta revisión se realizó en abril de 2019, en ese momento se identificaron tres artículos, pero algunos otros pudieron ser publicados en los siguientes meses. Esta tendencia general destaca el creciente interés en el tema porque cada vez más personas viven en las ciudades y hay muchas fuentes de partículas contaminantes que dañan la calidad ambiental y pueden ser perjudiciales para la salud humana.

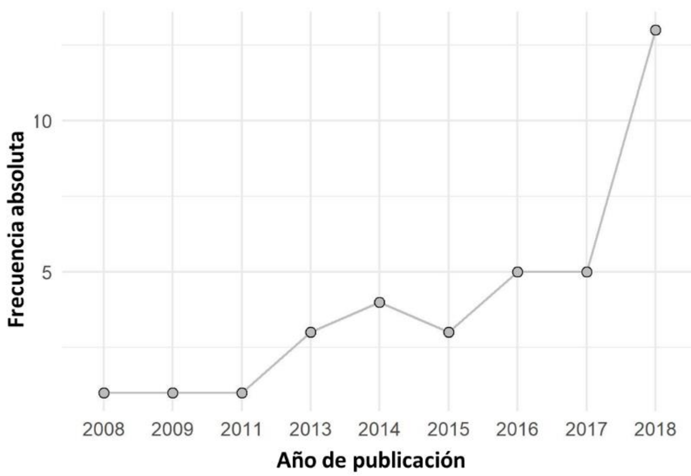

Fig. 1 Tendencia al alza de los artículos publicados relacionados con metales pesados en el polvo de la calle y la evaluación de riesgos para la salud humana.

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Health risk of heavy metals in street dust

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1. ABSTRACT

Heavy metals in street dust represent a risk to the human health due to their toxicity, persistence and bioaccumulation. Using the US Environmental Protection Agency (USEPA) assessment, here, we review the human health risks of such dust world-wide. The street dust in such cities is contaminated by *As*, *Cd*, *Cr*, *Cu*, *Hg*, *Mn Ni*, *Pb* and *Zn* beyond the median levels of the world soil background values. Among these elements, the median values of the hazard risk indices (non-carcinogenic risk) are highest for As, Cr and Pb and the median values of the risk indices (carcinogenic risk) for As are in the tolerable risk range for children and adults and in the case of Pb, the median value of the carcinogenic risk indices are also in the tolerable range for children. We emphasize that the level of heavy metals in street dust pose a considerable risk to the human health and require monitoring and approaches to reduce such toxic levels.

2. INTRODUCTION

By 2030, 60% of the world population are housed in the urban areas (1). The combined impact of the urban and the industrial development, use of vehicles and human activities, undoubtedly leaves a footprint on the quality of the environment, adversely impacts the quality of air and leads to increasing levels of heavy metals in the street dust (2-3).

Street dust is formed by solid particles deposited on impervious materials that originate from the interaction of solid, liquid and gaseous constituents in the urban environment (4). It originates from natural and anthropogenic sources. Special attention is paid to the latter because of the pollutants they may contain; anthropogenic sources include traffic-related emissions, industrial discharges, domestic activities, weathering of buildings and other atmospheric depositions (5,6). Therefore, street dust is a sink of pollutants, but it is also a reaction bed and a source of those pollutants which can be released back to the atmosphere, soils and water (4,6,7).

Among the complex components of street dust, heavy metals (arsenic (As), barium (Ba), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn) contamination have drawn public attention because of the high toxicity, concealment, persistence and biological accumulation in the ecosystem and humans (8). They can enter the human body via inhalation, ingestion and dermal exposure, and can have both a non-carcinogenic and carcinogenic risk (2). They may accumulate in the fatty tissues in the body and affect the central nervous and circulatory systems, disrupt the normal functioning of our internal organs, act as cofactors in other diseases and may cause DNA damage (6). At present, As, Cd, Cr (VI) and Ni have been identified as carcinogenic metals to humans, while Pb is classified as probably carcinogenic to humans (9,10).

The above underlines the importance of studying street dust. As it is a relatively new research field related to the environmental sciences, with the earliest studies dating from the 1980s and 1990s (11,12), its study object needs to be addressed from an interdisciplinary perspective. Now, this field has adopted a wide theoretical background and methods from the soil sciences (6,13,14), nevertheless, it is necessary to verify whether these adopted methods and knowledge work well for street dust, and if a specific body of knowledge for study street dust should be developed.

During the past decade, many isolated studies of human health risk assessment of heavy metals in street dust have been carried out employing the model developed by the US Environmental Protection Agency (USEPA) for soils. However, there is not a general view of the topic, and many structural and methodological differences have been found among studies; therefore, it is necessary to review the state of the art on this subject matter, and to establish guidelines for future studies. We reviewed the evolution, state of the art and future lines of research on the concentrations of heavy metals, sources and human health assessments of street dust, during the past decade.

3. PROGRESS IN THE STUDY OF HEAVY METAL CONTAMINATION IN STREET DUST

3.1. Sampling process established for street dust

Along the last ten years, different statistical samplings have been used. A very common one is systematic sampling because it is representative and very useful for spatial interpolations. However, in many studies the type of sampling is neither justified nor well explained and could lead to bias in samplings. Therefore, it is important to look for the best sampling type and to explain with sufficient detail how the sampling was made and the rationale for the method.

The sample size is also a point that requires attention. Most of the studies used a small sample size, between 13 and 74 sites. Mean sample sizes are around 65, and maximum ones are above 250. A small number of samples could not be representative of the entire city and could result in errors, especially when cities are large. The simplest way to define a sample size could be based on the area to be analyzed, with at least one sample per square meter to be taken. Another alternative is to take 100 samples as a minimum when spatial interpolations are to be undertaken (15).

The best practice of sampling should be based on surface area (m^2) and, if the amount is not sufficient, a bigger area must be sampled. The street dust loading (that is, the quantity of street dust per square meter) provides valuable information about the amount of dust and even the amount of heavy metals that is present in the environment, and therefore should be reported. At present, most of the sampling of street dust are based on an approximate quantity (300–500 g), however, the quantity of dust per square meter (*i.e.*, the street dust loading) must be reported from now on.

In relation to the equipment used to collect the samples, change in the dust loading is obtained by fraction sizes when different sampling methods are used (brushing and vacuuming). For smaller particle mass fractions (less than 74 micrometers), the vacuuming method is more efficient at collecting the sample. On the contrary, for bigger particle sizes (74–500 micrometers), the brushing method is more effective for collecting larger particles. Equations to transform the measured concentrations between methods have been developed by Yu *et al.*, in 2016 (16). Even when both sampling methods give similar concentrations, they can affect the heavy metal loading, so it is important to take this information into account.

With regards to the particle size, there is no consensus. Some authors sieve the street dust through a sieve of less than 250 micrometers, arguing that those particles are most likely to adhere to hands and therefore be involuntarily ingested (17). Others use sieves of less than 100 micrometers, arguing that particles less than 100 micrometers are easily re-suspended and therefore can be inhaled and capable of remaining airborne for considerable durations (3,6). However, less than 63 micrometers are the most preferable size because these particles can be considered to mainly arise from atmospheric deposition and transported by re-suspension (18). Furthermore, the smaller the particle size, the greater the surface area to volume ratio and thus the concentrations of heavy metals (19).

There are several possible explanations for higher concentrations of heavy metals in dust samples with smaller particles: 1) they can be direct by-products of vehicular and industrial activities; 2) their relatively larger available surface area per unit mass means a higher adsorption rate for heavy metals compared to larger particles (19); and 3) they might contain a greater proportion of organics and clay minerals that facilitate the adsorption of metals (5).

However, this is not consistent in the bibliography: depending on the heavy metals, the highest concentrations are identified in different particle sizes. For example, Chen *et al.* (20) report that the highest concentrations for Co, Zn, As, Sr, Cd and Sb were effectively found in the less than 63 micrometers fraction, but for Ni and Cu the highest concentrations occurred in the median sizes (125–500 micrometers), and the mean Pb level is relatively higher in the coarsest fraction (500–1000 micrometers) (20). In addition to these different results, it is recommended that the smallest particle size is analyzed. A fraction of less than 63 micrometers is easy to obtain in a laboratory with a mesh and better reflects the anthropogenic emissions of street dust (21,22).

Chemical and physical properties commonly measured in soils could be very helpful in street dust analysis; those properties are organic matter, clay percentage, pH and cation exchange capacity. Organic matter is a chelating agent, mineral clay adsorbs heavy metals in the surface, pH can modify the mobility of the heavy metals, and cation exchangeable capacity is the soil (dust) property where the heavy metals can be adsorbed (23). The analysis of these properties in street dust could elucidate the role of organics and clay minerals in the content of heavy metals; *e.g.*, González-Grijalva *et al.* (24) observed that kaolinite content in soils increases Pb bioaccessibility in the intestinal phase. Similar studies should be done for street dust. In relation to particle size fractions, in particular, the mineralogy of particles should be addressed, *e.g.*, rutile crystals commonly used worldwide have been identified in nanometric dust particles (25). In addition to mineralogy, the importance of pH and cation exchange capacity in the mobility of heavy metals in street dust also need to be studied.

3.2. Heavy metal contamination of street dust

3.2.1. Geochemical analysis

The most common analytical techniques used are: atomic absorption spectroscopy (AAS),

Table 1. Comparison of some characteristics for different analytical techniques

Characteristic/ Technique	ICP-OES	ICP-MS	AAS	GFAAS	XRF	PXRF
Cost	High	Very high	High	High	Moderate	Low to moderate
Multi or monoelemental	Multi	Multi	Multi (70)	Multi	Multi	Multi
Sample preparation	Acid digestion	Acid digestion	Acid digestion	Acid digestion	Pellet	Little preparation
Detection limits	ppb	ppb, even ppt	ppb	ppb	ppm	ppm
Precision	High	Very high	High	High	Acceptable	Moderate to low
Sample quantity	1 g	1 g	1 to 5 g	1 g	10 g	10 g

ICP-OES: inductively coupled plasma optical emission spectroscopy; ICP-MS: inductively coupled plasma mass spectroscopy; AAS: atomic absorption spectroscopy; GFAAS: graphite furnace atomic absorption spectrometry; XRF: X-ray fluorescence; PXRF: portable X- ray fluorescence; g: grams.

graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectroscopy (ICP-MS), inductively coupled plasma optical emission spectroscopy (ICP-OES), portable X-ray fluorescence (PXRF) and X-ray fluorescence (XRF). A comparison of the characteristics of these techniques is presented in Table 1.

Atomic spectroscopy comprises absorption, emission and fluorescence; all involve the process of excitation of an electron and decay to the ground state. With regards to the atomic absorption, AAS and GFAAS are examples of these techniques. In AAS, the concentrations are measured by passing light emitted by a radiation source, in a specific wavelength, through a cloud of atoms from a sample. The reduction in the amount of light intensity reaching the detector is seen as a measure for the concentration of an element. In GFAAS, samples are mixed with modifiers prior to the atomization processes and then dispensed into an atomizer; the sample is retained in the tube and the light path for a prolonged time, which leads to an improvement in sensitivity. Some disadvantages are a limited working range, slow analysis and high cost (14).

The techniques of ICP-AES consist of high energy emitted by a source that excites atoms, which subsequently emit light when they return to the ground state. ICP-OES is based on the emission of photons from excited atoms and ions in a radiofrequency discharge; the ionic excited state species may return to the ground state via emission of photons. The wavelength of the photons can be used to identify the elements and the number of photons is directly proportional to the concentration. ICP-MS uses an argon plasma source to dissociate the sample into its basic atoms or ions that are isolated according to their atomic mass-to-charge ratio by a quadrupole or magnetic sector analyzer. In this case, metal ions are detected rather than the light they emit (14). The fluorescence of the X-ray technique reported in the selected studies was the most common; it is a physical phenomenon that involves the interaction of X-rays with matter. X-ray radiation strikes an atom, detaching some electrons from the inner orbitals; this makes the atom unstable; the unoccupied spaces are filled by electrons from a higher orbital and the energy released is in the form of fluorescent X-rays (14). PXRF is based on the same physical phenomenon, but it is a portable device, smaller and lighter than the stationary equipment.

For the methods that require digestion of the samples to release the heavy metals, generally, standardized protocols are followed, such as the USEPA method 3051A: Microwave-assisted acid digestion of sediments, sludges, soils, and oils (26). This digestion is not intended to accomplish total decomposition of the samples; therefore, the concentrations do not reflect the total content. In the case of XRF the samples are ground and pressed in pellets. This method does not require acid digestion; thus, the concentrations could be higher than ICP.

Table 2. Descriptive statistics of the concentrations of heavy metals in street dust worldwide

HM	N	Mean (mg/kg)	Median (mg/kg)	Standard deviation	Minimum (mg/kg)	Maximum (mg/kg)	Earth-crust values[1]	World soil background[1]
As	22	27.1	12.7	39.2	2	148	1.8	6.83
Ba	6	156.7	194	95.3	12.2	248.5	400	460
Cd	28	3.7	1.1	5.8	0.3	21.4	0.1	0.41
Co	23	13.5	11.5	7.7	4	34	10	11.3
Cr	36	104.3	84.8	93.7	18.4	587.3	100	59.5
Cu	38	696.7	83.4	2731.3	27.5	16000	55	38.9
Fe	14	25522.2	22103	12775.6	8693.7	58300	NA	NA
Hg	10	56.5	0.2	177.2	0.1	560.9	0.07	0.07
Mn	24	601.8	532.9	619	189.9	3407.3	900	488
Ni	32	50.4	36.3	49.8	21	300	20	29
Pb	37	502.9	97.4	2283.3	0.9	14000	15	27
V	12	54.1	52.9	23.2	4	86	135	129
Zn	35	634.6	280.7	1167.7	56.6	6022	70	70

n: number of articles, NA: not available [1](29). Based on (1-9,13,16-18,20,21,27,28,32,33,36,41-44,50-58)

Regardless of the method, quality control must be carried out. This includes reagent blanks, duplicate samples and spiked samples. The detection and quantification limits must also be reported, as well as the recovery percentages with respect to the reference certified materials.

3.2.2. Overview of worldwide heavy metal concentrations in street dust

During the last decade, there has been an upward trend in the study of heavy metals in street dust around the world. In 2018 there was a boom in publications. This general trend highlights the increasing interest in the topic, because an increasing number of people now live in cities and there are many sources of polluted particles that decrease the environmental quality and can be harmful to human health.

Comparison of mean concentrations of heavy metals in street dust in different urban environments is a common practice, even though there are no universally accepted sampling and analytical procedures for geochemical studies of urban deposited materials. Moreover, concentrations of heavy metals in street dust particles vary considerably among cities depending on the local climate conditions, wind patterns and technologies, as well as the density of traffic and industrial activities (4,17).

The heavy metals that are almost always reported in street dust are Cu, Pb, Cr and Zn; the number of articles (n) that reported the concentrations for each heavy metal can be seen in Table 2. The main reasons why Cu, Pb, Cr and Zn are the most commonly measured heavy metals could be: 1) most interest is given to these elements because of their toxicity or extensive use, and 2) they are easier to measured compared to other metals, such as Hg.

Some studies have been carried out in very contaminated urban areas, for example, a mining area (27) and an e-waste processing area (28). In these places, very high concentrations of some heavy metals are found, that is, higher than the median ones for street dust worldwide. Thus, median values are more representative as a central tendency measure for the heavy metal concentrations around the globe (Table 2).

In relation to the variation of the data, the standard deviation reported for each heavy metal in this paper (Table 2) is higher than those reported in each individual study. However, it is expected that variation found in the worldwide data is greater than inside each city because each location has its own environmental conditions (climate, wind, traffic density, etc.), and different sampling and analytical procedures were used among studies.

To define a level of contamination, a reference value, known as the background, is needed. It should represent the natural or previous concentrations before anthropogenic activities have emitted the pollutants. The heavy metal concentration divided by the background is named the contamination factor (CF). Using the world soil background (29), the CF for the median concentrations of Zn and Pb (CF between 3 and 6) indicates a considerable contamination, and these are the heavy metals released in greater quantities in cities. Median concentrations of Hg, Cd, Cu, As, Co, Cr, Mn and Ni represent a moderate level of contamination worldwide (CF between 1 and 3). There is practically no contamination for Ba and V (CF less than 1), in urban environments.

Even when the soil background concentrations are commonly used as reference values to define a level of pollution for street dust, soils are not the only natural source of heavy metals in street dust, and it is very difficult to find soils unaffected by anthropogenic activities in cities. Therefore, the background values of heavy metals could be obtained from other materials, for example, from the coarse fraction of street dust, since this fraction is not the product of atmospheric deposition due to its large size. However, a possible problem is the fact that the coarse fraction could also be the result of anthropogenic activities, as the materials for construction transport can contribute to the presence of sands and gravels on the surfaces of streets. Nonetheless, we consider this is an alternative that needs to be tested.

No correlation between heavy metal concentrations and the number of inhabitants was found. This disagrees with previous results found in Spain, where increases in metal concentrations with population density were observed in street dust (30). Even when an increase in metal concentration with the number of inhabitants or population density could be expected, this hypothesis needs to be more deeply tested, as the present review shows a discrepancy.

To provide an overview of the concentrations of heavy metals in each country, variance analysis was undertaken. However, this was difficult because of the different number of samples for each country. China was the country for which more articles were published, with 58 percent of the selected studies carried out in Chinese cities. The next country with highest number of published articles was Iran (13 percent), then India (5 percent), and one article (3 percent) was found for each of the following countries: Algeria, Bangladesh, Chile, Mexico, Mongolia, Saudi-Arabia, Serbia, Turkey and Afghanistan. For the last article, two cities were studied, so the same study examined two places.

Among heavy metals only the concentrations of Cr had statistically significant differences between countries, according to Kruskal-Wallis test. China had the highest concentrations, followed by India, Iran and Afghanistan (Figure 1). For the remaining heavy metals, only the country with the highest mean concentration is mentioned, without significant differences: Chile had the highest mean concentration of As and V, in a mining port; Mexico for Ba; Changchun, China, for Cd and Co; an e-waste processing site in China for Cu and Pb, although those concentrations (16,000 mg/kg for Cu and 14,000 mg/kg for Pb) are excluded from Figure 1 for clarity; the same Chinese e-waste processing site for Ni and Zn; Xuanwei, China, for Fe; and an iron mining area in Mongolia for Mn.

The highest mean concentrations are found in urban areas with specific point sources, for example, mining and e-waste recycling. Thus, special attention must be paid to these sites in order to ensure the population health. Furthermore, this shows again the importance of separate industrial activities from population centers, and in this way, exposure can be diminished. Special security and control measures must be taken in those places where very high concentrations of heavy metals are emitted.

3.3. Sources of heavy metals in street dust

Different types of street dust are heterogeneous at a small-scale, due to their mobility, the rapid environmental alteration, and the variable

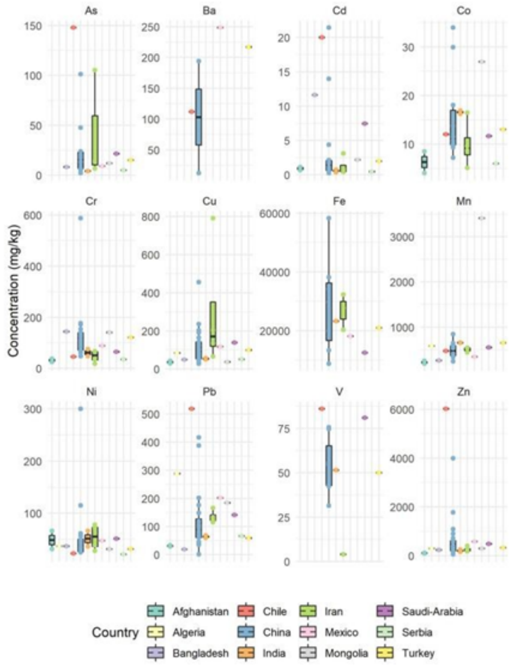

Figure 1. Comparison of the concentrations of heavy metals by country. The maximum concentrations of Cu (16,000 and 6103 mg/kg) and Pb (14,000 mg/kg) were excluded from plots in order to clarify the other concentrations in the figure.

distribution of their urban sources (31). Different approaches have been used to identify the possible sources of heavy metals in street dust. In 2017, studies focused on dividing the cities into different land uses or functional areas, such as industrial, commercial, residential and others (21,32,33). By 2018 and 2019, statistical methods were increasingly implemented, with the most commonly used being principal component analysis, cluster analysis and positive matrix factorization.

Principal component analysis (PCA) uses orthogonal transformation to convert an array of observations of correlated variables into a set of values of linearly uncorrelated variables that are defined as principal components. Therefore, PCA reduces data and extracts a small number of factors (principal components, PCs) for determining the relationships among the observed variables. The eigenvector with the largest eigenvalue is the direction of greatest variation, the one with the second largest eigenvalue is the (orthogonal) direction with the next highest variation, and so on. Each PC contains information on all of the elements combined into a single group, while the loadings of each element indicate their relative contribution to the group (34).

Positive matrix factorization is an efficient multivariate factor analysis tool (31). In the model, the sample concentration data matrices are decomposed into factor contribution matrices and factor profile matrices. Based on the decomposition result, the profile information collected, and the emission inventories investigated, the sources could be determined (7).

Hierarchical cluster analysis also helps in identifying relatively homogeneous groups of elements, using an algorithm that starts with each element in a separate cluster and combines clusters until only one is left (34). Combinations of many source identification methods are often considered as more efficient than one single method to increase the resolution of the dataset (8).

All these methods have been employed in diagnosis studies that determine the concentrations of heavy metals in street dust and their possible sources; however, some specific studies are needed to soundly identify the sources and to update the inventories. These kinds of studies include the analysis of car, industry and house emissions, as well as the weathering of buildings and roads, the releases from crops, etc. In some of these analyses, isotopes are used to track emissions (35). The most commonly cited sources of heavy metals are:

1. Arsenic, easily generated during coal combustion. Coal combustion can cause the emission of fly ash into the atmosphere, with the metals present in the fly ash being deposited on street dust (7).

2. Barium, mainly discharged by the brake systems of motor vehicles (36).

3. Chrome, naturally occurring element in rocks, animals, plants, soil, and volcanic dust and gases. Its most common anthropogenic sources

include the industrial oxidation of mined chromium deposits and possibly combustion of fossil fuels, wood, paper, etc., as well as industrial processes, such as refining (ore), processing (chemical and refractory), production (cement and automobile brake linings and catalytic converters) and tanning (leather) (5). Cr is also emitted through processes like stainless steel wear, auto part wear and tool manufacturing (16). Subsequently, chromium is used in motor parts and the motor's body (6), and it is also produced during coal combustion (7).

4. Cadmium, relatively rare metal that occurs naturally in combination with other elements. The primary sources of airborne Cd are the burning of fossil fuels and the incineration of municipal waste materials (5). Cd is used for the preparation of special alloys and solders, metal plating, pigments in yellow or brown paints (for coloring plastics, glass and polishes), nickel–cadmium rechargeable batteries, and electronic waste (6,16). Cd is an important element contained in lubricating oil and tires, which can release Cd to street dust.

5. Cobalt, mainly produced by the smelting industry (16).

6. Copper, essential trace element, widely distributed in the environment. It occurs naturally in elemental form and as a component of many minerals. Cu possibly originates from exhaust emissions from both gasoline and diesel-fueled road vehicles, wear of the automobile's oil pump, and brake pads of vehicles. Cu is released during industrial activities, such as metal processing and smelting, in addition to being present in building materials.

7. Iron and Manganese, produced by the smelting industry (16), by the wear of the braking system and by the general wear of the cars, are also easily generated during coal combustion (7).

8. Mercury, important element in pesticides and fertilizers, being volatile and easy to migrate. Thus, Hg could migrate into urbanized areas and could be released from pesticides used for creating green spaces in cities. In addition, hospitals and clinics are also typical activities that can cause the release of Hg (7).

9. Nickel, used in the body and parts of cars and is also readily generated during coal combustion (7).

10. Lead, ubiquitous metal in industrialized areas. High Pb concentration in street dust samples is associated with traffic burden, brick kilns and the use of leaded gasoline (5). It is discharged from fuel/oil leakage from automobiles with oil lubricants, and wear and tear of tires, brake linings and other parts. E-waste recycling contributes significant amounts of trace metals such as Pb (16).

11. Zinc, essential trace element widely distributed in the environment. Contamination in dust samples is strongly affected by traffic emissions, including engine emissions, mechanical abrasion of vehicles, and tire and brake wear (5). Zn is added to tire tread rubber mostly as zinc oxide (ZnO), and in lesser quantities as a variety of organo-zinc compounds to facilitate vulcanization of rubber. Zinc is also common in car lubricants and carburetors (6).

12. Vanadium, normally regarded as a marker for fuel oil or petroleum burning. The smelting industry can also produce vanadium (16).

3.4. Human health risk assessment

3.4.1. The human health risk model

Risk assessment implies the evaluation of the degree of exposure, measured as an estimated daily intake (in milligrams of contaminant per unit of body weight and unit of time). The intake received through ingestion, inhalation and dermal absorption of trace elements in street dust depends on four types of variables: contact rate, exposure frequency, exposure duration and the bodyweight of the potentially exposed population. These estimates are each affected by a variable degree of uncertainty (31).

The United States Environmental Agency has developed a model to assess the carcinogenic and non-carcinogenic human health risk to heavy metals present in soils. This model can be adopted for street dust based on the assumptions as follows: (a) intake rates and particle emission for street dust can be approximated by those developed for soil (37); (b) human beings are exposed to street dust through three main pathways: ingestion, inhalation and dermal contact; (c) relevant exposure parameters of children and adults in the study areas are similar to those of reference populations; (d) the overall non-carcinogenic and carcinogenic risk for each heavy metal can be calculated by summing the individual risks from the three exposure pathways (5,16,33).

The following equations are commonly used to calculate the estimated daily intake (EDI) in mg/kg per day by ingestion (EDI_{ing}), inhalation (EDI_{inh}) and dermal contact (EDI_{dermal}), and the lifetime average daily dose (LADD) (Eq. 1, 2, 3 and 4):

Equation 1 $$EDI_{ing} = \frac{C * IngR * EF * ED * CF}{BW * AT}$$

Equation 2 $$EDI_{inh} = \frac{C * InhR * EF * ED}{PEF * BW * AT}$$

Equation 3 $$EDI_{dermal} = \frac{C * SA * AF * ABS * EF * ED * CF}{BW * AT}$$

Equation 4 $$LADD = \frac{C}{PEF x AT_{can}} x \left(\frac{CR_{child} x EF_{child} x ED_{child}}{BW_{child}} + \frac{CR_{adult} x EF_{adult} x ED_{adult}}{BW_{adult}}\right)$$

CR is the contact (or absorption) rate. CR = IngR for ingestion, CR = InhR for inhalation, and CR = SA × AF × ABS for dermal contact.

Generally, C is used as the upper limit of the 95 percent confidence interval for the mean (95 percent UCL), which is considered as a conservative estimate of the "reasonable maximum exposure" but, in some studies, maximum concentrations are used. Instead, other authors consider that the risks are overestimated using 95 percent UCL, therefore, they prefer to use the arithmetic mean (16). The most common exposure factors are presented in Table 3.

In some articles a modified model is used which includes a daily time proportion (0.33 percent) for the ingestion and inhalation rates. In such cases, authors considered that the common rates provide a conservatively more protective assessment because they are based on exposure during a whole day, which is unrealistically long. They also argued that the dust particle size should to be considered (4,38).

Using local exposure factors for each study area is desirable, for example, in Beijing, the Municipal Research Institute of Environmental Protection has estimated the inhalation rate, particle emission factor, exposed skin area, skin adherence factor and dermal absorption factor (16). Using more local parameters improves the reliability of the model for local conditions.

The hazard quotients of ingestion, inhalation and dermal contact ($HQ_{ing/inh/derm}$) are found by dividing the EDI into the reference dose (RfDdemonstrated in Equation 5:

Equation 5 $$HQ_{ing/inh/derm} = \frac{EDI_{ing/inh/derm}}{RfD}$$

The RfD most commonly used can be seen in Table 4. The inhalation reference dose values are substituted sometimes by oral reference doses because it is assumed that, after inhalation, the absorption of the particle-bound toxicants will result in similar health effects when the particles had been ingested (39).

The hazard index (HI) is presented as the sum of the HQ for the three exposure pathways: ingestion, inhalation and dermal contact. The HI can evaluate the human health risk: if greater than 1, it is possible that non-carcinogenic effects may occur; if the HI value is less than 1 the opposite may be expected (37).

For carcinogens, the incremental lifetime cancer risk ($ILCR$) is commonly calculated with the following equation:

Equation 6 $$ILCR = LADD * CSF$$

The most common cancer slope factors used in the references cited are shown in Table 4.

Table 3. Most commonly reported exposure factors for human health risk assessment

Factor [units]	Value		Reference
	Child	Adult	
Ingestion rate (IngR) [mg/day]	200	100	37
Inhalation rate (InhR) [m^3/day]	7.63	12.8	9
Particle emission factor (PEF)	1.36E+09	1.36E+09	37
Surface of exposed skin area (SA) [cm^2]	2800	5700	37
Dermal absorption factor (ABS)	0.001	0.001	37
Skin adherence factor (AF) [mg/cm^2]	0.2	0.07	37
Duration of exposure (ED) [years]	6	24	37
Frequency of exposure (EF) [days/year]	350	350	28
Average time non-carcinogens (AT) [days]	ED*365	ED*365	9
Average time for carcinogens (Atcan) [days]	70*365	70*365	9
Body weight (BW) [kg]	15	70	18
Heavy metal concentration (C) [mg/kg]	95 percent UCL		Measured in each study
Conversion factor (CF)	1×10^{-6}		41
UCL: upper confidence limit, mg: milligrams, m^3: cubic meters, cm^2: ~~squirt~~ square centimeters, kg: kilograms.			

The RfD for Pb has not been established by the USEPA, therefore, the RfD for Pb is 3.561023 mg/kg/day calculated from the provisional tolerable weekly Pb intake limit (25 mg/kg body weight) recommended by the Food and Agriculture Organization and the World Health Organization (FAO/WHO) for adults. The acceptable or tolerable risk is over the range of 1E−06 to 1E−04 (37). These values indicate that one additional case in a population of between 1,000,000 and 10,000 is acceptable (40).

3.4.2. Overview of the health risk assessment worldwide

The heavy metals for which the HI is most commonly calculated are Cu (92 percent for both children and adults), Pb (87 percent for both), Cr (87 percent for children and 92 percent for adults) and Zn (85 percent for both); the number of articles (n) that reported the HI for each heavy metal can be seen in Table 5. The main reason why the number of articles for the HI is out of line with the number of articles that reported concentrations of Cu, Pb, Cr and Zn is because some authors only calculated the HI for children and others only for adults.

Because very high concentrations of some heavy metals are found in some locations, the mean worldwide HI may not be representative of the worldwide situation; therefore, the median concentrations are taken in this review as the central tendency measure. According to the median HI, there is no expected risk of developing adverse effects on human health (HI less than 1), either for children nor for adults (Table 5). Despite this, the median HIs for As, Cr and Pb are the highest of all the heavy metals (E−01) for children, which indicates that special attention should be paid to those heavy metals. Moreover, it has been reported that chronic exposure to an HI greater than 1E−01 may trigger many ailments (17). In the case of the HI for adults, the risk is less (E−02) than for children, but there are many heavy metals at this risk level, *i.e.*, As, Cr, Fe, Mn, Pb and V.

Even when the median HI is at a safe level, in some cities, possible adverse effects on the health of children and adults may occur due to the presence of As, Cu, Ni and Pb in street dust. Cd and Cr can also cause adverse effects for children; see the maximum HI in Table 5. At this point, it is worth mentioning that some extremely high HI values were deleted because they could be mistakes. These extremely high values were identified in boxplots by

Table 4. Reference doses (RfD) and cancer slope factors (CSF)

Heavy metal	Oral RfD	Dermal RfD	Inhalation RFD	Oral CSF	Dermal CSF	Inhal CSF
As	3.00E-04	1.23E-04	3.01E-04	1.50E+00	3.66E+00	1.51E+01
Cd	1.00E-03	1.00E-05	1.00E-03			6.30E+00
Co	2.00E-02	1.60E-02	5.71E-06			9.80E+00
Cr	3.00E-03	6.00E-05	2.86E-05			4.20E+01
Cu	4.00E-02	1.20E-02	4.02E-02			
Fe	8.40E+00	7.00E-02	2.20E-04			
Hg	3.00E-04	2.10E-05	8.57E-05			
Mn	4.60E-02	1.85E-03	1.43E-05			
Ni	2.00E-02	5.40E-03	2.06E-02			8.40E-01
Pb	3.50E-03	5.25E-04	3.52E-03	0.0085		4.20E-02
V	7.00E-03	7.00E-05	7.00E-03			
Zn	3.00E-01	6.00E-02	3.00E-01			

RfD: reference doses, CSF: cancer slope, E: exponential. Based on (6, 19, 35, 40)

country, and linear regressions between the concentrations and the HI; even when high, their corresponding concentrations were close to the median. The HIs deleted for children were: As = 221 (41), Cd = 180 (28), Co = 11.8 (41), Cr= 60 (28), Hg = 103, and Pb = 23,600 (28). The HIs deleted for adults were: Cd = 22 (28), Cr = 7.67 (28), Hg= 22.1, and Pb = 2942.86 (28). In the case of Hg, the concentration was high, but no explanation or discussion was provided.

A probable linear relationship between the HI and the concentrations of heavy metals was expected because the exposure parameters of children and adults in the study areas were close to those of reference populations, and only the concentrations of heavy metals varied. Indeed, for some elements, the correlation coefficients were higher than 0.7, indicating good linear relationships, and only a few points were far away from the central tendency. For other elements, however, no relationship was found, and, for Fe, a negative relationship was observed, *i.e.*, when the Fe concentration increased, the HI for adults decreased. This highlight possible errors in the calculations. Therefore, for future studies, a clear and detailed writing of the methodology is recommended.

Another important point is to always use bioavailable concentrations of heavy metals in street dust for assessing human health risks. The toxicity reference values used in risk assessments for ingestion are expressed in terms of absorbed doses and are often derived from assays that employ soluble salts or other easily available chemical forms of heavy metals. Consequently, human health-risk assessments assume that the concentration of heavy metals used in USEPA equations represents the concentrations of heavy metals that are bioavailable in the gastrointestinal tract (30).

In relation to the carcinogenic risks, where the distributions of frequencies were also skewed to the right, the median was used as a central tendency measure. According to the median RI, As and Pb are in the tolerable risk range (1E−06 to 1E−04) for children, and As was also tolerable for adults. Consequently, once again, special attention must be paid to As and Pb (Table 6). Although the median worldwide RIs were in or below the tolerable range, in some cities, the RI exceeded that range (see maximum RI in Table 6) for As, Cr, Ni and Pb, both for children and adults. Therefore, people could be at risk of developing cancer during a lifetime in those places.

Table 5. Non-carcinogenic indexes (HI) for children and adults

Heavy metal	n	Mean	Median	SD	Minimum	Maximum
Children						
As	18	1.07E+00	2.68E-01	2.32E+00	3.40E-03	9.00E+00[1]
Ba	5	4.29E-02	4.80E-02	4.51E-02	0.00E+00	1.10E-01
Cd	26	1.12E-01	1.07E-02	2.78E-01	1.33E-03	1.02E+00[2]
Co	21	1.03E-01	8.20E-03	1.80E-01	0.00E+00	6.00E-01
Cr	33	4.39E-01	2.79E-01	7.33E-01	0.00E+00	4.06E+00[3]
Cu	36	1.80E+00	1.47E-02	8.38E+00	1.70E-03	4.93E+01[4]
Fe	6	4.86E-02	4.15E-02	3.79E-02	1.21E-04	9.91E-02
Hg	8	1.09E-02	4.73E-02	6.42E-02	2.50E-03	1.72E-01
Mn	23	1.11E-01	7.55E-02	1.42E-01	0.00E+00	6.62E-01
Ni	30	3.33E-01	1.59E-02	1.73E+00	0.00E+00	9.50E+00[5]
Pb	33	2.23E-01	3.93E-01	4.84E-01	3.73E-03	2.19E+00[6]
V	11	6.37E-02	2.17E-02	8.46E-02	0.00E+00	2.70E-01
Zn	33	2.37E-02	7.79E-03	6.23E-02	0.00E+00	3.33E-01
Adults						
As	21	2.20E-01	3.09E-02	4.76E-01	3.33E-03	1.90E+00[1]
Ba	5	6.63E-03	8.23E-03	6.39E-03	0.00E+00	1.50E-02
Cd	28	1.49E-02	1.84E-03	3.55E-02	0.00E+00	1.53E-01
Co	23	1.54E-02	1.55E-03	2.48E-02	0.00E+00	7.50E-02
Cr	35	7.55E-02	3.77E-02	1.07E-01	0.00E+00	5.33E-01
Cu	36	2.05E-01	1.98E-03	1.05E+00	4.94E-04	6.25E+00[4]
Fe	6	1.76E-02	1.53E-02	1.91E-02	8.10E-06	5.30E-02
Hg	9	1.57E-03	1.14E-02	2.08E-02	2.10E-04	6.11E-02
Mn	23	1.90E-02	1.10E-02	2.23E-02	0.00E+00	9.61E-02
Ni	31	4.09E-02	2.30E-03	2.15E-01	0.00E+00	1.20E+00[5]
Pb	33	3.10E-02	4.65E-02	5.87E-02	5.77E-04	3.10E-01
V	12	2.44E-02	1.11E-02	3.30E-02	0.00E+00	1.10E-01
Zn	33	3.18E-03	1.17E-03	7.82E-03	0.00E+00	4.33E-02

n: number of articles, E: exponential, SD: standard deviation, HI: hazard index, When the HI is greater than 1, possible adverse effect on human health may occur. [1]HI greater than 1: (27,9), [2]HI greater than 1: (27, 41), [3]HI greater than 1: (42, 20, 6), [4]HI greater than 1: (28, 27), in addition, HI greater than 1 in reference: (1), [5]HI greater than 1: (28), [6]HI greater than 1: (41), (43), (44)

To reduce exposure to the pollutants, street cleaning is one of the best practices. Therefore, the street cleaning program and planning related to street dust in urban areas is important. Local conditions, climate and specific needs also need to be considered as critical determinants of the ideal street sweeping strategy (technology, frequency, speed, targeted areas, etc.) (4).

4. PERSPECTIVES

We identified the need to standardize the terms used referring the material (matrix) and

Table 6. Carcinogenic risk (RI) for children and adults

Heavy metal	n	Mean	Median	Standard deviation	Minimum	Maximum
Children						
As	14	2.54E-05	3.20E-06	5.84E-05	2.91E-09	2.10E-04[1]
Cd	16	9.54E-06	1.23E-09	2.08E-05	5.66E-11	6.19E-05
Co	14	1.29E-07	5.60E-09	3.22E-07	0.00E+00	1.07E-06
Cr	26	5.06E-05	6.05E-07	1.42E-04	4.61E-10	6.14E-04[2]
Ni	20	3.81E-02	6.06E-09	1.70E-01	4.00E-10	7.60E-01[3]
Pb	9	7.10E-05	2.66E-06	2.06E-04	8.08E-11	6.21E-04[5]
Adults						
As	12	2.34E-05	1.65E-06	7.15E-05	3.90E-10	2.50E-04[1]
Cd	13	1.55E-06	1.30E-09	3.06E-06	1.09E-10	8.69E-06
Co	10	4.39E-07	6.40E-09	1.31E-06	0.00E+00	4.16E-06
Cr	22	1.93E-05	4.90E-07	5.63E-05	1.16E-12	2.11E-04[2]
Ni	15	1.60E-05	4.08E-09	4.25E-05	2.00E-10	1.59E-04[4]
Pb	9	4.19E-05	1.20E-07	1.25E-04	1.08E-11	3.75E-04[5]

The tolerable risk is over the range of 1E-06 to 1E-04 (USEPA, 2001), USEPA= United States Environmental Protection Agency, [1](9), [2]RI is in the tolerable limit on references: (7, 20, 17), [3]RI is in the tolerable limit on: (39, 7, 17), [4]RI is in the tolerable limit on (7), [5] RI is in the tolerable limit on (20)

Figure 2. Some of the main highlights from this review are summarize in the figure: 1) it is necessary to record the sampled area in order to calculate street dust load, and to sieve to 63 µm; 2) there is worldwide contamination of lead and zinc in street dusts; 3) the main sources of heavy metals in street dust are automobiles and fossil fuels; and 4) arsenic, chromium and lead concentrations in street dust worldwide could be a possible risk to human health.

elements of analysis. We encourage readers to use the most common terms found in the literature: "street dust" and "heavy metals". These terms are increasingly recognized by the researchers in the field.

Important guidelines that came from this review (Figure 2) were: 1) Sampling must be clearly defined and preferably should be based on statistical methods. The number of samples must be enough to represent the study population; at least one sample per square kilometer should be taken, or 100 samples taken when spatial interpolations are required to be conducted, according to Oliver and Webster (2015). 2) All studies of heavy metals in street dust should collect samples per square meter, to report street dust loading and even heavy metals loadings. In this way, it is possible to have a general overview of the quantity of dust that is in the urban environment. 3) Particle size should be less than 63 micrometers. The adopted 2 mm size from soil sciences does not work well for street dust, as it is a very coarse fraction which does not represent airborne particles.

Lastly, lead and zinc were identified as the heavy metals most commonly released in cities, since they had the highest contamination category, with reference to the world soil background values. With regards to human health, arsenic, chromium and lead have the highest risk to human health; therefore, they should always be analyzed in studies of heavy metals in street dust.

Some suggestions for future studies are as follows:

A future research topic will be the creation of sorption, mobility and toxicity indices of heavy metals considering the quantity and type of clays, organic matter, aggregation and pH of urban dust (23, 24)

The mobile or bioaccessible fractions should always be used in estimations of the USEPA human health risk model of heavy metals in street dust. The exposition factors for at least each big city should be determined in order to make the health risk assessment more accurate. The case of Beijing (16) is a good example of this effort.

Other proxy methodologies, *e.g.*, color of street dust (45,46,47) and magnetic properties (42,48,49), could be applied to identify the more likely polluted sites, then deeper analysis could be made in those specific sites, saving time and resources. The burning of fossil fuels generates magnetite and maghemite particles that are black minerals and that have high values of magnetic susceptibility, this is the reason for the use of color and the magnetic signal as proxy technologies.

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Abbreviations: As: arsenic, Ba: barium, Cd: cadmium, Co: cobalt, Cr: chromium, Cu: copper, Fe: iron, Hg: mercury, Mn: manganese, Ni: nickel, Pb: lead, V: vanadium, Zn: zinc, USEPA: United States Environmental Protection Agency, DNA: deoxyribonucleic acid, AAS: atomic absorption spectroscopy, GFAAS: graphite furnace atomic absorption spectrometry, ICP-AES: inductively coupled plasma atomic emission spectroscopy, ICP-MS: inductively coupled plasma mass spectroscopy , ICP-OES: inductively coupled plasma optical emission spectroscopy, PXRF: portable X-ray fluorescence, XRF: X-ray fluorescence, PCA: Principal component analysis, PC: principal components, EDI: estimated daily intake, EDIing: estimated daily intake by ingestion, EDIinh: estimated daily intake by inhalation, EDIdermal: estimated daily intake by dermal contact, LADD: lifetime average daily dose, C: heavy metal concentration, IngR: ingestion rat, EF: exposure frequency, ED: exposure duration, CF: conversion factor, BW: body weight, AT: average time, InhR: inhalation rate, PEF: particle emission factor, SA: surface of exposed skin area, AF: skin adherence factor, ABS: dermal absorption factor, CR: contact or absorption rate, UCL: confidence interval for the mean, HQ: hazard quotient, HQing/inh/dermal: hazard quotient for ingestion/inhalation/dermal contact, RfD: reference dose, ILCR: incremental lifetime cancer risk, CSF: cancer slope factor, FAO: Food and Agriculture Organization , WHO: World Health Organization

Key Words: Heavy Metals, Sampling, Sources, Street Dust, Risk Assessment, Review

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Aportes del capítulo a la tesis

Este capítulo estableció los antecedentes de la tesis a nivel global, ya que se revisaron 39 ciudades alrededor del mundo. De esta manera adquirimos un panorama general sobre lo que se sabe y las metodologías que se han utilizado para analizar la contaminación por metales pesados en el polvo urbano (*street dust*) durante los últimos 10 años, aproximadamente (la revisión se hizo en el 2019).

Una de las aportaciones que nos dejó esta revisión fue que nos permitió utilizar los términos más aceptados en la comunidad científica especialista en el tema. Si bien al inicio del doctorado habíamos acordado titular la tesis como “Contaminación por elementos potencialmente tóxicos en ciudades mexicanas con ambientes contrastantes” después de esta revisión decidimos llamar a los elementos “metales pesados” porque, aunque es un término ambiguo, está ampliamente aceptado en la comunidad científica experta en contaminación y hace más fácil el seguimiento a los artículos publicados. Otro concepto básico era el de polvo urbano, el cual también ha recibido otros nombres. Nos parece que en español “polvo urbano” queda bien, sin embargo en inglés es poco utilizado, por tanto adoptamos el término más empleado que fue el de “*street dust*”, algunas veces también agregamos *road dust* en las palabras clave de los artículos, debido a que fue el segundo término más usado, según los resultados de esta investigación.

En cuanto a la metodología, observamos la relevancia de definir claramente cómo se hizo el muestreo en los artículos, ya que en varios artículos no se especificaba cómo se había hecho. Además, el muestreo debería basarse en métodos estadísticos (aleatorio, sistemático, etc.). El número de muestras debería ser suficiente para representar a la población de estudio, se debe tomar al menos una muestra por kilómetro cuadrado. Por esta razón, en los análisis particulares de esta tesis para la CDMX se hizo un muestreo extensivo de 482 muestras, para tratar de aumentar la representatividad en comparación con el muestreo del análisis de las seis ciudades mexicanas. Además, vimos que en todos los estudios sobre metales pesados en el polvo urbano se deberían utilizar muestras tomadas por metro cuadrado, para informar la carga de polvo urbano y la carga de metales pesados. De esta forma, es posible tener una visión general de la cantidad de polvo que hay en el entorno urbano.

La compresión de las metodología de evaluación de la contaminación y riesgos a la salud humana también nos permitió reportar, de la mejor manera posible, los resultados de los análisis de riesgo, evitando pequeños errores o deficiencias que observamos en estos estudios. Las tablas de resumen con los factores de exposición que se obtuvieron de esta revisión fueron las que se implementaron para hacer los cálculos de los índices de riesgo a la salud humana en los estudios subsecuentes para las ciudades de México.

La síntesis estadística de los estudios analizados sirvió como punto de comparación con los resultados obtenidos para las ciudades de estudio de México. Esta fue una manera efectiva de tener una referencia a nivel global para comparar los valores de las concentraciones de los metales pesados en polvos urbanos. Por un lado, ya nos habíamos asegurado de que los estudios incluidos a nivel mundial tuvieran objetivos y una metodología similar a la utilizada en los estudios en México. Por otra parte, evitamos tener que hacer comparaciones individuales entre ciudades, como se hacía en las discusiones de muchos artículos. Además, justo comparamos con estudios realizados en los últimos 10 años, que incluyen las fechas en las que se hicieron los muestreos de las seis ciudades mexicanas y el muestreo extensivo de CDMX. Comparar con estudios recientes es más apropiado que hacerlo con aquellos más antiguos ya que las concentraciones en el polvo urbano reflejan la contaminación de corto a mediano plazo.

CAPÍTULO II

"Heavy metal contamination (Cu, Pb, Zn, Fe, and Mn) in urban dust and its possible ecological and human health risk in Mexican cities"

Este capítulo conforma la espina dorsal de la tesis, según como se tenía planteada inicialmente, aunque el resto de los análisis particulares para el muestreo extensivo de la CDMX demoraron más tiempo que este análisis general con las seis ciudades mexicanas. En el equipo de trabajo se habían muestreado y analizado algunas de estas ciudades previamente, sin embargo, hacía falta hacer una comparación entre todas para tener un panorama general para México. Por tanto, se incluyeron tantas ciudades como fue posible, procurando que fueran diversas en cuanto a ubicación geográfica, geología, actividades económicas realizadas en cada una y número de habitantes.

Como se mencionó en la introducción general de la tesis, un problema común en los estudios de contaminación ambiental es precisamente determinar cuándo un sitio está contaminado. Para esto se han utilizado comúnmente índices de contaminación que comparan las concentraciones actuales del elemento respecto a un nivel de fondo que se podría encontrar en el sitio de manera natural. Sin embargo, establecer el valor de fondo natural es difícil, especialmente en sitios urbanos donde todo se podría considerar como alterado por el hombre y encontrar sitios naturales es casi imposible. Esta tarea es aún más difícil para una matriz como el polvo urbano, el cual por definición está compuesto por partículas de origen tanto natural como antrópico. A pesar de estas dificultades, en la práctica se han utilizado como referencia valores de fondo de los suelos para hacer los análisis de los polvos urbanos.

Después de las dificultades para establecer los valores de fondo, nos encontramos con otro asunto por resolver ¿los valores de fondo deberían ser generales para permitir hacer comparaciones entre sitios distintos o locales para reflejar las características y condiciones particulares de cada sitio? Existe un debate sobre cuál valor se debería utilizar. Por este motivo, hemos decido probar dos valores, uno general y otro local y reportar cómo cambia la contaminación en las ciudades mexicanas, según el valor de fondo utilizado.

Por último, establecer si un sitio está contaminado no solo depende de si las concentraciones superan un valor de referencia (valor de fondo) sino también de si esas concentraciones pueden representar un riesgo para la vida del sistema. La evaluación de riesgos es otro tema muy amplio con muchos matices, que puede requerir mucho tiempo de análisis y ser muy costoso. La manera más sencilla de hacer una primera aproximación es a través de índices de riesgo a los que se han denominado como "riesgo ecológico" para la vida en general, y de manera específica se han desarrollado los índices de riesgo a la salud humana, que implican riesgo de desarrollar cáncer (*Risk Index*) y riesgo de desarrollar otros padecimientos distintos al cáncer (*Hazard Index*). Nosotros utilizamos estos índices para evaluar los posibles riesgos de los metales pesados en el polvo urbano.

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Heavy Metal Contamination (Cu, Pb, Zn, Fe, and Mn) in Urban Dust and its Possible Ecological and Human Health Risk in Mexican Cities

Q2 Q3 Q4 Q1

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Q5 Q6 Q7

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Cities occupy a relatively small percentage of the Earth's surface. However, they influence the entire biosphere, affect biodiversity and environmental conditions, which end up affecting human health and well-being. Therefore, it is necessary to evaluate the level of contamination by heavy metals in urban environments, as well as the possible ecological and human health risks. In this study, the urban dust of six Mexican cities was analyzed and it was found that all studied cities were contaminated, except for Mérida, when soil world background value was used as reference. In contrast, Mérida and Morelia were the most contaminated when a local background was used (decile 1). The concentrations in the cities for the metals Cu, Pb and Zn, decreased in the order CDMX > San Luis Potosí > Toluca > Morelia-Ensenada > Mérida. In the particular case of Cu and Pb, SLP accompanied CDMX as the most polluted city. For Mn and Fe concentrations, the order was CDMX > Toluca > Ensenada > SLP > Morelia-Mérida. No potential ecological risk was found due to contamination by Cu, Pb, and Zn, in the urban dust of the studied cities. However, the higher metal contribution to the potential ecological risk in all the cities was from Pb; and it represented a moderate ecological risk of more than 25% on CDMX, SLP, and Toluca sites. Pb can also be a potential risk for children's health. In addition, chronic exposure to Fe and Mn could trigger many ailments. In the future, it is important to identify the main sources of Pb in cities and seek mitigation strategies to reduce the possible adverse effects that this metal may be causing.

Keywords: street dust, pollution load index, risk assessment, lead, Mexico Q9

1 INTRODUCTION Q10

Cities occupy a small percentage of the global land surface (~5%) but can influence the entire biosphere (Angeoletto et al., 2015). Between the multiple challenges of cities, the constant impact of human activities can have unintended repercussions on biodiversity, the functioning of ecosystems, and environmental quality, causing, in turn, a negative impact on human health and well-being (Lawrence 2003).

Urban dust is made up of solid particles deposited on impermeable materials that originate from the interaction of solids, liquids, and gases in the environment (Keshavarzi et al., 2018). Urban dust is a receptor for solid particles from different sources, therefore it becomes a sink for atmospheric particles. At the same time, urban dust can also be considered as a pollutant source into the atmosphere and soils, through the re-suspension of this material. It can also be a source of contaminants for water (Keshavarzi et al., 2018; Safiur Rahman et al., 2019), through rain runoff (Jayarathne et al., 2018).

Among the pollutants present in urban dust, heavy metals can be toxic or harmful to the environment and living beings, even at low concentrations. They are generally associated with relatively high densities (>5 g/cm^3) since their density is assumed to be related to toxicity. Additionally, heavy metals are persistent in the environment and bioaccumulate, thus gaining public attention (Lin et al., 2017). The mechanism of toxicity of heavy metals can be explained by their ability to interact with nuclear proteins and DNA, causing deterioration of biological macromolecules (Helaluddin et al., 2016).

Ensenada, San Luis Potosí, Mexico City, Toluca, Morelia, and Mérida are Mexican cities located at different latitudes and with different geological environments. These urban areas are within the 20 Metropolitan Zones with the highest total gross production and number of inhabitants (CONAPO and SEDESOL 2012) and they could highlight the current situation in terms of contamination by heavy metals and let us explore the influence of the city size (number of inhabitants) and geological environment (physiographic province) on the pollution.

Diagnoses of contamination by heavy metals in urban dust have been carried out in some of these cities of Mexico. In Mérida and Ensenada the color of urban dust has proved to be an indicator of heavy metal pollution, dark colors are more polluted than light ones (Cortés et al., 2015; Aguilar et al., 2021). In San Luis Potosí, the highest concentrations of heavy metals in street dust have been related to the metallurgical complex and the industrial park (Aguilera et al., 2019); and heavy metals in soils could also be an important pathway of exposure (Perez-Vazquez et al., 2015; Pérez-Vázquez et al., 2015), indeed metal concentrations have been identified in children (Flores-Ramírez et al., 2018). Mexico City has been identified as polluted by heavy metals in street dust (Delgado et al., 2019), and heavy metal concentrations have been measured in mothers and children (Lewis et al., 2018). However, the effects of urbanization on environmental quality vary between regions with different degrees of development, topography, natural resources, and public policies (Liang, Wang, and Li 2019).

In this study, we wonder whether there is heavy metal contamination in the urban dust of six Mexican cities and if this contamination may represent a potential ecological and human health risk. It is expected that the largest and most industrialized cities will have the highest concentrations of heavy metals, however, we do not know if this happens proportionally with size and if this is the case for all metals. We also explore the differences in the pollution between located in the same and different physiographic provinces.

2 METHODS

2.1 Data Collection

In previous studies, urban dust samples were collected during the dried season in Mexico City in 2011 (CDMX, $n = 89$), Ensenada in 2012 (ESE, $n = 86$), San Luis Potosí in 2017 (SLP, $n = 100$), Morelia in 2014 (MLM, $n = 100$), Mérida in 2016 (MID, $n = 101$) and Toluca in 2013 (TLC, $n = 89$). For all the cities, a standard sampling procedure was followed which consisted of sweeping 1 m^2 of street surface, following a systematic, homogeneously distributed sampling design. The samples were packed in plastic bags and georeferenced (**Supplementary Figure S1**). Description of the study sites can be seen in the Supplementary material. They were dried in the shade and at room temperature for 2 weeks to avoid any kind of oxidation. Subsequently, they were passed through a number 10 sieve with a 2 mm opening, to remove the coarse fragments.

Chemical analysis of heavy metals in cities was done by X-ray fluorescence energy dispersive (XRF-ED). Only in the case of Morelia inductively coupled plasma optical emission spectroscopy (ICP-OES) was used. The details of the methodology can be consulted in previous studies: CDMX (Delgado et al., 2019), Ensenada (Cortés et al., 2015), SLP (Aguilera et al., 2019), Mérida (Aguilar et al., 2021). We selected the heavy metals that were measured for all the cities, those metals were copper (Cu), lead (Pb), zinc (Zn), manganese (Mn), and iron (Fe).

2.2 Identification of the Most Polluted Cities

To evaluate the level of contamination of each heavy metal, the contamination factor (CF) was used, which is a technique used to find the state of contamination of each element, as well as the pollutant load index (PLI), which is the geometric average of the five metals studied (Tomlinson et al., 1980): Q11

$$CF = C_n / F_n \quad (1)$$

$$PLI = \sqrt[n]{CF1 * CF2 * \ldots * CFn} \quad (2)$$

C_n represents the concentration of a heavy metal n and F_n is the background value of the same heavy metal. Generally, the background values found in soils with little anthropization or a general reference value such as the world background values for soils are used (Kabata-Pendias 2011). This study used both the background values reported for soils worldwide (Kabata-Pendias 2011), as well as the first decile of the distribution of frequencies of the heavy metals in each city, to compare what happens when considering the particularities of each site against a general reference value.

A CF less than 1 indicates insignificant contamination, between 1–3 a moderate contamination, between 3–6 considerable and greater than 6 a high contamination level (Ihl et al., 2015). A PLI close to one indicates that the heavy metal load is close to the background level, while a PLI > 1 indicates contamination (Mehr et al., 2017).

Subsequently, Kruskal-Wallis analyzes were carried out to identify if there were statistically significant differences in the concentrations of heavy metals between cities. To perform the statistical analysis (descriptive statistics, Pearson correlation, and Kruskal-Wallis test) and the figures, the R Project software, version 4.0.4 (2021-02-15) "Lost Library Book" was used.

2.1.1 Ecological Risk Assessment

The ecological risk factor (E_i) for each heavy metal (Cu, Pb y Zn) was calculated with the **Eq. 4** (Hakanson 1980):

$$E_i = \left(T_f\right)_n x\ (CF)_n \tag{4}$$

where T_f is the toxic response factor of each metal, Cu = Pb = 5, Zn = 1, Mn = 1; and CF is the corresponding pollution factor, in this study we used the soil worldwide background (Kabata-Pendias 2011). E_i is classified as low potential ecological risk ($E_i < 40$), moderate potential ecological risk ($40 \leq E_i < 80$), considerable potential ecological risk ($80 \leq E_i < 160$), high potential ecological risk ($160 \leq E_i < 320$) and a very high potential ecological risk ($E_i \geq 320$) (Hakanson 1980; Hua et al., 2018; Jahandari 2020).

Toxic response factors (T_f) They are based on the principle of abundance, which indicates that the potential toxicological effect of an element is proportional to its abundance, or rarity, in nature. In addition, T_f considers the tendencies of each metal to be deposited in the lake sediments and a dimension correction (order of magnitude) was also made so that they could be compared with the CF (Hakanson 1980).

To obtain the potential ecological risk of several metals (PER) we used the following equation:

$$PER = \sum\nolimits_{n=1}^{n} (E_i)_n \tag{5}$$

Where E_i is the potential ecological risk index for each metal, and n is the number of heavy metals analyzed. PER is divided into four classes: low potential ecological risk ($PER \leq 150$), moderate potential ecological risk ($150 < PER \leq 300$), considerable potential ecological risk ($300 < PER \leq 600$), high potential ecological risk ($PER > 600$) (Yesilkanat et al., 2021).

2.1.2 Human Health Risk Assessment

To estimate the risk of heavy metals, present in urban dust on the health of the population, the USEPA methodology will be used. First, the estimated daily intakes were calculated per ingestion (EDI_{ing}), inhalation (EDI_{inh}) and dermal contact (EDI_{dermal}) (**Eqs 6–8**); as well as the average daily dose for life (LADD) to estimate the carcinogenic risk (CR) (**Eq. 9**).

$$EDI_{ing} = \frac{C*IngR*EF*ED*CF}{BW*AT} \tag{6}$$

$$EDI_{inh} = \frac{C*InhR*EF*ED}{PEF*BW*AT} \tag{7}$$

$$EDI_{dermal} = \frac{C*SA*AF*ABS*EF*ED*CF}{BW*AT} \tag{8}$$

$$LADD = \frac{C}{PEFxAT_{can}} x\left(\frac{CR_{child}xEF_{child}xED_{child}}{BW_{niño}} + \frac{CR_{adulto}xEF_{adulto}xED_{adulto}}{BW_{adulto}}\right) \tag{9}$$

CR is the contact or absorption rate. CR = IngR for ingestion, CR = InhR for inhalation, and CR = SA * AF * ABS for dermal contact. We calculated the $EDIs$ for each of the sampling points.

The use of local parameters improves the reliability of the model; however, exposure factors have not been estimated for any Mexican city, therefore those of reference populations were used in this study (**Supplementary Table S1**).

Hazard ratios for ingestion, inhalation, and dermal contact ($HQ_{ing/inh/derm}$) were obtained by dividing the EDI between the reference dose (RfD) as shown in **Eq. 10**. RfD are presented in **Supplementary Table S2**.

$$HQ_{ing/inh/derm} = \frac{EDI_{ing/inh/derm}}{RfD} \tag{10}$$

The non-carcinogenic risk index (HI) represents the sum of the HQ for all three routes of exposure. If HI is greater than 1, there could be non-carcinogenic effects on the health of the population, if it is less than 1 the opposite would be expected (USEPA 2001).

For carcinogenic elements, the risk of developing cancer during life ($ILCR$) is commonly calculated by the following equation:

$$ILCR = LADD * CSF \tag{11}$$

The accepted or tolerable risk is in the range of 1E-06 to 1E-04 (USEPA 2001). These values indicate that an additional case in a population of 1,000,000 and 10,000 people is acceptable (Lu et al., 2014).

3 RESULTS AND DISCUSSION

Considering all the cities, Mn and Fe had a strong positive correlation (r = 0.9), and a strong negative correlation with Cu, Pb, and Zn (r < −0.7). Cu and Zn were also strongly correlated (r = 0.82), and they had a weaker correlation with Pb (Pb-Cu, r = 0.5; Pb-Zn, r = 0.35). This seems to indicate that Fe and Mn are elements that can share similar sources; in fact, they have been reported as elements of natural or mixed origin (Dehghani et al., 2016), in studies of heavy metals. On the other hand, Zn and Cu may also be sharing similar sources, some of which may be the same as those for Pb, while the latter metal could have other sources, in addition to those shared with Zn and Cu.

In general, the distribution of frequencies of the metals in the different studied cities was asymmetric to the right, this can be seen due to the differences between the median and the mean (**Supplementary Table S3**). The city with the greatest differences between the median and the mean of Cu and Pb was Morelia, in the case of Mn and Zn it was SLP, and for Fe it was Mérida. Within each city, when comparing the mean and the median among the different metals, Pb had the greatest differences. Such differences have been considered as a qualitative indicator of an anthropic enrichment of metal in the urban environment (Aguilera et al., 2019).

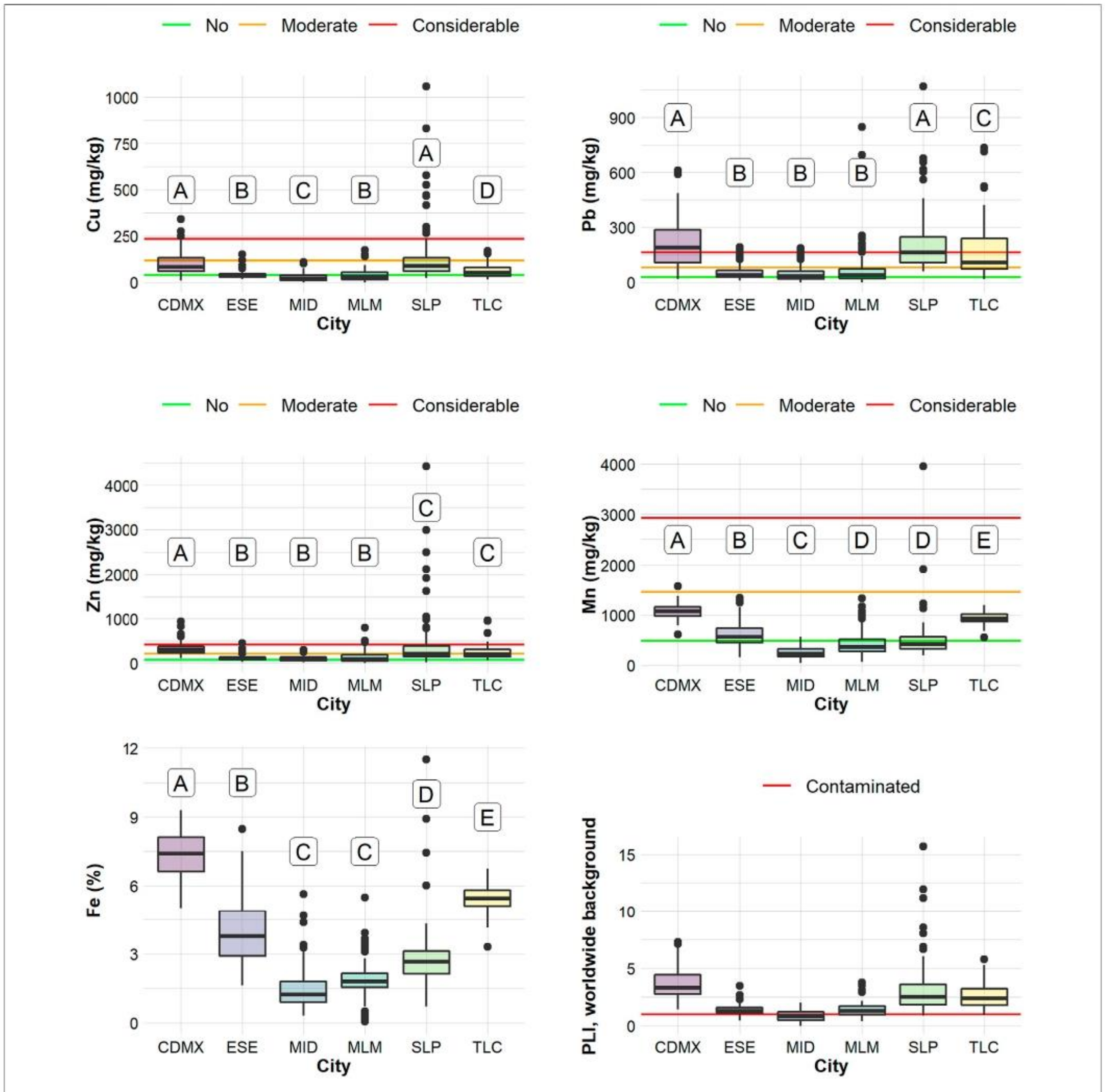

FIGURE 1 | Boxplots of the heavy metal concentrations. Different letters indicate significant differences. CDMX: Mexico City, ESE: Ensenada, MID: Mérida, MLM: Morelia, SLP: San Luis Potosí, TCL: Toluca. PLI: pollution load index. Horizontal lines represent the contamination levels using the background value established for soils worldwide (Kabata-Pendias 2011).

Previously, we did a systematic review to summarize the heavy metal concentrations in street dust worldwide, considering 39 cities (Aguilera, Bautista, Goguitchaichvili, et al., 2021). This is a more efficient way to compare with multiple studies, instead of doing it one by one. Compared to the median values of that review, Cu (Mexico: 46.83 mg/kg, world: 83.4 mg/kg) and Zn (Mexico: 149.9 mg/kg, world: 280.7 mg/kg) had a lower median in the Mexican cities analyzed in this study. While the median Fe concentration in Mexico was higher than that reported for the world (Mexico: 30,600 mg/kg, world: 22,103 mg/kg).

By cities, the median Fe concentrations in CDMX, Ensenada, Toluca, and SLP were higher than those reported worldwide (Aguilera, Bautista, Goguitchaichvili, et al., 2021). In addition, in CDMX and Toluca the medians of Mn and Pb were also higher than those reported worldwide (Aguilera, Bautista, Goguitchaichvili, et al., 2021). In SLP, the median Pb

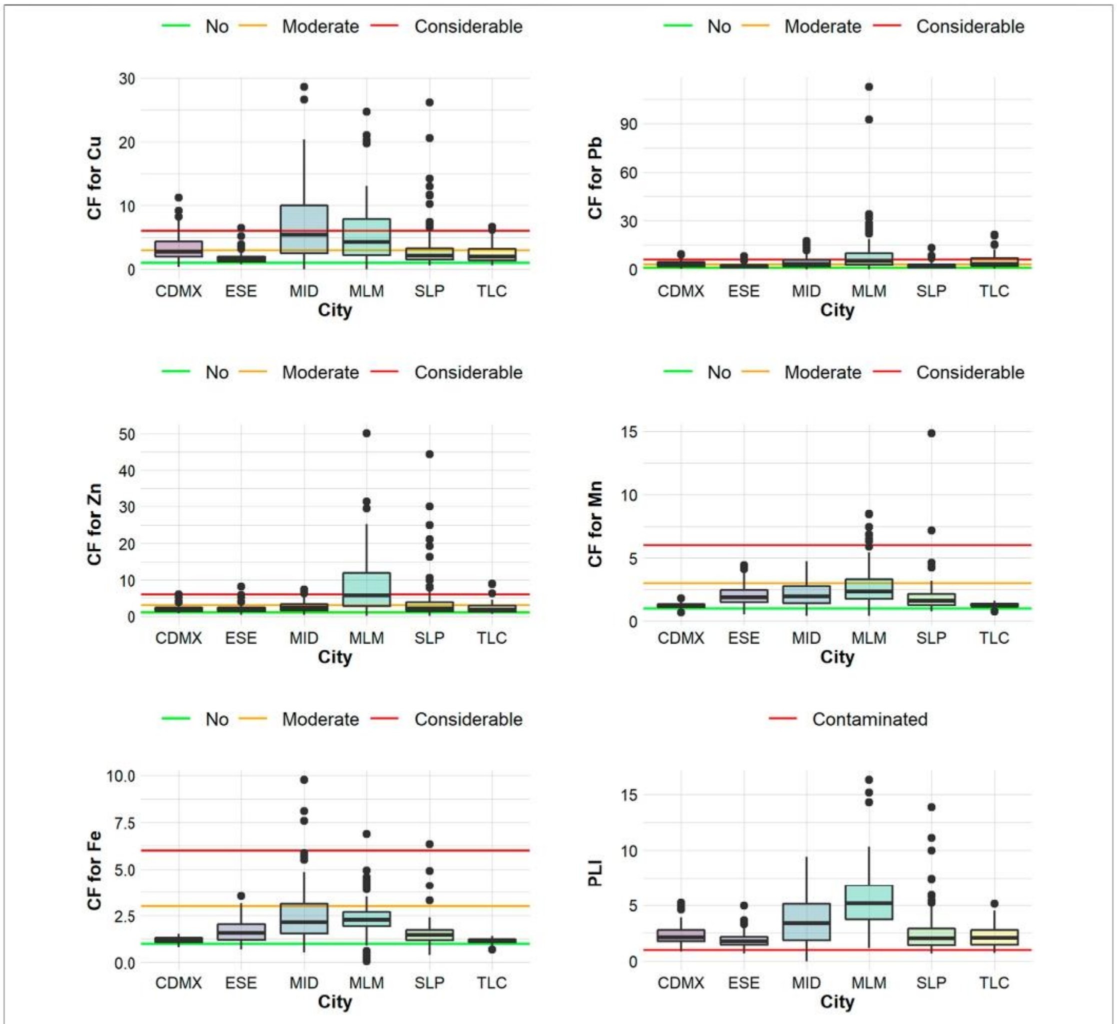

FIGURE 2 | Box plots of the contamination factors (CF), using decile 1 of each city as the background value. CDMX: Ciudad de México, ESE: Ensenada, MID: Mérida, MLM: Morelia, SLP: San Luis Potosí, TCL: Toluca. PLI: pollution load index. Horizontal lines represent the contamination levels.

concentration exceeded the world median While in Morelia and Mérida the median concentrations of all metals were lower than those of the world.

3.1 Most Polluted Cities

When the background value established for soils worldwide was considered (Kabata-Pendias 2011), all cities were contaminated, except for Mérida, since 75% of the data had a PLI greater than one (**Figure 1**). The median PLI decreased in the order CDMX > SLP > Toluca > Morelia–Ensenada > Mérida. It should be remembered that this indicates a general pattern of contamination by Cu, Pb, Zn, and Mn; Fe was not considered because there is no reported background value. This same order was maintained in the specific case of Cu, Pb, and Zn concentrations, with significant differences; particularly for Cu and Pb, SLP accompanied CDMX as the most polluted city. However, there were variations in the level of contamination for Mn and Fe by the city, the order was CDMX > Toluca > Ensenada > SLP > Morelia-Mérida (**Figure 1**).

On the other hand, when we estimated the level of contamination using decile 1 of each city as background values, the results changed. The cities with the lowest concentrations (Mérida and Morelia), and therefore the least contaminated using as a background value the one established for soils worldwide, became the most polluted (**Figure 2**). When comparing the results of both background values, we observe that Morelia and Mérida were the most susceptible cities to changes in their level of pollution.

Morelia and Mérida turned out to be the most polluted cities because deciles 1 of heavy metals in both cities were very low (**Supplementary Table S3**), while deciles 1 of CDMX, Toluca, and SLP were high. The values of the first decile of Morelia were between 3 (the case of Mn) and 5.5 (the case of Cu) times lower than the background values of soils worldwide; while, in CDMX, the values of the first decile were approximately double the background values of soils worldwide, except for Cu, which was very similar to the first decile.

The differences observed by the use of both background values highlight the problem that has been discussed for decades, when a general background value is used all local variations are ignored, while when particular background values are used for each site, all local differences are emphasized (Hakanson 1980). In this study it was clear that the concentrations of CDMX, SLP, and Toluca were higher than those of Morelia or Mérida, however, the local background values of these last two cities were so small that they turned out to be the most contaminated when compared.

Another point to consider was the fact that the analytical technique (ICP-OES) with which Morelia concentrations were obtained was more sensitive than that used in all the other cities (XRF-ED). For this reason, lower values could have been detected in Morelia.

It is noteworthy that the contamination of Pb and Cu in the largest city in Mexico (CDMX) was comparable to that of a metallurgical city (SLP). Metallurgical and mining activities are among the main emitters of heavy metals into the environment (Tapia et al., 2018; Li et al., 2015), however, a large number of minor sources (vehicles, industries, garbage incineration, etc.) in urbanization (CDMX) can lead to a similar level of contamination.

While it is a common idea that the largest or most populated cities should be the most polluted, this is not necessarily true. The population decreased in the order CDMX > Toluca > SLP > Mérida > Morelia > Ensenada (INEGI Instituto Nacional de Estadística y Geografia 2014). Mérida was the fourth most populated city; however, it was the least polluted, considering the global background value. SLP was the third most populated city, but its level of contamination by Pb and Cu was comparable to that of CDMX (the most populated). Ensenada was the least populated city, but its concentrations of Mn and Fe were higher than those of SLP, Morelia, and Mérida. At the global level, Aguilera et al. (2021) did not find a correlation between the number of inhabitants and the concentrations of heavy metals. At the local level, in CDMX, no relationship was found (Aguilera, Bautista-Hernández, et al., 2021). However, other studies have found this relationship (Acosta et al., 2015; Trujillo-González et al., 2016).

Among the cities of the Neovolcanic Belt (Morelia, Toluca, CDMX; **Supplementary Material**), there were significant differences in the level of contamination, CDMX was the most contaminated city by Cu, Pb, Zn, Mn, and Fe with significant differences from Toluca, while Morelia was the least contaminated; therefore, pollution must be caused by human activities, rather than natural causes.

Fe and Mn may be sharing the same sources, they are considered as elements of natural or mixed origin (Dehghani et al., 2016). Zn and Cu may also be sharing similar sources, some of which may be the same as for Pb, while the latter metal could have other sources.

In CDMX it has been recognized that the main sources of Cu, Pb, and Zn in street dust could be related to vehicular traffic (Aguilera, Bautista-Hernández, et al., 2021; Aguilera, Bautista, Gutiérrez-Ruiz, et al., 2021). In SLP, the main source of Cu and Zn is the metallurgical complex and to a lesser extent the industrial park, Pb could have the same sources, in addition to vehicular traffic (Aguilera et al., 2019). In Toluca, the main sources of Pb can be the combustion processes of food waste, paper, plastics, textiles, rubber, wood, and metal smelting; other sources, other than combustion, from these industries; as well as the old Pb deposit from leaded gasoline (Ávila-Pérez et al., 2019).

Little information is available on possible sources of heavy metals in the environment in Ensenada and Morelia. In Ensenada, using a bioindicator (mussel *Mytilus californianus*), it has been observed that Pb concentrations are affected by anthropic activities, in this study it was thought that Pb reached the mussel through the atmospheric deposition (Muñoz-Barbosa, Gutiérrez-Galindo, and Flores-Muñoz 2000). In Morelia, it was found that the highest concentrations of Zn in soils were located in primary roads with significant differences for the other roads. In addition, the concentrations of Mn, Pb, and Fe exceeded the maximum limits of the Mexican regulations for soils (Carranza et al., 2015), called NOM-147 (SEMARNAT 2007).

In Mérida, Cu, Zn, and Pb have been associated with vehicular traffic, because the highest concentrations have been found in the historic center and on primary roads. When observing the dust particles under a microscope, spherical particles of anthropic origin with these associated metals were found (Aguilar et al., 2021).

3.1.1 Potential Ecological Risk

The PER was below 150 for practically all cities; therefore, there is no potential ecological risk due to the concentrations of Cu, Pb, Mn, and Zn, together, in urban dust. Only two sites in SLP had a moderate potential ecological risk ($150 < PER \leq 300$) and one more site had a considerable risk ($300 < PER \leq 600$). The values of the medians of the PER decreased in the order CDMX > SLP > Toluca > Ensenada > Morelia > Mérida (**Figure 3**). Pb was the metal that most contributed to the PER in all cities, representing 67.3% of the PER in CDMX, 49.3% in Ensenada, 58.1% in Mérida, 55.1% in Morelia, 66.8.1% in SLP, and 64.1% in Toluca.

Even when no potential ecological risk was found due to Cu, Pb, Mn, and Zn, in the urban dust of the studied cities, it is important to remember that this index is the addition of the individual risks of each metal, as in this study only three metals could be analyzed, the risk may be lower than in other cities where more metals were considered (Yesilkanat et al., 2021). Therefore, if more metals were analyzed in Mexican cities, the ecological risk would change.

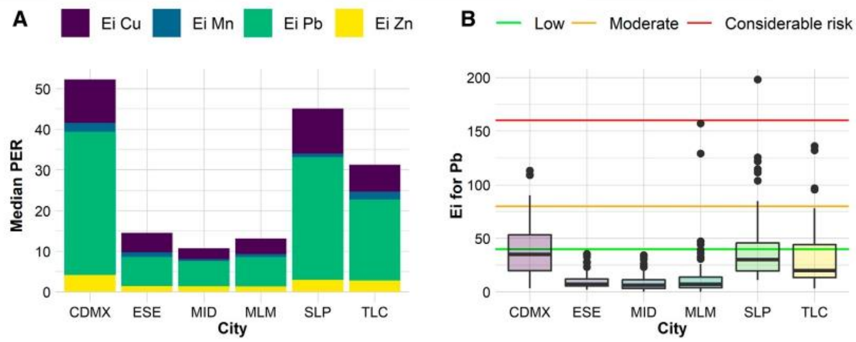

FIGURE 3 | In the **(A)**, the value of the median potential ecological risk (PER), divided according to the contribution of each of the metals risk factors (Ei). In the **(B)**, box plots of lead risk factors (Ei) for each studied city. CDMX: Mexico City, ESE: Ensenada, MID: Mérida, MLM: Morelia, SLP: San Luis Potosí, TCL: Toluca.

Pb alone did represent a potential ecological risk, according to the ecological risk factor (Ei). In more than 25% of sites of CDMX, SLP and Toluca a moderate risk was found, in some sites of these cities, a considerable risk was found, and only in one SLP site was a high risk (**Figure 3**). This result differs from that found in other studies where several cities were analyzed, in those cases different metals contributed the most to the ecological risk (Jahandari 2020; Yesilkanat et al., 2021). In fact, in the present work, Pb alone represents a moderate ecological risk in more than a quarter of the sampling sites of CDMX, SLP, and Toluca.

3.1.2 Human Health Risk

The main route of exposure to heavy metals was ingestion. The risk to human health was 10 times higher for children than for adults. Pb was the only metal that represented a non-carcinogenic risk for the health of children in the cities of CDMX, SLP, and Toluca since its HI was greater than one in ~25% of the sampling sites (**Figure 4**). Children are the most susceptible due to their hand-to-mouth habits and rapid growth rates (Kamali, Omidvar, and Kazemzadeh 2013).

Some points to consider are 1) the fact that the total concentrations of Pb were used to calculate the health risk indices, therefore the risk is being overestimated, it is necessary to use the bioavailable concentrations (Huang. 2016); 2) on the other hand, only the risk represented by urban dust is being considered, while that from other sources such as water, food, air, soil, and glazed ceramic also has its contribution to the total risk of this metal for the human health (H. H. Li et al., 2017); and 3) the effect that may have the combination of Pb with other metals and pollutants is still unknown.

Chronic exposure to an HI greater than 0.1 (1E-01) has been reported to trigger many ailments (Jadoon et al., 2018). In this sense, Fe represented a risk of generating ailments in children in all cities, since they all had HI greater than 0.1 (1E-01), in some sampling points; in CDMX and Toluca this happened for the entire city; in Ensenada, it happened in 87% of the cases and in SLP 46% of the cases had an HI greater than 0.1 (1E-01). In Morelia and Mérida, only the extreme values were in this situation. The Mn could also unleash health problems for children in all cities; especially in CDMX and Toluca, since their HI was greater than 0.1 in the entire city; in Ensenada, the HI was higher than 0.1 in 88% of the city, in SLP in 79%, in Morelia in 67% and Mérida in 29% of the city. In the case of Zn HI greater than 0.1 was only found in some sites of SLP; the same for Cu, together with one sampling point in CDMX. Cu and Zn were the metals that represented the least risk to human health.

Iron and manganese are generally not analyzed in heavy metal contamination studies, probably because they are not considered dangerous or relevant in the urban environment, however, that is not true (Kim, Lee, Seok et al., 2015; Kletetschka, Bazala, Takáč et al., 2021). We compared the mean HI for kids and adults in different cities and observed that HI for Fe commonly is higher than the one for other metals such as Cu and Zn (**Table 1**). In Mexico, the mean Fe HI for kids was higher than those reported in all the other cities. Black magnetite particles can be seen in the air filters of the air monitoring systems of Mexican cities. Mn has been analyzed only at sites where significant sources of this metal are known in advance (Menezes-Filho 2016; Rodrigues et al., 2018). The results of the present work indicated that it is important to include them and monitor their concentrations in cities. 04) (USEPA 2001).

In comparison with other cities (**Table 1**), the mean HI for Cu for kids was ten times higher than for Bandar-Abbas and Shiraz and the same for the other cities. For Zn were ten to twenty times lesser tan for the other cities. Mean Pb HI for kids in the six Mexican cities was higher than for Bandar-Abbas, lesser than for Düzce, and almost the same magnitude as for the rest of the cities. Mean Fe HI for kids in the six Mexican cities was higher than all the cities in comparison. Mn was higher than four of the six cities in comparison. The HIs for adults were similar but ten times lesser than for kids.

Pb was the only analyzed metal with the potential to generate cancer. However, the carcinogenic risk index (RI) indicated that this metal in street dust does not represent a risk of developing cancer in any of the cities, the median value was 1.1E-9, which is

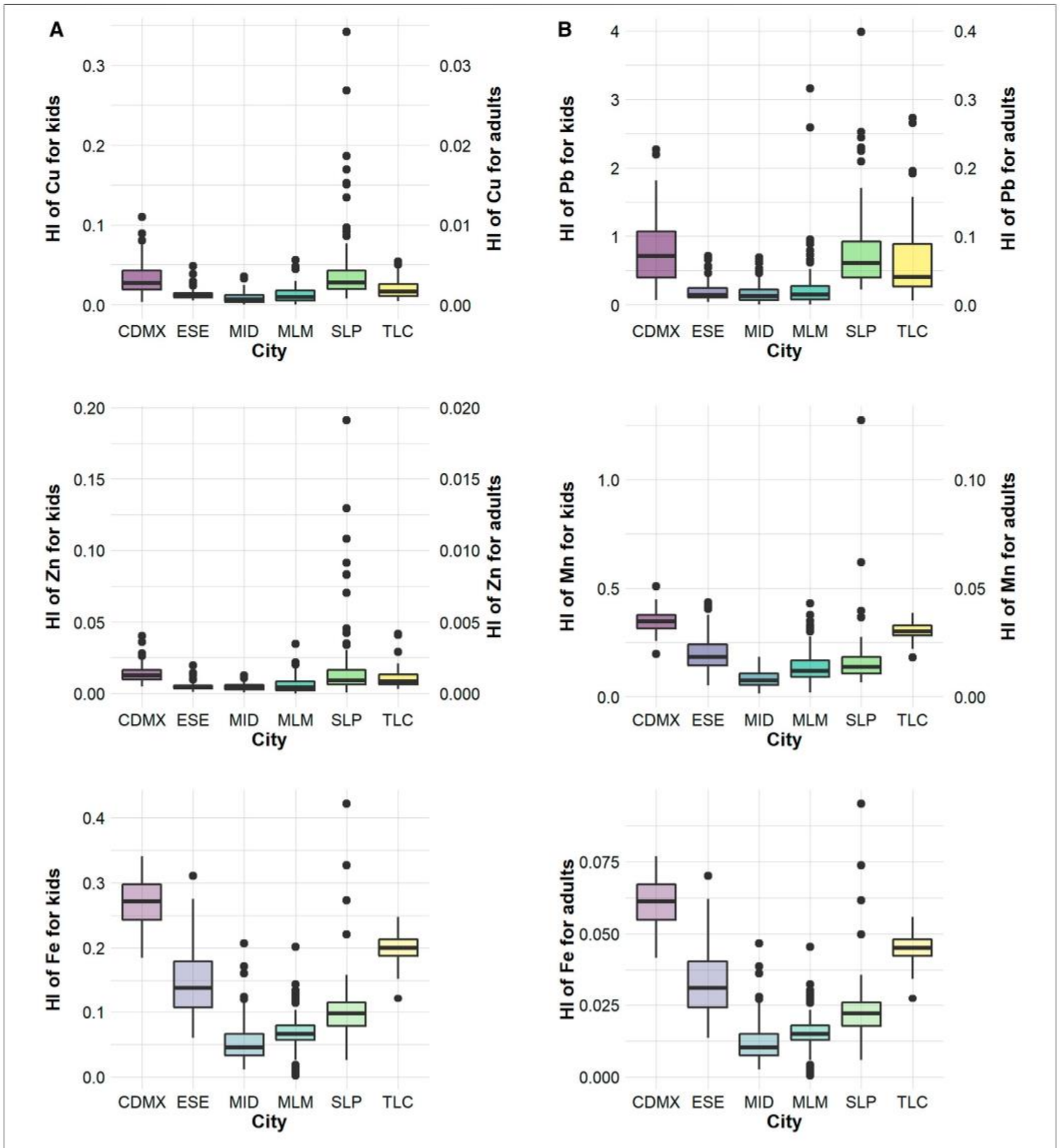

FIGURE 4 | Box plots of the human health risk indices (HI) for children **(A)** and adults **(B)**, of each heavy metal for Mexican cities. CDMX: Mexico City, ESE: Ensenada, MID: Mérida, MLM: Morelia, SLP: San Luis Potosí, TCL: Toluca.

below the accepted or tolerable risk (1E-06 a 1E- After analyzing the pollution and ecological and human health risk indices, we were able to observe that lead was the metal that causes the greatest concern in Mexican cities. Globally, Pb is also one of the metals of greatest concern, along with Cr (Aguilera, Bautista, Goguitchaichvili, et al., 2021). In the case of Mexico, practically in all cities, it is attributed the source of this metal in street dust to vehicular traffic, however, it is also investigated how much the deposit of old Pb from leaded gasoline contributes (Ávila-Pérez et al., 2019).

TABLE 1 | Comparison of mean Hazard Index (HI) for the studied heavy metals in other cities around the world.

City	–	Cu	Fe	Mn	Pb	Zn	Authors
Bandar-Abbas, Iran	Kids	1.70E-03	9.91E-02	7.61E-02	4.34E-03	5.61E-03	Keshavarzi et al. (2018)
	Adults	7.10E-04	1.38E-02	1.05E-02	5.77E-04	7.46E-04	
Düzce, Turkey	Kids	1.60E-02	4.00E-02	4.10E-02	1.40E+00	7.40E-03	Taşpınar and Bozkurt (2018)
	Adults	2.00E-03	2.00E-02	1.10E-02	3.10E-01	9.40E-04	
Jeddah, Saudi-Arabia	Kids	4.47E-02	4.29E-02	1.70E-01	5.20E-01	2.09E-02	Shabbaj et al. (2018)
	Adults	5.25E-03	1.67E-02	3.35E-02	6.63E-02	2.57E-03	
Suzhou, China	Kids	1.20E-02	8.70E-02	1.40E-01	1.80E-01	1.10E-02	Lin et al. (2017)
	Adults	2.70E-03	5.30E-02	3.80E-02	3.10E-02	1.70E-03	
Shiraz, Iran	Kids	8.70E-03	1.21E-04	2.60E-03	2.23E-01	6.36E-03	Keshavarzi et al. (2015)
	Adults	9.00E-04	8.10E-06	1.70E-04	4.85E-02	7.70E-04	
Nanjing, China	Kids	1.09E-02	2.22E-02	2.24E-02	1.76E-01	1.00E-02	Hu et al. (2011)
	Adults	1.17E-03	2.38E-03	2.40E-03	1.88E-02	1.08E-03	
Mexican cities	Kids	2.23E-02	1.36E-01	2.01E-01	4.80E-01	9.51E-03	This study
	Adults	2.39E-03	3.08E-02	2.60E-02	5.17E-02	1.03E-03	

On the other hand, it is necessary to establish a monitoring system for heavy metals in the dust of the streets, soils, and plants of Mexican cities, as well as pollution indicators with proxy characteristics (easy analysis and low cost) that allow the analysis of thousands of dust samples to identify the sites of high concentration of heavy metals. In this sense, magnetic (Sánchez-Duque et al., 2015; Aguilera et al., 2020) and colorimetric (Cortés et al., 2015; Sanleandro et al., 2018; Aguilar et al., 2021) techniques are promising.

4 CONCLUSION

In this study, we highlighted the current situation in terms of heavy metal contamination in Mexican cities. When the proposed value for soils worldwide was considered as the background, all cities were contaminated, except for Mérida. However, Mérida and Morelia were the most polluted cities when a local background value was used (decile 1). For the metals Cu, Pb and Zn, the concentrations in the cities decreased in the order CDMX > San Luis Potosí > Toluca > Morelia-Ensenada > Mérida. In the particular case of Cu and Pb, SLP accompanied CDMX as the city with the highest concentrations. For the Mn and Fe, the order slightly changed: CDMX > Toluca > Ensenada > San Luis Potosí > Morelia-Mérida.

The largest and most industrialized cities were expected to have the highest concentrations of heavy metals; however, we did not know if this was proportional to the size and if this was the case for all metals. The results showed that contamination was not necessarily related to the number of inhabitants, a populated city like Mérida was the least contaminated; on the contrary, a sparsely populated city like Ensenada was more polluted by Mn and Fe than other more populated ones like San Luis Potosí, Morelia, and Mérida.

No potential ecological risk was found due to contamination by Cu, Pb, and Zn, in the urban dust of the studied cities. However, Pb was the metal that contributed the most to potential ecological risk in all cities. Furthermore, Pb alone did represent a moderate ecological risk in more than 25% of the CDMX, San Luis Potosí, and Toluca sites. Pb could also represent a health risk for the children in these cities. Additionally, chronic exposure to Fe and Mn could trigger many ailments or illnesses.

The analysis of the level of contamination and the possible ecological and human health risk of heavy metals in the dust of six Mexican cities, allowed us to identify that Pb is the metal that causes the greatest concern in the urban environment of Mexico. Therefore, it is important to pay attention to this metal and inquire more deeply about its sources and mitigation strategies.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation. Q12

AUTHOR CONTRIBUTIONS

Conceptualization: FB; methodology: CD, YA, DA, JC, AA, and RC; validation: FB, PQ, and AG; formal analysis: AA; resources: FB, PQ, and AG; writing-original draft: AA; writing-review and editing: FB, PQ, and AG; visualization: AA; supervision: FB; Project administration: FB; funding acquisition: FB and AG. Q13

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SUPPLEMENTARY MATERIAL Q16

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenvs.2022.854460/full#supplementary-material

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. Q15

Aportes del capítulo a la tesis

En este capítulo se comparó la contaminación por metales pesados en el polvo urbano de seis ciudades mexicanas: Ensenada, San Luis Potosí, Morelia, Toluca, CDMX y Mérida. Con este estudio se cubrió el objetivo principal de la tesis y nos permitió indagar, posteriormente, en cuestiones más específicas relacionadas con el tema, utilizando como caso de estudio la CDMX.

Entre las principales reflexiones que surgieron de esta investigación pudimos observar que evidentemente el nivel de contaminación se ve muy afectado dependiendo de si se utiliza un valor de fondo local o global. A tal punto que Mérida pasó de ser la ciudad menos contaminada al poner como referencia un mismo valor de fondo para todas las ciudades (el establecido para suelos a nivel mundial), a ser la más contaminada cuando se utilizó un valor de fondo local. Esto se debió a que en esa ciudad se pueden encontrar valores muy bajos de los metales pesados de manera natural, incluso más bajos de los que se han reportado en suelos a nivel mundial.

Hacer la evaluación del nivel de contaminación con ambos valores de fondo, uno global y otro local, sirve para hacer comparaciones respecto a otros sitios urbanos y poder tener una idea de cómo varían las concentraciones de los metales pesados entre sitios. Sin embargo no es suficiente en un análisis de contaminación ambiental porque no podemos saber posibles repercusiones de cada nivel de contaminación ¿Qué ciudad será la más (más riesgosa para la salud), la que tuvo un nivel de contaminación alto respecto a los valores de fondo locales porque de manera natural hay muy bajas concentraciones o la que tuvo un nivel de contaminación bajo, pero concentraciones más altas porque sus valores de fondo locales son más alto de manera natural?

De hecho puede haber ciudades peligrosas o tóxicas de manera natural y otras que han sido intoxicadas por las actividades antrópicas del lugar. Estas distinciones son posibles gracias a la comparación de ambos valores de fondo: local y global. Claro que simplificamos los hechos para que sea más sencillo hacer clasificaciones, pero la realidad es que hay todo un gradiente y una mezcla entre la toxicidad natural y la intoxicación. Lo que podemos decir es que hay ciudades que de manera natural son más tóxicas que otras y que además han sido intoxicadas.

La evaluación de riesgo ecológico y a la salud humana también nos permitió complementar el análisis de la contaminación por metales pesados en el polvo urbano. Ya que estas evaluaciones se hacen con las concentraciones y no con los niveles de contaminación, pudimos observar que, independientemente del nivel de contaminación, no se identificó un posible riesgo ecológico. Aunque las ciudades con las concentraciones más altas sí representan un mayor riesgo. De entre los metales analizados, el plomo podría representar un riesgo para la salud de los niños de CDMX, Toluca y San Luis Potosí. En México (considerando las seis ciudades), el HI promedio de Fe para los niños fue más alto que el reportado en otras partes del mundo, en el caso del Mn fue más alto que para la mayoría de los demás sitios.

De manera visual, al comparar la clasificación de las ciudades más contaminadas con la clasificación de las ciudades más pobladas, nos dimos cuenta de que no hubo correspondencia; las ciudades más grandes no fueron necesariamente las más contaminadas. En cuanto al ambiente geológico, las ciudades de la misma provincia fisiográfica tuvieron distintos niveles de contaminación. Estas son cuestiones que se podrían analizar de manera estadística en futuras investigaciones. En el último capítulo de esta tesis hicimos un análisis estadístico inferencial para el muestreo extensivo de la CDMX. A futuro, podría hacerse un estudio similar, utilizando variables socioeconómicas y ambientales para otras ciudades de México.

CAPÍTULO III

"Heavy metal pollution of street dust in the largest city of Mexico, sources and health risk assessment"

Después del análisis general de las seis ciudades mexicanas, hicimos un muestreo extensivo de 482 muestras de polvo urbano en la CDMX para actualizar el anterior y tener una muestra más representativa del polvo urbano de la ciudad más grande del país.

Al ampliar la cantidad de muestras pudimos hacer un análisis más detallado. En esta ocasión se utilizó una técnica analítica más precisa con el fin de mejorar la evaluación de riesgo a la salud y la estimación del valor de fondo local (decil 1). En lugar de fluorescencia de rayos X utilizamos la espectroscopía óptica de plasma acoplada inductivamente (ICP-OES). Además, pudimos incluir más elementos en el análisis: Co, Cr, Cu, Fe, Mn, Ni, Pb, V y Zn.

En la evaluación del nivel de contaminación, además del factor de contaminación incluimos el índice de geoacumulación, el cual considera pequeñas variaciones en el valor de fondo al agregar una constante de 1.5 que multiplica al valor de fondo seleccionado. Al utilizar más índices en el análisis es posible comparar cómo cambia el nivel de contaminación. Entonces, la contaminación no solo depende del valor de fondo utilizado, sino también de la metodología de evaluación que se emplee.

Otra cuestión muy importante en los estudios de contaminación es poder identificar las posibles fuentes emisoras de los contaminantes. Este es un punto necesario para poder atender el problema desde la raíz y disminuir las concentraciones en el ambiente o evitar que sigan aumentando. Sin embargo, no es una tarea sencilla, especialmente en una ciudad tan grande y con múltiples actividades que pueden estar acrecentando el problema. Como primer intento para identificar las fuentes a partir de las concentraciones de los metales, utilizamos las relaciones estadísticas entre los mismos (correlaciones, análisis de componentes principales y de conglomerados). La idea detrás es que los elementos que están relacionados provienen probablemente del mismo sitio. Después de identificar las relaciones se busca en la literatura en dónde se utilizan esos mismos elementos.

Finalmente, hasta donde sabemos, no existen límites máximos permisibles o normativas que regulen las concentraciones de los metales pesados en el polvo urbano. El establecimiento de estos límites también es importante para controlar las emisiones y disminuir la contaminación. Por tanto, en este estudio establecimos algunos niveles de acción como recomendaciones sobre lo que se debería hacer en cada categoría de contaminación.

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Heavy metal pollution of street dust in the largest city of Mexico, sources and health risk assessment

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Abstract In large industrialized cities, tons of particles containing heavy metals are released into the environment and accumulate on street surfaces. Such particles cause a potential risk to human health due to their composition and size. The heavy metal contamination levels, main emission sources, and human health risks were identified in 482 samples of street dust. Heavy metal concentrations were obtained by microwave-assisted acid digestion and ICP-OES. The results indicated that street dust in Mexico City is contaminated mainly with Pb, Zn, and Cu, according to the contamination factor and the geoaccumulation index. The pollution load index of the street dust was made with the concentrations of Pb, Zn, Cu, Cr, and Ni. The main sources of Pb, Zn, Cu, and Cr are anthropic, probably due to vehicular traffic. The highest levels of Cr and Pb in urban dust represent a health risk for children. Contamination limits were proposed for heavy metals in street dust of Mexico City. These limits might be useful to generate and apply public policies to decrease anthropic emissions of the heavy metals studied, particularly Cr and Pb.

Keywords Contamination factor · Pollution load index · Heavy metal loads · USEPA health risk assessment

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Introduction

In several cities around the world, air (Son et al., 2018), soils (Ihl et al., 2015), dusts (Ali et al., 2017; Men et al., 2018; Aguilera et al., 2019), and plant contamination (Aguilar-Reyes et al., 2012) by heavy metals are a serious problem that affects population health (WHO, 2014; Budai & Clement, 2018). In the case of air and soil contamination, several countries have implemented official standards since decades ago that define the maximum permissible concentrations of heavy metals; however, there is no regulation for street dust and plants.

Street dust is composed of a mixture of naturally occurring pollutants (weathering of rocks, soil erosion, leaf litter, among others) (Cortés et al., 2015)

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and anthropic (brake and tire wear, engine components, and exhaust emissions) (Budai & Clement, 2018; Gunawardena et al., 2014; Świetlik et al., 2015), as well as polluting particles released by industries (Aguilera et al., 2019), homes, and the weathering of urban infrastructure (Lee et al., 2018). Street dust is a sink of particulate heavy metals that are deposited on the surface of streets, sidewalks, and windows (Rahman et al., 2019). At the same time, street dust can become a source of pollutants by resuspension and washed off by stormwater runoff (Wijesiri et al., 2018).

In particular, the study of street dust is interesting because it is in closer contact with the population than particulate matter (measured at 4 m above the ground) or soils. Heavy metals in street dust can enter the human body through three routes of exposure: inhalation, ingestion, or dermal. Depending on factors such as toxicity of the element, bioavailability, concentration, etc., as well as socioeconomic issues and the person's health status, heavy metals can generate adverse health effects (Calderón et al., 2001; Carrizales et al., 2006; Salustri et al., 2010). Therefore, establishing the levels and limits of heavy metal contamination in street dust, as well as identifying the sources of heavy metals and the risk to human health in each city, is of utmost importance to propose solution action plans.

Mexico City is one of the largest and most populous cities in the world, with high levels of contamination that cause different health problems, e.g., DNA damage, as well as respiratory and cardiovascular diseases (Son et al., 2018). The study of heavy metals in street dust, with a large number of samples, will make it possible to propose an official standard for Mexico City to define categories of action according to different contamination limits. The objectives of this study were (a) the identification of the levels of heavy metal contamination in street dust, (b) elucidate the possible sources of heavy metals, and (c) human health risk assessment by the heavy metals in street dust of Mexico City.

Materials and methods

Study site and sampling design

Mexico City is located in a basin at an altitude of 2240 m above sea level, with an area of 1485 km^2. The population stands at around 8.9 million inhabitants with a population density of 5966 inhabitants/km^2. Considering the metropolitan area, the population reaches 23,500,000 inhabitants. Moreover, 4,000,000 vehicles circulate every day, and 40,000 small and medium industries are in operation (Molina et al., 2010).

In Mexico City, there are two climatic seasons during the year: the dry winter season from November to April and the rainy season from May to October. During winter, thermal inversions are frequent, until the sun warms the cold air, around 9 or 10 am, the pollutants disperse. The prevailing winds have northeast to southwest direction; however, the "Sierra del Ajusco" prevents the passage of the wind and thus the dispersion of pollutants (Vallejo et al., 2003). An industrial center with a high population density is located in the northern part of the city. The central part includes the historical and socioeconomic center of the city, with a high urban and commercial activity. The southern area has been dominated by residential and commercial activities (Rodríguez-Salazar et al., 2011).

During April and May 2017, a systematic, homogeneously distributed sampling of 482 street dust samples was carried out (Fig. 1). To collect the sample, the dust present in 1 m^2 of the street was swept and the geographic coordinates of each site were taken. The samples were transferred to the laboratory where they were allowed to dry at room temperature and in the shade. After that, samples were sieved at 250 μm, since at this size, the particles adhere easily to the hands and can be ingested (Jadoon et al., 2018).

Geochemical analysis and contamination levels

To determine heavy metal concentrations, 0.4 g of each sample was digested with 20 mL of concentrated HNO_3, in an ETHOS Easy microwave digestion system (Millestone Inc) using Teflon PFA beakers. The temperature was brought to 175 ± 5 °C in approximately 5 min and was kept at that temperature for 4.5 min. After cooling, the digested samples were filtered with Whatman No. 42 paper, then transferred into 50-mL flasks, and graduated with water type A (US-EPA method 3051A). Quality controls for the acid digestion method included reagent blanks and sample duplicates. The quality assurance and quality control (QA/QC) results showed no signs of contamination or loss in any of the analyses.

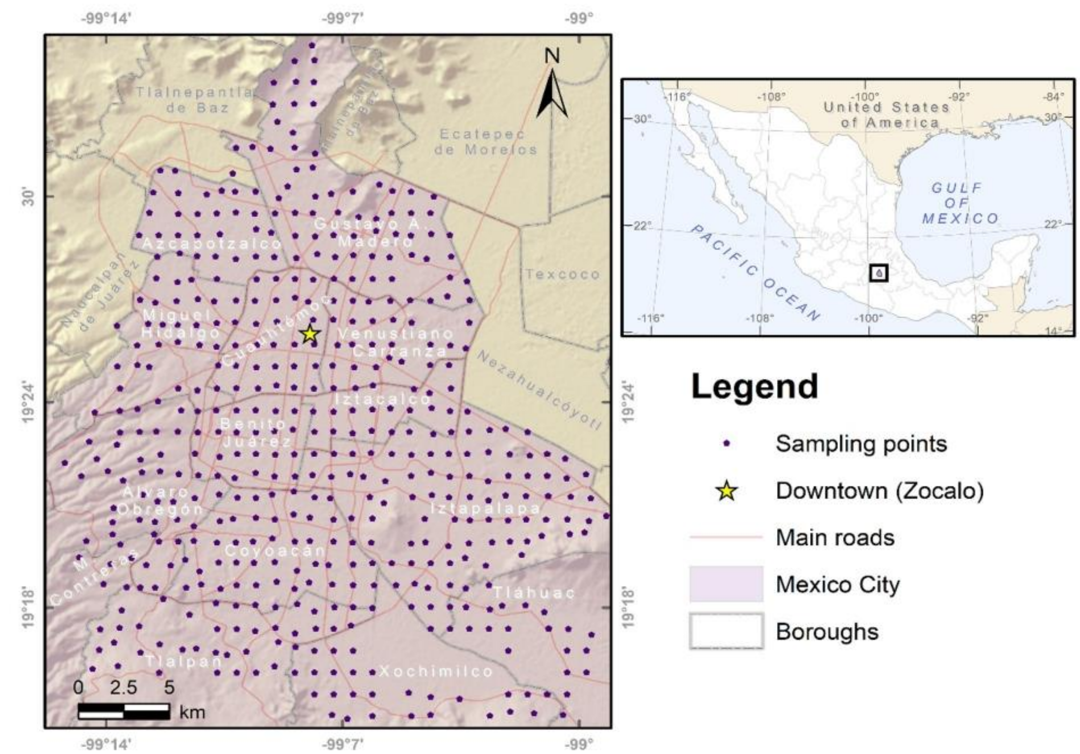

Fig. 1 Location map of the study site and sampling points

Digestions and quality controls were analyzed in triplicate with an Agilent Technologies 5100 Inductively Coupled Plasma Optical Spectrometer (ICP-OES) (US: EPA method 6010C). To prepare the calibration curve, multi-elemental QCS-26R reference-certified material was used (high purity brand). Radiofrequency power (RF power) was 1.2 kW, nebulization flow 0.7 L/min, and argon plasma flow was 12.0 L/min. The detection (DL) and quantification (QL) limits are presented in Table 1. DL and QL were estimated during validation by measuring low concentration repeats, DL was calculated as 3 times the standard deviation of the repeats, and QL was calculated as 10 times the standard deviation of the same repeats.

Two contamination indexes were calculated for each heavy metal: geoaccumulation index (I_{geo}) and contamination factor (CF), as well as the pollution load index (PLI) which is the geometric average of the five highest CF (Eq. 1–3) (Tomlinson et al., 1980).

$$I_{geo} = Log_2(C_n/1.5B_n) \tag{1}$$

$$CF = C_n/B_n \tag{2}$$

$$PLI = \sqrt[n]{CF1 * CF2 * \cdots * CFn} \tag{3}$$

C_n represents the concentration of the heavy metal n, and B_n is the background geochemical value. Constant 1.5 is used to compensate for natural fluctuations of the heavy metals studied and to compensate for small anthropic influences.

Generally, the background values found in healthy, non-degraded, or managed soils are used as background values; when this information is not available, the global background values for soils have been used (Kabata-Pendias, 2011) or even the minimum value found in the data under study (Declercq et al., 2019). In this research, the

Table 1 Detection (DL) and quantification (QL) limits for the elements analyzed in the wavelength used by Agilent Technologies 5100 ICP-OES

Metal	λ (nm)	DL (mg/kg)	QL (mg/kg)
Al	308.2	73.75	246.25
Ba	233.5	2.5	7.5
Ca	317.9	75	250
Co	228.6	1.25	5
Cr	267.7	1.25	5
Cu	324.7	1.25	2.5
Fe	238.2	27.5	93.75
Mg	279.0	52.5	177.5
Mn	257.6	5	15
Ni	231.6	1.25	6.25
Pb	220.3	3.75	15
V	292.4	2.5	6.25
Zn	213.8	2.5	12.5

first decile was used because no background values have been established for street dust. We use the first decile instead of the minimum value to allow some variation and tolerance. Besides, the global background values for soils were also used, to make comparisons between the two proposals. The interpretation of the I_{geo} (Müller, 1979) and CF (Ihl et al., 2015) is presented in Table 2. A *PLI* value close to one indicates that the heavy metal load is close to the bottom level, while a $PLI > 1$ indicates contamination (Mehr et al., 2017; Tomlinson et al., 1980).

Sources of heavy metals

Principal component analysis (PCA) was used as a qualitative pattern recognition method, which can indicate the sources that enrich the concentrations of the heavy metals studied. The PCA reduces the data and extracts a small number of factors (principal components PC), to determine the relationships between the observed variables. The eigenvector with the longest eigenvalue is the direction of greatest variation, the second largest eigenvalue is the orthogonal direction with the next largest variation, and so on. Each PC contains information on all the elements present in a single group, while loads of each element indicate their relative contribution to the formation of the group (Rout et al., 2014).

Table 2 Geoaccumulation index (I_{geo}) and contamination factor (CF) interpretation

I_{geo}	Interpretation
<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
CF	**Interpretation**
<1	Insignificant contamination
1–3	Moderate contamination
3–6	Considerable contamination
>6	High contamination

Human health risk by heavy metal contamination in street dust

To estimate the risk of heavy metals, present in street dust on the health of the population, the methodology developed by the United States Environmental Protection Agency (USEPA) was used. First, the estimated daily intakes for the three main exposure routes were calculated: ingestion (EDI_{ing}), inhalation (EDI_{inh}), and dermal contact (EDI_{dermal}) (Eqs. 4–6), as well as the lifetime average daily dose (LADD) to estimate the carcinogenic risk (Eq. 7).

$$EDI_{ing} = \frac{C \times IngR \times EF \times ED \times CF}{BW \times AT} \quad (4)$$

$$EDI_{inh} = \frac{C \times InhR \times EF \times ED}{PEF \times BW \times AT} \quad (5)$$

$$EDI_{dermal} = \frac{C \times SA \times AF \times ABS \times EF \times ED \times CF}{BW \times AT} \quad (6)$$

$$LADD = \frac{C}{PEF \times AT_{can}} \times \left(\frac{CR_{child} \times EF_{child} \times ED_{child}}{BW_{child}} + \frac{CR_{adult} \times EF_{adult} \times ED_{adult}}{BW_{adult}} \right) \quad (7)$$

Table 3 Exposure factors of reference populations for human health risk assessment

Factor	Definition and units	Value		Reference
		Child	Adult	
IngR	Ingestion rate (mg/day)	200	100	USEPA (2001)
InhR	Inhalation rate (m^3/day)	7.63	12.8	Li et al. (2001)
PEF	Particle emission factor	1.36E+09	1.36E+09	USEPA (2001)
SA	Surface of exposed skin area (cm^2)	2800	5700	USEPA (2001)
ABS	Dermal absorption factor	0.001	0.001	USEPA (2001), Ali et al. (2017)
AF	Skin adherence factor (mg/cm^2)	0.2	0.07	USEPA (2001)
ED	Duration of exposure (years)	6	24	USEPA (2001)
EF	Frequency of exposure (days/year^1)	350	350	Zheng et al. (2010)
AT	Average time non-carcinogens (days)	ED*365	ED*365	USEPA (1989)
Atcan	Average time for carcinogens (days)	70*365	70*365	USEPA (1989)
BW	Body weight (kg)	15	70	Zheng et al. (2010), Mohmand (2015), Kurt-Karakus (2012)
C	Heavy metal concentration (mg/kg)	This study		
CF	Conversion factor (kg/mg)	1×10^{-6}		Li et al. (2001)

All the exposure factors used in this study are those established for reference populations (Table 3). The use of local factors could improve the reliability of the model; however, exposure factors have not been estimated yet for any Mexican City. CR is the contact (or absorption) rate. CR = IngR for ingestion, CR = InhR for inhalation, and CR = SA × AF × ABS for dermal contact. The type of CR used for each carcinogenic metal depends on the exposure route by which it can cause cancer (Table 4).

Risk ratios for ingestion, inhalation, and dermal contact ($HQ_{ing/inh/derm}$) were obtained by dividing the *EDI* by the reference dose (*RfD*) as shown in Eq. 8:

$$HQ_{ing/inh/derm} = \frac{EDI_{ing/inh/derm}}{RfD} \quad (8)$$

The hazard index (HI) represents the sum of the *HQ*s for the three routes of exposure. If HI is greater than 1, non-carcinogenic effects on the health of the population could occur; if it is less than 1, the opposite would be expected (USEPA, 2001).

For carcinogenic elements, the incremental lifetime cancer risk (ILCR) is commonly calculated using the following equation:

$$ILCR = LADD \times CSF \quad (9)$$

The accepted or tolerable risk is in the range of 1E-06 to 1E-04 (USEPA, 2001). These values indicate that an additional case in a population of 1,000,000 and 10,000 people is acceptable (Lu et al., 2014).

Table 4 Reference doses (RfD) and cancer slope factor (CSF) for each route of exposure

	Oral RfD	Inhalation RfD	Dermal RfD	Oral CSF	Dermal CSF	Inhalation CSF
Co	2.00E-02	5.71E-06	1.60E-02			9.80E+00
Cr	3.00E-03	2.86E-05	6.00E-05			4.20E+01
Cu	4.00E-02	4.02E-02	1.20E-02			
Fe	8.40E+00	2.20E-04	7.00E-02			
Mn	4.60E-02	1.43E-05	1.85E-03			
Ni	2.00E-02	2.06E-02	5.40E-03			8.40E-01
Pb	3.50E-03	3.52E-03	5.25E-04	0.0085		4.20E-02
V	7.00E-03	7.00E-03	7.00E-05			
Zn	3.00E-01	3.00E-01	6.00E-02			

Results

Contamination levels by heavy metals in street dust in Mexico City

All the analyzed elements (Ba, Co, Cr, Cu, Mn, Ni, Pb, Ti, V, Zn, Al, Ca, Fe, and Mg) had an asymmetric distribution (not normal) according to the Shapiro test; therefore, the median is used as a reference of central tendency. The median concentrations of the elements decreased in the order Ca > Al > Mg > Fe > Ti > Zn > Mn > Ba > Pb > Cu > Cr > Ni > V > Co (Table 5). The first five elements and the Mn are considered as major elements because they are more abundant in the Earth's crust, while the rest are called trace elements due to their small concentrations.

Both the lack of normality in the frequency distribution and the wide differences between the mean and the median are considered qualitative indicators of the anthropic origin of the elements. The elements that showed the greatest differences between the mean and the median were Fe, Pb, Cu, Zn, Al, Cr, V, and Ca. Besides, the highest coefficients of variation corresponded to Fe, Pb, Zn, Cu, and Cr. These characteristics are the first indications that the concentrations of these elements have been enriched by the anthropic activities in Mexico City. This is logical due to the widespread use of these elements. Especially, these elements are related to the vehicle fleet, body materials, auto part wear, brake lining, motor body, wear and tear of the tire, and other parts (Rahman et al., 2019; Jiang et al., 2018).

Table 6 also summarizes the descriptive statistics of the loadings of the analyzed elements. The loadings were obtained by multiplying the concentrations of each element by the amount of dust, in kg, present on 1 m^2 of the surface. None of the loads had a normal distribution, according to the Shapiro test. The medians decreased in the same order as the concentrations of the elements: Ca > Al > Mg > Fe > Ti > Zn > Mn > Ba > Pb > Cu > Cr > Ni > V > Co.

Table 5 shows the global background values for soils, which were used in this study, along with the first decile of the frequency distribution of each element. Comparing both values highlights the fact that the world background values of soils for Ba, Mn, Ti, and V are more than three times greater than the values proposed in this article (first decile); in the case of Ti, it is 27 times greater. This is because these elements are abundant in soils; however, they are not so abundant in street dust. The opposite occurs for Pb and Zn, the first decile of the frequency distribution is greater than the global background value for soils, which indicates that the Pb and Zn of street dust come mainly from anthropic sources.

Contamination factor

When the first decile was considered as the background value of street dust from Mexico City, most of the data for all the elements were located at the threshold of

Table 5 Statistical summary of the heavy metal concentrations in mg/kg and background values

Heavy metal	*n*	Min	Max	Median	Mean	CV	Background decile 1	Global soils background value[a]
Ba	482	41.2	446.0	122.5	128.2	0.4	77.4	460.0
Co	482	2.5	82.4	7.5	7.4	0.6	5.0	11.3
Cr	482	15.0	441.0	43.7	51.4	0.7	28.8	59.5
Cu	482	6.2	847.1	81.2	99.7	0.8	36.2	38.9
Mn	482	100.0	990.5	223.7	235.2	0.3	166.3	488.0
Ni	482	13.7	148.7	35.0	36.3	0.4	22.5	29.0
Pb	481	8.8	1907.8	101.2	128.2	1.0	38.7	27.00
Ti	422	96.3	1677.1	365.5	412.3	0.5	254.9	7038.0
V	482	11.2	160.0	26.2	26.8	0.3	18.8	129.0
Zn	482	18.7	4827.6	229.9	280.7	1.0	113.8	70.0
Al	482	2823.6	59,285.2	9045.5	10,853.3	0.6		
Ca	482	1450.0	261,937.5	51,411.8	57,430.1	0.6		
Fe	482	653.3	61,326.8	3817.0	5722.2	1.0		
Mg	482	984.8	30,780.7	6484.5	6948.9	0.5		

Min minimum, *Max* maximum, *CV* coefficient of variation

[a] Kabata-Pendias (2011)

Table 6 Statistical summary of the heavy metal loads in mg/m^2

Heavy metal load	*n*	Min	Max	Median	Mean	CV
Ba	482	0.47	18.90	5.47	5.74	0.55
Co	482	0.02	3.42	0.31	0.34	0.73
Cr	482	0.18	15.10	1.91	2.28	0.74
Cu	482	0.12	33.12	3.50	4.45	0.87
Mn	482	0.92	33.56	9.82	10.69	0.53
Ni	482	0.14	9.67	1.45	1.70	0.68
Pb	481	0.12	52.78	4.19	5.46	0.93
Ti	422	0.96	109.31	15.49	18.69	0.71
V	482	0.11	7.82	1.12	1.22	0.56
Zn	482	0.42	195.29	9.99	12.25	1.00
Al	482	33.16	3346.18	399.23	481.67	0.73
Ca	482	53.39	17,132.74	2138.60	2615.96	0.82
Fe	482	6.88	2213.50	160.70	260.51	1.13
Mg	482	13.89	1950.83	283.55	335.01	0.74
Dust load (g/m^2)	482	5.4	173.3	43.00	46.40	0.5

Min minimum, *Max* maximum, *CV* coefficient of variation

moderate contamination (Fig. 2). The Pb, Cu, and Zn concentrations had the highest CF, the extreme CF values of these elements (Pb, Cu, and Zn) were located in the category of high contamination.

When considering as a background value the one established worldwide for soils, then a greater variation in the levels of contamination was observed, between elements. The elements with the highest CFs were Pb and Zn, with more than 25% of the data in the category of considerable contamination, followed by Cu and Ni with ~50% of the data in the moderate contamination category. More than 75% of the Cr, Co, and Mn data were located in the insignificant contamination category, and practically, all the Ba, Ti, and V data were found in the same category (insignificant contamination).

In the case of the PLI for the five elements with the highest CF (Pb, Cu, Zn Cr, and Ni), more than 50% of the data had a value greater than 1, both for the first decile and for the global background value for soils, this indicates that street dust from Mexico City is contaminated by heavy metals, regardless of the background value used in this study.

It is difficult to establish the (natural) background values of the elements when it comes to such a mobile matrix, i.e., street dust, located in urban sites full of anthropic activities. Background values of soils may be inappropriate because they are not the only source of heavy metals in street dust and because the particle size at which both matrices are analyzed is very different. On the other hand, the results of this study show that the use of the first decile can be limiting by homogenizing the variation for the contamination factors.

Geoaccumulation index

One of the benefits of the geoaccumulation index, regarding the contamination factor, is that it admits small variations in the background values. When using the first decile as the background value, it was observed that about 50% of the Pb, Zn, and Cu data were found in the category of *uncontaminated to moderately contaminated*; for the rest of the elements, with exception of Mn and V, just over 25% of the data was located in that category. Only Mn and V had most of the data in the *uncontaminated* category.

On the other hand, when considering the global background values for soils, the level of Pb and Zn contamination increased, compared with what was found with the first decile, with more than 25% of the data in the category of *moderate contamination*. Next, about 50% of the Cu data was in the *uncontaminated to moderately contaminated* category. All other elements were located as *uncontaminated*, in ascending order Ti < V < Ba < Mn < Co < Cr < Ni.

The most polluting elements in urban Mexico City dust were Pb and Zn, followed by Cu, regardless of the background value used in this work. However, when using the global background value for soils, the level of contamination was higher. Furthermore,

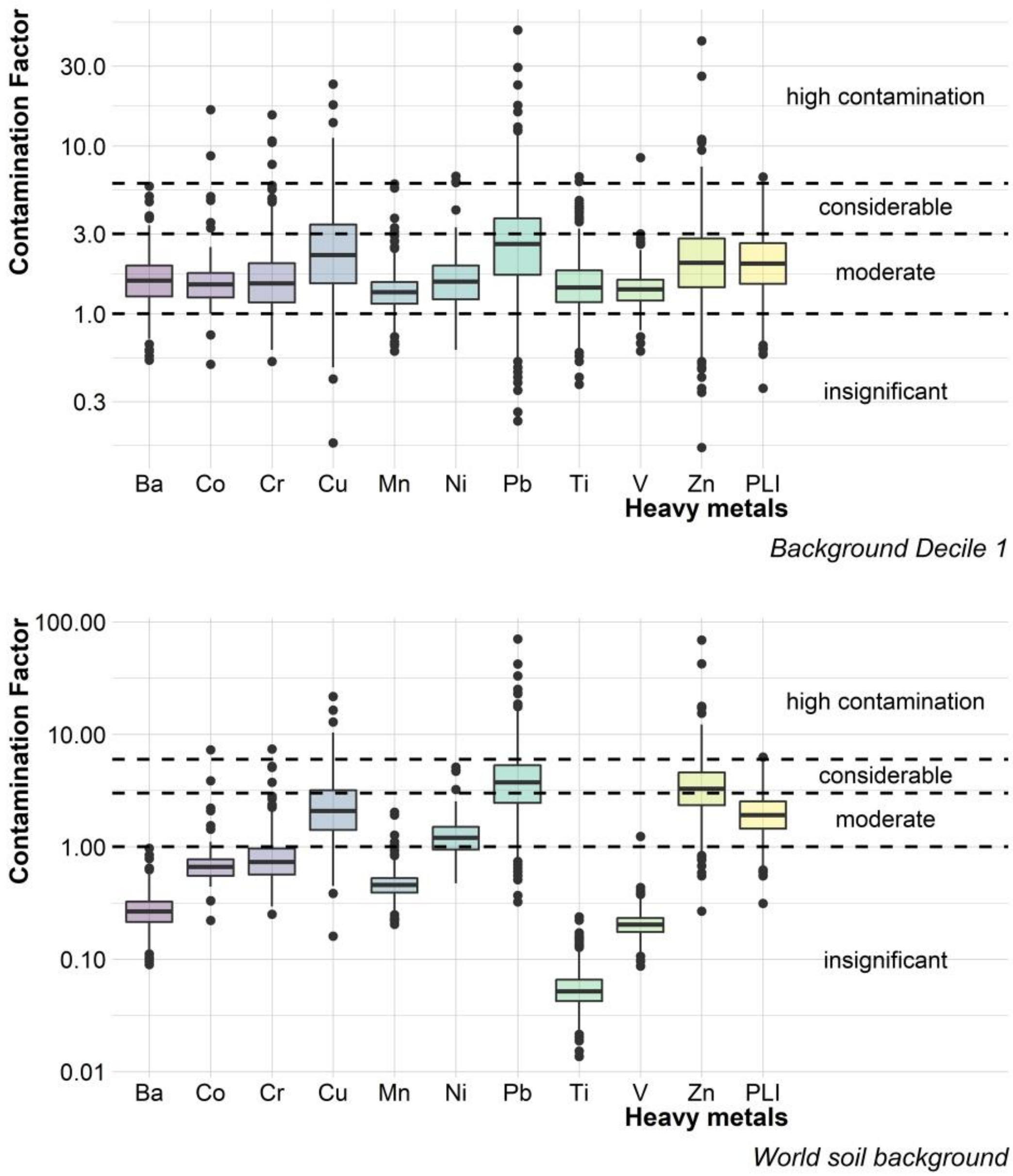

Fig. 2 Boxplots for heavy metal contamination factors using the first decile (top image) and the global background value for soils (Kabata-Pendias, 2011) (bottom image) as the background value

even when the median was at an *uncontaminated to moderately contaminated* level when the first decile was used, and *moderately contaminated* when the global background value for soils was used; in both cases, some sampled sites reached the category of highly to very highly contaminated by Pb and Zn.

Heavy metals with the highest contamination in street dust from Mexico City were Pb, Zn, and Cu, secondly Ni and Cr; considering CF and Igeo, with two different background levels (global value for soils and the first decile). Recognizing that these elements are related to vehicular traffic (Budai & Clement, 2018; Świetlik et al., 2015; Gunawardena et al., 2014), this sector could be pointed out as one of the most, if not the most influential, in heavy metal contamination in street dust in Mexico City. The PLI (Fig. 2) indicated that the level of contamination by the most polluting heavy metals (Pb, Zn, Cu, Ni, and Cr) is moderate, regardless of the background value considered (first decile and world soil background).

Proposal of contamination limits

The need to establish levels of regulation of heavy metal concentrations in street dust is evident; however, it is a complicated issue, starting with the difficulties of establishing a reference value or background value that represents a state of non-contamination. In the present work, we have compared the CF and Igeo using two background levels: (1) the first decile of the frequency distribution and (2) the global background value for soils. Each has its advantages and disadvantages; however, we consider that it is more appropriate to use the first decile as it is a specific value for Mexico City.

Using the first decile as the background value, contamination limits were established taking the CF as a reference (Table 7). The categories proposed for these limits are those used by Galán and Romero (2008) for Spain: (1) reference value (CF < 1): equivalent to the background value, indicates that there is no contamination below that level. (2) Recommended investigation level (CF: 1–3): there could be an insignificant to moderate degree of contamination, so it is recommended to be alert and, if possible, analyze bioavailable concentrations for the human body. (3) Mandatory investigation level (CF: 3–6): a considerable to a high level of contamination is assumed; therefore, it is considered mandatory to investigate bioavailable concentrations or to carry out a sequential chemical extraction. (4) Intervention level (CF > 6): a high level of contamination is assumed; therefore, mitigation actions must be carried out to reduce contamination.

The existence of a moderate level of contamination in Mexico City highlights the need to regulate heavy metal concentrations in street dust. The contamination limits are a simple first proposal to start regulating the concentrations of heavy metals in Mexico City. Following the contamination limits proposed in this article, it would be advisable to carry out more exhaustive analyzes on anthropic metals (Pb, Zn, Cu, Ni, and Cr); it is mainly recommended to analyze bioavailable concentrations for humans. Although the contamination limits are based on total concentrations, toxicological analyses are also required. The proposed categories (Galán & Romero, 2008) allow having a reference on the action measures required at each level of contamination, which is very useful for decision-makers.

Main sources of heavy metals in street dust of Mexico City

Correlation coefficients have been widely used to identify those elements that came from the same sources. In this study, Spearman's method was used

Table 7 Proposed contamination limits for heavy metals in street dust in Mexico City

Heavy metal	Reference value	Recommended investigation level	Mandatory investigation level	Intervention level
	(mg/kg)			
Ba	77.4	77–232	232–465	> 465
Co	5.0	5–15	15–30	> 30
Cr	28.8	29–86	86–173	> 173
Cu	36.2	36–109	109–217	> 217
Mn	166.3	166–499	499–998	> 998
Ni	22.5	23–67	67–135	> 135
Pb	38.7	39–116	116–232	> 232
Ti	254.9	255–765	765–1529	> 1529
V	18.8	19–56	56–113	> 113
Zn	113.8	114–341	341–683	> 683

as the correlation method, since none of the elements had a normal distribution. Pb-Cr-Cu-Zn concentrations showed a strong and significant correlation (Fig. 3), with a coefficient greater than 0.6. The Mn-V-Al-Fe also maintained a strong and significant correlation between them. On the other hand, Fe had a

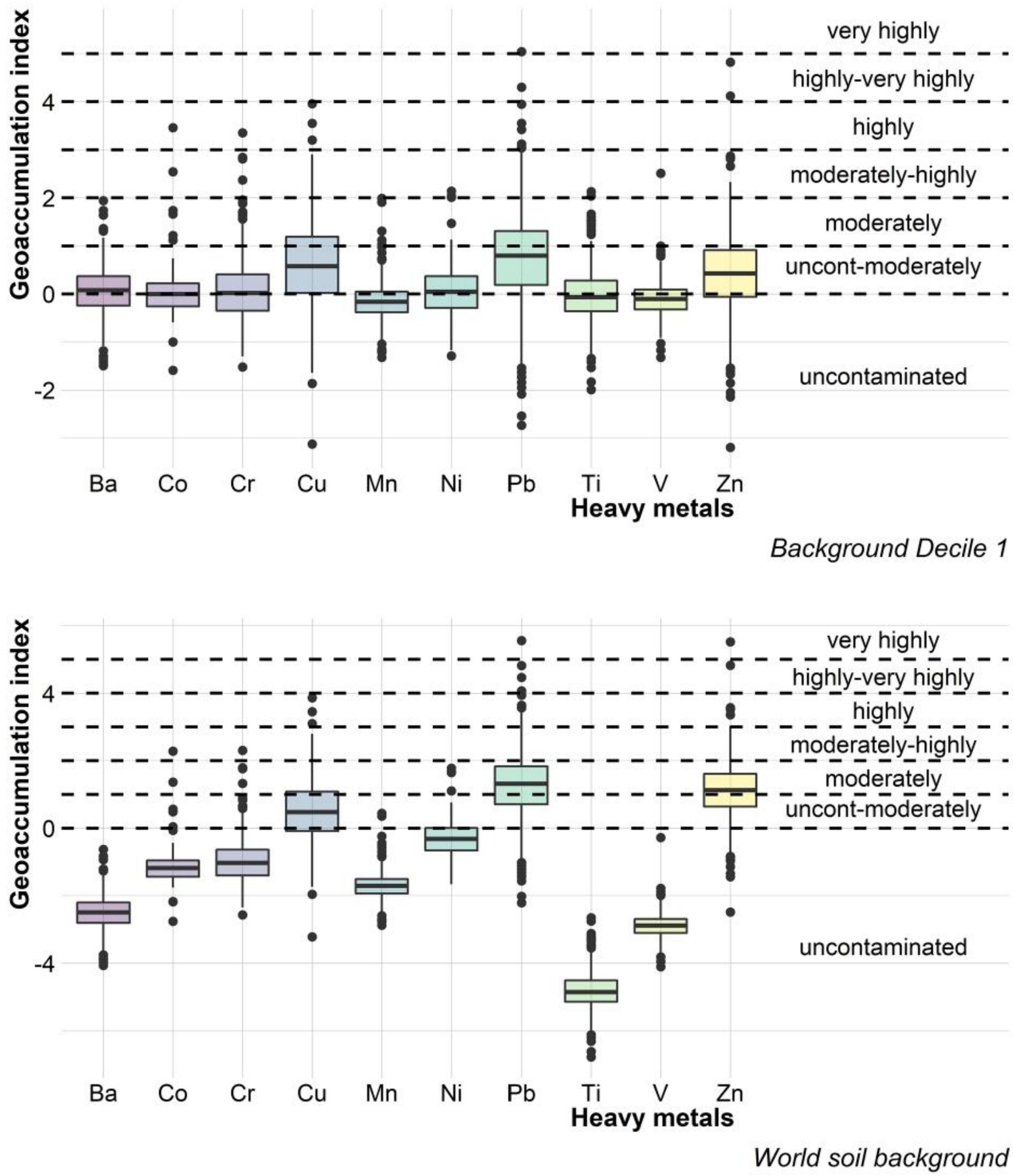

Fig. 3 Boxplots for heavy metal geoaccumulation index using the first decile (top image) and the global background value for soils (Kabata-Pendias, 2011) (bottom image) as the background value

strong and significant, but indirect, relationship with Ca, Cr, Cu, and Ni. Also, other significant correlations were found between pairs of elements that can be reviewed in detail in Fig. 4.

The principal component analysis (PCA) was applied on log-transformed data to reduce the influence of high values because data were not normally distributed. Moreover, data were centered and scaled before the analysis was performed. PCA has been a useful method to identify anthropic pollution sources of heavy metals in soils (Liao et al., 2018) and dust (Chen et al., 2014).

The first two PC had eigenvalues greater than one; therefore, they were extracted and are shown in Table 8. Mg, Ca, and Ni concentrations were excluded from the analysis due to poor representability. PC1 explained 40.41% of data variance and it was dominated by Fe, Mn, V, and Al; the elements identified as the natural ones. On the other side, PC2 explained 25.9% of the data variance and it was dominated by the anthropic elements: Pb, Cr, Zn, and Cu. These four metals were the most polluting elements of the street dust in Mexico City (Cr, Cu, Pb, and Zn), according to the contamination indexes previously calculated; this also suggests that they are elements of anthropic origin.

It has been recognized in the literature that Cu, Pb, Zn, and Cr are traffic-related metals (Budai & Clement, 2018; Świetlik et al., 2015; Gunawardena et al., 2014).

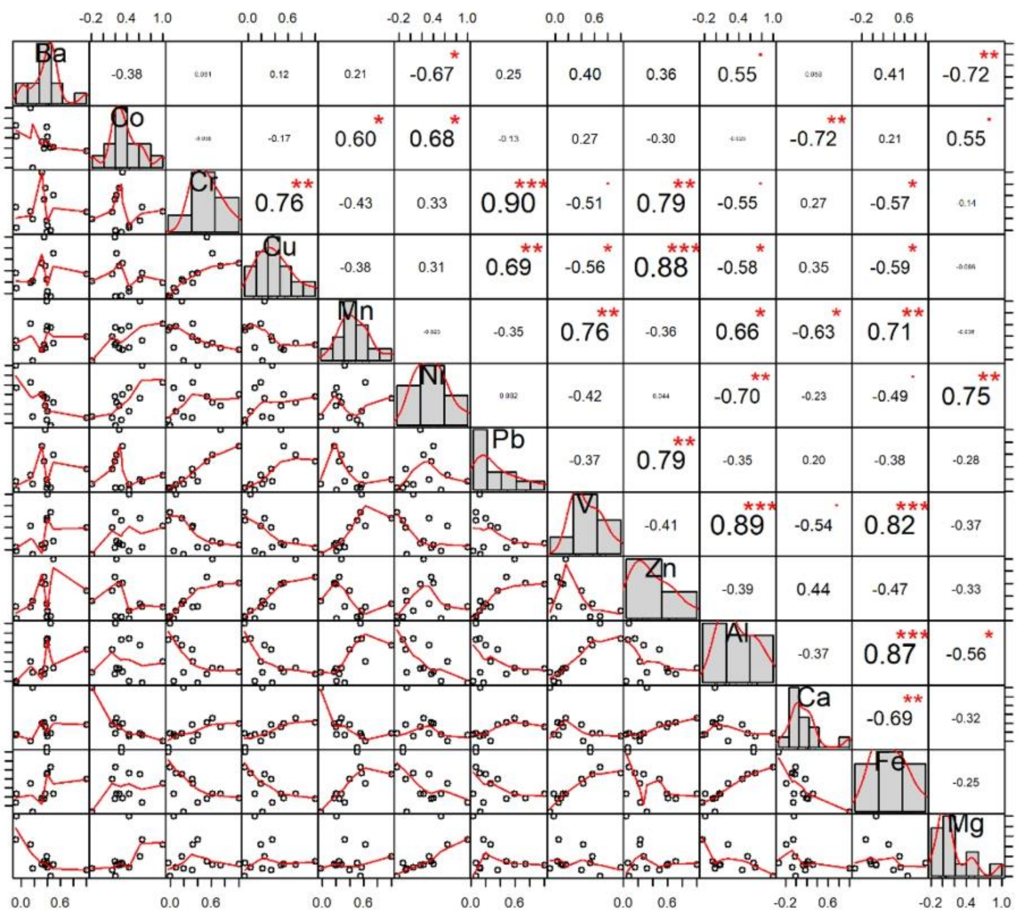

Fig. 4 Spearman correlation coefficients at the top, * indicates statistical significance with $p=0.05$. In the lower part, the scatter plots of the corresponding pairs of variables can be seen

Table 8 Component matrix for data of Mexico City street dust

Elements	Component 1 Fe, Mn, V, Al	Component 2 Pb, Cr, Zn, Cu
Ba	0.31	0.16
Co	0.31	0.04
Cr	0.18	0.40
Cu	0.16	0.43
Mn	0.38	−0.08
Pb	0.20	0.44
Ti	0.30	−0.33
V	0.38	−0.17
Zn	0.20	0.43
Al	0.35	−0.29
Fe	0.42	−0.19
Eigenvalue	4.45	2.85
Cumulative variance (%)	40.41	66.29

Although in varying quantities, Cu and Pb emissions are known to originate from brake wear, Pb can also come from the loss of lead wheel weights, while Zn is mainly emitted by tire and brakes wear, as well as from diesel exhaust emission, and some Zn compounds are used as additives for motor oil (Budai & Clement, 2018; Świetlik et al., 2015). Cr can originate from exhaust emissions (Gunawardena et al., 2014).

In the present study, the results of the Spearman correlation coefficients and PCA showed an association between Pb and Cr; this has also been previously observed in studies on street dust (Lee et al., 2018; Legalley & Krekeler, 2013). Lee et al. (2018) concluded that lead chromate in dust particles originates from yellow street paint; furthermore, they argued that the paint containing lead chromate is one of the largest sources of Pb contamination in street dust; therefore, lead chromate paint could be a probable source of Pb and Cr in Mexico City street dust. Once the lead chromate begins to deteriorate due to abrasion, humidity, and temperature, as well as the exposure of the pigments to light (it is a photo-sensitive pigment), paint and pigments crack, peel, and turn to chalk, mobilizing metal particles into the urban environment (Legalley & Krekeler, 2013).

In Mexico City, only one previous study on heavy metals in street dust has been carried out, whose sampling took place in 2011. Compared with that study, the same heavy metals continue to have the highest degree of contamination: Cr, Cu, Pb, and Zn (Delgado et al., 2019). In comparison with Mexico City soils, previous studies also identified Pb, Cu, and Zn as anthropic elements; however, Cr was considered as a natural element in soils, while in street dust, it seems to be anthropic. In the case of the present study, the very strong Spearman's correlation coefficient ($r = 0.9$) found between Pb, which is consensually anthropic, and Cr indicates that the origin of Cr in street dust is mainly anthropic.

Human health risk by heavy metal contamination in street dust

The evaluation of the health risk using the USEPA methodology showed that the mean concentrations of the elements were within the level considered to be safe for the population health (children and adults). This indicates that there is no risk of developing adverse health effects due to exposure to the analyzed heavy metals (HI < 1) (Table 9).

The average HI of Cr and Pb for children was the closest to the safe limit, being in the order of E-01; at that level, it has been reported that ailments of different types can be triggered (Jadoon et al., 2018). Furthermore, the maximum HIs of Cr and Pb can indeed represent a health risk for children exposed to these sites, since they exceed the threshold considered safe. Therefore, attention should be paid to the concentrations of these elements present in street dust; as a conservative action, maximum values should be considered.

The maximum IR (2.13E-05) and average (2.48E-06) of Cr are within the tolerable risk, which means that ~2 cases of cancer in a population of 100,000 people may occur for the maximum RI, and 2.5 cases in a population of 1 million people may occur for the average RI. However, it depends on the oxidation state, since only Cr (IV) is carcinogenic, while in this study, the total concentrations were used for the risk assessment. In another study of Cr in street dust, it was found that around 45% of the Cr present in the sample corresponds to Cr (VI) (Lee et al., 2018); if the same occurs for Mexico City, the risk would be reduced in more than a half; however, this should be corroborated in the future.

Table 9 Hazard indexes (HI) for children and adults and risk index (RI)

Heavy metal	Minimum	Maximum	Median	Mean	Standard deviation	Coefficient of variation
	Children					
Co	1.76E-03	5.81E-02	5.28E-03	5.26E-03	3.12E-03	5.94E-01
Cr	7.30E-02	2.15E+00	2.13E-01	2.50E-01	1.67E-01	6.67E-01
Cu	2.02E-03	2.73E-01	2.62E-02	3.22E-02	2.45E-02	7.60E-01
Fe	2.39E-03	2.25E-01	1.40E-02	2.10E-02	2.13E-02	1.02E+00
Mn	3.22E-02	3.19E-01	7.21E-02	7.58E-02	2.54E-02	3.34E-01
Ni	8.88E-03	9.61E-02	2.26E-02	2.35E-02	8.98E-03	3.83E-01
Pb	0.00E+00	7.10E+00	3.77E-01	4.75E-01	5.01E-01	1.05E+00
V	2.63E-02	3.74E-01	6.13E-02	6.27E-02	2.06E-02	3.29E-01
Zn	8.10E-04	2.09E-01	9.94E-03	1.21E-02	1.27E-02	1.05E+00
Sum	2.60E-01	9.39E+00	8.32E-01	9.58E-01	6.59E-01	6.88E-01
	Adults					
Co	2.28E-04	7.54E-03	6.85E-04	6.82E-04	4.05E-04	5.94E-01
Cr	8.28E-03	2.44E-01	2.41E-02	2.84E-02	1.89E-02	6.67E-01
Cu	2.17E-04	2.94E-02	2.82E-03	3.46E-03	2.63E-03	7.60E-01
Fe	5.40E-04	5.07E-02	3.16E-03	4.73E-03	4.81E-03	1.02E+00
Mn	4.17E-03	4.14E-02	9.34E-03	9.82E-03	3.28E-03	3.34E-01
Ni	9.55E-04	1.03E-02	2.43E-03	2.52E-03	9.67E-04	3.83E-01
Pb	0.00E+00	7.67E-01	4.07E-02	5.13E-02	5.41E-02	1.05E+00
V	3.08E-03	4.38E-02	7.18E-03	7.34E-03	2.41E-03	3.29E-01
Zn	8.70E-05	2.25E-02	1.07E-03	1.31E-03	1.37E-03	1.05E+00
Sum	2.92E-02	1.03E+00	9.57E-02	1.10E-01	7.26E-02	6.63E-01
	Risk index					
Co	2.82E-08	9.30E-07	8.45E-08	8.42E-08	5.00E-08	5.94E-01
Cr	7.25E-07	2.13E-05	2.11E-06	2.48E-06	1.66E-06	6.67E-01
Ni	1.33E-08	1.44E-07	3.38E-08	3.51E-08	1.35E-08	3.83E-01
Pb	0.00E+00	1.11E-07	5.88E-09	7.42E-09	7.83E-09	1.06E+00
Sum	1.00E-06	2.20E-05	2.00E-06	2.64E-06	1.70E-06	6.45E-01

Conclusions

Based on a striking and representative number of samples, the contamination factor and the geoaccumulation index showed that the street dust in Mexico City is moderately contaminated by Pb, Zn, and Cu. In addition to these three elements, Cr and Ni, together, were part of the polluting load of street dust, which indicated that more than 90% of Mexico City was contaminated (polluting load index higher than one). Moreover, the maximum values of Cr and Pb concentrations could represent a health risk for children in Mexico City. These results highlight the necessity to monitor and regulate the heavy metals in the street dust; to the best of our knowledge, this regulation is not made anywhere in the world, at the moment.

Cu, Cr, Pb, and Zn in the street dust of Mexico City must have a similar origin since those elements were associated; we assumed they must be anthropic probably due to vehicular traffic, Cr and Pb could come from the lead chromate used in the yellow paint, Cu is known to originate from brake wear, Zn is emitted by tire and additives to motor oil, and Cr can originate from exhaust emissions. Fe, Mn, V, and Al must also have a common origin; those can come from natural sources or a mix of natural and anthropic sources. In future studies, it will be important to analyze the possible sources identified in this study; this will be very useful to control the emissions of heavy metals in Mexico City.

With the idea of improving the health of the population of the largest city in the country, we proposed categories of action according to the contamination levels identified by the contamination factor; we hope these contamination limits will help to launch public policies to decrease the polluting load of heavy metals in street dust of Mexico City. Government actions are needed around the reduction of emissions, a street dust managing program, and citizen cleaning campaigns, as well as education campaigns on potential health problems due to contact with street dust.

Author contribution All authors contributed to the study conception and design. Data collection was performed by Ruben Cejudo, geochemical analysis was performed by Margarita Gutiérrez-Ruiz and Agueda E. Ceniceros-Gómez. The first draft of the manuscript was written by Anahi Aguilera and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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Aportes del capítulo a la tesis

En estudios sobre la contaminación por metales pesados es deseable analizar el mayor número de elementos posible. Al aumentar los metales bajo análisis en este artículo, respecto a los estudiados en el capítulo anterior, nos dimos de cuenta de que, además del Pb, el Cr también representó un riesgo para la salud de los niños de la CDMX. Junto con las concentraciones, analizamos la carga de los metales pesados y del polvo, i.e. la cantidad de cada elemento por metro cuadrado. Los límites de los metales para polvos de interiores en Estados Unidos están establecidos por metro cuadrado, tal vez en el polvo de la calle se desarrollen límites en las mismas unidades.

Al utilizar dos métodos para analizar el nivel de contaminación observamos que el nivel cambia dependiendo de la cantidad de categorías que tenga cada método y de qué tanto se permita que varíe el nivel de fondo. Debido a que el índice de geoacumulación tiene más categorías de contaminación y permite variaciones en el valor de fondo, pareciera que la contaminación disminuye cuando se utiliza este índice respecto al factor de contaminación.

Incrementar el número de muestras nos permitió hacer análisis más robustos y tener más confianza en los resultados, aunque esto representó un mayor esfuerzo de muestreo y análisis de laboratorio, lo que implica más costos y tiempo. Podría esperarse que el aumentar el muestreo disminuyera la variación de los datos, sin embargo, en estudios de contaminación urbana por metales pesados no necesariamente sucede así. Hay múltiples fuentes y los polvos son móviles, lo que genera mucha variación en las concentraciones entre sitios. Esto se analizó más a detalle en el último capítulo.

El análisis de las asociaciones entre los elementos nos permitió agruparlos, al menos distinguimos dos grandes grupos que clasificamos como elementos de origen principalmente natural o antrópico. Los elementos en cada grupo se relacionaron de manera positiva entre ellos y de manera inversa con los elementos del otro grupo. Si bien creemos que el Cu, Zn, Pb y Cr deben ser de origen antrópico y el Mn, Fe, V y Al pueden ser principalmente de origen natural, esto no implica que solo los elementos de origen antrópico pueden ser peligrosos para la salud humana. El Cr y el Pb representaron el mayor riesgo para la salud de la población, pero enseguida se posicionaron tanto el Cu y el Zn como el Fe, Mn y V. En el capítulo anterior ya se observaba la importancia de incluir a elementos como el Fe y el Mn, ya que llegan a representar un riesgo aún mayor que los metales comúnmente analizados, como el Cu y el Zn; en este capítulo se corroboró dicha importancia.

Después de encontrar las asociaciones y revisar en la literatura cuáles podrían ser las fuentes, es necesario hacer estudios para corroborar los hallazgos. Por ejemplo, encontramos una correlación positiva fuerte entre el Pb y el Cr, mientras que en la literatura se ha reportado que la pintura amarilla contiene cromato de plomo y es una fuente importante de estos metales al polvo; ahora sería conveniente analizar la pintura amarilla de las calles de la CDMX y el polvo urbano de los alrededores. Esto es aún más relevante ya que la evaluación de riesgo a la salud mostró que ambos metales representan un riesgo para los niños. Si comparten fuentes similares, se puede atacar el problema al mismo tiempo.

Ciertamente establecer categorías de acción es una labor ardua que requerirá más trabajo a futuro, sin embargo, proponer niveles basados en las niveles de contaminación fue un primer ejercicio que se queda como un antecedente para seguir trabajando en este tema. Los valores de las categorías propuestas deberán establecerse por ciudad y posteriormente se podrá hacer un análisis de comparación entre las ciudades del país y de otras partes del mundo.

Si bien las concentraciones biodisponibles son útiles para estimar la cantidad de metal que podría ser absorbida por el cuerpo humano a través del aparato gastrointestinal, pierden relevancia cuando la vía de ingreso o ruta de exposición es la inhalación, en especial cuando el tamaño de partícula es muy fino y el polvo puede pasar directamente a la sangre o al cerebro. Además, para metales como el plomo no existe un valor en sangre que se considere seguro; pensando en esto y para garantizar la salud de la población, sería necesario prohibir el uso de este metal en los productos de uso diario, especialmente en las pinturas y barnices de todo tipo.

Una vez diagnosticada la “enfermedad” (contaminación por metales pesados) de las ciudades, es necesario buscar un tratamiento pensando en la resiliencia urbana. Es importante crear ciudades resilientes que puedan ser capaces de reponerse y adaptarse ante eventos adversos como la contaminación. La resiliencia basada en la planeación de la ingeniería moderna utiliza infraestructuras sociales, técnicas y ecológicas para asegurar que las geografías urbanas existentes sigan siendo viables y gobernables.

CAPÍTULO IV

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

De acuerdo con los resultados de los dos capítulos anteriores, nos dimos cuenta de la importancia de considerar al Fe y Mn en los estudios de contaminación urbana por metales pesados. Estos elementos comúnmente se consideran como inofensivos porque los seres humanos tenemos mecanismos para regular sus concentraciones; de hecho, el Fe y Mn son considerados elementos esenciales para el correcto funcionamiento del cuerpo humano. Sin embargo, en exceso también pueden ser tóxicos. La evaluación del riesgo a la salud en las seis ciudades mexicanas (Capítulo II) y en el muestreo intensivo de la CDMX (Capítulo III), mostraron que la exposición a estos metales podría causar padecimientos en la salud de los niños.

La eliminación gradual de los compuestos de plomo de la gasolina ha llevado al uso de otros compuestos que tienen características antidetonantes, como el metilciclopentadienil manganeso tricarbonilo (MMT). El MMT se convierte rápidamente en sulfato de manganeso II ($MnSO_4$), el cual genera la mayor concentración de Mn en el cerebro después de la inhalación, porque es el más soluble de todos los compuestos.

En condiciones de alta exposición por ingestión o inhalación, el sistema humano que regula los niveles de Mn parece fallar, por lo que el Mn se acumula en el cerebro y otros tejidos, generando efectos potencialmente tóxicos. Esta acumulación puede ocurrir incluso a niveles bajos de manganeso en el aire durante la exposición a largo plazo porque la eliminación de manganeso en el cerebro parece ser lenta.

Recientemente, ha surgido una preocupación médica en la Ciudad de México debido a que los niños y jóvenes ya están mostrando las características neuropatológicas tempranas de la enfermedad de Parkinson (Calderón-Garcidueñas et al., 2017). El Mn podría ser una causa; sin embargo, no hay información sobre las concentraciones de Mn en el ambiente de la Ciudad de México. Para obtener un primer indicador de la extensión y distribución de la contaminación en el entorno urbano de la Ciudad de México, optamos por examinar la concentración y carga de Mn en el polvo de las calles de la ciudad, así como identificar las áreas más contaminadas.

En este capítulo se hizo un análisis espacial de la contaminación, evaluándola con el factor de contaminación y el índice de geoacumulación. La autocorrelación espacial se analizó a través de la semivarianza y se interpoló con el método de kriging indicador, utilizando las categorías de contaminación de los índices como umbrales de corte. El Mn fue uno de los metales que obtuvo más autocorrelación espacial, por eso fue posible hacer los mapas de la distribución espacial.

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

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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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Scientific concern about the contamination due to manganese (Mn) has been raised because of its increasing presence in the environment, related to anthropogenic sources such as mining and smelting,[1] Mn alloy production,[2,3] welding, dry alkaline battery manufacturing, Mn salt production, ceramics, glass, aluminum cans and electronic components manufacture,[4] agrochemicals containing Mn such as fungicides and fertilizers,[5] as well as vehicle emissions.[6]

The phasing out of lead compounds from gasoline has led to the use of other compounds that have antiknock characteristics, such as the methylcyclopentadienyl manganese tricarbonyl (MMT).[4,7] MMT is quickly converted to complex manganese phosphate, sulfate ($MnSO_4$) and oxides (most likely Mn_3O_4). From these compounds, $MnSO_4$ generates the highest Mn concentration in the brain after inhalation, because it is the most soluble of all compounds.[8]

Under conditions of high exposure via ingestion or inhalation, the human system that regulates Mn levels appears to fail, thus Mn accumulates in the brain and other tissues, generating potentially toxic effects.[6,8] This accumulation can even occur at low levels of airborne Mn during long-term exposure because Mn clearance in the brain seems to be slow.[4,9]

The main effects of long-term exposure to inorganic Mn include neurological manifestations and biochemical alterations: in the initial stages of the disorder one may find reduced response speed, irritability, intellectual deficit, mood changes and compulsive behaviors to more prominent and irreversible extrapyramidal dysfunction resembling Parkinson disease upon protracted exposure.[9]

Recently, medical concern has been raised in Mexico City because children and youth are already exhibiting early Parkinson disease neuropathological hallmarks.[10] Mn could be a cause; however, there is no information on Mn concentration amounts in Mexico City's environment.

Mexico City has more than 20 million inhabitants, 53 000 industries and approximately 5 million vehicles. Settled street dust constitutes a good surrogate for air pollution. It is easy to sample and manipulate, and it reflects the potential risk of population exposure.[11,12] Mn in street dust can be estimated as concentration (mg/kg), as load per area unit (mg/m^2) or as rate load (mg/m^2/30 days). All these measurements turn up important information.[2,5]

In order to obtain the first indicator of pollution extent and distribution in Mexico City's urban environment, we chose to examine Mn concentration and load in the city's street dust, as well as to identify the most contaminated areas.

Materials and methods

Sampling

Systematic sampling was designed for a 703 km^2 area (figure 1). We collected 482 street dust samples during the dry season (March to April 2017) in a 1 m^2 area in the streets, next to the sidewalks. Stones, leaves, and branches were removed. Dust was gathered in four mounds at the ends of each street block. Then it was collected with plastic tools and deposited in labeled and georeferenced polyethylene bags. Dust samples were dried for two weeks under the shade at room temperature to avoid metal oxidation. They were sieved with a 250 μm mesh and then weighed.

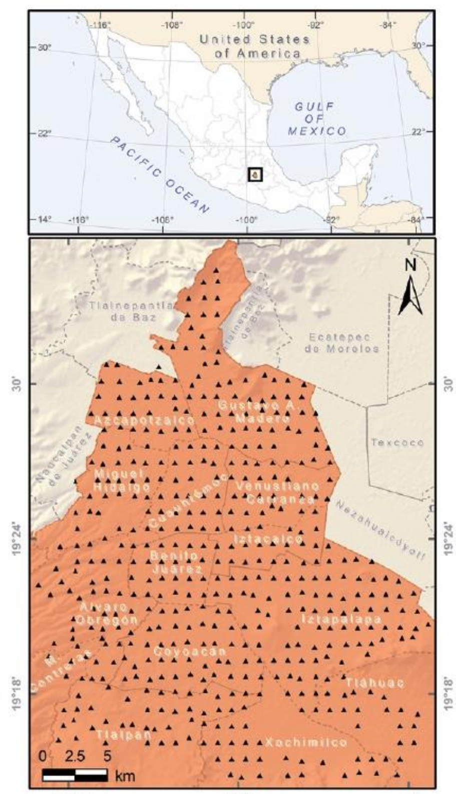

Figure 1. Sampling sites of street dust in Mexico City, 2017

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_3 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^2) and Mn load (mg/m^2) on street dust were carried out, as well as Spearman correlation coefficients for non-normal distribution. Mn load in street dust (mg/m^2) was calculated by multiplying Mn concentration (mg/kg) and street dust load in kg/m^2.

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*.[13]

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[14] or even the minimum value of the study data have been used.[15] 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^2 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);[14] 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.

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

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 geostatistical analysis using GS+ software. The interpolation method was kriging, equations can be found elsewhere.[13] 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_{ing}), 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 HQing/inh/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

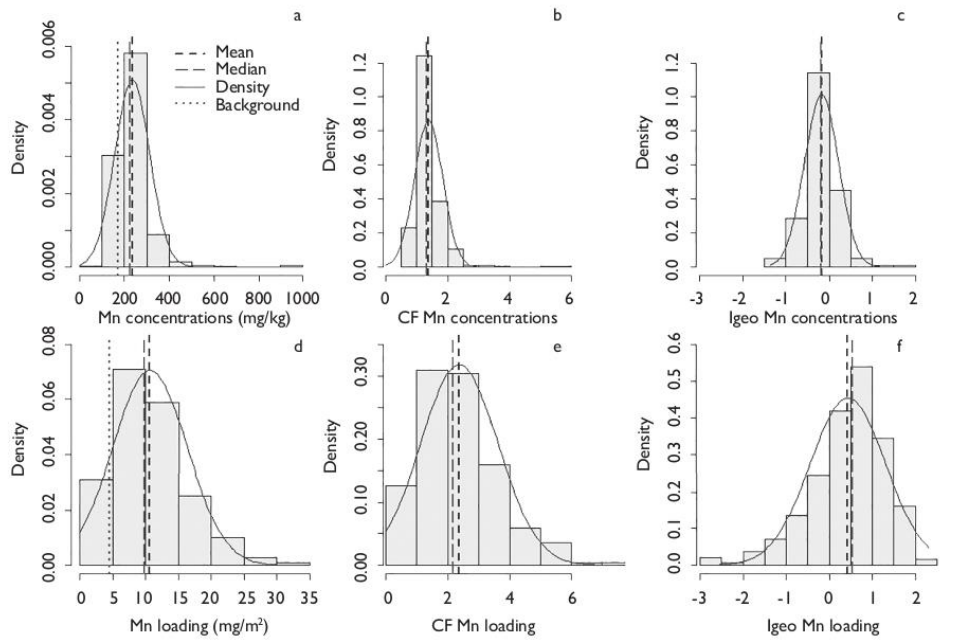

Figure 2. Frequency distribution for manganese (Mn) concentration and load (a and d), for their contamination factors (CF) (b and e) and geoaccumulation index (Igeo) (c and f)

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 g/m^2 with an interval from 5-173 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.

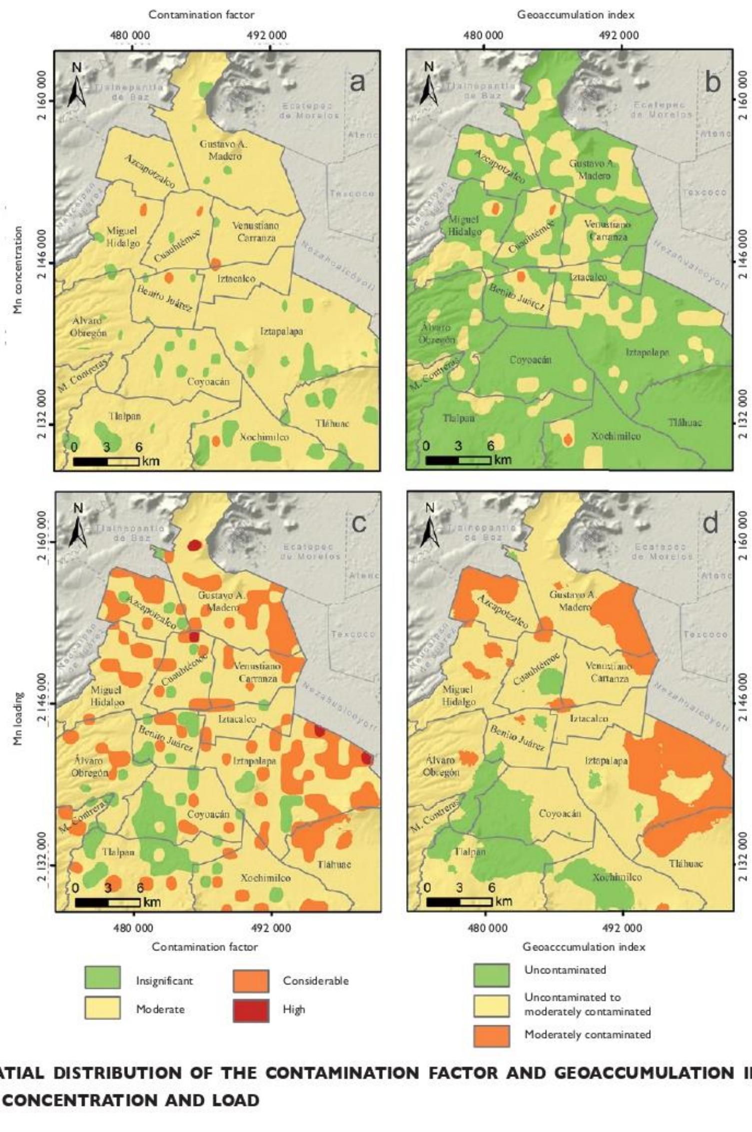

Figure 3. Spatial distribution of the contamination factor and geoaccumulation index for manganese (Mn) concentration and load

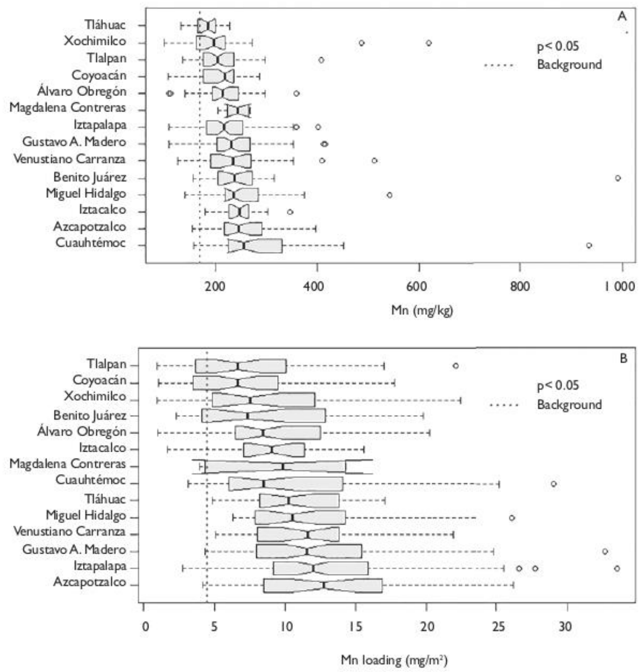

Figure 4. Box and whisker plot for manganese (Mn) concentrations (a) and Mn load (b) by municipality, ordered from lower to higher according to Dunn's non-parametric test

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 Iztpalapa 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.[13,16] 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.[13,17,18]

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.[19,20] 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.[6] 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,[2] in Mexico City's children. Children are most vulnerable because they have higher absorption rates and have not fully developed Mn excretion mechanisms.[4,6]

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^2) than those of Salinas Valley, California intramural dust (171 mg/kg and 1.9 mg/m^2).[5] 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^2/30 days).[2] 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^2/30 day)	12*		9.0-38	2
Salinas, USA	Fungicides maneb and mancozeb	House dust	Load (mg/m^2)	1.9		0.001-25	5
Mexico City	Atmospheric contamination	Street dust		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_{10} and $PM_{2.5}$ concentrations with high levels of the following metals: Mn, Zn, Cu, Pb, Ti, Sn, V and Ba.[10]

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 Popocatépetl volcano, as the volcanic activity is one of Mn main natural sources.[4]

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.[5]

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[5] 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.[1]

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 ($HI_{children}$=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^2. 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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Aportes del capítulo a la tesis

En esta investigación específica para el Mn corroboramos que el nivel de contaminación no necesariamente refleja el peligro que esta representa. El grado de contaminación resultó ser moderado, pero la evaluación de riesgo a la salud indicó que la exposición crónica a Mn podría desencadenar malestares en la salud de los niños de la CDMX. De hecho, al comparar las concentraciones y cargas de Mn de este análisis con otros estudios reportados en la literatura, encontramos que los valores de Mn en el polvo urbano son equivalentes a los de otros sitios donde se reconoce que se utiliza metilciclopentadienil manganeso tricarbonilo en las gasolinas y que, incluso, se han medido concentraciones de Mn que superan los límites de la Agencia para Sustancias Tóxicas y el Registro de Enfermedades (ATSDR), en la sangre de los niños.

En comparación con un sitio con un amplio uso de pesticidas con manganeso, la concentración y la carga promedio de manganeso en el polvo de las calles de la Ciudad de México fueron más altas que las del polvo intramuros del Valle de Salinas, California. En comparación con un sitio adyacente a una planta de producción de aleaciones de manganeso (menos de 2 km), la carga principal de manganeso en la Ciudad de México estuvo muy cerca de la tasa de carga principal de manganeso en Simões Filho, Brasil. Sin embargo, en Brasil, los autores analizaron una tasa de 30 días, mientras que en la Ciudad de México no sabemos cuánto Mn se acumula en ese tiempo.

El análisis espacial resaltó la importancia de considerar tanto la concentración como la carga del elemento, ya que las áreas con los valores más altos fueron distintas para ambas variables y la exposición de la población depende de las dos. Por un lado, entre más concentrado esté el Mn en el polvo, con una pequeña cantidad de polvo que entra al organismo implica una cantidad alta de Mn. Mientras que entre mayor sea la carga de Mn aumenta la probabilidad de que la ingesta de Mn sea mayor.

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CAPÍTULO V

"Is the Urban Form a Driver of Heavy Metal Pollution in Road Dust? Evidence from Mexico City"

En algunas ciudades existen ciertas fuentes que son las que más contribuyen a las concentraciones de los metales pesados en el polvo urbano; sin embargo, hay ciudades que tienen múltiples fuentes y un comportamiento mucho más complejo, como es el caso de la CDMX. Esto lo pudimos observar en el estudio del capítulo III de esta tesis. De hecho, se decidió hacer un muestreo intensivo en la CDMX con la idea de que mejoraría la autocorrelación espacial de las concentraciones de los metales, respecto al muestreo que se utilizó para hacer el análisis del capítulo II. Ya que entre más cercanía espacial mayor similitud. Sin embargo, la sorpresa fue que la autocorrelación espacial disminuyó al aumentar la cercanía entre muestras, por lo cual no pudimos presentar, en esta tesis, mapas geoestadísticos para todos los metales, utilizando métodos de kriging.

Lo anterior nos llevó a buscar otras manera de analizar espacialmente la contaminación por metales pesados y relacionar las características de la forma urbana con la contaminación, para identificar los factores que podrían estar incrementando o disminuyendo las concentraciones de los metales, ya que la influencia de las estructuras y patrones urbanos en el medio ambiente no se comprende bien.

Liang et al. (2019) encontraron que la tasa de urbanización, la formación de metrópolis, el desarrollo económico e industrial, así como la construcción de edificios y carreteras agravan la contaminación ambiental. Jung et al., (2019) encontraron que algunos factores de la estructura urbana que empeoran la contaminación del aire (PM10 y PM2.5) en Corea son la población total, el área comercial, el área industrial, el área total y el producto interno bruto por persona. En la Ciudad de México se ha demostrado que las emisiones de gases de efecto invernadero, provocadas por los desplazamientos, pueden reducirse aumentando la mezcla de usos residenciales y económicos, así como concentrando los puestos de trabajo cerca de los centros de empleo y corredores de actividad económica (Muñiz y Sánchez, 2018). Con base en esos resultados, pensamos que los factores relacionados con la mezcla de usos del suelo residencial y económico, y la densidad de empleo podrían estar relacionados con las concentraciones de metales pesados asociados con el tráfico, como el Pb, Cu y Zn.

La centralización también es un factor importante para determinar la distribución espacial de los metales pesados en el polvo de las calles. Las concentraciones de los metales pesados aumentan gradualmente hacia el centro en algunas ciudades (Alharbi et al. 2019). Solo encontramos este estudio que aborda los efectos de la estructura urbana sobre los metales pesados en el polvo de las calles.

En este capítulo, partimos de las preguntas: (1) ¿Existe una correlación espacial en los contenidos de metales pesados de los puntos muestreados en la Ciudad de México? (2) ¿Cuáles son los principales factores que explican la distribución y concentración de metales pesados en el polvo de las vías urbanas? La primera pregunta se abordó aplicando la prueba de correlación espacial I de Moran a las concentraciones de metales pesados y la segunda pregunta utilizando modelos de regresión lineal para analizar la relación entre los metales pesados y los factores de la forma urbana.

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Article

Is the Urban Form a Driver of Heavy Metal Pollution in Road Dust? Evidence from Mexico City

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Abstract: Environmental pollution is a negative externality of urbanization and is of great concern due to the fact that it poses serious problems to human health. Pollutants, such as heavy metals, have been found in urban road dust; however, it is unclear whether the urban form has a role in its accumulation, mainly in cases where there is no dominant unique source. We collected 482 samples of road dust, we determined the concentrations of five heavy metals (Cr, Cu, Pb, Zn, and Ni) using inductively coupled plasma optical emission spectrometry (ICP-OES), and then we derived the pollution load index (PLI). After estimating the mostly anthropogenic origin of these pollutants based on global levels of reference, there were two main aims of this study. Firstly, to analyze the spatial correlation of heavy metals, and secondly, to identify the main factors that influenced the heavy metal concentrations in the road dust of Mexico City. We did this by using a spatial autocorrelation indicator (Global Moran's I) and applying ordinary least squares (OLS) and spatial regression models. The results indicated low levels of positive spatial autocorrelation for all heavy metals. Most variables failed to detect any relationship with heavy metals. The median strip area in the roads had a weak (significance level of 90%) but consistent positive relationship with Cr, Cu, Ni, Pb, and the PLI. The distance to the airport had a weak (significance level of 90%) and inverse relationship with Pb. Manufacturing units were associated with an increase in Cu (significance level of 95%), while the entropy index was associated with an increase in Ni (significance level of 95%).

Keywords: road dust; heavy metals; Mexico City; urban pollution; urban form

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1. Introduction

The world is becoming increasingly urban. In the developing world, Latin America has already achieved this transition toward an urbanized society. For example, in Mexico, it is estimated that 80% of the population lives in urban areas [1]. The capital, Mexico City, along with its metropolitan area, concentrates around 17.5% of the country's population and has over 40,000 industries and 4 million vehicles that consume more than 40 million liters of fossil fuels per day, releasing, as a result, thousands of tons of pollutants into the urban environment [2]. Environmental pollution is one of the main negative externalities of huge urban agglomerations, especially in the developing context where weak institutions and planning efforts aggravate the problem [3].

Air pollution has attracted a great deal of attention, as it is considered one of the main causes of death in cities [4]; therefore, air pollution has been widely researched. Less attention has been paid to road dust pollution [5]; however, we assume that they are likely interlinked. Research reported that road dust is a sink for polluting emissions, which are deposited on the surface of streets, sidewalks, and windows [6]. At the same time, road dust is a source of pollutants of atmospheric particulate matter [7]. Studies found that urban structure factors, such as land use, industrial development, and building construction, worsened the pollution in urban areas [8,9]. From a social point of view, aspects such as tax revenue and education level are associated with a decrease in urban pollution [9]. In terms of country-level data, researchers have tested the environmental Kuznets curve (EKC) hypothesis, which states that the relationship between gross domestic product (GDP) per capita and different environmental indicators exhibit an inverted-U curve [10,11].

Heavy metals are some of the major pollutants found in road dust [12–14]. Due to their abundance, toxicity, persistence, and bioaccumulation, heavy metals can cause permanent damage to ecosystems and humans [15]. The severity of health problems due to heavy metal toxicity depends on several factors, such as the type and form of the element, the route and duration of exposure, and to a greater extent, the susceptibility of each person [16]. Low concentrations of non-essential heavy metals (As, Hg, Pb, Cr, and Cd) can be lethal to animals. In Mexico City, the median levels of lead in children's blood were found to be close to the reference level for public health interventions (5.0 μg/dL) [17]. Prenatal lead exposure has been associated with a decrease in child growth [18]. Even essential metals (Zn, Cu, and Ni), required for the proper function of different enzymes, can become toxic in high concentrations, inducing the generation of reactive nitrogen and oxygen species. This can result in the peroxidation of lipids, as well as the functional deterioration of DNA and proteins [19]. Nickel diminishes the protection that taurine provides against neurodegeneration [16].

The sources of heavy metals in road dust can be diverse. In some cities, the origins are very specific to major stationary emitting sources; for example, the smelting industry [13], e-waste recycling [20,21], and mining activities [22]. Natural processes may also be the cause of an increase in the concentrations of trace metals [23]. Using pollutant-tracing approaches, mobile sources of heavy metals have also been identified, such as vehicular emissions [24]. It is considered that Cu, Pb, Zn, and Cr are traffic-related metals [25–27]. The quantities emitted vary, but some metals can be linked to specific vehicle parts. For example, Cu emissions are generally related to brake abrasion [28,29]; Zn is mainly emitted by tire wear [25], as well as from diesel exhaust emissions [27]. Some Zn compounds are used as additives for motor oil [30]. In the case of Cr, this metal can originate from exhaust emissions [26]. Pb can come from brakes and the loss of lead wheel weights [27]; Cr and Pb have been reported to originate also from yellow street paint which contains lead chromate. Paint and pigments crack, peel, and turn to chalk, mobilizing metal particles into the urban environment [31,32]. Ni can come from mixed industrial/fuel-oil combustion [30].

In cities with an economy mostly related to the service sector, there are multiple small and scattered possible sources, which can be mobile or fixed. Therefore, it is vital to determine what characteristics of the urban form act as driving factors of heavy metal pollution in road dust to obtain a better understanding of the cycle in the city. This would bring insights to help plan measures that limit the exposure of the population to these pollutants.

This work goes beyond the description of heavy metals in urban road dust. To the best of our knowledge, this is the first attempt to make systematic statistical inferences regarding the characteristics of the urban form that could influence the concentration of heavy metals in urban road dust. In this paper, we respond to two main questions: (1) Is there a spatial correlation in the heavy metal contents of points sampled across Mexico City? (2) What are the main factors that explain the distribution and concentration of heavy metals in urban road dust? The first question is addressed by applying the Moran's I spatial correlation test to the heavy metal concentrations, and the second question by using linear regression models to analyze the relationship between heavy metals and the urban form.

2. Literature Review

There have been several approaches to evaluate the effects of the built environment on urban pollution, mainly in the air and taking the city as the unit of analysis. Liang et al. [9] in the Beijing–Tianjin–Hebei urban agglomeration, using a geographically weighted regression model, found that the rate of urbanization, the formation of metropolises, and the level of economic and industrial development, as well as building and road construction aggravate the environmental pollution (measured as an index for air, soil, and water pollution).

Predictors associated with a decrease in urban pollution include the industrial level, tax revenue, education level, and the use of the internet. Implementing taxes to protect the environment promotes the modernization of highly polluting industries, while an increase in resident incomes promotes a shift in the regional economy to low-pollution, knowledge-based industries. An improvement in the educational level drives environmental protection technology, improving the environmental quality.

Jung et al. [8], in Korea, applying a Bayesian spatial regression model, found that the total population, the commercial area, the industrial area, the total area, and the gross domestic product per person are factors associated with worse air pollution (nitrogen oxides, sulfur oxides, PM10, and PM2.5). Zhang et al. [33] in Calgary, Canada, using a land-use regression model, found that the main factors that increased the heavy metal concentrations in airborne particulate matter were industrial point sources.

Industrial and commercial zoning, as well as traffic indicators and population density, were also good predictors for most elements. In the case of specifically addressing the pollution by heavy metals in road dust, Alharbi et al. [14] compared the spatial distribution in two metropolitan cities (a typical corridor city and a compact city) of Saudi Arabia. They found that centrality was an important factor for determining the spatial distribution of heavy metals in road dust, which increased in concentration gradually toward the city center.

In Mexico City, research demonstrated that greenhouse gas emissions, caused by commuting, can be reduced by increasing the mix of residential and economic uses, as well as concentrating jobs near employment centers and economic activity corridors [34]. Studies determined that the sources of heavy metals in the urban road dust in Mexico City must be anthropogenic [35]. Therefore, we hypothesized that factors related to industrial land use, mixed land-use, and job density could be related to the concentrations of heavy metals associated with traffic, like Pb, Cu, and Zn. We hypothesized a negative association with the urban vegetation cover assuming a depuration effect.

3. Study Site

The Mexico City metropolitan area had a population of around 21,000,000 inhabitants in 2015 and was among the four largest urban agglomerations in the world [36]. The metropolitan area is formed by the urban areas of three states: Mexico City, the State of Mexico, and Hidalgo. Mexico City comprises mostly the central and south parts of the metropolitan area. The metropolitan area is located in a valley at 2240 m.a.s.l. The unique topography, with mountains surrounding the metropolis, results in thermal inversions preventing the dispersion of pollutants during the winter season from November to April.

Sierra del Ajusco's mountains in the southwest prevent the passage of the prevailing winds (northeast to southwest direction) and, thus, the dispersion of pollutants [37]. The land use geography in Mexico City is complex, but as a general description, Rodríguez-Salazar et al. [38] stated that the main industrial center, with a high population density, is located in the northern part of the city. The central part includes the historical and business center of the city, with high commercial activity.

The southern area has been dominated by residential and commercial activities. It was in the 1980s with the liberation of the economy that a process of absolute and relative deindustrialization related to the global economy began in the metropolis [39]. Factories were obligated to settle beyond the limits of Mexico City (formerly called the Federal

District) and the consolidation of light manufacturing began; overall, the tertiarization of the economy led to commercial and services activities beginning to dominate the economy in the city [40].

4. Materials and Methods

4.1. Data Collection

We collected 482 road dust samples associated with 482 sampling points for this study in a semi-grid pattern of approximately 1-km-wide squares across the urban area of Mexico City (Figure 1). The project was executed only within this political jurisdiction given that this was a project funded by the government. Thus, this sampling can be considered systematic, which covered the urban and peri-urban parts of the city. The collection of samples was done during the dry season in April and May (30 days) of 2017. The atmospheric conditions were stable; the temperature was between 15 and 20 °C, with winds in a north to south direction and speeds between 4 and 8 km/h [41]. During the sample collection campaign, there were no rains. All samples were collected under the same conditions: in a square meter of area on the pavement, below the sidewalk, the distance from the pedestrian area was between 0 and 1 m. All samples were taken in horizontal streets and without sedimentary traps (holes or potholes) to avoid biases. Because the sampling was systematic, the distance to the traffic lights was not considered. The urban road dust was sampled by brushing it from a 1 m^2 area at each point. The dust load in each sample point is defined as the amount of dust (<250 μm) per area of street space—in this case, 1 m^2—after the coarse material is removed [42,43]. Particles of less than 250 micrometers are most likely to adhere to hands and therefore be involuntarily ingested [44]. This particle size can be easily obtained in the laboratory using a sieve, which is very useful when analyzing a large number of samples.

The concentrations (mg/kg) of 14 elements were determined via inductively coupled plasma optical spectrometer (ICP-OES), which is a methodology used previously to this end [20,45,46]. However, only the most polluting metals identified in a previous study [47] were considered in the present work. Those elements were Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb), and Zinc (Zn). The concentrations were determined by digesting 0.4 g of each sample with 20 mL of concentrated HNO_3, using Teflon PFA beakers, in an ETHOS Easy microwave digestion system (Millestone Inc, Milan, Italy). The temperature was brought to 175 ± 5 °C in approximately 5 min and was kept for 4.5 min. After cooling, the digested samples were filtered with Whatman No. 42 paper, transferred into 50 mL flasks, and graduated with water type A (US-EPA method 3051A). Quality controls for the acid digestion method included reagent blanks and sample duplicates. The quality assurance and quality control (QA/QC) results showed no signs of contamination or loss in any of the analyzes. An Agilent Technologies 5100 ICP-OES (US: EPA method 6010C), sourced from Santa Clara, CA, USA, was used to analyze, in triplicate, the digestions and quality controls. A multi-elemental QCS-26R reference certified material was used (high purity brand) to prepare the calibration curve. The radiofrequency power (RF power) was 1.2 kW, the nebulization flow was 0.7 L/min, and the argon plasma flow was 12.0 L/min.

The pollution load index (PLI) was calculated as the geometric average of the Cr, Cu, Ni, Pb, and Zn results divided by their corresponding background value [48]. The contamination factors were obtained by dividing the concentrations of each heavy metal at each sampling point by the background value. We used the world background values for soils [49], which were obtained by determining heavy metal concentration in soils from places with the least anthropic disturbance possible. A PLI value close to 1 indicates that the heavy metal load was close to the naturally occurring level, while a PLI > 1 indicates contamination [48,50]. In Table 1, we can see the descriptive statistics of the dependent variables. The concentration of Pb in one sample was below the detection limit (Pb = 3.75 mg/kg). We took that limit as the Pb content in the sample because the statistical analysis requires numerical variables.

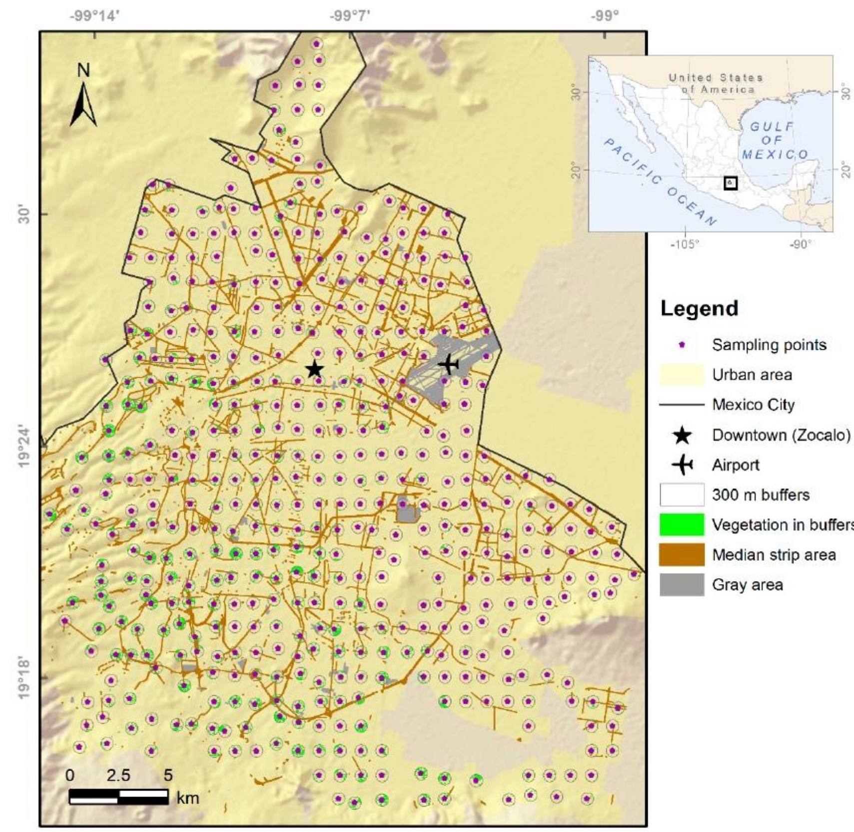

Figure 1. The study site and sampling point locations.

Table 1. The descriptive statistics of the heavy metal concentrations (mg/kg) in the 482 road dust samples.

Heavy Metal	Global [1] Background	Minimum	Maximum	Median	Mean	Standard Deviation
Cr	59.5	15.0	441.0	43.7	51.4	34.3
Cu	38.9	6.2	847.1	81.2	99.7	75.8
Ni	29	13.7	148.7	35.0	36.3	13.9
Pb	27	8.8	1907.8	101.2	128.2	134.6
Zn	70	18.7	4827.6	229.9	280.7	294.4
PLI [2]		0.3	6.3	2.0	1.9	0.8
Dust load [3]		5.4	173.3	43.0	46.4	23.2

Note: [1] Kabata-Pendias (2011); [2] unitless; [3] Amount of dust <250 μm in 1 m^2 of the street (g/m^2).

Different explanatory variables were measured at each sampling point (Table 2). The population density was measured as inhabitants per hectare at the census tract level using the 2010 census data from the National Institute of Statistics and Geography [51]. The population density can determine the intensity of various socioeconomic activities that worsen air pollution [8]. Job density considered the number of jobs per hectare within the traffic analysis zone (TAZ) according to the 2017 Household Origin-Destination Survey [52]. Jobs were estimated according to the number of trips to work to a certain TAZ.

Table 2. Descriptive statistics of the covariates in the analysis. n = 482.

Covariate	Minimum	Maximum	Median	Mean	Standard Deviation
Population density (hab/ha)	0.0	443.1	132.4	139.8	81.1
Job density (jobs/ha)	4.2	349.7	30.0	43.9	50.7
Street intersections	0.0	162.0	38.0	45.4	29.2
Road surface (m^2)	2922.8	99,909.4	47,475.6	47,196.8	15,477.1
Distance to the airport (m)	803.2	25,424.3	12,792.8	12,571.7	5329.5
Distance to the city center (m)	633.9	24,361.9	10,304.1	10,977.3	5245.1
Manufacturing units	0.0	377.0	13.0	15.5	21.1
Potentially polluting units	0.0	24.0	1.0	1.4	2.7
Gray area (ha)	0.0	15.7	0.0	0.3	1.4
Entropy index	0.0	0.8	0.3	0.3	0.2
Vegetation (%)	0.0	65.6	5.5	10.0	11.9
Distance to vegetation (m)	0.0	329.3	22.0	40.2	48.2
Median strip area (m^2)	0.0	67,855.0	1498.0	4531.3	8161.5
Marginalization index	−1.4	1.3	−0.7	−0.7	0.5

Note: A minimum value of zero is expected when the covariate is not present at any of the road dust sampling points.

For the rest of the covariates, we considered a 300 m ring buffer around each sampling site. Street intersections were identified using the street network shapefiles from the official geostatistical framework [51], and, with the network analysis tool in ArcGis 10.0, we counted all intersections within the buffers. The road surface was estimated using this same layer. Street classification is not consistent between the municipalities of Mexico City; thus, for simplicity, we assumed three types of roads and their dimensions: local streets as 7 m wide, intermediate roads as 15 m wide, and highways as 25 m wide. We propose that this classification produces a conservative estimation of the road surface in each buffer.

Based on the 2014 urban geostatistical framework, we calculated the total area of polygons corresponding to large concrete surfaces, such as civil airfields, malls, markets, aviation tracks, and electrical substations. We called these surfaces "gray areas". The median strip area, which is usually covered with vegetation, was estimated using this same dataset, which has polygons explicitly categorized with this name, road median strip. The distance to the city center was calculated using the Euclidean distance (the straight line that connect two points assuming there are no obstacles in the space) from each sampling point to the historical center of downtown (also called Zócalo-Tenochtitlán).

The distance to the airport also considered the Euclidean distance to the Benito Juarez International Airport. The number of manufacturing units in each buffer was calculated based on those classified by the North American industry classification system in 2018. The number of potentially polluting units considered the economic units related to mining, construction, and pipelines in the National Statistical Directory of Economic Units (Directorio Nacional de Unidades Económicas, DENUE) [53].

We calculated the entropy index as a measure of the land-use mix, considering the relative percentages of different land-use types within an area. The entropy index varied from 0 to 1, with 0 indicating a homogeneous area with only one land-use type, and the mix level increasing as the index increases. Here, P^j is the percentage of each land-use type j in the area, and $k \geq 2$ is the number of land-use types j.

$$ENT = -\left[\sum_{j=1}^{k} P^j ln\left(P^j\right)\right] / ln(k) \quad (1)$$

The entropy index was calculated using information from the publicly available urban data website "Portal de Datos de la Ciudad de México" [54]. Each land-use polygon was georeferenced as a data point, and information about the land use type and the area was provided. Thus, all polygons whose centroid lay within the 300 m buffer were considered in the estimation. There were 113 categories of land-use descriptions, and two categories were excluded (no zoning—"sin zonificación"—and existing uses—"usos existentes").

Then, the 111 categories were simplified to six general categories: (1) green areas, parks, open spaces, and agricultural areas; (2) residential; (3) office and commercial; (4) industrial; (5) mixed-use; and (6) institutional and public facilities. The official information did not provide concrete and clear definitions of the 111 initial categories; thus, a series of assumptions were made in the collapsing process. For example, land use corresponding to residential and low-scale retail was considered residential. It is very common that, in middle and low-income neighborhoods, small-scale retail coexists with residential uses.

Every original category that includes office and services, was counted in category 3. The mixed-use category included all polygons that were explicitly considered as this on the website as well as those centers of traditional towns and suburbs called "Centros de Barrio". Different land uses, such as residential, commercial, office, and open spaces, converge in these places. The column open area was used for those polygons lacking information about their area. Other corrections were made through a visual inspection on Google Earth for polygons with an important area within the buffer but not initially taken into account when their centroid was not within the buffer.

We calculated the mean normal difference vegetation index (NDVI) in each buffer zone from satellite images (March to May 2017) obtained from Planet Scope for Mexico City to estimate the urban vegetation. A supervised classification was made from the NDVI raster file in the QGIS version 3.4 software, using the "Semi-automatic Classification Plugin" tool. Two classes were determined: (1) vegetation, for the highest NDVI values (>0.6); and (2) no vegetation or the remainder of the urban area. Subsequently, the results of the classification were transformed into a shapefile to obtain the vegetation polygons and to calculate their area.

The vegetation polygons intersecting the buffers were summed up to obtain the total area of vegetation within each buffer. Finally, the total vegetation area was divided by the buffer surface and multiplied by 100 to obtain the percentage of vegetation present in each buffer, referred to here as "vegetation (%)". Another variable related to vegetation is the Euclidean distance from the sampling point to the closest vegetation polygon. Finally, as a measure of the socioeconomic characteristics, the index of marginalization was extracted at the census tract level for each sampling point. This index can have negative and positive values; the highest positive values correspond to the highest levels of marginalization [55].

We considered local variables as those related to characteristics of the immediate urban environment that surrounds the sample point. Examples of these are population density, percentage of vegetation, and the number of potentially polluting units. On the other hand, regional variables were those that characterize a sample with respect to a metropolitan point of reference. Examples are the distance from the city center, and the distance to the airport.

4.2. Spatial Autocorrelation

The univariate spatial autocorrelation was examined using Moran's I statistics for global measurements of spatial dependence [56]. The formula for standard correlation is expanded to incorporate a spatial weight matrix. Thus, its formula is defined as:

$$I = \frac{n}{S_o} \frac{\sum_{i=1}^{n} \sum_{j=1}^{n} w_{i,j} z_i z_j}{\sum_{i=1}^{n} z_i^2} \tag{2}$$

where n is the number of sample points indexed by i and j, Z_i is the deviation of an attribute (in this case, the heavy metal content) for point i from its mean, $W_{i,j}$ is the spatial weight between point i and j, while So is the aggregate of all spatial weights.

We defined neighbors as those spatial units within a specific distance threshold. For this analysis, we tested different thresholds of contiguity (1600, 5000, 10,000, and 15,000 m). All neighbors were weighted equally and then row standardized. This means that it depends on the number of neighbors to determine the final weight, as the larger the number, the lower the weights.

The range of Moran's I varies with the weights matrix, but it is usually expected to vary from -1 to 1. The sign corresponds to the type of autocorrelation, i.e., positive or negative. Values close to 1 indicate high spatial autocorrelation while values close to zero mean null spatial autocorrelation. The Moran's test for spatial autocorrelation uses the spatial weights matrix and tests the null hypothesis statement of 'no spatial autocorrelation'. In other words, the alternative hypothesis is if the Moran's I is greater than zero. Then, a p-value lower than 0.05 means there is strong evidence to reject the randomization null hypothesis in favor of an alternative hypothesis. We used the function "moran.test" of the R Project program to test the spatial autocorrelation. These results were compared with a Moran Monte Carlo permutations test and also using an inverse distance criterion to determine weights for neighbors. These results were relatively consistent with the moran.test function.

4.3. Regression Models

When two variables are close to a perfect linear combination of one another, it is called collinearity. Thus, when more than two variables are involved, it is called multicollinearity. This represents a problem when applying linear regression models given that it can result in unstable regression estimates with high standard errors. Variance inflation factors (VIF) measure how much the variance of the estimated regression coefficient is inflated by the existence of correlation among the predictor variables. The general rule of thumb is that VIFs exceeding 4 warrant further investigation, while VIFs exceeding 10 signify serious multicollinearity requiring correction. Thus, the variance inflation factor (VIF) was used to test the multicollinearity between the factors.

Ordinary least squares (OLS) regressions were tested for all response variables, i.e., the heavy metals contents. Due to a lack of normality evaluated through the Shapiro test, all covariates and dependent variables were log-transformed using a natural logarithm. Some variables with zero values were transformed using the natural logarithm of 1+x. An OLS model can be described in the form:

$$\mathrm{Y} = \beta\mathrm{X} + \varepsilon \tag{3}$$

where Y is the dependent variable, X is the independent variable, and β its coefficient. If we consider several covariates, then we have a vector of X and β. Finally, ε is the error term. Coefficients of log-log regression models can be interpreted in the following way, given a coefficient in the form "0.X". We expect about X increase in heavy metal content when the covariate increases by 10%.

After that, a spatial diagnostic of the OLS residuals was applied to select the appropriate spatial regression model for each of these dependent variables [57,58]. There are two main sources of spatial dependence: (1) spatial diffusion, which occurs when spatially proximate units are influenced by the behavior of their neighbors. This was modeled via a Lagrange multiplier spatial lag model (LMlag), estimated by the maximum likelihood; and (2) the geographic clustering of covariates, also called attributional dependence. This was modeled via a spatial error model (LMerror), estimated either with the maximum likelihood or with the generalized method of moments.

The Spatial lag model takes the form:

$$\mathrm{Y} = \beta\mathrm{X} + \rho\mathrm{Wy} + \varepsilon \tag{4}$$

Here, to the OLS equation it is added a W term that stands for the spatial weights matrix and the ρ coefficient.

In the case of the Spatial error model, this takes the form:

$$\varepsilon = \lambda\mathrm{W}\varepsilon + \mathrm{v} \tag{5}$$

We can see that this model is related to the error term, where W is also the spatial weights matrix, it is included the lambda coefficient and v is an uncorrelated additional error term.

Lagrange multiplier diagnostics for spatial dependence in R use the regression object and the object of neighbors and weights. In the case of the Spatial lag model, we test for a missing spatially lagged dependent variable, in other words, the null hypothesis is that rho = 0. In the case of the Spatial error model, the null hypothesis is that lambda (λ) = 0. The first step was to run the non-robust LMlag and LMerror diagnostic tests, the results of which can lead to three different paths: (1) if none of these diagnostic tests are statistically significant, then the OLS estimates are sufficient to model the dependent variable; (2) if only one of the diagnostics determined the presence of spatial dependence, the corresponding model was estimated; (3) if both diagnostic tests were significant, then both the robust LMlag and the robust LMerror diagnostics were tested, and the model with the largest value was used [58]. All the statistical analyses were done with the R Studio program, version 3.6.1.

5. Results

The median concentrations of the heavy metals were higher than the global background value in the soils, except for Cr. In the case of Ni, the median concentration is only 6 units above the global background level. Indeed, 91.5% of the samples had a pollution load index (PLI) greater than 1 (median=2) (see above Table 1). We propose that this is an important indication of the anthropogenic origin of the heavy metals found in the road dust from Mexico City. The dust load varied considerably from 5.4 to 173.3 g/m^2. As it is very difficult to control aspects related to the deposition of dust in the points of sampling, we decided to work with the heavy metal concentrations instead of the total heavy metal contents as dependent variables.

The mean concentrations of the heavy metals reported here are lower than those reported in a previous study in Mexico City (sampling in 2011) [35]. Even though there are not yet maximum permissible levels in urban road dust, the content of heavy metals in the samples is fortunately still lower than the closest regulation, i.e., the content of heavy metals in soils from residential areas. Therefore, it is important to continue monitoring for long-term fluctuations to avoid an increase in these pollutants and prove the good performance of the environmental policies.

5.1. Spatial Autocorrelation

Moran's I was significant for Cr only at a vicinity distance of 5000 m; however, the coefficient of autocorrelation was only 0.03. Therefore, a general pattern of clustering was not expected (Table 3). Cu had a significant Moran's I at all vicinity distances, but, again, the coefficient was very small. Moran's I for Ni became significant at a distance of 10,000 m and was even more significant at 15,000 m; however, the coefficient was only 0.01.

Contrary to Ni, Moran's I for Pb was significant at short distances (1600 and 5000 m), but, again, the coefficients were smaller than 0.1. Zn had a significant Moran's I at all distances, except at 5000 m, with the coefficient smaller than 0.1. Moran's I for the PLI was significant at all distances, and it was greater than 0.1 at 1600 m; hence, a general pattern of clustering could be expected at a short vicinity distance. The dust load had a significant Moran's I at all distances; thus, the coefficients (and consequently the autocorrelation) decreased as the distance increased.

As the global Moran's I was very close to 0 for all heavy metals, indicating low levels of positive spatial autocorrelation, it was not necessary to explore the local version of this index to identify any spatial clustering pattern. This is an initial sign that the local aspects are more relevant than any regional process in determining the concentrations of these metals.

Table 3. The global Moran's I and test of statistical significance at different vicinity distances (1600, 5000, 10,000, and 15,000 m).

Variable	1600 m	*p*-Value	5000 m	*p*-Value	10,000 m	*p*-Value	15,000 m	*p*-Value
Cr	0.05	0.07	0.03	0.00 ***	0.00	0.41	0.00	0.72
Cu	0.08	0.00 **	0.05	0.00 ***	0.02	0.00 ***	0.01	0.00 ***
Ni	0.00	0.11	0.02	0.06	0.01	0.01 *	0.01	0.00 ***
Pb	0.06	0.02	0.03	0.00 **	0.00	0.14	0.00	0.49
Zn	0.06	0.01 *	0.01	0.14	0.01	0.01 *	0.01	0.00 ***
PLI	0.13	0.00 ***	0.06	0.00 ***	0.02	0.00 ***	0.01	0.00 ***
Road dust load	0.18	0.00 ***	0.16	0.00 ***	0.10	0.00 ***	0.04	0.00 ***

* Significance at 95% confidence, ** 99% confidence, and *** 99.9% confidence.

In Table 4, we can see the *p*-values of the diagnostic tests of the OLS residuals. All non-robust tests were non-significant. In the case of the robust versions, for Cu, Ni, Zn, the PLI, and the dust load, the tests were also non-significant, which indicates that OLS is a suitable modeling approach. For Pb, the spatial error model was significant (alpha at 5%); thus, for this metal, the results of the spatial error regression model were analyzed.

Table 4. *p*-values of the diagnosis of the ordinary least squares (OLS) regression residuals.

Test	Cr	Cu	Ni	Pb	Zn	PLI	Dust Load
Lm (lag)	0.11	0.15	0.51	0.51	0.89	0.65	0.50
LM (error)	0.06	0.24	0.75	0.14	0.56	0.47	0.24
Robust LM (lag)	0.11	0.35	0.14	0.07	0.31	0.50	0.18
Robust LM (error)	0.06	0.65	0.17	0.02 *	0.24	0.38	0.10

* Significance at 95% confidence.

5.2. Factors Influencing the Heavy Metal Concentrations

The VIF indicators were below 4.3 for our vector of covariates, which indicates a low risk of multicollinearity that could bias the coefficient estimations. Overall, there were few significant relationships between the covariates and the heavy metal concentrations, including the road dust load (Table 5). Population density had a null association with all of the heavy metals, which indicates that the number of people in the surroundings of the sample point was not relevant to explain the presence of our dependent variables.

Table 5. Results of the ordinary least squares regressions.

Covariate	Cr			Cu			Ni			Pb		
	beta	*p*		*beta*	*p*		*beta*	*p*		*beta*	*p*	
Intercept	**4.94**	**0.00**	***	**3.64**	**0.03**	*	3.30	0.00	***	6.76	0.00	**
Population density (inhabitants/ha)	0.00	0.98		−0.03	0.40		−0.02	0.36		0.03	0.49	
Job density (jobs/ha)	−0.04	0.46		0.11	0.10	.	−0.01	0.76		0.04	0.61	
Street intersections	0.02	0.71		−0.06	0.49		0.02	0.63		0.01	0.93	
Road surface (m^2)	−0.07	0.48		0.03	0.85		−0.07	0.35		−0.09	0.59	
Distance to the airport (m)	−0.06	0.38		0.05	0.57		0.10	0.06	.	−0.18	0.11	
Distance to the city center (m)	0.01	0.87		−0.04	0.71		0.02	0.79		−0.03	0.84	
Manufacturing units	0.04	0.34		0.10	0.04	*	0.02	0.37		0.07	0.27	
Potentially polluting units	0.08	0.12		−0.03	0.62		−0.02	0.58		0.00	0.96	
Gray area (ha)	0.00	0.97		0.08	0.45		0.05	0.43		−0.03	0.81	
Entropy index	0.02	0.93		-0.17	0.46		0.37	0.01	**	0.15	0.60	
Vegetation (%)	−0.01	0.82		−0.03	0.60		−0.05	0.10		−0.01	0.90	
Distance to vegetation (m)	−0.01	0.68		0.02	0.53		−0.03	0.21		0.01	0.84	
Median strip area (m^2)	0.01	0.10	.	0.02	0.09	.	0.01	0.09	.	0.02	0.08	.
Marginalization index	−0.01	0.67		−0.01	0.80		0.01	0.80		−0.06	0.26	
r^2	−0.01			0.06			0.02			0.05		

Table 5. *Cont.*

Covariate	Zn			PLI			Dust Load		
	beta	*p*		*beta*	*p*		*beta*	*p*	
Intercept	2.98	0.07	.	0.59	0.62		8.13	0.00	***
Population density (inhabitants/ha)	−0.02	0.59		-0.01	0.77		−0.01	0.81	
Job density (jobs/ha)	0.08	0.22		0.04	0.43		−0.16	0.01	**
Street intersections	−0.11	0.16		-0.02	0.69		0.09	0.25	
Road surface (m^2)	0.23	0.09	.	0.00	0.98		−0.30	0.02	*
Distance to the airport (m)	0.03	0.76		−0.01	0.84		−0.06	0.44	
Distance to the city center (m)	−0.03	0.78		−0.01	0.86		−0.03	0.79	
Manufacturing units	0.08	0.10		0.06	0.08	.	−0.04	0.43	
Potentially polluting units	−0.03	0.65		0.00	0.99		0.12	0.05	.
Gray area (ha)	0.05	0.60		0.03	0.69		−0.01	0.91	
Entropy index	−0.15	0.51		0.04	0.79		0.39	0.07	.
Vegetation (%)	−0.04	0.43		−0.03	0.46		−0.13	0.00	**
Distance to vegetation (m)	0.03	0.37		0.01	0.84		0.01	0.77	
Median strip area (m^2)	0.01	0.21		0.01	0.04	*	0.01	0.28	
Marginalization index	−0.04	0.29		−0.02	0.41		0.02	0.51	
r^2	0.07			0.04			0.10		

beta is the slope; *p* represents the *p*-value; . Significance at 90% confidence, * 95% confidence, ** 99% confidence, and *** 99.9% confidence.

Job density had a weak positive association (significance level of 90%) with Cu. However, there was not any significant relationship with the rest of the metals. Our initial expectation was that in places with high job density, the heavy metal concentrations would be high due to an increased number of trips to work and, therefore, increased levels of polluting emissions. Thus, the association found between job density and Cu supports our initial hypothesis since the emission of this metal from vehicles has been associated with tire wear and brake abrasion [29] With the dust load, job density had a significant inverse association (significance level of 99%). We could expect about a 1.6% increase in the dust load when the job density decreased by 10%. This could be explained if we consider that employment centers in Mexico City are related to tertiary types (offices and commerce) that are not necessarily highly polluting activities. These workplaces tend to be better cared for and cleaner than lower-class areas.

The street intersections variable was not significant with any metal. The initial expectation was that this variable could represent the emissions of heavy metals due to car braking, with the higher the number of street intersections representing higher braking frequency. However, the braking emissions are likely not large enough to be detected through street intersections.

The road surface had a weak positive relationship with Zn (significance level of 90%). The emissions of Zn from vehicles have been associated with the combustion of lubricating oil [30], tire wear [25], and diesel exhaust emissions [27]. Therefore, this result supports the expectation that the road surface is a suitable proxy variable for traffic flow as a determinant of Zn in the road dust. On the other hand, there was a significant inverse association between the road surface and the dust load (significance level of 95%). We could expect about a 3% increase in the dust load when the road surface decreased by 10%. These surfaces are likely maintained and cleaned as brigades of cleaning workers sweep the larger roads.

The distance to the airport had a positive but weak relationship with Ni (significance level of 90%). Higher concentrations of this metal were found further away from the airport; therefore, the airport might not be an important source of this metal. An inverse weak association (significance level of 90%) was found for Pb and the distance to the airport in the spatial error model (Table 6). The coefficient tells us that we could expect about a 2% increase in the Pb content when the distance to the airport decreased by 10%. Our hypothesis is that tire wear in the aircraft take-off and landing could emit dust particles containing Pb. In the case of the distance to the city center, there was a null association with the other heavy metals.

Table 6. Spatial error model results for Pb.

Covariate	**Pb**	
	beta	***p***
Intercept	7.12	0.00
Population density (inhabitants/ha)	0.03	0.41
Job density (jobs/ha)	0.03	0.68
Street intersections	0.01	0.88
Road surface (m^2)	−0.10	0.56
Distance to the airport (m)	−0.19	0.08
Distance to the city center (m)	−0.05	0.68
Manufacturing units	0.08	0.19
Potentially polluting units	0.00	0.96
Gray area (ha)	−0.01	0.94
Entropy index	0.17	0.54
Vegetation (%)	0.00	0.95
Distance to vegetation (m)	0.01	0.87
Median strip area (m^2)	0.02	0.08
Marginalization index	−0.06	0.20
AIC	757.01	

Note: AIC (Akaike Information Criterion), lower AIC value suggest a better fit.

Manufacturing units had a positive significant association with Cu with an alpha level of 5%. We could expect about a 1% increase in Cu when manufacturing units increased by 10%. It is very likely that behind this variable there are a variety of chemical processes in the manufacturing; therefore, there could be several sources of Cu from these processes as well as traffic-related emissions. The relationship with PLI was also positive but less significant (significance level of 90%). Potentially polluting units failed to show any association with the heavy metals. This means that possible major pollutant units were not properly identified with our variable. Thus, other alternatives must be tackled in future research such as the use of other classification schemes to differentiate potentially polluting units from the whole census of economic units. Only in the case of the dust load was there a positive significant association at the 90% significance level. Thus, these units are associated with an increase in dust, but are not associated with an increase in the heavy metal content.

The gray area variable also failed to detect any association with the heavy metals. Our initial expectation was that this variable could be related to heavy metals due to the polluting emissions of activities related to large concrete surfaces (markets, aviation tracks, and electrical substations). The null association of the gray areas could be due to the huge diversity of activities considered in the covariate. The entropy index had a positive relationship at the alpha level of 5% with Ni. We could expect about a 4% increase in Ni when the entropy index increased by 10%. A high entropy index means a similar proportion of the six land uses considered; thus, these places could have a variety of potential sources of Ni together, such as sites of fuel combustion.

There was also a weak positive relation (alpha level of 10%) of the entropy index with the dust load. The difficulty in obtaining a clear relationship between the land-use covariates and heavy metal contents in urban dust in México City could be related to the tertiary-oriented economy. We assume that mobile sources of traffic emissions would be more relevant but also more difficult to trace. In the case of air pollution, industrial point emissions have been identified as the source of pollution, such as in the studies of Zhang et al. [33] in Alberta, Canada, and Jung et al. [8] in Korea, where commercial and industrial areas were associated with increased particulate matter pollution.

The percentage of vegetation in the buffer and the distance to the closest vegetation spot failed to show any association with the heavy metal content. In the case of the former, there was a significant negative association (significance level of 99%) with the dust load, which indicates that vegetated areas tended to have less dust but not necessarily a higher heavy metal content. The median strip area had a weak (significance level of 90%) but consistent positive relationship with Cr, Cu, Ni, Pb, and PLI. This led us to hypothesize that these areas may act as sinks of pollution in the roads, acting as places of heavy metal accumulation. For example, during the sweeping of the road, the dust may be dumped there. The positive relationship between the median strip area and Pb remained for the spatial error model at the alpha level of 10% (Table 6).

Initially, we considered the median strip area part of the vegetation area because it frequently has a vegetation cover. After testing the initial models, the previous vegetation area covaried positively with Pb and Cr. That result was unexpected, and we therefore decided to separate the components of the vegetation covariation and, finally, identified that only the median strip area was positively related to Cr, Pb, Zn, and the PLI. It will be important to untangle the relationship between heavy metals and the median strip area to define the best way to manage such areas. It is important to clarify that covariates of urban form do not necessarily represent specific detailed sources of heavy metals. They represent general characteristics (places) of the urban environment where these pollutants could be being emitted or places of concentration (sinks of pollution (from other mobile or fixed sources of pollution)).

Finally, there was no differential exposition to heavy metals according to the socioeconomic status of households, as we found a null association with the marginalization index. The good news is that road dust is not an important source of exposure to Pb for those in low-income areas, as they are at higher risk of developing health problems [59]. However, attention should be paid to keep the streets clean, because marginalized areas tended to be dustier than middle-income and affluent areas.

The study of the relationships between the urban form and heavy metals is incipient; further investigation is needed to develop a conceptual framework that guides the development of more robust models. The present study is an exploratory analysis in this sense, and we tested the group of covariates that we considered the most relevant. Although some of these variables did not show any association, the inclusion was supported by a deep reflection of what we considered could be the route of heavy metals in the urban environment.

The study of temporal variation in the short term is also important to design better sampling processes that minimize and control the effects of potential confounding factors. For example, natural cleaning mechanisms, such as rain and air currents, and the different practices of street sweeping. From a methodological point of view, we propose to test smaller buffers, which might be at 100 or 150 m around the sampling points, since the characteristics of the immediate surroundings are very important. A better characterization of the urban form might also benefit from more consistent and refined publicly available data regarding the urban environment. The characterization of the local urban environment is key to devising the sampling strategy. Further research lines also include the application of other modeling approaches and inter-city comparisons to test if the phenomena studied here present similar behavior in cities of different sizes and economic conditions. Furthermore, we suggest the inclusion of covariates related to atmospheric processes as well as covariates with more detailed georeferenced data about emission sources.

6. Conclusions

According to the global Moran's I, there were low levels of positive spatial autocorrelation in all the heavy metals analyzed. We interpret this as an indication of the greater relevance of the local aspects over regional processes as determinants of the heavy metal content in urban road dust. Any mapping exercise based on statistical interpolation would not be reliable. A lack of major unique sources of these pollutants could also cause a lack of spatial autocorrelation. In our regression exercise, the most striking finding was that the median strip area in urban roads had a weak but consistent positive relationship with Cr, Cu, Ni, Pb, and the Pollution Load Index. Other significant positive relationships were found for Cu with the manufacturing units, and Ni with the entropy index. More disaggregated indicators would be relevant to unveil the nature of these associations.

Certain variables failed to show any association with the heavy metals, such as the population density, street intersections, distance to the city center, gray area, distance to vegetation, and marginalized areas. Other variables that failed to be associated with heavy metals but showed an association with the dust load were the potentially polluting units (significance level of 90%) and vegetation (significance level of 99%), positive in the former and negative in the latter. The job density (significance level of 99%) and road surface (significance level of 95%) significantly reduced the dust load as well. For Pb, the spatial error model showed the correct specification, unlike the other metals where OLS was found to be appropriate. In this model, distance to the airport had a weak (significance level of 90%) and an inverse association with Pb. This presents an important suggestion to consider this place as a potential source of this metal in urban dust.

Thus, we can conclude that some features of the urban form, as described above, are important drivers of heavy metal pollution in the road dust. A better understanding of how road dust pollution is associated with the urban form will be important to design measures that mitigate the exposure of people to those pollutants.

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Aportes del capítulo a la tesis

Después de utilizar el índice I de Moran para analizar la correlación espacial, corroboramos que los niveles de autocorrelación espacial positiva fueron muy bajos para todos los metales pesados analizados. Interpretamos esto como una indicación de que los aspectos locales tienen mayor relevancia que los procesos regionales como determinantes del contenido de metales pesados en el polvo urbano. Por tanto, no son grandes fuentes puntuales las que deben estar determinando la distribución espacial de los metales pesados en el polvo urbano.

En una ciudad con tanta densidad poblacional y dedicada principalmente al sector de servicios como lo es la CDMX, puede haber múltiples fuentes pequeñas que liberan cantidades variables de metales pesados. Por ejemplo, a través de los modelos de regresión lineal múltiple, nosotros encontramos que el área de los camellones tuvo una relación positiva consistente con las concentraciones de Cr, Cu, Ni, Pb y el índice de carga contaminante (PLI). Esto nos llevó a plantear la hipótesis de que estas áreas podrían estar actuando como una fuente de estos metales. Sin embargo, no solo podrían ser una fuente, sino también lugares de acumulación de los metales pesados. Por ejemplo, si durante el barrido de la carretera el polvo se va depositando en los camellones, los metales pesados se pueden ir concentrando.

Al comenzar la investigación creímos que algunos indicadores relacionados con la mezcla de usos del suelo residencial y económico, y la densidad de empleo podrían estar incrementando las concentraciones de metales pesados asociados con el tráfico, como el Pb, Cu y Zn. Sin embargo, los indicadores que utilizamos relacionados con los usos de suelo y los empleos, solo mostraron que a mayor densidad de empleo menor la cantidad de polvo urbano. Esto puede deberse a que en las zonas donde se concentran los empleos formales generalmente se mantienen más limpias las calles. Otras relaciones significativas fueron entre del Ni con el índice de Entropía (mezcla de usos de suelo), así como entre el Cu y las unidades de Manufactura. En el futuro, indicadores más desagregados serían relevantes para desvelar la naturaleza de estas asociaciones.

En el capítulo III se comentó que en futuras investigaciones sobre los metales pesados en el polvo urbano de la CDMX será necesario analizar las posibles fuentes identificadas en esta tesis como lo fue la pintura amarilla de las calles, la cual podría estar aportando Pb y Cr al mismo tiempo. Con los resultados de este capítulo (V) se pone de manifiesto la necesidad de investigar también la relación que hay entre las concentraciones de los metales pesados y el área de los camellones. Algunas posibles explicaciones son 1) en el suelo de los camellones se pueden estar acumulando los metales y después las partículas del suelo pasan al polvo urbano, por lo que será conveniente analizar las concentraciones de los metales en esos suelos; 2) hay mayor tráfico vehicular en las calles con camellones ya que generalmente son vías muy transitadas; y 3) la vegetación de los camellones limita la dispersión de las partículas atmosféricas o favorece la acumulación de polvo en estas calles.

A través de este análisis establecimos las bases para el estudio de las relaciones entre la forma e infraestructura urbana y las concentraciones de los metales pesados en el polvo de las calles. Entender estas relaciones permitirá ir conociendo el comportamiento, los mecanismos de transporte y destino de los metales pesados en el polvo de las ciudades. A su vez, enriquecer la teoría de la contaminación por metales pesados en los polvos urbanos ayudará a ir precisando los indicadores.

El estudio de los polvos urbanos necesita tratarse de la mano con la teoría urbana para buscar estrategias de remediación y adaptación para disminuir las emisiones, establecer programas de limpieza de las calles y campañas de limpieza ciudadana, así como, campañas de educación sobre los problemas de salud potenciales por el contacto con el polvo urbano, entre otras acciones. Por el momento, los hallazgos de esta investigación servirán como telón de fondo para evaluar futuros cambios potenciales en las concentraciones ambientales de los metales pesados.

Estudiar la variación temporal en el corto plazo también es importante para diseñar mejores procesos de muestreo que minimicen y controlen el efecto de los factores de confusión. Por ejemplo, los mecanismos de limpieza naturales como la lluvia y las corrientes de aire, y las prácticas de barrido de calles. Desde un punto de vista metodológico, proponemos probar áreas de amortiguamiento más pequeñas, que pueden estar a 100 o 150 m alrededor de los puntos de muestreo, ya que las características del entorno inmediato son muy importantes. Una mejor caracterización de la forma urbana también podría beneficiarse de datos públicos disponibles más consistentes y refinados sobre el entorno urbano. Otras líneas de investigación también incluyen la aplicación de otros enfoques de modelado y comparaciones entre ciudades para probar si los fenómenos aquí estudiados tienen un comportamiento similar en ciudades con diferentes tamaños y aparatos económicos.

El estudio de las relaciones entre la forma urbana y los metales pesados es incipiente, se necesita más investigación para desarrollar un marco conceptual que oriente el desarrollo de modelos más robustos. El presente estudio es un análisis exploratorio en este sentido, y terminamos probando el grupo de covariables que consideramos más relevantes. Si bien algunas de estas variables no mostraron asociación alguna, su inclusión se apoyó en una profunda reflexión de lo que pensamos que podría ser la ruta de los metales pesados en el medio urbano. Es importante seguir monitoreando las fluctuaciones a largo plazo para evitar un aumento de estos contaminantes y demostrar el desempeño de las políticas ambientales.

CONCLUSIONES

Esta tesis aportó información sobre el estudio de la contaminación por metales pesados en el polvo urbano de seis ciudades de México.

A continuación, se enlistan las conclusiones generales:

- ⇒ Las ciudades estudiadas estuvieron contaminadas por Pb, Cu, Zn, Mn y Fe, con excepción de Mérida, tomando como referencia el valor de fondo mundial para suelos. Sin embargo, al comparar cada ciudad con sus valores de fondo locales (decil uno) Mérida fue de las ciudades más contaminadas.
- ⇒ A nivel nacional, el plomo fue el metal que representa mayor riesgo ecológico y a la salud humana en todas las ciudades estudiadas.
- ⇒ La contaminación no se relacionó necesariamente con el número de habitantes, ciudades pobladas como Mérida fueron las menos contaminadas, por el contrario, ciudades poco pobladas como Ensenada estuvieron más contaminadas por Mn y Fe que otras más pobladas como San Luis Potosí, Morelia y Mérida.
- ⇒ En la evaluación individual de la Ciudad de México, después de un muestreo intensivo (n=482), encontramos contaminación por Pb, Zn y Cu en los polvos urbanos. Además, las concentraciones máximas del Cr y Pb representaron un riesgo para la salud de los niños. Esperamos que la propuesta de límites de contaminación que hicimos en esta investigación pueda ayudar en el establecimiento de políticas públicas para disminuir la carga contaminante de metales pesados en el polvo urbano de la Ciudad de México.
- ⇒ Específicamente en el caso del manganeso, en el 90% de la Ciudad de México se encontró un grado de contaminación moderado. Las áreas con mayores concentraciones de Mn se localizaron al centro y norte de la Ciudad de México.
- ⇒ El análisis espacial tanto de las concentraciones como de la carga de Mn puso de manifiesto la importancia de considerar ambas variables en los estudios de contaminación y exposición a metales pesados, como el Mn, ya que las áreas con los valores más altos fueron distintas para ambas variables y si sólo se considerara una de ella se perdería información sobre la extensión de la contaminación. Además, los resultados mostraron evidencia de que la carga de polvo tiene un fuerte impacto en la carga de Mn ya que se encontró una fuerte correlación entre ambas variables.
- ⇒ Para los metales Cr, Cu, Pb, Zn y Ni, en la Ciudad de México, tuvimos indicios de que los aspectos locales tienen mayor relevancia que los regionales como determinantes del contenido de metales pesados en el polvo urbano, ya que, se encontraron bajos niveles de autocorrelación espacial positiva. La falta de fuentes únicas importantes de estos contaminantes también podría estar causando una falta de autocorrelación espacial.
- ⇒ El hallazgo más importante fue que el área de los camellones tuvo una relación positiva débil pero constante con el Cr, Cu, Ni, Pb y el índice de carga contaminante. Esto nos llevó a plantear la hipótesis de que estas áreas podrían estar actuando como lugares de acumulación de metales pesados, por ejemplo, si al barrer las calles se vierte el polvo allí.

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