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Determinación espacial y temporal de metales en PM_{2.5} en el Área
Metropolitana de la Ciudad de México

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PRESENTA

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Resumen.

La contaminación del aire es una preocupación de salud pública ya que causa daños a la población. En años recientes, diversas investigaciones epidemiológicas han asociado morbilidad y mortalidad con partículas suspendidas (material particulado [PM]) en la atmósfera. Los estudios de la caracterización química, la distribución espacio-temporal, la identificación de fuentes de PM en ambientes urbanos ha cobrado relevancia en las ciencias ambientales, ya que son herramientas claves para tomadores de decisiones. Además, estos estudios pueden impactar positivamente en la calidad del aire y en la salud de las poblaciones.

Este trabajo presenta los resultados del conjunto de acciones que permitieron: caracterizar la composición química de metales y metaloides en la fracción fina del material particulado ($PM_{2.5}$) en concentraciones traza; identificar las fuentes de emisión y realizar un *prorratio* del aporte de dichas fuentes. Además, este trabajo demuestra la distribución, dispersión y acumulamiento de los metales en el $PM_{2.5}$ por efectos meteorológicos dentro de la cuenca de la Zona Metropolitana de la Ciudad de México (ZMCM).

La caracterización elemental se llevó a cabo mediante la técnica analítica instrumental ICP-MS (*inductively coupled plasma mass spectrometry*) en muestras colectadas de $PM_{2.5}$ de dos campañas de muestro (2011 y 2013). Se aseguró la calidad analítica mediante materiales de referencia certificados (MRC): 1649a (polvo urbano), 1648a (material particulado urbano) y BCR 723 (polvo de camino). El método desarrollado incluyó digestión ácida asistida por microondas.

Las muestras disponibles sometidas al protocolo de digestión y análisis pertenecen a dos campañas de colecta de $PM_{2.5}$ efectuadas en 2011 y 2013. Las características de ejecución de las campañas de muestreo fueron similares: simultáneamente se colectó $PM_{2.5}$ en cinco sitios de la ZMCM pertenecientes a la infraestructura de monitoreo de la SEDEMA (Secretaría de Medio Ambiente de la Ciudad de México): Tlalnepantla (TLA-NW, northwest), San Agustín (SAC- NE northeast), La Merced (MER-C, Center), Coyoacán (COY-SW, southwest), Universidad Autónoma Metropolitana campus Iztapalapa (UAM-I, SE, southeast) una vez cada 6 días durante un mes representativo de las temporadas seca (abril – Dry Warm -DW), lluvias (agosto – Rainy-R) y fría (noviembre – Dry Cold - DC). El $PM_{2.5}$ se colectó con muestreadores de altos volúmenes (*Hi-vol*) por 24 h.

Las bases de datos anuales conformadas por las concentraciones de los metales distinguiendo los sitios y temporadas fueron evaluadas mediante los programas computacionales *Statistica 10.1*, *Wind Plot* y *R* con la paquetería de *Open Air*.

Los elementos estudiados fueron: Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Rb, Sr, Cd, Sb, Cs, Th, Pb, Tl, La, Ce, Sm y Eu; también Pt y Hg. Los elementos con mayor concentración fueron Fe y Ti, asociados a emisiones geogénicas. Las concentraciones significativamente ($p < 0.05$) más altas para la mayoría de los metales se encontraron en NW o NE, y durante DW. Esta tendencia se observó en los resultados de la campaña de 2011 y se corroboró con los correspondientes de 2013. A pesar de las similitudes entre 2011 y 2013 se observó un aumento del 17% en la concentración en masa de $PM_{2.5}$. Se destacó la importancia de la

intensidad del viento en el impacto de las fuentes de emisión. El efecto de la intensidad del viento se reveló mediante *wind plots* siendo este el mecanismo de control para el aumento de las concentraciones de los metales. Esto permitió concluir que los episodios de alta velocidad ($>5 \text{ m s}^{-1}$) son los responsables de elevar las concentraciones de metales geogénicos. Mediante factores de enriquecimiento (EF) y análisis de componentes principales (PCA) fue posible atribuir a los metales analizados con sus fuentes: geogénicas o antropogénicas respectivamente; de igual manera se pudo identificar metales con fuentes de procedencia mixta.

Las mediciones de concentración Pt en $\text{PM}_{2.5}$ se han empleado para monitorear las emisiones vehiculares, debido a que son producto de la emisión por desgaste de los convertidores catalíticos incorporados en vehículos automotores con el propósito de disminuir la emisión de gases de combustión incompleta tal como CO. La comparación con información previa en la zona confirma un aumento del 19.6% en las concentraciones de Pt. Este aumento corresponde con el de la flota vehicular entre 2011 y 2013. Mostrar esta tendencia es importante para contribuir con información para que los tomadores de decisiones construyan políticas públicas favorables al medio ambiente y su relación con la salud de los habitantes.

Se presentan también las concentraciones de Hg en $\text{PM}_{2.5}$. Se investigó la variabilidad estacional y temporal por primera vez en este tamaño de partícula para la ZMCM. Se logró identificar episodios localizados de altas emisiones, lo que confirmó los sitios donde se encuentran sus fuentes. La evaluación de los datos permitió mostrar la tendencia decreciente de Hg. La información obtenida permite conocer la evolución en el tiempo de las emisiones de este contaminante; esto cobra importancia tras la firma y promulgación del convenio de Minamata por parte de las autoridades mexicanas.

Abstract.

Polluted air is a public health concern because it causes damage to the population. In recent years, various epidemiological investigations have been able to associate high morbidity and mortality with atmospheric particulate matter (PM). Studies of chemical characterization, spatio-temporal distribution, identification of PM sources in urban environments have gained relevance in environmental sciences as they are key tools for decision makers. In addition, these studies may positively impact the quality of the air and health of populations.

In this work, a set of actions were carried out that allowed: To characterize the elemental composition of metals and metalloids in trace concentrations in the fine fraction of the particulate material (PM_{2.5}); to identify the sources of emission and make apportionment of that contribution sources. In addition, an interpretation of the distribution, dispersion and accumulation of metals in PM_{2.5} is provided by meteorological effects within the basin of Mexico City Metropolitan Area (MCMA).

The chemical characterization was carried out using the instrumental analytical methodology ICP-MS (inductively coupled plasma mass spectrometry) in PM_{2.5} collected samples. Analytical quality was assured by validating the method based on certified reference materials (CRM): 1649a (urban dust), 1648a (urban particulate material) and BCR 723 (road dust). The method developed and validated for this characterization included microwave-assisted acid digestion of the samples.

The available samples for digestion and analysis protocols were obtained from two PM_{2.5} collection campaigns carried out in 2011 and 2013. The execution characteristics of the sampling campaigns are similar: PM_{2.5} was simultaneously collected at five sampling sites within the MCMA that belongs to the monitoring infrastructure of the SEDEMA (Secretary of Environment of Mexico City): Tlalnepantla (TLA-NW, northwest), San Agustín (SAC-NE northeast), La Merced (MER-C, Center), Coyoacán (COY-SW, southwest), Metropolitan Autonomous University Iztapalapa campus (UAM-I, SE, southeast). The samples were taken once every other six days during a representative month of the dry-warm season (April - DW), rainy season (August - Rainy- R) and dry-cold season (November - DC). The PM_{2.5} samples were collected with high volume samplers (Hi-vol) during 24 h.

The annual databases formed by the concentrations of the metals considering the sampling sites and seasons were evaluated using the Statistica 10.1, Wind Plot computer programs; R with Open Air package.

The metals studied were: Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Rb, Sr, Cd, Sb, Cs, Th, Pb, Tl, La, Ce, Sm and Eu, as well as Pt and Hg. The elements with the highest concentrations were Fe and Ti, which are associated with geogenic emissions. By statistical analysis it can be determined that significantly higher concentrations ($p < 0.05$) for most metals were found in the NW or NE locations during DW. This trend was observed in the 2011 PM_{2.5} campaign sampling and was corroborated with that of 2013. Despite the similarities between 2011 and 2013, a 17% increase in the mass concentration of PM_{2.5} was observed. The importance of

wind intensity in the impact of emission sources was highlighted. The effect of wind intensity was revealed by wind plots, as the control mechanism for this increase. This enables to conclude that high-speed episodes (5 m s^{-1}) were responsible for raising the concentrations of geogenic metals. Through the enrichment factor (EF) and principal component analysis (PCA), it was possible to attribute the analyzed elements to geogenic and anthropogenic sources, as well as identify a group of elements with sources of mixed origin.

Pt concentration measurements in $\text{PM}_{2.5}$ have been used to monitor vehicle emissions, as they are the result of the emission of catalytic converters incorporated in motor vehicles with the purpose of reducing gas emissions such as CO. The comparison with previous information in the area confirms 19.6% of increase in Pt concentrations. This corresponds to the increase in the vehicle fleet between 2011 and 2013 that sampling campaign were carried out. Publicizing these increasing trends in the MCMA is important for the construction of public policies favorable to the environment and its relationship with the health of the inhabitants.

Hg concentrations are also determined in $\text{PM}_{2.5}$. Seasonal and temporal variability is investigated for the first time in this particle size for the MCMA. It was possible to identify localized high-emission episodes that confirmed the sites where the emission sources are located. The decreasing tendency of Hg was shown by comparing the results from this work with those available. To know the evolution in time of the emissions of this pollutant becomes important with the signing and promulgation of the Minamata agreement by the Mexican authorities.

Introducción.

Generalidades.

En las últimas décadas el crecimiento poblacional en zonas urbanas ha traído afectaciones al ambiente. Evidencia de ello es el deterioro de la calidad del aire provocado por emisiones de contaminantes a la atmósfera. La contaminación atmosférica, a su vez, provoca daños a la salud, mismos que pueden ir desde malestares agudos del tracto respiratorio hasta enfermedades crónico degenerativas o mortales. Los efectos adversos varían en función de la composición química, de su concentración y de la frecuencia de exposición a los contaminantes, entre de otros (Englert, 2004; Nemmar, et al., 2013).

Los problemas de salud asociados con la contaminación atmosférica han sido reconocidos por la *Organización Mundial de la Salud* (OMS) desde 2013 mediante la *Agencia Internacional de Investigación en Cáncer* (IARC por sus siglas en inglés); al clasificar a la contaminación del aire como un agente carcinogénico para los seres humanos. (International Agency for Research on Cancer, 2013)

Es por ello que los estudios <como el presente> que brinden información referente a la caracterización, distribución, tendencias, etc., del contenido químico de la atmósfera (o parte de sus constituyentes) son fundamentales para elaborar programas de gestión de la calidad del aire que permitan ofrecer medidas y acciones que favorezcan la solución de problemas ocasionados por la contaminación del aire.

Aire, aerosoles y material particulado (PM).

De acuerdo con la fisicoquímica, el *aire* es una mezcla gaseosa prácticamente homogénea compuesta principalmente de N₂ (71%), O₂(28%) y Ar (<1%). En él se encuentran suspendidas porciones diminutas de sólidos y líquidos que son lo suficientemente pequeñas para no sedimentarse en la superficie terrestre debido a la gravedad. Al sistema termodinámico comprendido por una fase discontinua de sólidos inmersa en una fase continua gaseosa se le denomina *aerosol* (García-Colín & Varela, 1996). Las partículas suspendidas detectables más pequeñas varían desde cúmulos moleculares hasta partículas microscópicas con radios a partir de 10⁻³ μm. Se originan tanto de procesos naturales como antropogénicos (Harrison & Van Grieken, 1998; McNeill & Parisa, 2014).

Se emplea el término *material particulado* (PM —del inglés *particulate matter*—) o solo *partículas* para referirse a los sólidos y líquidos suspendidos presentes en los aerosoles. El tamaño es una característica importante para su clasificación. El PM químicamente está constituido por una compleja mezcla de compuestos inorgánicos como óxidos, aniones (sulfatos, nitratos, cloruros, etc.), cationes (como el amonio, K⁺, Na⁺, etc.) y también de compuestos orgánicos (como carbono elemental, ácidos, compuestos semivolátiles, etc.), agua, metales, etc. La proporción de estos constituyentes depende de gran variedad de condiciones.

Estas partículas presentan heterogeneidad de formas que comprenden esferas y figuras irregulares (Stevenson, 1982; Hamilton, et al., 1994). Un criterio útil para clasificarlas en función de su tamaño es el diámetro aerodinámico, que se define como el diámetro de una

partícula esférica con densidad uno que mantiene algunas propiedades idénticas a las de la partícula real, como por ejemplo la velocidad de sedimentación (García-Colín & Varela, 1996).

El tamaño del material particulado es una característica muy importante relacionada con la salud. Se ha encontrado que entre menor sea el tamaño del PM, mayor será su posibilidad para penetrar en el sistema respiratorio. Inicialmente se empleó como indicador de la calidad del aire a las partículas suspendidas totales (PST), las cuales comprenden un intervalo de tamaño entre $0.005 \mu\text{m}$ y $100 \mu\text{m}$ (García-Colín & Varela, 1996). Posteriormente, diversos estudios sobre los efectos de las partículas suspendidas en la salud (Nriagu, 1979; Englert, 2004) se enfocaron sobre partículas que pudieran ser inhaladas, y se encontró que las partículas menores que $10 \mu\text{m}$ (PM_{10}) tienen esta característica. Se ha designado como la fracción respirable o fracción gruesa a las partículas cuyos diámetros aerodinámicos se encuentra entre $2.5 \mu\text{m}$ y $10 \mu\text{m}$. Así mismo, se les llama fracción fina a las partículas con diámetro menor que $2.5 \mu\text{m}$ ($\text{PM}_{2.5}$). De acuerdo con recientes investigaciones epidemiológicas, el $\text{PM}_{2.5}$ ha mostrado estar más correlacionado con efectos negativos a la salud, ya que pueden alcanzar a penetrar hasta la región alveolar en los pulmones (Kok, et al., 2006; Nemmar, et al., 2013).

Conocer el proceso que dio origen al PM es importante para el diseño de políticas públicas y estrategias para mejorar la calidad del aire. El tamaño y la composición química del PM proporcionan información del proceso que les dio origen (coagulación, condensación, etc.) así como de la fuente que las emitió. El PM puede ser emitido a la atmósfera ya sea por fuentes naturales (como proceso de erosión, quema de bosques, polvo de desiertos, etc.) o por actividades antropogénicas (como la minería, la actividad industria, quema de combustibles fósiles, etc.) (Godish, 2004). El análisis elemental de metales traza en PM provee información para la atribución y reconocimiento de fuentes de emisión.

Los muestreadores son dispositivos de colecta de PM en aire. Comercialmente existen muestreadores disponibles con gran variedad de características y capacidades diferentes. Algunos de ellos son: el impactador de cascada en multietapa, el muestreador de grandes volúmenes (Hi-Vol, $>30 \text{ m}^3 \text{ h}^{-1}$) y el muestreador de bajos volúmenes (low-vol, $\sim 1 \text{ m}^3 \text{ h}^{-1}$), estos últimos dos, con la capacidad de seleccionar diferentes tamaños de partícula (Godish, 2004). A menudo se emplean los muestreadores de altos volúmenes durante periodos de 24 h, lo que permite la comparación de los resultados entre diferentes sitios o temporadas.

Generalmente las muestras se colectan en filtros y de éstos los hay disponibles en materiales de diferente composición como: filtros de policarbonato, de fibra de vidrio (con y sin recubrimiento de teflón), de fibra de cuarzo, membranas de teflón y de celulosa (Baron, 2001). La selección del filtro depende tanto de la fracción de PM que se va a colectar como de la caracterización química que se efectuará.

Metales en la atmósfera de las ciudades.

Los metales en la atmósfera están presentes mayoritariamente en la fase particulada y varían entre el 1 % y el 10 % en masa (Cheng et al. 2010). Existe una relación entre el proceso de

emisión que les dio origen en la atmósfera y el tamaño de la fase particulada en el que se encuentran. Conocer qué metales se encuentran en los diferentes tamaños de partícula, su intervalo de concentración, la relación que guardan tales elementos entre ellos, etc. permite identificar las fuentes de contaminantes atmosféricos. En la Tabla 1 se reportan algunas fuentes de metales reconocidas por algunos grupos de trabajo.

Tabla 1 Metales reportados típicamente con sus fuentes de aporte ⁽¹⁾

PM	Metales	Fuente	Lugares	autores
PM ₁₀	Fe, Ba, Zn, Cu, Pb	Tráfico y emisiones de vehículos automóviles	Areao, Portugal Milán, Italia Barcelona, España	(Pio, et al., 1989) (Alastuey, et al., 2006)
PM _{2.5}	Al, Si, Ca, Fe, K	Masa mineral Polvo de ciudad	Huelva, España Barcelona, España	(Alastuey, et al., 2006) (Querol, et al., 2008)
PM ₁₀ PM _{2.5}	Na, Cl, Mg	Brisa marina	Areao, Portugal Barcelona, España	(Pio, et al., 1989) (Querol, et al., 2008)
PM _{2.5}	V, Ni	Combustión de combustibles fósiles	Barcelona, España	(Querol, et al., 2008)
PM _{2.5}	Mn, Zn, Pb, Cd	Industria Metalurgia	Llodio, España	(Alastuey, et al., 2006)
Fracción fina Fracción gruesa	Si, S, K, Ca, Ti, Fe, Mn S, Cl, V, Cr, Ni	Suelos Combustibles	Ciudad de México, tres locaciones	(Miranda, et al., 2005)

¹Modificada de (Vianna, et al., 2008)

Influencia temporal a la concentración de metales en PM en ciudades.

La composición química en el PM varía debido a factores meteorológicos como la temperatura, humedad, velocidad dirección del viento, dentro de otras. La dependencia de la concentración de metales en PM con factores meteorológicos ha sido reportada en ciudades de todo el mundo (Cheng, et al., 2010; Saliba, et al., 2010; Aldabe, et al., 2011; Warneck & Willimas, 2012).

Las temporadas frías se caracterizan por la ocurrencia de inversiones térmicas, así como la prevalencia de vientos de baja intensidad. Estas son características que favorecen el acumulamiento de contaminantes en la atmósfera local, hecho que ocasiona aumento en las concentraciones de metales. Contrariamente, en algunas ciudades durante la temporada invernal suceden nevadas o precipitaciones, lo que puede disminuir la cantidad de PM y por ende la concentración de metales.

Se ha observado que durante las temporadas cálidas en clima seco se favorece la resuspensión y transporte de partículas de polvo, lo que puede elevar las concentraciones en la atmósfera de elementos provenientes de la corteza terrestre (Kulshrestha, et al., 2009; Dongarrá, et al., 2010; Saliba, et al., 2010).

Las estaciones climáticas también provocan variabilidad en las concentraciones de metales en los centros urbanos. Durante la época invernal el aumento del uso de calefacción (ya sea por quema de combustibles fósiles o por generación eléctrica), provoca aumento de las emisiones de material particulado trayendo consigo el aumento de metales que son aportados por estas fuentes.

Otro efecto estacional observado en la concentración de metales en PM, está relacionado con la temporada de lluvias. En la investigación llevada a cabo en la ciudad de Agra, India, se presentan los resultados para un muestro de mayo 2006 a marzo 2008 comprendiendo las estaciones de verano (marzo-junio), monzón (julio-octubre) e invierno (noviembre a febrero). En este estudio se colectaron muestras de PM_{2.5} y PM₁₀. Los autores reportan que, durante la estación del monzón, la cantidad de PM en el aire disminuye y a su vez la cantidad de metales. Este fenómeno es conocido como *barrido húmedo*: se dice que la atmósfera es lavada por la lluvia. (Kulshrestha, et al., 2009).

Influencia espacial a la concentración de metales en PM en ciudades.

La concentración de los metales en PM está condicionada a la distancia entre las fuentes de emisión y la ubicación de los muestreadores; esto debe tomarse en cuenta para el diseño de campañas de colecta. Se han reportado variaciones espaciales tanto regionales (países o porciones de continentes) como locales.

Por ejemplo, se ha observado un gradiente descendiente de en la concentración metales emitidos por brisa mariana en función de la distancia entre las ciudades y la costa, como es el caso de la región mediterránea en Europa (Alastuey, et al., 2006; Querol, et al., 2009; Dongarrá, et al., 2010; Aldabe, et al., 2011). Del mismo modo se ha observado variabilidad en la concentración de metales emitidos en función de la posición geográfica otras fuentes como desiertos, volcanes, zonas rurales, etc.

Los estudios no sólo deben considerar a la ubicación geográfica de una ciudad, sino que también deben de tomar en cuenta el ordenamiento territorial de la zona; es decir, considerar las ubicaciones de aéreas industriales, residenciales, comerciales, zonas de desechos municipales e inclusive la presencia de áreas rurales aledañas, entre otras.

Para un sustancial número de ciudades el tráfico vehicular es una importante fuente de emisión de metales antropogénicos. Por ello, se han llevado a cabo diversos estudios referentes a la distribución espacial del contenido químico en función de la distancia de avenidas con gran flujo vehicular, túneles o cruces carreteros (Thorpe & Harrison, 2008).

Estudios urbanos reportan variación espacial de contaminación atmosférica de acuerdo con las cercanías a centros o parques industriales. Un estudio en Venecia, Italia reporta emisiones de As, Se y Cd provenientes de la industria manufacturera de vidrio

establecida en Murano y también emisiones de V y Co provenientes de un parque petroquímico situado en la parte continental llamado Venecia Mestres (Saliba, et al., 2010).

Cabe mencionar que, para otras localidades, la contaminación petroquímica es evidenciada por variaciones de las emisiones de Ni y V. Tal es el caso de los poblados situados en Castelló, España; en donde se ha encontrado que el origen de emisiones de contaminación por industrias petroquímicas están ubicadas entre 20 km y 200 km (Querol, et al., 2007).

Efectos de vientos sobre la concentración de contaminantes en ciudades.

Las condiciones eólicas juegan un papel fundamental en el acumulamiento y dispersión de contaminantes. Los vientos pueden acarrear materiales emitidos lejanamente o que, provoquen resuspensión de partículas previamente depositadas. También el viento intenso puede no permitir la floculación de partículas gruesas y por ende las partículas finas cobren importancia contaminante, o que, durante episodios intensos de vientos fuertes se remuevan las partículas de la atmósfera local.

Para hacer un estudio adecuado es necesario conocer la información del sitio (información local) en términos de los regímenes de vientos incluyendo episodios ciclónicos o anticiclón, así como otros factores geográficos y topológicos que puedan aportar material a la zona de estudio.

Por ejemplo, se ha encontrado que los vientos de origen norafricano transportan polvo del desierto del Sahara: ciudades europeas no costeras como Milán y Pamplona han reportado aumento de las concentraciones de metales provenientes de la corteza terrestre atribuibles a esta fuente (Aldabe, et al., 2011). En un estudio realizado en Beirut, Líbano, se reporta el incremento en la concentración de metales de origen geológico durante el otoño (Saliba, et al., 2010), mientras que en ciudades del Mediterráneo occidental como Palermo (Dongarrá, et al., 2010), Barcelona (Querol, et al., 2009), Tarragona, (Querol, et al., 2008) etc. muestran elevación similar de metales de origen geológico durante el verano, en todos los casos aportados eólicamente desde África.

Identificación proporcional (prorratio) de fuentes contaminantes de metales a la atmósfera.

Caracterizar las variaciones espacio-temporales de concentraciones de metales permite identificar las fuentes que aportan materiales al aire troposférico. Además, estas variaciones permiten conocer la proporcionalidad del impacto de las fuentes, a esto se le conoce como prorratio e identificación de fuentes de aporte (*Source apportionment*). Esta tarea, aunque no es sencilla, se puede abordar desde diferentes perspectivas. En años recientes la aplicación de herramientas estadísticas a datos de concentraciones de metales, permite lograr acertadas caracterizaciones de los perfiles de emisión.

Un procedimiento simple para atribuir contaminación antropogénica (producto de actividades humanas en entornos urbanos) es la comparación directa de las concentraciones de metales encontradas en ciudades frente a las encontradas en zonas rurales vecinas. Este

procedimiento presenta limitaciones. Actualmente, las campañas de muestro toman los valores de zonas rurales dentro de sus concentraciones de fondo (Kulshrestha, et al., 2009; Dongarrá, et al., 2010; Saliba, et al., 2010).

Factor de enriquecimiento (EF).

Otro procedimiento que permite identificar a los metales cuyas concentraciones han aumentado como producto de actividades antropogénicas, es mediante la identificación del incremento de metales corticoides en comparación con metales en el PM: se emplea el factor de enriquecimiento (EF –enrichment factor- por sus siglas en inglés). Éste se calcula a partir del cociente de la abundancia relativa de un metal analito entre la abundancia relativa promedio del mismo metal en la corteza terrestre, o bien en el suelo del lugar si es que se encuentra caracterizado. El factor de enriquecimiento se define por (Vianna, et al., 2008)

$$EF_X = \frac{\left(\frac{[X]}{[Ref]}\right)_{PM}}{\left(\frac{[X]}{[Ref]}\right)_{corteza}} \quad (1)$$

Donde:

[X] Es la concentración de un metal, tanto en la muestra en el PM como en la corteza terrestre o en el suelo de la localidad.

[Ref] Es la concentración elemento de referencia elegido. Los elementos empleados con mayor frecuencia son Al, Fe, Si, y Ti.

La interpretación de los valores de EF es sencilla, pero se deben establecer criterios específicos para hacer una adecuada conclusión. Los metales cuyo valor EF sea cercano a uno, se asociarán con origen cortical: polvo geogénico resuspendido, principalmente. Algunos metales podrían ser emitidos tanto de fuentes naturales como antropogénicas. Los investigadores establecen criterios diversos para especificar qué metales se encuentran bajo qué categoría. En general, se indica que los metales cuyos valores de EF se encuentran entre 1 y 5 corresponden a metales emitidos por dos fuentes; otros investigadores toman un intervalo de 1 a 10 para esta misma categoría. Muchos de los autores concuerdan que los valores de EF mayores a 10 o 100 implican que la fuente de emisión de sus correspondientes metales es antropogénica (Qureshi, et al., 2006; Alleman, et al., 2010; Zereini, 2010; Xu, et al., 2012; Ledoux, et al., 2017).

El EF probablemente es la herramienta de identificación de fuentes de emisión de metales a la atmósfera más empleada a nivel mundial. Sin embargo, una de sus limitaciones es suponer que no existe contaminación del metal de referencia seleccionado respecto a la corteza (Marks & McGowan, 2010). La gran mayoría de los estudios contemporáneos combinan este procedimiento con técnicas estadísticas de análisis multivariado. También es necesario considerar el valor de referencia utilizado. A veces las conclusiones correctas se obtienen usando composiciones de suelos locales en vez de la de corteza terrestre promedio.

Herramientas estadísticas.

Muchos trabajos relacionados con la determinación de las fuentes de emisión de contaminación de metales a la atmósfera se basan en procedimientos estadísticos. Los más sencillos utilizan correlación por pares de metales, tal que, los metales que presenten correlación significativa implicarían que han sido emitidos por la misma fuente. Sin embargo, en muchas campañas de muestreo se obtienen gran cantidad de datos por lo que se requieren técnicas estadísticas más robustas y sofisticadas. Un ejemplo es el *modelo receptor* (Belis, et al., 2014).

Uno de los fundamentos principales del modelo receptor es asumir que la masa del contaminante se conserva entre la fuente de emisión y el sitio de colecta. Otro fundamento es el análisis de balance de masa que puede usarse para identificar y prorratear las fuentes de contaminantes atmosféricos mediante la resolución de la ecuación:

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (2)$$

Donde x_{ij} es la concentración de la j -ésima especie en la i -ésima muestra; g_{ik} es la contribución de la k -ésima fuente a la i -ésima muestra; f_{kj} es la concentración de la j -ésima especie en la k -ésima fuente, y e_{ij} es el término residual (ejemplo: la diferencia entre el valor medido y el valor ajustado) (Belis, et al., 2014).

Para encontrar una solución se requiere de una base de datos de constituyentes químicos (concentraciones elementales). Entre mayor sea la cantidad de datos en la matriz, mayor serán las posibilidades de identificar los distintos factores que identifiquen a las fuentes (Belis, et al., 2014).

El modelo receptor proporciona información sobre características de la fuente a partir de las mediciones de la composición química de las partículas en un sitio de muestreo. Las metodologías del modelo receptor más utilizadas en los estudios de prorrateo de fuentes hasta ahora son: el Análisis de Componentes Principales (PCA- del inglés *principal component analysis*), el Análisis de Factores con Factorización de Matriz Positiva (PMF –*Positive Matrix Factorization*) y el Balance Químico de Masas (CMB por sus siglas en inglés).

Existen ventajas y limitaciones teóricas de estos modelos en la identificación e interpretación de las principales fuentes de PM. Sin embargo, diversos autores han recomendado la combinación de estos modelos para obtener soluciones más adecuadas para la identificación de fuentes contaminantes. Stortini y co-autores (Stortini, et al., 2009) aplicaron una combinación de PCA-PMF para identificar las principales fuentes de emisión y sus aportaciones medias a partículas contaminantes. Los autores concluyeron que los modelos combinados son superiores para muchos receptores relativamente complicados.

Metodologías analíticas Instrumentales.

Existe un gran número de técnicas que permiten la determinación del contenido químico en PM, tales como, cromatografía iónica para el caso de especies iónicas, para metales se puede emplear: espectroscopia de emisión atómica de plasma acoplado inductivamente (ICP-AES

– del inglés, *inductively coupled plasma atomic emission spectrometry*), espectrometría de emisión de rayos X inducida por partículas (PIXE– del inglés, *Particle induced X-ray emission spectrometry*), fluorescencia de rayos X; y en el caso particular de metales traza y ultratrazas, la espectrometría de masas de plasma acoplado inductivamente (ICP-MS– del inglés *inductively coupled plasma mass spectrometry*).

Una adecuada metodología para la determinación química de metales en PM debe considerar el procedimiento de extracción/digestión de los analitos de interés para su análisis, lo que implica un reto en sí de la calidad analítica de la investigación. Para el caso de la técnica por ICP-MS se establecen parámetros de calidad que incluyen la mezcla de ácidos para realizar digestiones asistidas por microondas. A su vez se contemplan parámetros que aseguran la calidad mediante materiales de referencia certificados (MRC), así como la información referente a límites de detección y curvas de calibración.

La Zona Metropolitana de la Ciudad de México.

La Zona Metropolitana de la Ciudad de México (ZMCM) es una de las megalópolis más pobladas del mundo con más de 20 millones habitantes en un área aproximada de 2000 km². La zona comprende a la Ciudad de México (16 alcaldías, antes delegaciones), un municipio en Hidalgo y 59 en el Estado de México (Instituto Nacional de Estadística y Geografía, 2014). Las actividades antropogénicas en esta zona han provocado un incremento en los niveles de contaminantes ambientales, producto de las emisiones industriales no controladas, los desechos industriales y domésticos; así como las emisiones de millones de automóviles que circulan en la ciudad. Con esto la calidad ambiental se ha visto mermada, particularmente se ha observado en estudios de vegetación urbana y de suelos urbanos el incremento de los metales traza (Guzmán-Morales, et al., 2011).

El primer trabajo sobre contaminación en la Ciudad de México es reportado en 1960 (Bravo, 1960). Para 1971 se aprobó la “Ley para Prevenir y Controlar la Contaminación Ambiental” como medida para resguardar el ambiente ante el rápido crecimiento urbano. En los 80’s se publicaron trabajos sobre la composición química de las PST. En 1984 entra en operación la Red Automática de Monitoreo Atmosférico (RAMA) que incorpora mediciones de Pb y PM₁₀, En 2003 se añade muestreo de PM_{2.5}. El Sistema de Monitoreo atmosférico (SIMAT) realiza mediciones de contaminantes para formular el Índice Metropolitano de la Calidad del Aire (IMECAS), monitorea rutinariamente la cantidad de PST, concentración de Pb en PST, concentración PM₁₀ y PM_{2.5}. (Dirección de Monitoreo Atmosférico de la Secretaría del Medio Ambiente, 2013) (Raga, et al., 2001).

Las investigaciones en torno a la calidad del aire y su mejoramiento en ZMCM se han abordado desde diferentes áreas, algunas de éstas han estudiado el contenido biológico, (Rosas Pérez, et al., 2007), el contenido de compuestos orgánicos (Sosa, et al., 2009), (Amador-Muñoz, et al., 2013), compuestos inorgánicos (Moya, et al., 2003), caracterización de elementos en PM_{2.5} mediante PIXE (Miranda, et al., 2004). Además, Vega y colaboradores (Vega, et al., 2009) encuentran diversos perfiles de emisión y los aportes de emisión de fuentes contaminantes mediante CMB y PCA: se resaltan la contaminación aportada de fuentes móviles, material geológico y aerosoles secundarios entre otros.

Para contribuir en la mejora continua de la calidad del aire en la ZMCM, se requiere de estudios que puedan ser ejecutados rutinariamente y que puedan evaluar dicha mejora. Se requieren estudios que aborden las causas de variabilidad en las concentraciones de contaminantes, ya sea variabilidad espacial, temporal; o los mecanismos meteorológicos que controlen éstas variaciones. Se requiere también de investigaciones sobre (posibles) contaminantes no contemplados en la normatividad y que puedan requerir ser normados en función de su presencia en la atmósfera, etcétera.

El presente trabajo de tesis extiende el conocimiento existente sobre el contenido químico elemental de las partículas en el aire de la zona metropolitana de la Ciudad de México (ZMCM). Cubriendo con esto requerimientos de investigación y necesidad del conocimiento sobre potenciales contaminantes. A lo largo de los cuatro artículos de investigación, ya publicados, se presentan resultados de gran valor e interés para tomadores de decisiones y para otros científicos. A demás se sientan bases para la realización de análisis que ejecutados rutinariamente (y al paso del tiempo) podrán brindar las tendencias del contenido químico en términos de metales, metaloides, EPG y Hg, dentro de otros y por consecuencia, impactar positivamente en a calidad del aire en beneficio de las personas que habitan la ZMCM.

Objetivo

Determinar la concentración de metales, metaloides, elementos del grupo de platino (EGP) y mercurio en material particulado ($PM_{2.5}$) en la Zona Metropolitana de la Ciudad de México (ZMCM).

Objetivos Particulares

- Proponer un método multielemental de cuantificación de metales en material particulado que permita la evaluación de concentraciones de metales traza y ultra traza por ICP-MS y que dicho método pueda ser empleado de manera rutinaria.
- Asegurar la calidad analítica mediante materiales de referencia certificados (MRC) de un método analítico de cuantificación por ICP-MS de metales colectados en filtros atmosféricos de fibra de vidrio, recubiertos con teflón y sometidos a digestión ácida asistida por microondas.
- Determinar las concentraciones de metales, metaloides, EGP y mercurio en material particulado en $PM_{2.5}$ colectando en la ZMCM.
- Caracterizar la variabilidad de las concentraciones de metales en $PM_{2.5}$ en términos espaciales en la ZMCM.
- Caracterizar la variabilidad de las concentraciones de metales en $PM_{2.5}$ en términos temporales durante dos años de muestreo.
- Determinar el impacto de factores meteorológicos que provocan variabilidad en la dispersión o acumulamiento de metales en $PM_{2.5}$ en la ZMCM.
- Identificar las fuentes de emisión de los metales, metaloides, *EGP* y *mercurio* mediante metodologías estadísticas, y determinar, por ende, el nivel de importancia proporcional de tales fuentes (prorratio).

Metodología

Los cuatro artículos de la presente investigación son suma de la combinación de: ejecutar muestreos atmosféricos (2011 o 2013), cuantificar metales por ICP-MS (método cuya calidad analítica se ha evaluado), incorporar datos meteorológicos disponibles de la SEDEMA, emplear metodologías estadísticas para la inferencia de información, discutir los resultados obtenidos junto con la correspondiente sustracción de conclusiones. A continuación, se describen las características del muestreo atmosférico, los procedimientos de digestión de las muestras, así como los parámetros y controles analíticos de las cuantificaciones.

Muestreos Atmosféricos:

Los muestreos atmosféricos de 2011 y 2013 se llevaron a cabo con la infraestructura pertenecientes a la Red Automática de Monitoreo Atmosférico (RAMA), subsistema del Sistema de Monitoreo Ambiental de la Ciudad de México, (SIMAT) de la Secretaría del Medio Ambiente (SEDEMA) de la Ciudad de México. Ambos muestreos de ejecutaron bajo las mismas condiciones de operación:

Se colectó PM_{2.5} atmosférico en filtros de fibra de vidrio recubiertos con teflón (Fiberfilm Pallflex), pretratados a 180 °C por 24 h para remover impurezas. Los filtros se transportaron y almacenaron envueltos en papel aluminio y bolsas zip-lock a 4°C. Se emplearon muestreadores de alto volumen con selector de partícula <2.5 µm (Andersen General Metal Works and Tish) con flujo promedio de 1.13 m³ min⁻¹ ± 10 % por 24 h durante tres temporadas: seca caliente (abril), lluvias o húmeda caliente (agosto) y seca fría (noviembre). En la Tabla 2 se presentan las fechas calendario de colecta.

Tabla 2 Calendario indicativo de fechas de colecta para los muestreos ejecutados durante 2011 y 2013. Las fechas en las que se ejecutó la colectadas se resaltan en casillas **Negras**.

Muestreo 2011																							
Temporada Seca Cálida ^A Abril 2011							Temporada de Lluvias ^B Agosto 2011							Temporada Seca Fría ^C Noviembre 2011									
Lu	Ma	Mi	Ju	Vi	Sa	Do	Lu	Ma	Mi	Ju	Vi	Sa	Do	Lu	Ma	Mi	Ju	Vi	Sa	Do			
				1	2	3	1	2	3	4	5	6	7		1	2	3	4	5	6			
4	5	6	7	8	9	10	8	9	10	11	12	13	14	7	8	9	10	11	12	13			
11	12	13	14	15	16	17	15	16	17	18	19	20	21	14	15	16	17	18	19	20			
18	19	20	21	22	23	24	22	23	24	25	26	27	28	21	22	23	24	25	26	27			
25	26	27	28	29	30	29	30	31	28	29	30												
Muestreo 2013																							
Temporada Seca Cálida ^A Abril 2013							Temporada de Lluvias ^B Agosto 2013							Temporada Seca Fría ^C Noviembre 2013									
Lu	Ma	Mi	Ju	Vi	Sa	Do	Lu	Ma	Mi	Ju	Vi	Sa	Do	Lu	Ma	Mi	Ju	Vi	Sa	Do			
1	2	3	4	5	6	7				1	2	3	4					1	2	3			
8	9	10	11	12	13	14	5	6	7	8	9	10	11	4	5	6	7	8	9	10			
15	16	17	18	19	20	21	12	13	14	15	16	17	18	11	12	13	14	15	16	17			
22	23	24	25	26	27	28	19	20	21	22	23	24	25	18	19	20	21	22	23	24			
29	30	Mayo 2013				26	27	28	29	30	31	25	26	27	28	29	30						
		1	2	3	4	5																	

^A en los artículos la temporada es referida como Dry Warm (DW).

^B en los artículos la temporada es referida como Rainy (R).

^C en los artículos la temporada es referida como Dry Cold (DC).

Durante cada día de muestro se colectó simultáneamente PM_{2.5} en cinco localidades (Figura 1): Tlalnepantla, San Agustín, La Merced, Universidad Autónoma Metropolitana – campus Iztapalapa y en Coyoacán. En la Tabla 3 se muestran las características para cada sitio. Se empleó un filtro blanco (filtro de campo) por cada día del muestreo.

Tabla 3. Características de los sitios de muestreo de PM_{2.5} en la ZMCM 2011 y 2013

Nombre del sitio	Orientación en ZMCM	Características	Coordenadas geográficas
Tlalnepantla (TLAL) ^A	Noroeste, NO	Zona industrial, comercial y residencial. Congestionamiento vehicular	19°31'42"N 99°12'42"O
San Agustín (SAG) ^B	Noreste, NE	Zona industrial, comercial y residencial. Congestionamiento vehicular	19°31'56"N 99°01'48"O
La Merced (MER) ^C	Centro, C	Zona comercial. Congestionamiento vehicular	19°25'28"N 99°07'09"O
Coyoacán (COY) ^D	Suroeste, SO	Zona residencial, comercial y escolar con tráfico regular	19°20'58"N 99°09'26"O
Universidad Autónoma Metropolitana- Iztapalapa (UAM-I) ^E	Sureste, SE	Zona residencial, comercial y escolar con tráfico regular.	19°21'45"N 99°04'16"O

^A en los artículos el sitio es referido como Northwest (NW).

^B en los artículos el sitio es referido como Northeast (NE).

^C en los artículos el sitio es referido como Center(C).

^D en los artículos el sitio es referido como Southwest (SW).

^E en los artículos el sitio es referido como Southeast (SE).

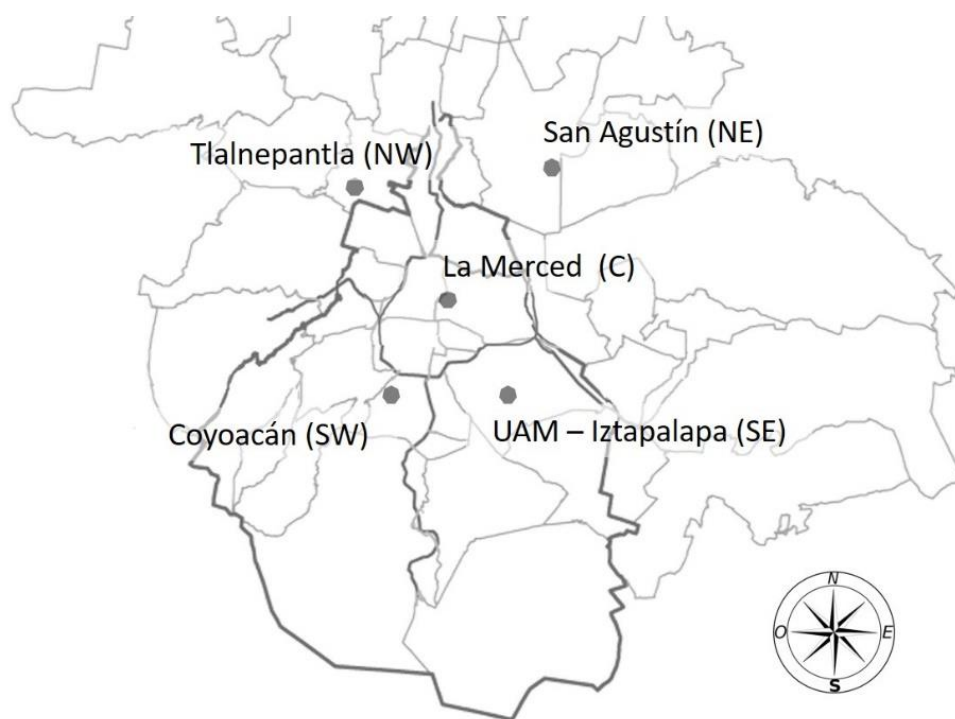


Figure 1 Sitios dónde se ejecutaron los muestros en 2011 y 2013

Evaluación de la calidad analítica y Digestión de Filtros Atmosféricos.

El método de cuantificación de los elementos químicos de interés, se realizó mediante ICP-MS (modelo iCAP-Q de la marca Thermo Scientific) ubicado en el Instituto de Geofísica de la Universidad Nacional Autónoma de México. Este instrumento está equipado con una celda de colisión con discriminador de energía cinética (KED por sus siglas en inglés).

La evaluación de la calidad analítica del método de digestión los filtros colectados durante el muestreo de 2011 se llevó a cabo con el material de referencia certificado (MRC): polvo urbano 1649a del NIST (*National Institute for Standard and Technology*, Estados Unidos). Este MRC 1649a proporciona valores de concentraciones para los siguientes elementos químicos: V, Cr, Mn, Fe, Co, Ni, Cu, Rb, Cd, Sb, Cs, La, Ce, Sm, Eu, Pb, Th. Los resultados de la evaluación de la calidad analítica se encuentran en el artículo titulado “Recognition of the importance of geogenic sources in the content of metals in PM_{2.5} collected in the Mexico City Metropolitan Area”, pp. 29 de la presente tesis.

Del mismo modo, la evaluación de la calidad analítica del método de cuantificación de metales en PM_{2.5} de los filtros colectados durante el muestreo de 2013 se realizó con el mismo procedimiento de digestión, pero utilizando dos materiales de referencia:

El MCR 1648a *material particulado urbano*, proporciona valores certificados para los siguientes elementos: Al, Ti, V, Cr, Mn, Co, Ni, Zn, As, Se, Ag, Cd, Sb y Pb. Los resultados de esta evaluación se reportan en: “Spatial and temporal distribution of metals in PM_{2.5} during 2013: assessment of wind patterns to the impacts of geogenic and anthropogenic sources”. (pp. 48 de la presente tesis). También se incluye en este MCR el valor certificado de concentraciones de Hg. El resultado de la evaluación de la calidad analítica para este metal se encuentra reportado en “Atmospheric PM_{2.5} mercury in the metropolitan area of Mexico City” (pp. 81 de la presente tesis).

El MCR de la Comisión Europea *polvo de camino* BCR-723 proporciona valores certificados de los elementos EGP: Pt, Pd y Rh. El resultado de la evaluación de la calidad analítica por ICP-MS para Pt se reporta en el artículo titulado “Platinum concentration in PM_{2.5} in the Mexico City Metropolitan Area: relationship to meteorological conditions” (pp. 68 de la presente tesis).

La preparación de los MRC y la de las muestras (filtros con) PM_{2.5} provenientes de ambos muestreos (2011 y 2013) se realizaron mediante digestión asistida por microondas. Se empleó el digestor Ethos One de la marca Milestone (Italia). Los vasos de teflón del digestor fueron sometidos a un método de limpieza especializado. Se utilizó un juego de vasos “Pro 24” para la digestión de MRC 1649a y también para la digestión de las muestras de los filtros colectados durante la campaña de 2011; mientras que un juego de vasos “SK-10” se empleó para la digestión de filtros colectados en la campaña de 2013 con los MRC 1648a y BCR-723.

Los MRC fueron preparados de la siguiente manera: a un fragmento de alrededor de 0.1 g de filtro (fibra de vidrio recubierto con Teflón[®], previamente desecado a peso constante), fue *cargado* con aproximadamente 20 mg de MRC (NIST 1649a[2011], NIST

1648a y BCR-723 [2013]). Tanto los filtros cargados con MRC como los filtros atmosféricos (un décimo) con $PM_{2.5}$ fueron colocados en predigestión una noche con una mezcla ácida de 8 mL de agua regia más 1 mL de HF. Posteriormente, se realizó la digestión asistida con el Ethos One. En cada *carrusel* de vasos del rotor de digestión de muestras se consideraron tres blancos: blancos de ácidos, blancos de filtros y blancos de campo (los manipulados en los muestreos atmosféricos). El programa de digestión partió de temperatura ambiente y se llevó hasta 180 °C durante 20 min, esta temperatura se mantuvo por 15 minutos. Posteriormente y tras enfriamiento, las muestras fueron llevadas a sequedad, se les añadieron 3 mL de HCl, y nuevamente se llevaron a sequedad para eliminar restos de HF. Las muestras digeridas fueron aforadas a 50 mL con HNO_3 al 2%.

Cuantificación analítica por ICP-MS

Para efectuar la cuantificación de metales mediante ICP-MS, se emplearon curvas de calibración con estándares multielementales de 0 a 5 $ng\ ml^{-1}$ a 6 puntos para todos los elementos en los MCR 1649a y 1648a excepto el Hg cuya curva se preparó de 0 a 2.5 mgL^{-1} a 12 puntos.

El Pt en el BCR-723 y el Hg en el 1648a fueron determinados por separado. La cuantificación de Hg por ICP-MS presenta complicaciones particulares: el procedimiento requiere de lavados con solución de Au. Por otra parte, la cuantificación de EGP mediante ICP-MS requieren de minimizar eficazmente las interferencias espectrales. El principal interferente para ^{195}Pt es ^{179}Hf ^{16}O (Niemelä, et al., 2004). Todas las soluciones estándar se prepararon por dilución de la solución patrón de multielemental (*High Purity Standards*) con 2% de HNO_3 (v/v). La deriva instrumental se corrigió empleando un patrón interno de ^{115}In ($10\ \mu g\ kg^{-1}$), preparado a partir de una solución certificada “stock” de $1000\ mg\ L^{-1}$ (Merck).

Resultados:

Los resultados constituidos por: determinaciones de concentraciones de metales en PM_{2.5}, evaluación de la calidad analítica de las determinaciones, análisis de variabilidad espacio-temporal e identificación de fuentes de emisión son tan extensos que, además de ser de gran valor científico, han sido publicados en cuatro artículos en revistas científicas internacionales. La Tabla 4 presenta los metales analizados, y las referencias correspondientes de la publicación

Tabla 4 Artículos comprendidos en el presente Tesis.

Metales Estudiados	Artículo publicado	Revista	Referencia
Muestreo atmosférico de 2011			
Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Rb, Sr, Cd, Sb, Cs, Th, Pb, Tl La, Ce, Sm y Eu.	Recognition of the importance of geogenic sources in the content of metals in PM _{2.5} collected in the Mexico City Metropolitan Area	Environmental Monitoring and Assessment	(Morton-Bermea, et al., 2018)
Muestreo atmosférico de 2013			
Ti, V, Cr, Mn, Co, Ni, Cu, Mo, Ag, Cd, Sb, Pb, La, Sm, Ce, y Eu.	Spatial and temporal distribution of metals in PM _{2.5} during 2013: assessment of wind patterns to the impacts of geogenic and anthropogenic sources	Environmental Monitoring and Assessment	(Garza-Galindo, et al., 2019)
Pt	Platinum concentration in PM _{2.5} in the Mexico City Metropolitan Area: relationship to meteorological conditions	Human and Ecological Assessment: International Journal	(Garza-Galindo, et al., 2018)
Hg	Atmospheric PM _{2.5} mercury in the Metropolitan Area of Mexico City	Bulletin of Environmental Contamination and Toxicology	(Morton-Bermea, et al., 2018)

En general, los resultados de estos artículos detallan los patrones de distribución de los metales analizados en PM_{2.5} e identifican las localidades y temporadas en que ocurrieron episodios de altas concentraciones. La comparación de los resultados entre ellos y con los resultados de trabajos reportados previamente en la zona de estudio permite conocer la tendencia (crecientes o decrecientes) a lo largo del tiempo. La comparación de estos resultados con los *informados* (reportados) para otras ciudades en el mundo dimensiona las consecuencias de los factores de urbanización, movilidad, desarrollo económico, entre otros,

y también las posibilidades de evolución del escenario en función de estos factores. Estas comparaciones se encuentran reportadas respectivamente en estos artículos.

El artículo “Recognition of the importance of geogenic sources in the content of metals in PM_{2.5} collected in the Mexico City Metropolitan Area” corresponde a la *precuela* del artículo “Spatial and temporal distribution of metals in PM_{2.5} during 2013: assessment of wind patterns to the impacts of geogenic and anthropogenic sources” (Título semejante al de la presente tesis):

Determinar las concentraciones de metales en PM_{2.5} [antecedida de su correspondiente evaluación de la calidad analítica] en el muestreo de 2011 confirmó la capacidad analítica en esta matriz novedosa para el grupo de trabajo. Este logro es importante en sí mismo ya que marcó la pauta para no sólo realizar una caracterización química del PM colectado, sino también para marcar precedentes en la implementación de análisis rutinarios; tal que, el procedimiento se repitió con muestras del 2013 pero con diferencias sutiles en la digestión y empleo de materiales de referencia disponibles.

Profundizar en la obtención de resultados evaluados estadísticamente se pudo lograr al contar con una segunda base de datos correspondiente el muestreo realizado en 2013. Las concentraciones de elementos en las bases de datos de 2011 y 2013 fueron analizadas empleando estadística descriptiva e inferencial para conocer y confirmar las variaciones espaciales y estacionales. Así como las fuentes de emisión. Las similitudes entre estos años de muestreo brindaron certeza a los procedimientos efectuados, así mismo, las diferencias entre ellos brindaron la posibilidad de ser reportados en dos publicaciones independientes y complementarias.

Los metales Pt y Hg en los artículos “Platinum concentration in PM_{2.5} in the Mexico City Metropolitan Area: relationship to meteorological conditions” y “Atmospheric PM_{2.5} mercury in the metropolitan area of Mexico City” merecen un *apartado* respecto a los demás metales por sus implicaciones ambientales en el contexto urbano. Estos metales, como contaminantes han sido poco estudiados en comparación con los demás, así que, estos trabajos aportan información novedosa para su comprensión y del entendimiento del papel que juegan en la atmosfera local

A continuación, se presentan las correspondientes publicaciones:

“Recognition of the importance of geogenic sources in the content of metals in PM_{2.5} collected in the Mexico City Metropolitan Area”

Resumen:

Se determinaron las concentraciones medianas, promedio y desviaciones estándar para Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Rb, Sr, Cd, Sb, Cs, Th, Pb, Tl, La, Ce, Sm y Eu en PM_{2.5} colectado en el muestreo de 2011 (Tabla 4 del artículo).

Mediante diagramas de cajas y bigotes (Fig. 3 del artículo) y comparación de medianas (u test Mann-Whitney, Tablas 6 y 7 del artículo) se identificó la variación espacial y temporal: En las localidades al norte (NW y NE) se registraron las concentraciones más altas para la mayoría de los metales estudiados; éstas ocurrieron durante DW.

Mediante PCA se reconoció la importancia que tiene las fuentes geogénicas en el aporte de metales en PM_{2.5} (Factores 1: Cr, La, Ce, Sm y Th; Factor 2: Ti, Fe, Mn, Co y Cu, Factor 3: Rb, Sr, y Eu). Las fuentes antropogénicas identificadas: Factor 4 (Ni y V), Factor 5 (Cd, Pb), Factor 6 (Sb). Las fuente que aporte Ni y V se propone ser mixtas: argumentos que soportan este hecho se discuten en extenso en (Garza-Galindo et al 2019).

Se confirmó la importancia de las fuentes geogénicas en el aporte de metales al aire respirable en la fracción fina mediante la Figura 4 (del artículo) “distribución de patrones de elementos de las tierras raras (o lantanoideas) normalizados con condrita.

Se concluye que las fuentes que aportan metales geogénicos son importantes, que las concentraciones más altas de estos metales se encuentran al norte de ZMCM y que son coherentes con los patrones dominantes de viento, también que las concentraciones más altas para esto metales ocurren en la temporada seca y calurosa. Las fuentes de emisiones de metales son menores en comparación con las geogénicas para la ZMCM y que son homogéneas espacialmente.

Recognition of the importance of geogenic sources in the content of metals in PM_{2.5} collected in the Mexico City Metropolitan Area

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Abstract The study of airborne metals in urban areas is relevant due to their toxic effects on human health and organisms. In this study, we analyzed metals including rare earth elements (REE) in particles smaller than 2.5 μm (PM_{2.5}), collected at five sites around the Mexico City Metropolitan Area (MCMA), during three periods in 2011: April (dry-warm season, DW), August (rainy season, R), and November (dry-cold season, DC). Principal component analysis allowed identifying factors related to geogenic sources and factors related to anthropogenic sources. The recognition of the high impact of geogenic sources in PM_{2.5} is in agreement with the REE

distribution patterns, which show similar behavior as those shown by igneous rocks, confirming the influence of the regional geogenic material. Metals associated to geogenic sources showed higher concentration ($p < 0.05$) at NE of the MCMA and a significant correlation with prevalent winds. Geogenic metals show similar seasonal distribution, with the highest concentration during DW ($p < 0.05$), suggesting a possible metal resuspension effect which affects more significantly at lower relative humidity (RH). The metals associated with anthropogenic sources are in agreement with the urban complexity of the area, showing homogenous distribution throughout MCMA ($p > 0.05$) and no similar seasonal pattern among them. These unexpected results exposed outstanding information regarding the identification of different geogenic sources as the main contributors of metals in the atmospheric environment in the MCMA and highlighted the importance of meteorology in the spatial and seasonal metal patterns.

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Keywords PM_{2.5} · Atmospheric pollution · Metals · Rare earth elements · Spatial distribution pattern · Seasonal distribution pattern

Introduction

During the last decade, atmospheric contamination in urban areas has attracted attention due to increased

anthropogenic emissions. In order to evaluate the degree of air quality degradation, chemical studies on suspended particulate matter are of particular relevance because by identifying their sources, these studies can help to develop efficient strategies for air quality control. Atmospheric particulate matter (PM) is a mixture of solid particles and liquid droplets with diameter less than 100 μm . The size and composition of PM depend on the sources and formation processes (Finlayson-Pitts and Pitts 2000). This is an important issue due to the effects on human health risk, especially those particles with diameter less than 2.5 μm ($\text{PM}_{2.5}$) (Dockery and Pope 1994; Pope et al. 1995; Pinkerton et al. 2000; Pope et al. 2002; Gauderman et al. 2004; Hu 2009; Feng et al. 2016; Ma et al. 2017; Zhou et al. 2017).

Many studies have focused on the determination of elemental constituents, inorganic ions, and organic components of $\text{PM}_{2.5}$ (Querol et al. 2004; Moreno et al. 2006a, b; Ragosta et al. 2008; Kulshrestha et al. 2009; Ravindra et al. 2008; Zhao et al. 2009; Amador-Muñoz et al. 2011; Xu et al. 2012; Chen et al. 2014; Gao et al. 2016). Metals in $\text{PM}_{2.5}$ vary over a wide range of concentrations. Furthermore, reported inhomogeneity in pollution levels in the same urban area has led to the identification of punctual sources.

Geogenic and anthropogenic emissions can contribute as sources of metals onto PM. Geogenic sources may result from volcanic activity, erosion of crustal minerals, sea salt aerosols, etc., while anthropogenic sources include vehicular traffic, fossil fuel burning, waste incineration, and industrial metallurgical processes, among others.

Although anthropogenic activities are recognized as the main contributors of PM into the urban air, metals from geogenic sources have been less highlighted. Multivariate analysis has been widely used to determine specific sources based on metal markers (Kulshrestha et al. 2009). In this context, the rare earth elements (REEs) provide relevant information. REEs have similar configuration of valence electrons and ionic ratios. As they have similar chemical and physical behavior, REE can be used as geochemical tracer to characterize igneous rocks and to determine geogenic sources. In several urban areas over the world, environmental enrichment of REE has been related to the use of products enriched with REE in different fields, including ceramics, electronics, optoelectronics, superconductors,

pharmaceutical, and fertilizers. However, the genetic information of REE contained in $\text{PM}_{2.5}$ can also be used to identify regional geogenic sources.

The Mexico City Metropolitan Area (MCMA) has experienced a substantial uncontrolled development in the suburban part of the city over the past 30 years. The impact of the urbanization and industrialization growth in the urban area of the MCMA has increased the metal content in the environment, as in the case for soils (Morton-Bermea et al. 2009a, b; Rodríguez-Salazar et al. 2011), biological material (Guzmán-Morales et al. 2011), and air (Rosas et al. 1995; Miranda et al. 2000; Chow et al. 2002; Querol et al. 2008). Regarding atmospheric contamination in MCMA, Rosas et al. (1995) reported lead on particles smaller than 10 μm (PM_{10}) during 1990–1991, originated by the use of leaded gasoline (used in Mexico up to 1989). Miranda et al. (2000) reported 15 elements in particles < 15 μm (coarse fraction) and $\text{PM}_{2.5}$ (fine fraction) collected during summer of 1995 in the south of Mexico City. Chow et al. (2002) described 36 metals, ions, and carbon collected in $\text{PM}_{2.5}$ and PM_{10} around Mexico City during winter 1992. Miranda et al. (2000; 2005) and Chow et al. (2002) associated the metals in the air with the emission from natural (suspended dust) and anthropogenic sources (vehicular traffic and industrial sources). Moreover, Querol et al. (2008) published chemical speciation of PM_{10} , $\text{PM}_{2.5}$, and PM_1 , collected during March 2006 at different sites in the MCMA, as part of the MILAGRO (Megacity Initiative: Local and Global Research Observations) campaign. They associated the high metal levels with resuspension of mineral dust, as well as with industrial emissions, local traffic, and oil combustion.

Since 1986, the local government authorities of Mexico City, through the Dirección de Monitoreo Atmosférico (SEDEMA), has established a network of air quality monitoring stations, including $\text{PM}_{2.5}$ among other parameters. Nowadays, there are more than 13 stations collecting TSP (total suspended particles), PM_{10} , and $\text{PM}_{2.5}$ around MCMA. Despite the big effort done by the air quality monitoring program, no extensive data on spatial and temporal variations of $\text{PM}_{2.5}$ elemental composition have been published. The objective of this study was to investigate the chemical components (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Rb, Sr, Cd, Sb, Cs, Th, Pb, Tl, La, Ce, Sm, and Eu) of $\text{PM}_{2.5}$ to evaluate, in terms of meteorological parameters, their temporal and spatial variation. The

Table 1 Sampling sites

Site in MCMA	Site name	Main characteristics
Northwest, NW	Tlalnepantla	Industrial, residential, and commercial
Northeast, NE	San Agustín	Residential and commercial with few industrial settlement
Central, C	Merced	Commercial and residential
Southwest, SW	Coyoacán	Residential
Southeast, SE	Universidad Autónoma Metropolitana-Iztapalapa	Residential with small factories

assessment of this data is a key point to identify source apportionment and their contribution.

Experimental method

PM_{2.5} sampling

A PM_{2.5} sampling campaign was conducted in the MCMA in 2011. Twenty-four-hour PM_{2.5} samples were collected simultaneously every sixth day, at five representative sites with different urban conditions in the MCMA (Table 1 and Fig. 1): northwest (NW, Tlalnepantla), northeast (NE, San Agustín), center (C Merced), southwest (SW, Coyoacán), and southeast (SE, Universidad Autónoma Metropolitana, Iztapalapa).

Sampling was performed during three seasons in 2011: April (dry-warm season, DW), August (rainy

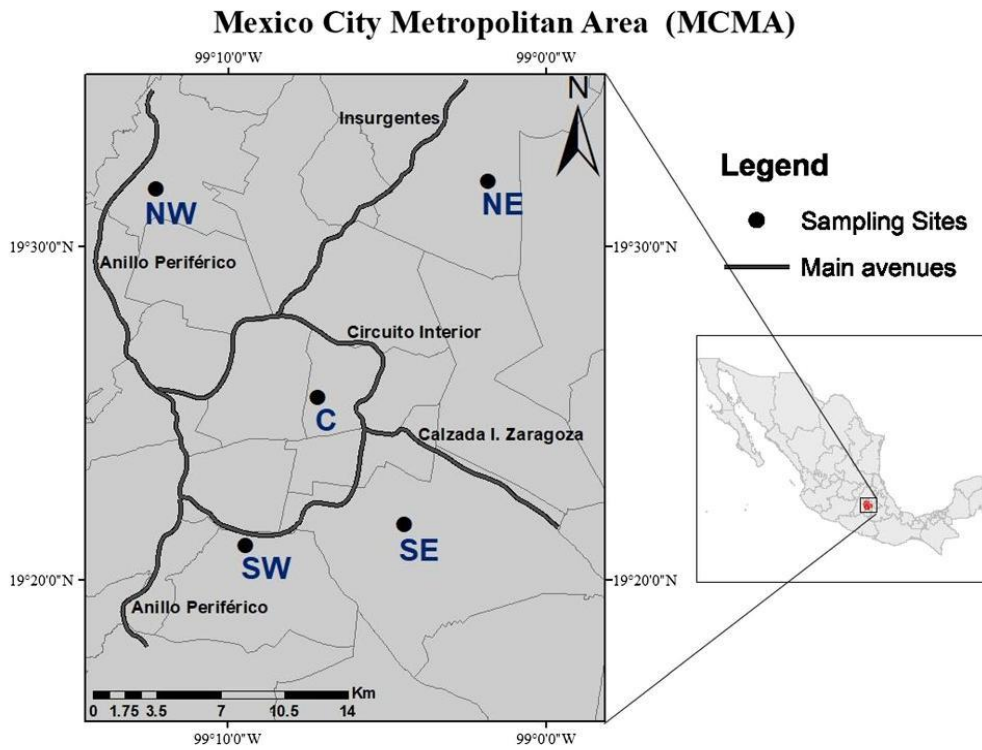


Fig. 1 Sampling sites in MCMA

Table 2 Analytical method efficiency. Recovery percentages of metals from NIST 1649a ($n = 22$)

	NIST 1649a Reference concentration (mg kg ⁻¹)	NIST 1649a Experimental concentration (mg kg ⁻¹)	DL (µg kg ⁻¹)	Recovery rate (%)	% CV
V	345	254	0.17	73.8	3.7
Cr	211	203	0.26	96.6	5.6
Mn	237	272	0.95	115.0	6.7
Fe	29,800	27,624	2.7	92.7	5.9
Co	16.4	13.2	0.56	80.5	5.8
Ni	166	128	0.44	77.7	7.2
Cu	223	175	1.09	78.5	6.1
Rb	48	59	1.76	124.0	6.8
Cd	22	23	0.05	108.8	9.8
Sb	29.9	27	0.08	92.4	6.0
Cs	2.84	3.02	0.17	106.6	10.1
La	33	25	0.07	76.4	9.3
Ce	52	40	0.9	78.2	9.9
Sm	4.7	3.9	0.23	82.1	8.3
Eu	0.87	0.92	0.08	106.6	8.7
Pb	12,400	8928	1.2	72.0	2.9
Th	6.6	6.7	0.03	101.4	4.8

DL detection limit

season, R), and November (dry-cold season, DC). Thereby, 73 PM_{2.5} samples were collected.

The airborne particles were accumulated with a high volume sampler (Tisch and Andersen General Metal Works) with a flow rate of 1.13 m³ min⁻¹ ± 10% on Teflon-coated glass fiber filters (20 cm × 25 cm) pre-baked to 180 °C for at least 24 h. Blank test background contamination was monitored by using operational blanks (unexposed filter), which were processed in parallel with field samples.

Analytical treatment

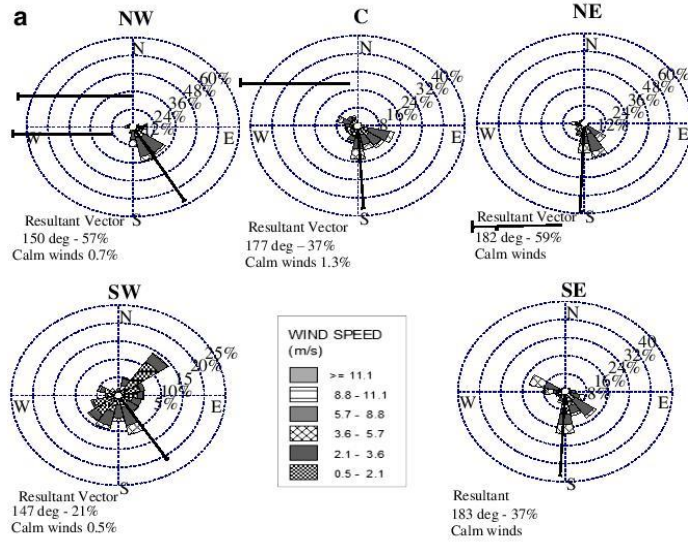
All samples and blank filters were kept in a desiccator for 48 h. A fraction (about 1/20) was exactly weighted and digested in Teflon vessels where 8 mL aqua regia and 2 mL HF were added. The mixture was left to stand overnight. Thereafter, the mixture was subjected to microwave-assisted digestion procedure using an ETHOS ONE (Millipore) microwave oven equipped with a rotor system for 10 Teflon vessels (PRO-24).

Table 3 Seasonal comparison of PM_{2.5} and meteorological parameters. Significantly higher values are in italics ($p < 0.05$)

2011	DW			R			DC			Trend ($p < 0.05$)
	Mean	Median	SD	Mean	Median	SD	Mean	Median	SD	
PM _{2.5} (µg m ⁻³)	29.8	<i>31.0</i>	6.5	12.4	13.0	5.9	22.9	23.5	6.5	DW > DC > R
RH (%)	44.8	45.8	16.7	54.4	<i>59.8</i>	18.5	52.0	<i>60.0</i>	17.2	DC = R > DW
T (°C)	20.7	<i>20.9</i>	1.9	17.6	17.6	1.2	14.2	14.5	2.2	DW > R > DC
Wsp (m s ⁻¹)	1.8	1.7	0.3	2.5	<i>2.40</i>	0.4	2.1	1.7	0.6	R > DC = DW

SD standard deviation

Fig. 2 **a** Wind roses for the sampling sites in MCMA during 2011. **b** Representative HYSPLIT back trajectories during the sampling period in the study area (Stein et al. 2015; Rolph et al. 2017)



b NOAA HYSPLIT MODEL
Backward trajectories ending at 0600 UTC 10 Apr 11
GHDA Meteorological Data

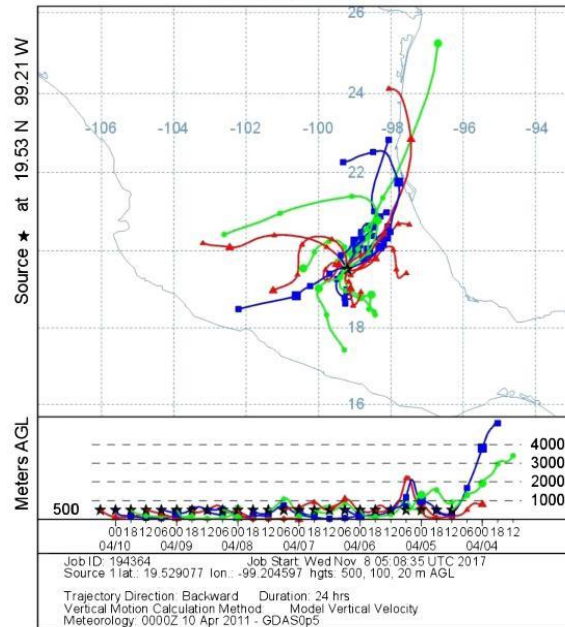


Table 4 Metal concentration (ng m^{-3}) in $\text{PM}_{2.5}$ ($\mu\text{g m}^{-3}$). Individual metal (M) mass contribution respect to metal total mass (M_T) (M/M_T)

	Mean $\mu\text{g m}^{-3}$	Median	Min	Max	SD	RSD (%)	M/M_T (%)
$\text{PM}_{2.5}$	21.6	21.00	5.00	43.00	9.08	41.9	–
			ng m^{-3}				
Ti	113.81	107.58	25.55	329.34	54.24	0.477	10.11
V	14.41	8.93	0.58	76.5	15.49	1.075	1.28
Cr	17.94	17.97	2.72	30.35	6.33	0.353	1.59
Mn	15.52	13.63	0.57	53.07	8.72	0.562	1.38
Fe	762.41	601.56	73.46	3351.43	520.82	0.683	67.72
Co	0.32	0.23	0.04	1.49	0.25	0.781	0.03
Ni	5.86	5.04	0.82	19.53	3.77	0.643	0.52
Cu	59.58	26.89	1.74	363.14	71.54	1.201	5.29
Rb	7.44	7.80	1.62	13.33	2.55	0.343	0.66
Sr	94.31	90.00	2.60	203.38	48.74	0.512	8.38
Cd	1.29	1.27	0.02	2.73	0.53	0.411	0.11
Sb	5.37	4.61	0.17	21.61	3.31	0.616	0.48
Cs	0.24	0.15	0.06	0.76	0.17	0.708	0.02
Th	0.24	0.12	0.02	1.54	0.31	1.292	0.02
Pb	24.7	20.78	1.12	69.01	13.38	0.542	2.19
Tl	0.10	0.10	0.00	0.25	0.04	0.400	0.01
La	0.63	0.44	0.06	3.18	0.55	0.873	0.06
Ce	1.33	1.06	0.18	6.55	1.04	0.782	0.12
Sm	0.16	0.11	0.02	0.78	0.14	0.875	0.01
Eu	0.24	0.21	0.01	0.59	0.13	0.542	0.02

SD standard deviation, Min minimum, Max maximum, RSD relative standard deviation

The digestion temperature ranged from room temperature to 190 °C in 25 min and maintained for 15 min. After cooling, the solution was transferred to a Teflon vessel and evaporated to dryness. To ensure full removal of HF, 3 mL HCl was added to the digestate and evaporated twice. The final digested samples were taken to a volume of 50 mL with 2% HNO_3 (v/v).

Instrumental analysis

Metal concentration measurements (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Rb, Sr, Cd, Sb, Cs, Th, Pb, Tl, La, Ce, Sm, and Eu) were carried out using an ICP-MS (iCAP Q Thermo) at the Instituto de Geofísica, Universidad Nacional Autónoma de México. Prior to ICP-MS analysis, a calibration curve was performed using a five-point curve (0, 0.01, 0.1, 1, and 5 ng mL^{-1}) with standard solutions that were prepared by diluting a multi-element standard solution (High Purity Standard) with 2% HNO_3 (v/v). Instrumental drift was corrected using ^{115}In as

internal standard, prepared from a certified stock solution of 1000 mg L^{-1} (Merck). Urban dust reference material 1649a (National Institute for Standard and Technology) was used to evaluate the method's efficiency.

Statistical analysis

Statistica Software version 10.0 (Statsoft, Dell Inc.) was used to calculate all statistical metrics. Median comparison was made by Mann–Whitney U test. Correlation analysis was carried out by Spearman R . Factor analysis with PCA as an extraction method and varimax rotation was used to identify the sources. Results from PCA were compared using either the Spearman or Pearson correlation matrix showing coherent results.

Meteorological data

The weather in MCMA can be divided in three climatic periods per year: warm-dry season (DW) from April to

Table 5 Comparison of metal concentration of our study with other cities, ng m⁻³

	This work (median, PM _{2.5})	Fuzhou, China 2007–2008 (mean, PM _{2.5}) ¹	Ulsan, Korea Spring 2008 (average, PM _{2.5}) ²	Ulsan, Korea Sommer 2008 (average, PM _{2.5}) ²	Barcelona 2001 (mean, PM _{2.5}) ³	Hong Kong 2003 (average, PM _{2.5}) ⁴
Ti	107.58	44.8 ± 31.3			26.3	12 ± 7.9
V	8.93	3.7 ± 2.1			9.5	15 ± 12
Cr	17.97	15.7 ± 9.3	8.1	11.6	2.9	1.2 ± 0.28
Mn	13.63	47.5 ± 30.3	10.2	21.5	9.6	19 ± 12
Fe	601.56	655.1 ± 437.7	302.6	357.9		200 ± 110
Co	0.23					1.1 ± 0.79
Ni	5.04	4.2 ± 3.1	20.0	5.2		6.4 ± 4.6
Cu	26.89	179.7 ± 132.9	44.9	42.1	31.7	33 ± 13
Rb	7.80					5.6 ± 5.9
Sr	90.00				1.9	
Cd	1.27		3.8	5.6	0.6	
Sb	4.61				4.3	6.8 ± 4.1
Cs	0.15					
Th	0.12					
Pb	20.78	39.6 ± 19.8	61.1	127	40.3	80 ± 78
Tl	0.10					
La	0.44					
Ce	1.06					
Sm	0.11					
Eu	0.21					

¹ Xu et al. 2012

² Hieu and Lee 2010

³ Moreno et al. 2006a, b

⁴ Cheng et al. 2010

June, rainy season (R) from July to October, and cold-dry season (DC) from November to February (Jáuregui 2000). Data of relative humidity (RH, %), temperature (T, °C), wind speed (m s⁻¹), wind direction (grades), and PM_{2.5} mass concentration for the corresponding sampling days were downloaded from the Automatic Monitoring Network website (<http://www.aire.cdmx.gob.mx/default.php?opc=aKBhnmI=&opcion=Zw==>).

Results and discussion

Quality control

The analytical procedure of simultaneous analysis of metals contained in particulate matter was evaluated. Detection limits were calculated as three times the standard deviation of 10 replicates of the blank filter.

Blank test background contamination was monitored using operational blanks (unexposed filter papers), which were processed with field samples. All analyzed metals are above the detection limits. Accuracy was evaluated by means of recovery rates of 22 aliquots of SRM NIST 1649a, loaded in Teflon-coated glass fiber filters (the same filter employed to collect PM_{2.5}). Good agreement is observed between the data and reference concentration for all metals. The average recoveries ranged between 72 and 124%. Results obtained from ICP-MS metal analysis and recovery percentages as well as detection limits are reported in Table 2.

Good recoveries are due to combined effect of an optimum digestion procedure and the optimal ICP-MS instrumental conditions that lead to obtaining low detection limits and low production of mass interferences. It must be mentioned that Ti, Sr, and Tl are not included

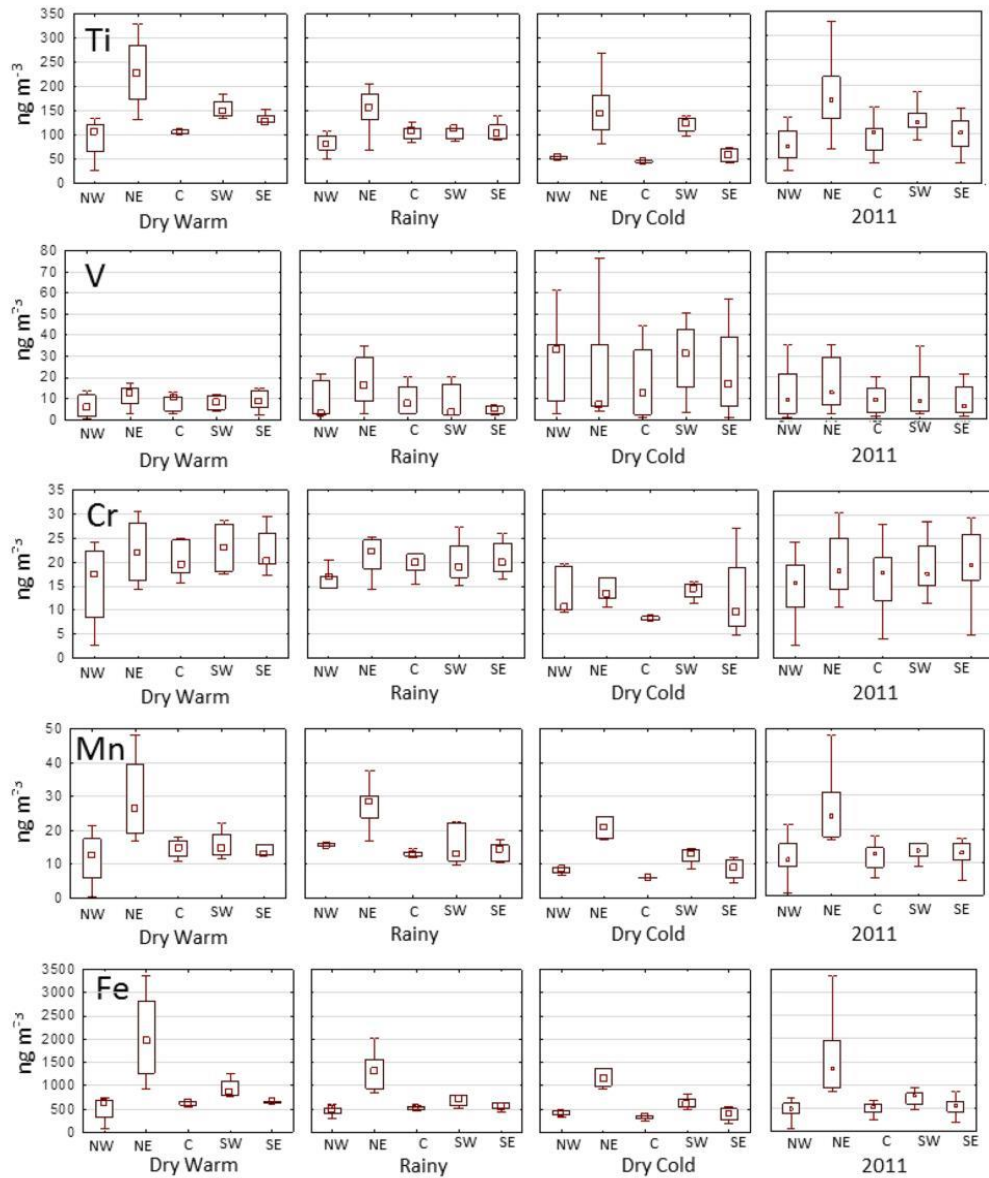


Fig. 3 Spatial and seasonal distribution pattern of metals in $PM_{2.5}$. Middle square—median, box—25th and 75th percentiles, and bars—10 and 90 percentiles

in as certified elements in NIST 1649a; the analytical method showed good reproducibility, with a relative

standard deviation (RSD = 0.42–1.7%, $n = 22$). Therefore, they were analyzed routinely in $PM_{2.5}$ samples.

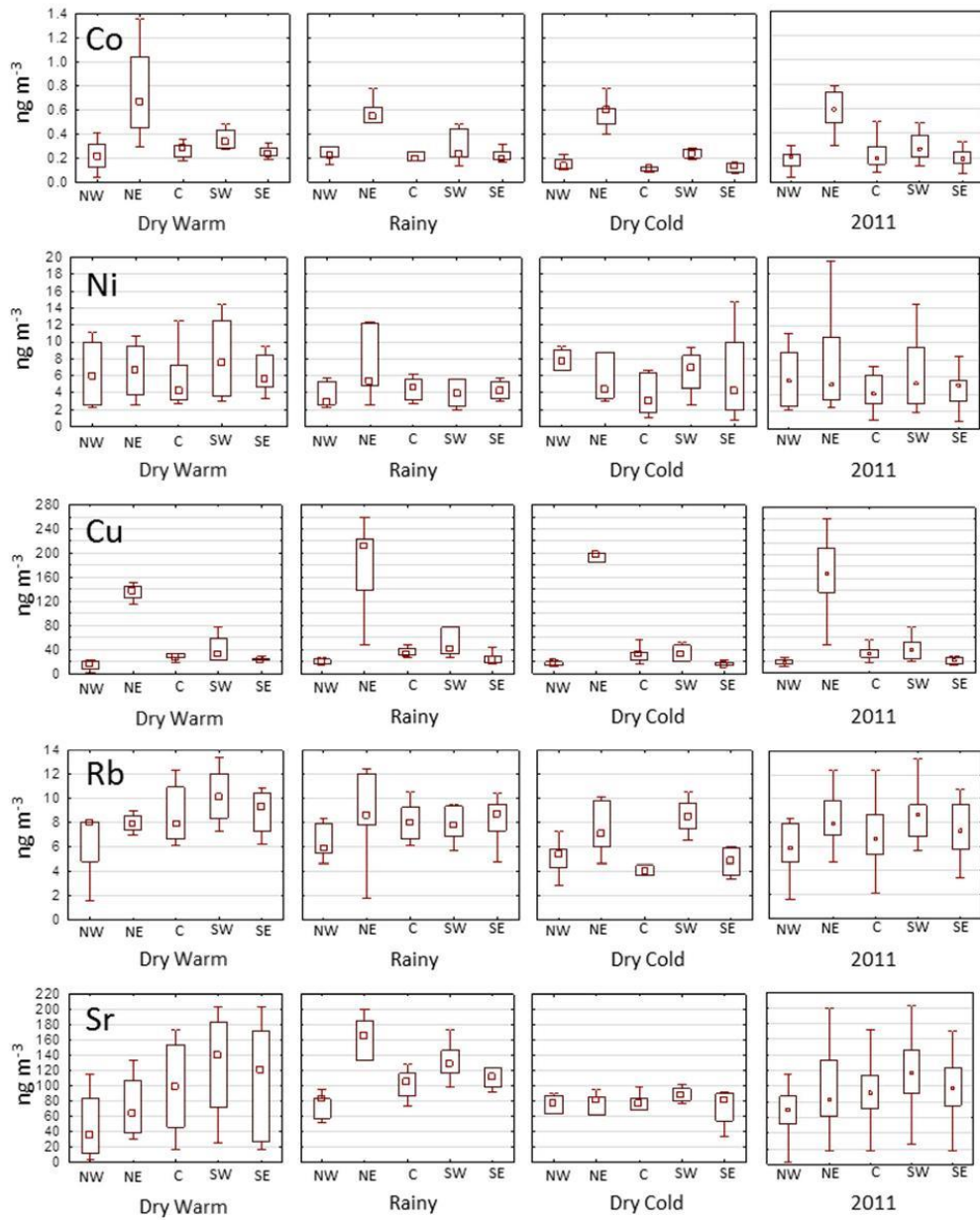


Fig. 3 (continued)

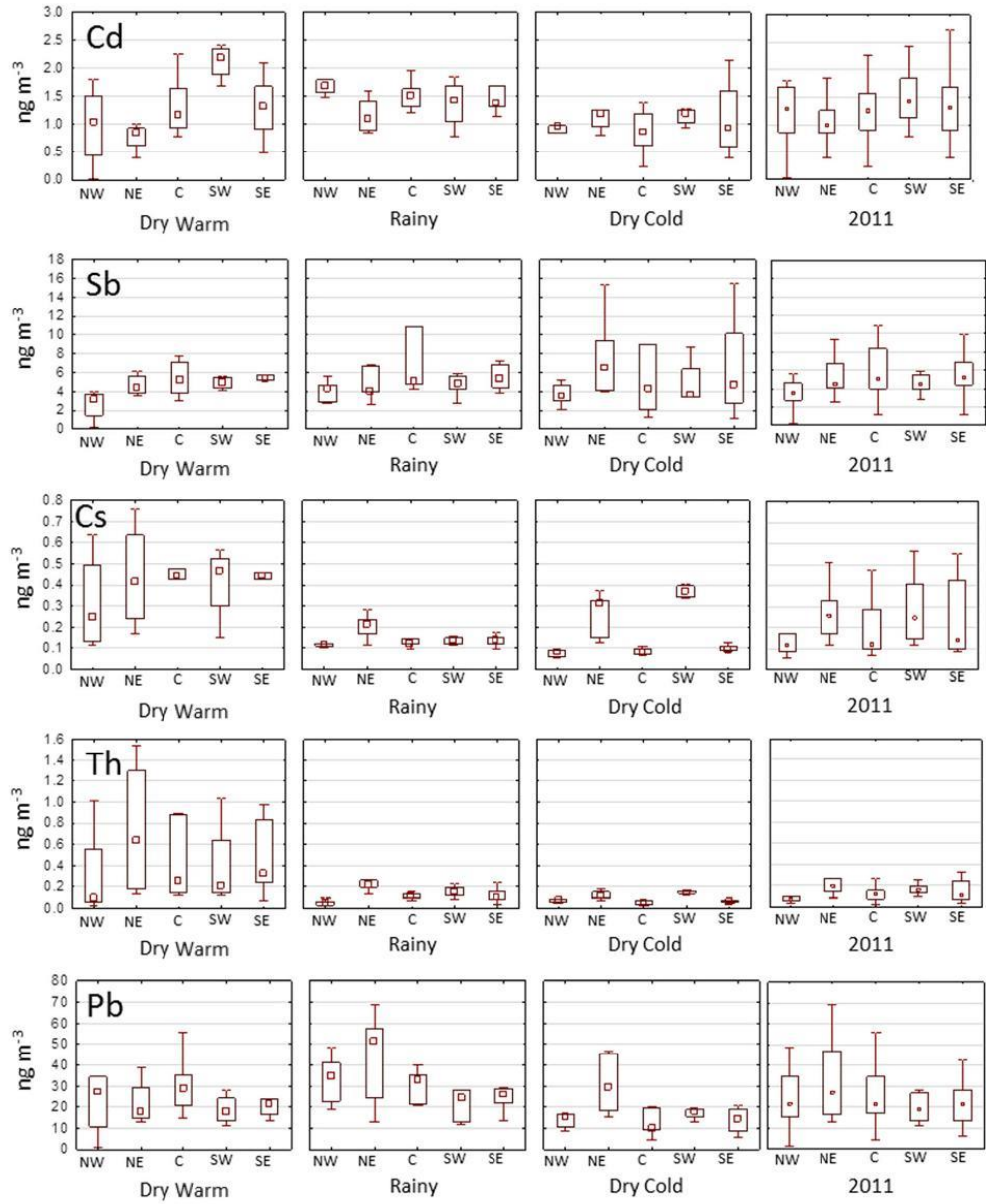


Fig. 3 (continued)

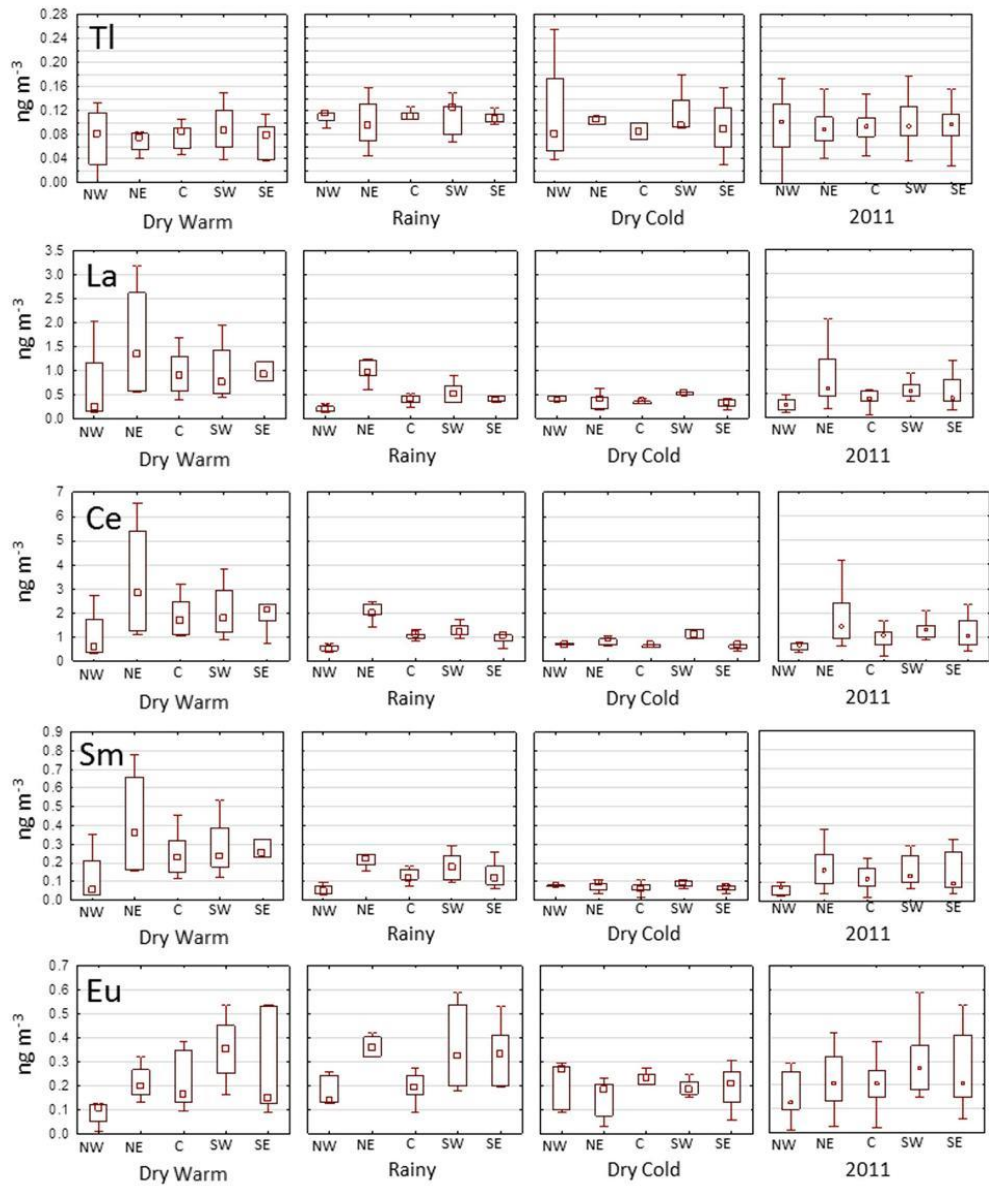


Fig. 3 (continued)

Recoveries in Table 2 are in the same range than those reported elsewhere by other groups using different

digestion parameters (concentration and volume of acids and oxidizing agents), as well as microwave oven

Table 6 Annual median comparison of metal concentration among sites ($p < 0.05$). Sites in *italic* form contain a higher metal concentration. *Equal sign* means similar concentrations between sites

Comparison of median	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Rb	Sr	Cd	Sb	Cs	Th	Pb	Tl	La	Ce	Sm	Eu
NW Vs NE	<i>NE</i>	=	=	<i>NE</i>	<i>NE</i>	<i>NE</i>	=	<i>NE</i>	<i>NE</i>	=	=	<i>NE</i>	<i>NE</i>	<i>NE</i>	=	=	<i>NE</i>	<i>NE</i>	<i>NE</i>	=
NW Vs C	=	=	=	=	=	=	=	<i>C</i>	=	=	=	=	=	=	=	=	=	<i>C</i>	<i>C</i>	=
NW Vs SW	<i>SW</i>	=	=	=	<i>SW</i>	=	=	<i>SW</i>	<i>SW</i>	<i>SW</i>	=	<i>SW</i>	<i>SW</i>	<i>SW</i>	=	=	<i>SW</i>	<i>SW</i>	<i>SW</i>	<i>SW</i>
NW Vs SE	=	=	=	=	=	=	=	=	=	=	<i>SE</i>	<i>SE</i>	=	=	=	=	=	<i>SE</i>	<i>SE</i>	<i>SE</i>
NE Vs C	<i>NE</i>	=	=	<i>NE</i>	<i>NE</i>	<i>NE</i>	=	<i>NE</i>	=	=	=	=	<i>NE</i>	<i>NE</i>	=	=	=	=	=	=
NE Vs SW	=	=	=	<i>NE</i>	<i>NE</i>	<i>NE</i>	=	<i>NE</i>	=	=	<i>SW</i>	=	=	=	=	=	=	=	=	=
NE Vs SE	<i>NE</i>	=	=	<i>NE</i>	<i>NE</i>	<i>NE</i>	=	<i>NE</i>	=	=	=	=	=	=	=	=	=	=	=	=
C Vs SW	<i>SW</i>	=	=	=	<i>SW</i>	=	=	=	=	=	=	=	<i>SW</i>	<i>SW</i>	=	=	=	=	=	=
C Vs SE	=	=	=	=	=	=	=	<i>C</i>	=	=	=	=	=	=	=	=	=	=	=	=
SW Vs SE	=	=	=	=	<i>SW</i>	<i>SW</i>	=	<i>SW</i>	=	=	=	=	=	=	=	=	=	=	=	=

settings (Karanasidou et al. 2005; Karthikeyan et al. 2006).

PM_{2.5} mass concentration and meteorological conditions

Seasonal PM_{2.5} concentrations and meteorological parameters are summarized in Table 3. During DW season, the PM_{2.5} median was the highest (31 $\mu\text{g m}^{-3}$, $p < 0.05$), when RH was the lowest (45.8%, $p < 0.05$). The associations between concentration and chemical composition of PM_{2.5} with meteorological conditions are well known. For instance, Kulshrestha et al. (2009) in a study of both urban and rural environment of Agra, India, found that PM₁₀ and PM_{2.5} concentrations were determined by temperature, relative humidity, and wind speed; this explains the high concentration found during the winter months. Zhao et al. (2009) point out that seasonal variations of temperature and relative humidity can be responsible for changes in concentrations of PM_{2.5} collected in Beijing. Nonetheless, they highlight the importance of wind patterns in those changes.

Moreover, for Fuzhou, China, Xu et al. (2012) report that higher PM_{2.5} concentrations are associated with low temperatures, high relative humidity, and low wind speed prevailing during winter. However, the effect of cold season in the increase of PM_{2.5} mass concentration was not observed in our study. The increase of PM_{2.5} concentration during DW seems to be influenced by low RH, with no spatial variation of observed in the MCMA ($p > 0.05$). The prevailing wind direction in the sampling area during 2011 was from north to south as shown in Fig. 2. Wind speed median values ranged from 1.7 to 2.4 m s^{-1} , with maximum speeds around 6 m s^{-1} . PM_{2.5} was positively correlated with T ($R = 0.31$) and inversely with RH ($R = -0.24$) and Wsp (-0.57) ($p < 0.05$) (Table 8).

Metal concentration in PM_{2.5}

Table 4 shows the metal concentration in PM_{2.5} as well as annual median concentration of PM_{2.5} in the MCMA during 2011. High variability was observed among metals, rising up to four orders of magnitude. The most abundant metals were Fe (67.7%), Ti

Table 7 Annual median comparison of metal concentration among seasons ($p < 0.05$). Season in *italic* form contain a higher metal concentration. *Equal sign* means similar concentrations between seasons

Comparison of median	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Rb	Sr	Cd	Sb	Cs	Th	Pb	Tl	La	Ce	Sm	Eu
DW Vs R	<i>DW</i>	=	=	=	<i>DW</i>	=	=	=	=	=	=	=	<i>DW</i>	<i>DW</i>	=	<i>DW</i>	<i>DW</i>	<i>DW</i>	<i>DW</i>	=
DW Vs DC	<i>DW</i>	<i>DC</i>	<i>DW</i>	<i>DW</i>	<i>DW</i>	<i>DW</i>	=	=	<i>DW</i>	=	=	=	<i>DW</i>	<i>DW</i>	=	=	<i>DW</i>	<i>DW</i>	<i>DW</i>	=
R Vs DC	<i>R</i>	<i>DC</i>	<i>R</i>	<i>R</i>	=	<i>R</i>	=	=	<i>R</i>	<i>R</i>	<i>R</i>	=	=	=	<i>R</i>	=	=	<i>R</i>	<i>R</i>	<i>R</i>

(10.1%), and Sr (8.4%), while the least abundant were Th (0.01%) and Tl (0.01%). This suggests geogenic emission as an important source to the PM_{2.5} of MCMA.

Table 5 shows a comparison of metal concentration in our study versus other urban areas. Most of the metals in our study were in the concentration range reported in other parts of the world (Moreno et al. 2006a, b; Cheng et al. 2010; Hieu and Lee 2010; Xu et al. 2012). However, Ti and Sr were the higher in our study, suggesting that geogenic emissions in the MCMA are more important sources than in the other cities.

Spatial and seasonal variation

Spatial, seasonal, and annual distribution patterns of metals are depicted in box plots (Fig. 3). Spatial and seasonal comparisons are described in Tables 6 and 7, respectively. Two metal groups with similar behavior among them were observed: Ti, Mn, Fe, Co, and Cu; and Rb, Sr, Cs, Th, La, Ce and Sm. The highest concentrations for both groups were observed at NE ($p < 0.05$) (Table 6). This two elements groups are related to geogenic sources. The recognition of geogenic sources as contributors in PM has been reported for other urban areas worldwide (Moreno et al. 2006a, b; Zhao et al. 2009; Hieu and Lee 2010; Xu et al. 2012). In particular, for the MCMA, Miranda et al. (2000, 2005) had also identified soil-derived dusts as the main contributor for metallic components in PM_{2.5}, regardless of the site where sampling was carried out. Most of the detected elements show a similar seasonal distribution (Fig. 3, Table 7), with the highest concentration during DW ($p < 0.05$). This pattern suggests a possible resuspension of metals by the wind from the top soil, stimulated by dry conditions where the lowest RH and the highest T values ($p < 0.05$) were observed (Table 3). This behavior is opposite to what has been observed during cool season in other parts of the world (Kulshrestha et al. 2009; Zhao et al. 2009; Xu et al. 2012).

Europium presented a different pattern as compared to the other metals, with the highest concentration observed at south of MCMA and during rainy season. V, Cr, Ni, Pb, Cd, and Tl are a group of metals showing also a different pattern, with a homogenous distribution throughout the studied area ($p > 0.05$) (Fig. 3, Table 6), suggesting similar

sources around the MCMA or a regular transport from the emitting sources. Sb was also homogeneously distributed, except at NW, where the lowest concentration was found. Eu, V, Cr, Ni, Pb, Cd, Tl, and Sb did not show the same seasonal pattern than the other metals, neither among them.

Source recognition

The analysis of the information in Table 8, which shows the Spearman correlation coefficients between the concentration of the metals and the PM_{2.5}, allows us to recognize at least two groups of elements with different origin.

Principal component analysis (PCA) was used to provide information for the identification of major metal sources. PCA results are consistent regardless of the nature of the database (raw or normalized). The number of factors retained was selected based on the scree test, which yielded six meaningful factors (Costello & Osborne 2005). Factor loadings had eigenvalues higher than 0.8. This number of factors provided the best solution, with eigenvalues above 1 for factors 1 to 5 and 0.87 for factor 6.

A total explained variance of 84.14% was observed. The main three factors explained 64.91% of the total variance, while the rest only explained 19.24%. Chromium, Cs, La, Ce, Sm, and Th were related with factor 1 (36.36%); Ti, Fe, Mn, Co, and Cu with factor 2 (17.44%); and Rb, Sr, and Eu with factor 3 (11.11%). Factors 4 to 6 clustered Ni, V, Cd, Pb, and Sb (Table 9).

Understanding results from similar works (Amato et al. 2009; Chen et al. 2014; Moreno-Rodríguez et al. 2015), along with the clear evidence gained from previous works related to the identification of the main sources of metals in MCMA (Morton-Bermea et al. 2009a, b; Guzmán-Morales et al. 2011), allows us to attribute the metals contained in factors 1 to 3 to geogenic sources.

The metals identified in factor 4 (Ni and V) are typically attributed to sources associated with fossil fuel combustion (Yuan et al. 2006; Dongarrà et al. 2010). On the other hand, previous works reported evidence associating these metals with geogenic sources of the studied area (Morton-Bermea et al. 2009a, b; Guzmán-Morales et al. 2011). Based on these two issues, we classify elements grouped in factor 4 as product of mixed sources.

Table 8 The Spearman rank correlation between metal data and meteorological parameters. Significant (positive) correlations are in bold ($p < 0.05$). Significant (negative) correlations are underlined

	PM _{2.5} (ng)	T	%RH	Wsp	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Rb
PM _{2.5} (ng)	1.00	0.31	<u>-0.24</u>	<u>-0.57</u>	0.03	0.42	-0.06	-0.19	0.09	-0.04	0.34	-0.15	-0.16
T	0.32	1.00	-0.22	-0.17	0.32	0.01	0.30	0.29	0.36	0.36	0.16	0.15	0.17
%RH	<u>-0.24</u>	-0.22	1.00	0.31	0.04	0.03	0.19	0.03	-0.022	0.08	0.19	0.12	0.10
Wsp	<u>-0.57</u>	-0.17	0.31	1.00	0.02	-0.24	-0.01	0.09	-0.12	-0.03	-0.18	-0.11	0.11
Ti	0.03	0.32	0.04	0.02	1.00	0.06	0.61	0.75	0.85	0.71	0.27	0.58	0.72
V	0.42	0.01	0.03	-0.24	0.06	1.00	0.04	0.11	0.24	0.17	0.72	0.12	-0.12
Cr	-0.06	0.30	0.19	-0.01	0.61	0.04	1.00	0.51	0.47	0.50	0.47	0.30	0.43
Mn	-0.19	0.29	0.03	0.09	0.75	0.11	0.51	1.00	0.81	0.81	0.24	0.66	0.45
Fe	0.09	0.36	-0.02	-0.12	0.85	0.24	0.47	0.81	1.00	0.76	0.34	0.69	0.50
Co	-0.04	0.36	0.08	-0.03	0.71	0.17	0.50	0.81	0.76	1.00	0.39	0.64	0.38
Ni	0.34	0.16	0.19	-0.18	0.27	0.72	0.47	0.24	0.34	0.39	1.00	0.18	0.02
Cu	-0.15	0.15	0.12	-0.11	0.58	0.12	0.30	0.66	0.69	0.64	0.18	1.00	0.25
Rb	-0.16	0.17	0.10	0.11	0.72	-0.122	0.43	0.45	0.50	0.38	0.02	0.25	1.00
Sr	<u>-0.33</u>	-0.07	0.11	0.19	0.29	-0.10	0.01	0.19	0.26	0.06	<u>-0.31</u>	0.09	0.59
Cd	-0.08	-0.01	-0.10	0.05	0.15	0.13	0.18	0.27	0.20	0.13	0.04	0.07	0.27
Sb	0.09	0.08	-0.12	<u>-0.29</u>	0.29	0.10	0.30	0.21	0.21	0.25	0.17	0.29	0.29
Cs	0.35	0.51	-0.01	<u>-0.17</u>	0.69	0.01	0.48	0.35	0.54	0.53	0.35	0.29	0.55
La	0.27	0.31	0.04	-0.25	0.52	0.11	0.59	0.36	0.49	0.52	0.46	0.35	0.28
Ce	0.15	0.42	0.02	-0.19	0.62	0.08	0.70	0.43	0.56	0.56	0.45	0.45	0.37
Sm	0.15	0.45	0.03	-0.15	0.55	0.000	0.71	0.38	0.49	0.51	0.39	0.37	0.34
Eu	-0.19	-0.18	0.03	0.07	0.16	-0.06	0.01	0.15	0.17	0.06	-0.25	0.02	0.38
Pb	-0.14	0.28	0.01	-0.01	0.34	0.17	0.42	0.56	0.42	0.55	0.27	0.36	0.27
Tl	-0.18	<u>-0.26</u>	0.24	0.29	0.03	0.27	-0.14	0.11	0.06	-0.04	0.04	-0.01	0.22
Th	0.21	0.45	0.07	-0.20	0.67	0.09	0.68	0.43	0.58	0.59	0.46	0.42	0.39

	Sr	Cd	Sb	Cs	La	Ce	Sm	Eu	Pb	Tl	Th
PM _{2.5} (ng)	<u>-0.33</u>	-0.08	0.099	0.35	0.27	0.15	0.15	-0.19	-0.14	-0.18	0.21
T	-0.07	-0.01	0.08	0.51	0.31	0.42	0.45	-0.18	0.28	<u>-0.26</u>	0.45
%RH	0.11	-0.10	-0.12	-0.01	0.04	0.02	0.03	0.03	0.01	0.24	0.07
Wsp	0.19	0.05	<u>-0.29</u>	-0.17	<u>-0.25</u>	-0.19	-0.15	0.07	-0.01	0.29	-0.20
Ti	0.30	0.15	0.29	0.69	0.52	0.62	0.55	0.16	0.34	0.03	0.67
V	-0.10	0.13	0.10	0.01	0.11	0.08	0.00	-0.06	0.17	0.27	0.09
Cr	0.01	0.18	0.30	0.48	0.59	0.70	0.71	0.01	0.42	-0.14	0.68
Mn	0.19	0.27	0.21	0.35	0.36	0.43	0.38	0.15	0.56	0.11	0.43
Fe	0.26	0.20	0.21	0.54	0.49	0.56	0.49	0.17	0.42	0.06	0.58
Co	0.06	0.13	0.25	0.53	0.52	0.56	0.51	0.06	0.55	-0.04	0.59
Ni	<u>-0.31</u>	0.04	0.17	0.35	0.46	0.45	0.39	<u>-0.25</u>	0.27	0.04	0.46

Table 8 (continued)

	Sr	Cd	Sb	Cs	La	Ce	Sm	Eu	Pb	Tl	Th
Cu	0.09	0.07	0.29	0.29	0.35	0.45	0.37	0.02	0.36	-0.01	0.42
Rb	0.59	0.27	0.29	0.55	0.28	0.37	0.34	0.38	0.27	0.22	0.39
Sr	1.00	0.34	0.09	-0.11	-0.08	-0.03	-0.02	0.80	0.08	0.48	-0.10
Cd	0.34	1.00	0.27	-0.07	-0.06	0.03	0.02	0.27	0.45	0.51	-0.06
Sb	0.09	0.27	1.00	0.18	0.12	0.22	0.18	0.03	0.45	0.09	0.16
Cs	-0.11	-0.07	0.18	1.00	0.66	0.72	0.64	-0.18	0.16	-0.37	0.80
La	-0.08	-0.06	0.12	0.66	1.00	0.92	0.92	0.17	0.17	-0.35	0.896
Ce	-0.03	0.03	0.22	0.72	0.92	1.00	0.96	0.05	0.29	-0.32	0.94
Sm	-0.02	0.02	0.18	0.64	0.92	0.96	1.00	0.11	0.21	-0.34	0.91
Eu	0.80	0.27	0.03	-0.18	0.17	0.05	0.11	1.00	-0.02	0.35	-0.03
Pb	0.08	0.45	0.45	0.16	0.17	0.29	0.21	-0.02	1.00	0.28	0.23
Tl	0.48	0.51	0.09	-0.37	-0.35	-0.32	-0.34	0.35	0.28	1.00	-0.36
Th	-0.10	-0.06	0.16	0.80	0.90	0.94	0.91	-0.03	0.23	-0.36	1.00

The metals contained in factors 5 and 6 are interpreted as resulting from anthropogenic emissions, possibly related to vehicular traffic and/or industrial activities (Zhai et al. 2014; Zhang et al. 2013).

It is evident that metals associated with geogenic sources explained the maximum variance and allowed the differentiation of several geogenic sources as responsible for the enrichment of a large group of metals present in PM_{2.5}. Such enrichment may be interpreted as a consequence of regional transport of geogenic material, influenced by the direction of the prevalent winds coming from the north (Fig. 2), as well as to the contribution of local geogenic material and/or resuspension of soil dust/geogenic material. The high concentration of geogenic metals at NE (Fig. 2, Table 6) confirms this argument.

The recognition of the high impact of geogenic sources in PM_{2.5} collected in MCMA is in agreement with the information obtained by means of REE assessment. Figure 4 shows the REE distribution patterns considering all REEs (normalized to chondrite, Evensen et al. 1978), in spite that only La, Ce, Sm, and Eu were included in the validation of the analytical procedure applied in this study. The low concentration of REE limited the assessment of REE pattern behavior in eight samples; all of them were collected during DW, when PM_{2.5} is higher and RH lower. The REE patterns in PM_{2.5} collected in MCMA clearly show a similar behavior as those shown by igneous rocks, confirming in this case, the influence of the regional geogenic material.

The metals in factors 4–6 were associated with different anthropogenic sources, not necessarily common among them. Anthropogenic sources can be associated to industrial activities and traffic emissions, which show up the complexity of the urban air in the MCMA.

Conclusion

We showed the importance of local geogenic material and/or resuspension of soil dust/geogenic material as the main source of metals associated to the PM_{2.5} in the MCMA. Anthropogenic metal sources are minor sources to the PM_{2.5} of MCMA. Geogenic metal concentrations identified in the factors 1, 2, and 3 were found at NE of the MCMA which is in agreement with the dominant wind direction from north to south during

Table 9 Identification of major metal association using principal component analysis (PCA). Associated metals are presented in italics

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Ti	0.46	<i>0.76</i>	0.33	-0.01	0.04	0.09
V	-0.11	0.05	-0.12	<i>0.93</i>	-0.02	0.00
Cr	<i>0.64</i>	0.25	0.27	0.02	0.42	-0.01
Mn	0.22	<i>0.91</i>	0.11	0.05	0.22	0.04
Fe	0.38	<i>0.84</i>	0.17	0.11	0.00	0.05
Co	0.30	<i>0.75</i>	-0.07	0.00	0.21	-0.07
Ni	0.43	0.15	-0.10	<i>0.79</i>	0.11	-0.01
Cu	-0.05	<i>0.87</i>	0.04	0.10	-0.15	0.06
Rb	0.25	0.31	<i>0.76</i>	-0.14	0.10	0.20
Sr	-0.21	0.14	<i>0.92</i>	-0.07	0.06	0.01
Cd	0.02	-0.11	0.34	0.07	<i>0.75</i>	0.17
Sb	-0.05	0.09	-0.01	-0.01	0.13	<i>0.94</i>
Cs	<i>0.80</i>	0.16	0.05	-0.03	-0.20	0.18
La	<i>0.94</i>	0.19	-0.01	0.07	0.02	-0.05
Ce	<i>0.93</i>	0.25	0.03	0.02	0.06	-0.03
Sm	<i>0.95</i>	0.16	0.03	0.00	0.08	-0.08
Eu	-0.01	0.02	<i>0.87</i>	-0.05	0.00	-0.15
Tl	-0.43	0.10	0.38	0.46	0.42	-0.06
Pb	0.08	0.47	-0.13	0.02	<i>0.71</i>	0.13
Th	<i>0.96</i>	0.11	-0.21	0.02	0.00	0.00
Eigenvalue	7.27	3.49	2.22	1.69	1.29	0.87
% Total—variance	36.36	17.44	11.11	8.43	6.46	4.35
Cumulative—% variance	36.36	53.80	64.91	73.33	79.79	84.14

2011. The contribution of geogenic materials transported by prevalent winds represents a significant influence on the air quality in the MCMA. Although previous studies in the MCMA had already signaled the importance of geogenic sources in $PM_{2.5}$, the use of

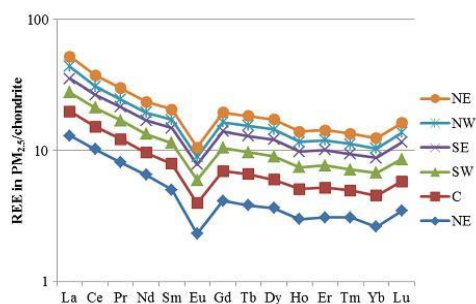


Fig. 4 Distribution patterns of REEs normalized to chondrite (Evensen et al. 1978) in $PM_{2.5}$. Patterns were calculated for samples collected during DW

ICP-MS might allow identifying the emitting sources in a more definite way, due to the detection of REE. Dry-warm season was the period with the highest geogenic metal concentrations. No significant differences in the spatial distribution of metals from anthropogenic sources were observed, suggesting common sources around MCMA.

Because the MCMA is a complex area with more than 20 million inhabitants exposed to this environment, the information obtained from this study, related to the impact of geogenic sources, the spatial and temporal behavior of metals in $PM_{2.5}$, and the influence of meteorological parameters must be confirmed with further studies, in order to establish public policies aimed to improve the air quality of the area.

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Spatial and temporal distribution of metals in PM_{2.5} during 2013: assessment of wind patterns to the impact of geogenic and anthropogenic sources.

Esta segunda publicación referente al tema del contenido metálico de PM_{2.5} para la ZMCM ha podido verificar los resultados en Morton-Bermea et al. (2018a) y también ampliar la competencia de los objetivos en la presente tesis.

En esta publicación se reportan las concentraciones medias y su variación para los siguientes metales: Ti, V, Cr, Mn, Co, Ni, Cu, Mo, Cd, Sb, Pb, Ag, La, Sm, Eu y Ce (Tabla 4 del artículo).

La variabilidad en las concentraciones de estos metales obedece a la distribución espacio-temporal: se confirmaron los patrones registrados del muestreo de 2011 mediante diagramas de cajas y bigotes (Anexo 1 de la presente tesis) y comparación de medianas tanto para los sitios como para las temporadas (Supporting Information del artículo: Tablas S1 y S2). En esta publicación las distribuciones espacio-temporales se reportan en la Figura 1 la distribución temporal confirmó que las concentraciones de metales se acumulan mayoritariamente en DC (temporada seca y fría). Este acumulamiento se explica por la combinación de la compactación de la capa de mezclado y por la ocurrencia de vientos de baja intensidad a causa la estabilidad atmosférica.

Se observó un aumento significativo ($p < 0.05$) del 17% de la masa de PM_{2.5} colectado en comparación con el muestreo de 2011, con lo que se esperaba un alza generalizada de metales, sin embargo esto sucedió únicamente para los metales identificados con fuentes geogénicas, ya que las concentraciones de metales antropogénicos disminuyeron ($p < 0.05$) sus concentraciones (Cd, Sb, Pb, Ni y V). Además, en el sitio SW (suroeste, Coyoacán) se registraron menores ($p < 0.05$) concentraciones de metales provenientes de ambas fuentes.

A través de evaluar los factores de enriquecimiento estacionalmente para los metales, se pudo no solo profundizar en la identificación de las fuentes sino también evidenciar el impacto de las fuentes antropogénicas; sobre todo en los metales emitidos por fuente mixtas (Ni y V), tal que, durante la temporada fría la componente antropogénica es sobresaliente.

El análisis de las concentraciones de metales en función de la intensidad y dirección de los vientos (Figura 3) manifiesta el mecanismo gobernante del aumento de concentraciones de metales geogénicos: son los episodios de viento intenso (mayores a 5 m s^{-1}).

Es importante construir una amplia base de datos para continuar el monitoreo de las tendencias de metales y sus razones de variabilidad. Información relevante para los tomadores de decisiones.

Spatial and temporal distribution of metals in PM_{2.5} during 2013: assessment of wind patterns to the impacts of geogenic and anthropogenic sources

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Abstract The Mexico City Metropolitan Area (MCMA) was the object of a chemical elemental characterization (Ti, V, Cr, Mn, Co, Ni, Cu, Mo, Ag, Cd, Sb, Pb, La, Sm, Ce, and Eu) of PM_{2.5} collected during 2013 and analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Sampling campaigns were carried out at five

locations simultaneously—northwest, northeast, center, southwest, and southeast—during dry-warm season (April), rainy season (August), and dry-cold season (November). By means of enrichment factor (EF) and principal component analysis (PCA), it was possible to attribute the analyzed elements to geogenic and anthropogenic sources, as well as to identify a group of elements with mixed provenance sources. The highest concentrations for most metals were found in northwest and northeast, and during dry-warm (DW), confirming the trend observed in PM_{2.5} samples collected in 2011. Despite similarities between 2011 and 2013, an increase of 17% in PM_{2.5} mass concentration was observed, mainly attributable to geogenic sources, whereby the importance of wind intensity to the impact of emission sources is highlighted. The effect of wind intensity was revealed, by means of polar plots, as the controlling mechanism for this increase. This allowed us to conclude that high-speed episodes (5 m s^{-1}) were responsible for raising geogenic metal concentrations rather than wind direction.

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Keywords PM_{2.5} · Metals · Mexico City · Wind plots · Geogenic and anthropogenic sources

Introduction

The study of atmospheric particulate matter (PM) is relevant due to its toxic effects in humans and other living organisms as they are associated, according to the World Health Organization, to a broad spectrum of

acute and chronic illnesses, such as lung cancer, chronic obstructive pulmonary disease (COPD), and cardiovascular diseases (WHO 2016). Santibáñez-Andrade et al. 2017, Michael et al. 2013, and Kampa and Castanas 2008 have reported the relationship between long-term exposure of high concentrations of PM with increased risk of lung cancer and respiratory and cardiovascular diseases. Besides, transition metals present in PM are able to damage DNA, induce mutations, and initiate carcinogenesis (Perrone et al. 2013; Wang et al. 2016). In recent years, the elemental characterization of particulate matter with less than 2.5 μm of aerodynamic diameter ($\text{PM}_{2.5}$) has raised concern because this size represents the breathable fraction. Studies related to chemical characterization of metals in $\text{PM}_{2.5}$ in different areas of the world have increased both in urban and remote areas (Kulshrestha et al. 2009; Aldabe et al. 2011; Warneck and Williams 2012). Most of them discussed not only metal concentration levels but also their spatial distribution, concluding that these two features are mainly dominated from local factors at each given area (Dongarrà et al. 2010; Saliba et al. 2010; Moreno et al. 2011).

The need to identify and weigh the sources of metals in $\text{PM}_{2.5}$ has led to the combined application of sophisticated statistical tools to the chemical characterization of the data. In this way, natural and anthropogenic sources have been recognized (Alleman et al. 2010; Cheng et al. 2010). Natural emission sources include volcanic eruptions, mineral dust, and weathering of soils and rocks. The anthropogenic sources of metal emissions have been associated with punctual industrial activities, such as petrochemistry, manufacturing, smelting, mining, and mobile sources from vehicle transit.

However, the quantity of each single metal in $\text{PM}_{2.5}$ does not depend only on the magnitude of the source, but also on weather conditions; meteorological factors, such as wind direction and intensity, spread, dilute, or even accumulate metals in breathable air. The relationship between pollutant concentrations in the atmospheric environment and meteorological factors has been reported by Ledoux et al. (2017), Zhang et al. (2015), and Uria-Tellaetxe and Carslaw (2014). For instance, Zhang et al. 2015 report the cross-correlation between $\text{PM}_{2.5}$ concentration and meteorological factors. $\text{PM}_{2.5}$ concentration decrease when (1) temperature raises, which leads to diffusion and dilution of particulate matter due to frequency of air convection; (2) humidity

raises, since particles will adsorb moisture and condensation will occur; and (3) wind speed raises, causing the spread of pollutants, which results in a lower concentration of $\text{PM}_{2.5}$, and vice versa. Conversely $\text{PM}_{2.5}$ increases by lower pressure, since this is not conducive to pollutant diffusion. Uria-Tellaetxe and Carslaw (2014) developed a new receptor modeling method (conditional bivariate probability function, CBPF) which requires wind speed as a variable to identify and characterize emission sources. Moreover, the same method was applied by Ledoux et al. 2016, finding the provenance of metals in $\text{PM}_{2.5}$ according to highest concentrations downwind as a first step for the identification of pollution sources related to their studied area. The Mexico City Metropolitan Area (MCMA) is one of the largest megacities in the world. It is located in a basin surrounded by mountains on the west, east, and south, with an average altitude of 2200 m above sea level. Only a few studies concerning atmospheric pollution have been conducted within the area; Megacity Initiative: Local and Global Research Observations (MILAGRO) campaign offers the results of several pollutant concentrations, such as CO, CO_2 , SO_x , NH_4^+ , O_3 (DeCarlo et al. 2008; Querol et al. 2008; Stone et al. 2008; Mugica et al. 2009; Molina et al. 2010). In recent years, content and composition of organic compounds in PM have been reported by Amador-Muñoz et al. (2011, 2013), while metal content by particle-induced X-ray emission (PIXE) analysis has been reported by Miranda et al. (2005), Barrera et al. (2012), and Hernández-López et al. (2016) and Pt concentration by Morton-Bermea et al. (2014).

In a first stage of a research project to characterize the long-term variations in composition and temporal and spatial distribution of $\text{PM}_{2.5}$ in MCMA, we reported the seasonal and spatial behavior of elemental composition during 2011 (Morton-Bermea et al. 2018), highlighting the importance of local geogenic material and/or resuspension of soil dust, as the main source of metals to the $\text{PM}_{2.5}$ in the area, with anthropogenic sources having a minor contribution. Further, geogenic metal concentrations were consistent with the dominant wind direction from north to south. Despite the recognition of the importance of geogenic sources, further research was needed to confirm changes in the apportionment of such sources.

In this contribution, we aim to achieve a number of innovative goals relevant to the area first, to strengthen the $\text{PM}_{2.5}$ chemical database and link it to previous

results obtained with similar studies; second, to identify and assign metal enrichments to their geogenic and anthropogenic sources; and finally, to unravel the mechanism that causes shifts to the impact of these sources. This was accomplished by assessing metal concentrations to meteorological parameters, fundamentally wind patterns. The methodology implemented in this work is intended to become the basis for a monitoring program that would help to exhaustively understand the chemistry, meteorology, and temporal-spatial distribution of PM_{2.5} in MCMA.

Methods

PM_{2.5} sampling

Sampling of PM_{2.5} was carried out in 2013 during three different seasons: dry-warm season (DW, April), rainy season (R, August), and dry-cold season (DC, November) at five sites simultaneously collected and located within MCMA: northwest (NW, Tlalnepantla), northeast (NE, San Agustín), central (C, Merced), southwest (SW, Coyoacán), and southeast (SE, Universidad Autónoma Metropolitana-Iztapalapa) (Fig. 1). The main features of the sampling sites are given in Table 1. PM_{2.5} samples were collected for 24 h, every 6 days, on Teflon-impregnated glass fiber filter (20.4 cm × 25.2 cm; TIGF, Pallflex), previously baked at 280 °C. Samplings were carried out at $1.13 \pm 10\% \text{ m}^3 \text{ min}^{-1}$, in high-volume samplers (Tisch and Andersen General Metal Works) previously calibrated according to Federal Register (1987). This sampling campaign belongs to a continuous program of environmental monitoring carried out by our research team employing infrastructure from the local government agency. In this way, 75 samples were collected for this study as well as for other researches. Unexposed filter for each sampling day was employed as field blank. Filters were enveloped in aluminum foil, kept in ziplock bags, and transported at 4 °C to the laboratory.

Sample treatment

PM_{2.5} samples on filters were treated to analyze 16 elements (Ti, V, Cr, Mn, Co, Ni, Cu, Mo, Ag, Cd, Sb, Pb, La, Sm, Ce, and Eu). One-tenth of each filter was

subjected to a microwave-assisted digestion procedure (Ethos One, Milestone) employing a mixture of aqua regia and HF. The digestion program was set from room temperature to 220 °C and kept for 20 min. The digested solution was taken to dryness and HNO₃ was added to ensure complete removal of HF. Finally, the digested solution was brought to 25-mL volume with 2% HNO₃ (v/v).

Instrumental analysis and quality control

Metal concentrations were obtained by means of inductively coupled plasma mass spectrometry (ICP-MS) in an iCAP Q spectrometer (Thermo Scientific) at Instituto de Geofísica, Universidad Nacional Autónoma de México. A multi-elemental calibration curve was performed including 0 ng mL⁻¹, 0.01 ng mL⁻¹, 0.1 ng mL⁻¹, 1 ng mL⁻¹, and 5 ng mL⁻¹ concentration points as part of analytical controls. All standard solutions were prepared from a High Purity Standard (USA) solution with 2% HNO₃ (v/v) (Merck, Germany). Instrumental drift correction was made with ¹¹⁵In as internal standard, prepared from a certified stock solution of 1000 mg L⁻¹ (Merck, Germany).

Analytical quality was evaluated with the standard reference material SRM 1648a (urban particle matter) from NIST. Ten aliquots of SRM 1648a were prepared and analyzed in the same way as PM_{2.5} samples. Blank test background contamination was monitored using operational blanks (unexposed filter papers), which were processed and analyzed with field samples. Detection limits were calculated as three times the standard deviation of 18 replicates of the procedural blank.

Data analysis

Mann-Whitney *U* test was used to compare medians among seasons and sites. The significant difference was defined as $p < 0.05$. Spearman's correlation was used to evaluate association among variables. Principal component analysis (PCA) with Spearman's correlation matrix and varimax rotation algorithm was used to identify sources. Statistica Software V 10.0 (StatSoft, USA) was used for the statistical analyses. Metal enrichment factors (EF) were computed based on metal crust data from Wedepohl (1995).

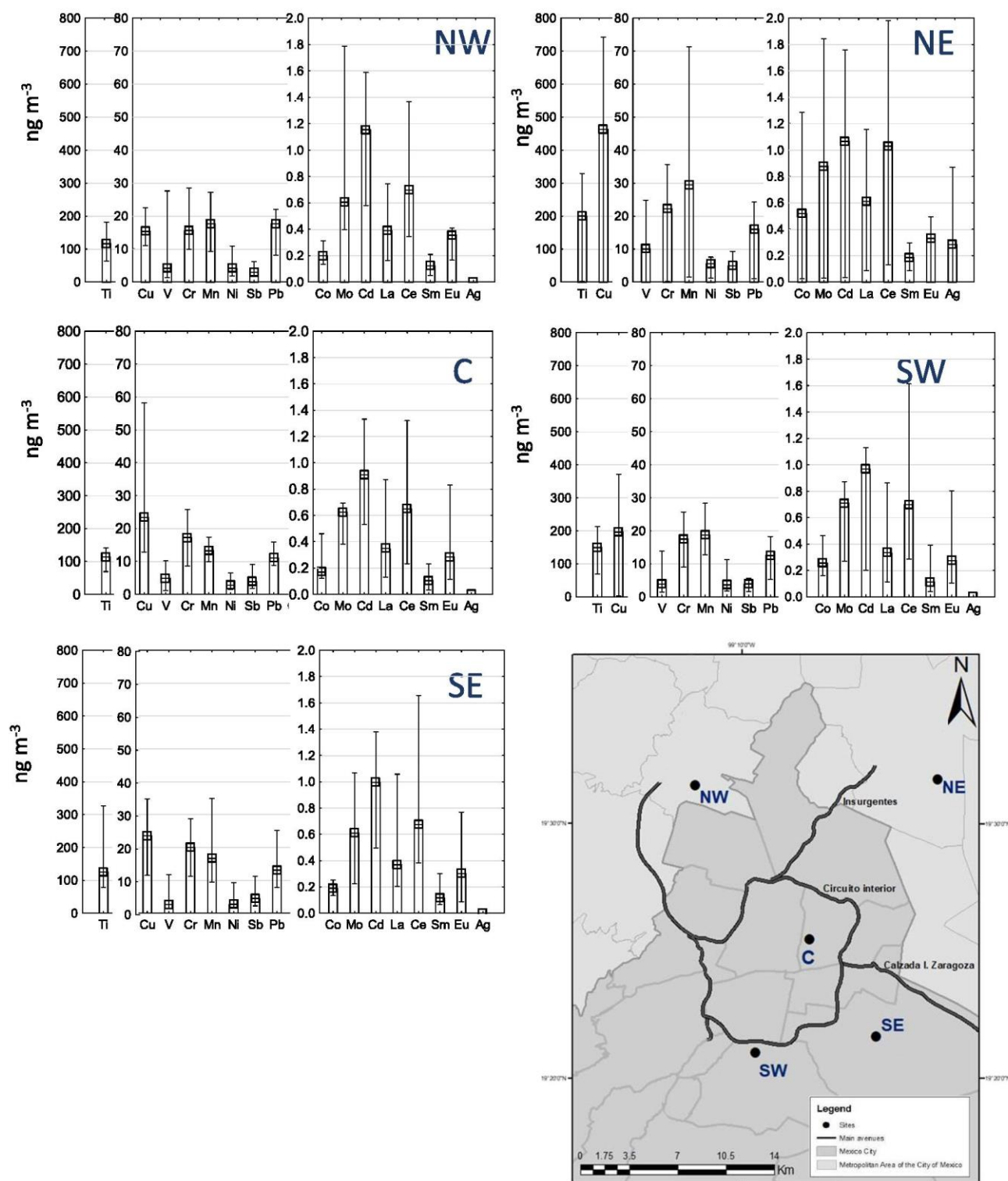


Fig. 1 Spatial distribution for the 16 metals analyzed in PM_{2.5}

Meteorological data

Meteorological parameters comprising temperature (*T*), relativity humidity (RH), wind speed (Wsp), and wind flow

(Wfl), along with PM_{2.5} mass concentration, were obtained from the local air quality monitoring authority SEDEMA (available online database at: <http://www.aire.df.gob.mx/default.php?opc=%27aKBhnmI=%27&opcion=Zw>).

Table 1 Sampling site characteristics

Site name	Position in MCMA	Main characteristics
Tlalnepantla	Northwest, NW	Residential and commercial area with industrial settlement and traffic avenues
San Agustín	Northeast, NE	Residential and commercial area with few industrial settlement and avenues
Merced	Central, C	Commercial and residential zone with vehicular avenues
Coyoacán	Southwest, SW	Residential zone and vehicular avenue
Universidad Autónoma Metropolitana-Iztapalapa	Southeast, SE	Residential zone and vehicular avenue with small manufactories

Results and discussion

Quality control

Metal recoveries and relative standard deviation (RSD) are given in Table 2. Recoveries ranged from 60 to 102%. Mo and Eu are not included as certified elements in SRM1648a; however, they were considered in this study because the analytical method resulted in RSD between 0.86 and 1.1%, $n = 18$. The accurate recovery rates are comparable to other reported ICP-MS analytical procedures, including microwave-assisted digestion and different mixtures of acids and SRM (Dongarrà et al. 2010; Aldabe et al. 2011; Hays et al. 2011; Morton-Bermea et al. 2018).

Relationship between PM_{2.5} mass concentration and meteorological parameters

Seasonal PM_{2.5} concentrations and meteorological parameters are tabulated in Table 3. The annual median PM_{2.5} mass concentration found for the sampling period is $28 \mu\text{g m}^{-3} \pm 15 \mu\text{g m}^{-3}$. This value exceeds two times the local recommended limit ($12 \mu\text{g m}^{-3}$, NOM-025-SSA1-2014) and almost three times the international recommendation ($10 \mu\text{g m}^{-3}$, WHO 2005). The Mann-Whitney U test shows that the highest mass concentration was registered during DW ($38 \mu\text{g m}^{-3}$, $p < 0.05$) by lowest RH and W_{sp} ($p < 0.05$) (Table 3). These observations agree with the conditions imposed by the low RH and W_{sp} that does not favor the dispersion of PM, as well observed by Zhang et al. 2015.

Elemental composition of PM_{2.5}: spatial and seasonal behavior

Metal concentrations in PM_{2.5} are listed in Table 4. Titanium was the most abundant metal with more than 50% relative abundance and Cu represents 13%, while Mn, V, Cr, Pb, Ni, and Sb sum for 27%; metals such as Mo, Cd, La, Sm, Eu, and Ce computed for less than 0.1% each. The spatial metal behavior is depicted in Fig. 1 with metal median concentrations at the five sites during the sampling season. The spatial comparison via Mann-Whitney U test (reported in Table S1) shows no significant differences for Cr, V, and Sb; this can be interpreted as the result of homogenization processes, or of a similar impact of the same source within the study area. On the other hand, Cd, Ni, and Pb present a significant difference at NE and NW. The remaining analyzed metals (Ti, Mn, Co, Cu, Mo, and Ag) have significant differences among the regions of MCMA, with concentrations in the following order: NE > NW > SW = C = SE. These findings align with those previously reported in Morton-Bermea et al. 2018. The contribution of this study, obtained from a more in-depth analysis (“Source apportionment” and “Relationship between metal concentration and wind patterns” sections) of the effects of winds on the dispersion allowed us to weigh the sources responsible for the high concentrations of metals observed in the north sites (NW and NE). The attribution of the enrichment of metals in the north of the studied area is complicated because of an industrial settlement and its proximity to arid areas further north of MCMA which Morton-Bermea et al. 2018 identify as a source of geogenic contamination in the studied area.

Table 2 Metal recoveries from SRM1648a

Analyte	NIST 1648a (mg kg ⁻¹)	Experimental (mg kg ⁻¹)	% Recovery	RSD	Detection limit (mg kg ⁻¹)
Ti	4021	4107	102.1	9.8	2.40
V	127	105	83.2	7.3	0.25
Cr	402	335	83.4	8.2	0.24
Mn	790	667	84.5	5.8	0.43
Co	17.93	12.68	70.8	5.1	0.02
Ni	81.1	66.73	82.3	5.2	0.36
Cu	610	379	62.1	8.7	1.10
Ag	6.0	3.5	59.1	9.6	0.07
Cd	73.7	64.1	86.9	4.1	0.25
Sb	45.4	36.4	81.1	7.8	0.11
Pb	0.655	0.48	73.3	7.0	0.25
La	39	27.8	71.3	9.8	0.07
Ce	54.6	35.6	65.2	9.3	0.90
Sm	4.3	2.8	65.1	9.5	0.23

$n = 18$. Al, Fe, and Zn could not be satisfactorily recovered

RSD relative standard deviation

A comparison by means of a U test for the seasonal data (Table S2) shows two behaviors: Cu, Cr Ni, V, Cd, and Mo with concentrations increasing in the following order $R < DW < DC$ and Ti, Mn, Co, Sb, and Pb present no seasonal significant variation. This behavior can derive mainly from two phenomena: (1) variations in the magnitude of the sources of these metals and (2) atmospheric processes of dispersion and accumulation.

Table 5 and Table 6 compare data obtained in this study with data obtained for PM_{2.5} collected during 2011 using the same sampling protocol (Morton-Bermea et al. 2018). There was an increase in PM_{2.5} mass concentration during 2013 of up to 17% as

compared to that during 2011 ($p < 0.05$). According to this, an increase of metal concentrations could be expected; nonetheless, this is only true for metals identified as geogenic (Morton-Bermea et al. 2018). Ti, Mn, Sm, Eu, and Ce were increased by 30%. Conversely, concentration of metals commonly considered from anthropogenic origin decreased: Cd and Sb both reduced in 18%, Pb in 37% and Ni and V in 30% and 56%, respectively. Spatial trends showed similar behavior in 2011 and 2013, except for the SW sampling site, where metal concentrations in general decreased from 2011 to 2013. Assuming small changes in emission sources for this period, these changes could be attributed to

Table 3 Meteorological parameters for MCMA during 2013 sampling campaign. Significant differences ($p < 0.05$) are indicated in **bold** when values are the highest among seasons, and values

are **bold italics** when values are significantly the lowest, analysis by Mann-Whitney U test

	2013			DW ($n = 25$)			R ($n = 25$)		DC ($n = 25$)			U test trend	
	X	M	SD	X	M	SD	X	M	SD	X	M		SD
PM _{2.5} ($\mu\text{g m}^{-3}$)	28.1	24.5	15.1	40.0	38.0	17.4	17.9	16.0	11.1	31.5	25.0	23.3	DW > DC > R
T ($^{\circ}\text{C}$)	17.0	16.9	3.7	21.1	21.3	4.6	17.1	16.1	3.7	14.4	13.9	4.3	DW > R > DC
RH	52.6	57.5	21.4	28.9	25.0	16.5	65.0	68.0	19.7	61.5	65.0	18.4	R > DC > DW
W_{sp} (m s^{-1})	2.2	2.1	0.5	2.2	1.8	1.2	2.3	2.2	1.0	2.1	1.9	0.9	R > DC = DW

T temperature, RH relative humidity, W_{sp} wind speed, X mean, M median, SD standard deviation, DW dry-warm, R rainy, DC dry-cold

Table 4 Statistical data of metal concentrations found in PM_{2.5}

Metal	Median (ng m ⁻³)	Mean (ng m ⁻³)	SD (ng m ⁻³)	Min (ng m ⁻³)	Max (ng m ⁻³)	% RSD	Relative abundance (%)
Ti	139	227	466	2.08	3862	205	57
V	4.6	29	93	0.09	761	322	2
Cr	18	25	31	0.19	217	122	8
Mn	18	32	69	1.46	567	213	7
Co	0.24	0.55	1.7	0.02	15	307	0.1
Ni	3.6	7.9	15.7	1.21	114	199	1.5
Cu	31	213	614	0.64	5181	289	13
Mo	0.66	1.02	1.61	0.03	12	158	0.3
Cd	0.99	1.33	1.74	0.03	13	131	0.4
Sb	4.0	5.6	8	0.03	54	142	2
Pb	13	17	17	1.07	125	102	5
Ag	0.01	0.10	0.31	0.0	2.8	310	<0.1
La	0.40	0.70	1	0.1	7.8	143	<0.1
Sm	0.10	0.20	0.3	0.0	1.9	150	<0.1
Eu	0.30	0.50	0.8	0.0	6.5	160	<0.1
Ce	0.70	1.20	1.7	0.1	10	142	<0.1

SD standard deviation, CV coefficient variation, RSD relative standard deviation

Table 5 Comparison of PM_{2.5} and meteorological parameters between 2011 and 2013

	2011 ^a				2013			
	N	Mean	Median	SD	N	Mean	Median	SD
PM _{2.5} (µg m ⁻³)	78	21.7	21.0	9.1	74	28.1	24.5	15.1
T (°C)	62	17.6	17.6	2.9	68	17.0	16.9	3.7
RH	69	50.7	57.5	17.7	67	52.6	57.5	21.4
Wsp (ms ⁻¹)	74	2.2	2.2	0.6	65	2.2	2.1	0.5
	DW 2011 ^a				DW 2013			
PM _{2.5} (µg m ⁻³)	25	29.8	31.0	6.5	25	39.4	41.5	10.6
T (°C)	18	20.6	20.9	1.9	24	21.1	20.8	1.9
RH	20	44.8	45.8	16.7	24	28.4	24.5	12.2
Wsp (ms ⁻¹)	20	1.8	1.7	0.3	25	2.2	2.1	0.5
	R 2011 ^a				R 2013			
PM _{2.5} (µg m ⁻³)	28	13.3	13.5	5.0	24	16.2	14.3	6.6
T (°C)	29	17.6	17.6	1.2	20	16.2	16.3	1.8
RH	24	54.4	59.8	18.5	20	67.5	61.5	13.1
Wsp (ms ⁻¹)	29	2.5	2.4	0.4	20	2.3	2.2	0.5
	DC 2011 ^a				DC 2013			
PM _{2.5} (µg m ⁻³)	25	22.9	23.5	6.5	25	28.4	24.0	16.4
T (°C)	15	14.2	14.5	2.2	24	13.6	13.1	2.0
RH	25	52.0	60.0	17.2	23	64.9	66.5	8.7
Wsp (ms ⁻¹)	25	2.1	1.7	0.6	20	2.1	1.9	0.6

Values marked in bold are significant higher (p<0.05)

^aData from Morton-Bermea et al. (2018)

Table 6 Comparison of metal concentrations found in this study and those coincident from the 2011 campaign (Morton-Bermea et al. 2018)

Metal	Mean ng m ⁻³ 2011 ^a	Median ng m ⁻³	SD ng m ⁻³	Mean ng m ⁻³ 2013	Median ng m ⁻³	SD ng m ⁻³	Mean ng m ⁻³ DW 2011 ^a	Median ng m ⁻³	SD ng m ⁻³	Mean ng m ⁻³ DW 2013	Median ng m ⁻³	SD ng m ⁻³
Ti	115.4	107.6	58.4	227.0	138.8	466.3	146.6	130.6	70.5	197.2	125.3	217.5
V	15.0	10.4	15.2	28.8	4.6	92.6	10.6	11.0	4.1	37.5	6.1	150.8
Cr	18.1	18.0	6.4	25.4	18.4	31.0	21.3	22.2	6.3	21.7	16.0	30.1
Mn	15.7	13.6	9.4	32.3	17.6	68.7	17.1	13.8	11.0	27.6	16.7	28.6
Co	0.3	0.2	0.3	0.5	0.2	1.7	0.4	0.3	0.3	0.4	0.2	0.5
Ni	6.0	5.2	3.6	7.9	3.6	15.7	7.1	7.6	3.1	8.2	3.6	22.0
Cu	60.2	28.3	72.4	212.6	30.5	614.3	49.5	26.0	50.2	168.3	65.5	184.6
Cd	1.2	1.2	0.5	1.3	1.0	1.7	1.1	0.9	0.7	1.7	1.1	2.4
Sb	5.5	4.8	3.3	5.6	3.9	8.0	5.2	5.1	2.2	7.4	4.9	10.0
Pb	25.1	20.8	14.3	16.9	13.1	17.3	25.1	20.5	15.4	17.2	11.7	19.3
La	0.72	0.46	0.63	0.66	0.40	1.02	1.31	1.23	0.82	0.62	0.33	1.50
Sm	0.18	0.11	0.16	0.21	0.14	0.25	0.33	0.32	0.20	0.18	0.11	0.36
Eu	0.22	0.20	0.13	0.49	0.32	0.78	0.20	0.13	0.14	0.49	0.11	1.25
	R 2011 ^a			R 2013			DC 2011 ^a			DC 2013		
Ti	112.2	106.8	35.7	183.7	123.8	245.4	89.4	75.0	56.2	300.1	148.0	744.6
V	10.3	6.2	9.3	4.7	2.5	5.3	24.9	20.9	22.1	44.2	19.3	52.6
Cr	19.7	19.0	4.2	28.2	20.0	39.7	13.1	11.5	5.8	26.2	23.2	21.4
Mn	16.8	14.9	6.7	26.6	18.0	39.0	12.9	9.1	10.2	42.7	20.6	109.7
Co	0.3	0.2	0.3	0.3	0.2	0.5	0.3	0.2	0.2	0.9	0.3	2.9
Ni	5.0	4.9	3.1	4.3	3.3	4.0	6.2	6.3	4.5	11.3	5.6	15.3
Cu	63.8	31.9	73.6	339.6	25.0	1028.1	66.2	23.2	88.9	129.9	21.0	215.9
Cd	1.5	1.5	0.4	1.1	0.8	1.6	1.0	1.0	0.4	1.1	1.1	0.8
Sb	5.2	4.9	2.0	4.9	2.8	9.2	6.1	4.3	5.1	4.5	3.9	2.6
Pb	29.9	27.9	13.8	18.9	13.5	22.4	19.1	17.4	11.8	14.7	14.3	5.8
La	0.51	0.40	0.30	0.65	0.53	0.56	0.40	0.38	0.22	0.70	0.61	0.80
Sm	0.15	0.13	0.08	0.23	0.18	0.19	0.08	0.08	0.06	0.21	0.17	0.18
Eu	0.28	0.25	0.14	0.52	0.35	0.42	0.19	0.20	0.09	0.47	0.35	0.34

Values marked in bold are significant higher ($p < 0.05$)

SD standard deviation

^aData from Morton-Bermea et al. (2018)

Table 7 Spearman correlation rank. Significant values ($p < 0.05$) are marked in **bold**

	PM _{2.5}	Ti	V	Cr	Mn	Co	Ni	Cu	Mo	Cd	Sb	La	Ce	Sm	Eu	Pb	Ag
PM _{2.5}	1.000	0.082	0.649	-0.170	0.119	0.184	0.371	0.165	0.290	0.351	0.641	-0.059	-0.141	-0.164	0.073	0.018	-0.017
Ti	0.082	1.000	0.335	0.730	0.938	0.811	0.374	0.473	0.554	0.092	0.362	0.588	0.722	0.670	0.391	0.417	0.493
V	0.649	0.335	1.000	0.194	0.419	0.491	0.722	0.255	0.708	0.420	0.619	0.277	0.196	0.175	0.249	0.338	0.339
Cr	-0.170	0.730	0.194	1.000	0.663	0.458	0.326	0.198	0.452	0.023	0.101	0.707	0.736	0.774	0.605	0.444	0.305
Mn	0.119	0.938	0.419	0.663	1.000	0.862	0.457	0.477	0.648	0.193	0.351	0.585	0.686	0.624	0.385	0.528	0.466
Co	0.184	0.811	0.491	0.458	0.862	1.000	0.525	0.544	0.685	0.244	0.410	0.512	0.587	0.504	0.302	0.478	0.483
Ni	0.371	0.374	0.722	0.326	0.457	0.525	1.000	0.213	0.571	0.274	0.331	0.464	0.386	0.388	0.451	0.544	0.350
Cu	0.165	0.473	0.255	0.198	0.477	0.544	0.213	1.000	0.316	0.099	0.466	0.229	0.264	0.161	-0.019	0.279	0.459
Mo	0.290	0.554	0.708	0.452	0.648	0.685	0.571	0.316	1.000	0.443	0.506	0.425	0.408	0.376	0.312	0.473	0.529
Cd	0.351	0.092	0.420	0.023	0.193	0.244	0.274	0.099	0.443	1.000	0.631	-0.091	-0.124	-0.141	-0.035	0.501	0.140
Sb	0.641	0.362	0.619	0.101	0.351	0.410	0.331	0.466	0.506	0.631	1.000	0.100	0.095	0.040	0.094	0.365	0.301
La	-0.059	0.588	0.277	0.707	0.585	0.512	0.464	0.229	0.425	-0.091	0.100	1.000	0.929	0.914	0.834	0.282	0.335
Ce	-0.141	0.722	0.196	0.736	0.686	0.587	0.386	0.264	0.408	-0.124	0.095	0.929	1.000	0.966	0.742	0.303	0.334
Sm	-0.164	0.670	0.175	0.774	0.624	0.504	0.388	0.161	0.376	-0.141	0.040	0.914	0.966	1.000	0.787	0.301	0.321
Eu	0.073	0.391	0.249	0.605	0.385	0.302	0.451	-0.019	0.312	-0.035	0.094	0.834	0.742	0.787	1.000	0.226	0.179
Pb	0.018	0.417	0.338	0.444	0.528	0.478	0.544	0.279	0.473	0.501	0.365	0.282	0.303	0.301	0.226	1.000	0.343
Ag	-0.017	0.493	0.339	0.305	0.466	0.483	0.350	0.459	0.529	0.140	0.301	0.335	0.334	0.321	0.179	0.343	1.000

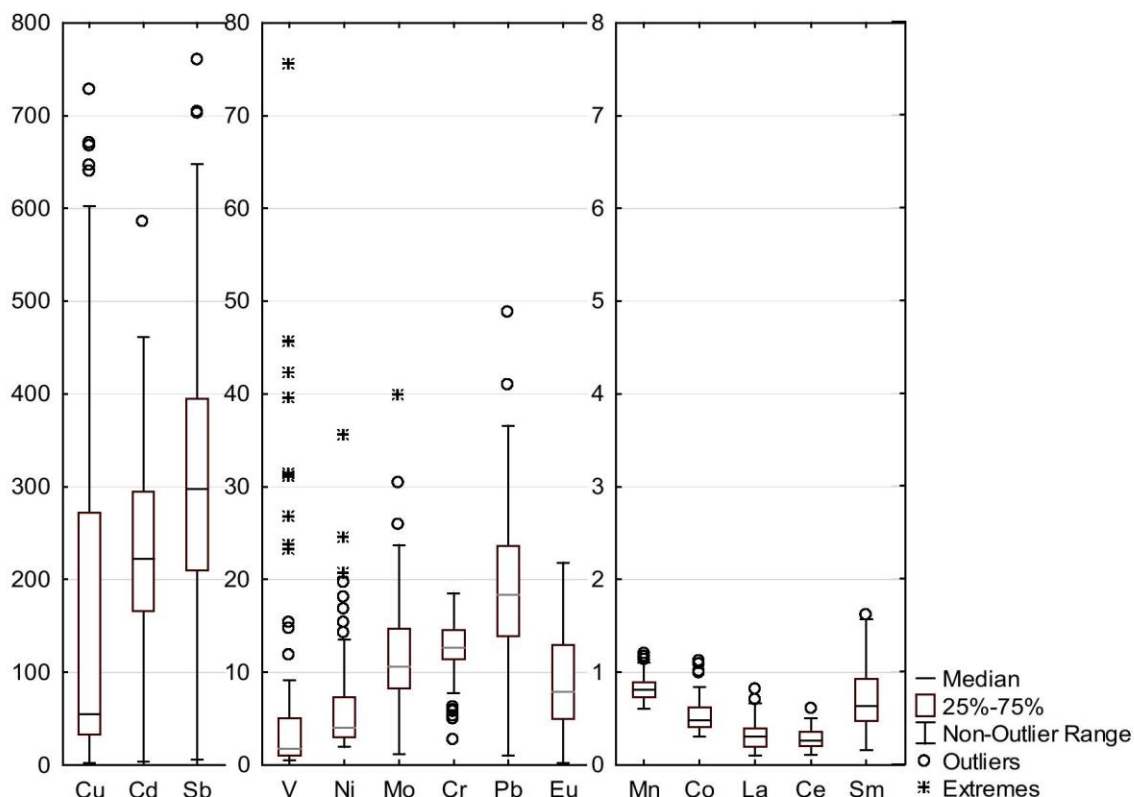


Fig. 2 Enrichment factors (EF) for all analyzed metals. EF computed considering Ti as the reference crustal component of the upper continental from Wedepohl (1995)

Table 8 Metal enrichment factors (EF) in PM_{2.5}. EF values have been computed, using Ti as a reference element employing upper crustal data reported by Wedepohl (1995). For seasonal median

values, values in **bold** are significantly the highest ($p < 0.05$). Values in **bold italics** are significantly higher than one value ($p < 0.05$). Values in *italics* are significantly the lowest ($p < 0.05$)

	2013 EF					Seasonal median EF value		
	Mean	Median	Minimum	Maximum	Std. dev.	DW	R	DC
Sb	315.8	293.3	6.2	760.1	157.4	366.7	223.8	278.3
Cd	265.2	221.3	3.4	2116.9	257.6	257.9	215.3	221.3
Cu	203.2	59.3	2.3	1360.4	273.8	105.2	55.8	<i>33.1</i>
Pb	20.2	18.4	1.0	94.1	11.9	17.1	20.0	18.4
Cr	12.2	12.6	2.7	18.5	3.1	<i>11.4</i>	14.5	13.0
Mo	12.2	10.5	1.2	39.8	6.6	9.7	9.5	13.2
Eu	8.8	7.6	0.2	27.2	5.4	<i>5.4</i>	9.3	9.1
Ni	7.6	4.0	1.9	97.7	12.2	3.9	3.7	5.3
V	6.7	1.7	0.5	75.6	12.7	2.3	<i>1.0</i>	5.5
Mn	0.9	0.8	0.6	4.2	0.4	0.8	0.8	0.8
Sm	0.8	0.6	0.2	3.5	0.5	<i>0.5</i>	0.9	0.7
Co	0.6	0.5	0.3	3.2	0.4	0.5	0.4	0.5
La	0.4	0.3	0.1	4.1	0.5	<i>0.2</i>	0.4	0.3
Ce	0.3	0.3	0.1	3.0	0.3	<i>0.2</i>	0.4	0.3
Ag	20	0	0	225.9	45.7	0.0	0.0	0.0

Table 9 Principal component analysis. Loadings of metals in PM_{2.5} related with factors

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Ti	0.468	0.123	0.816	0.164	0.042	0.207
V	0.054	0.982	0.080	0.032	0.064	0.078
Cr	0.698	0.314	0.260	-0.003	0.122	0.388
Mn	0.348	0.137	0.845	0.217	0.028	0.193
Co	0.117	0.128	0.925	0.214	0.018	0.013
Ni	0.080	0.937	0.076	0.145	0.048	0.116
Cu	0.085	0.058	0.309	0.853	-0.074	-0.001
Mo	0.194	0.866	0.269	0.110	0.184	0.158
Cd	-0.086	0.174	0.079	-0.075	0.935	0.096
Sb	-0.068	0.355	0.642	-0.017	0.315	0.161
La	0.881	0.299	0.131	0.175	-0.028	-0.088
Ce	0.934	-0.004	0.284	0.118	-0.045	0.044
Sm	0.937	-0.069	0.121	0.038	-0.133	0.147
Pb	0.122	0.203	0.255	0.319	0.258	0.746
Ag	0.154	0.195	0.189	0.849	-0.033	0.105
Eu	0.855	0.279	-0.069	-0.157	-0.042	0.166
Eigenvalue	7.7	3.2	2.2	1.4	0.8	0.8
% Total	43.0	17.5	12.2	7.6	4.5	4.2
Cumulative	43.0	60.5	72.7	80.3	84.8	89.0

Values marked in bold are significant higher ($p < 0.05$)

meteorological variations (wind conditions) between 2011 and 2013, especially during DW (Table 5), as explained in the “Source apportionment” and “Relationship between metal concentration and wind patterns” sections.

Source apportionment

Correlations and enrichment factors of metals in PM_{2.5}

Assigning metals to geogenic and anthropogenic sources is a complex task. Local authorities recognize anthropogenic activities as the main sources to atmospheric pollution in MCMA. Conversely, Morton-Bermea et al. (2018) identified the important influence of geogenic sources in PM_{2.5} within the studied area. In the current study, Spearman’s rank correlation (Table 7) led to recognize the association between PM_{2.5} with V, Ni, Mo, Cd, and Sb. There is ambivalent information regarding the origin of these metals; V, Ni, and Mo have been pointed as indicators of oil fuel processes (Yuan et al. 2006; Alleman et al. 2010; Pandolfi et al. 2011), whereas, a geogenic origin of V and Ni in this area has been reported, attributed to the local host rock (Morton-Bermea et al.

2009). Thus, it could be considered that these metals come from both geogenic and anthropogenic sources. However, the mechanisms that control the impact of these sources are unclear and it will be explored in the “Source apportionment” and “Relationship between metal concentration and wind patterns” sections.

To obtain a better insight, enrichment factors (EF) have been computed, using Ti as a reference element and data from the upper crustal reported by Wedepohl (1995). Because EF values of metals are fixed by their origin, they can be used to assign elements to their geogenic or anthropogenic source. In this way, metals with $EF \approx 1$ values were assigned as unaffected by anthropogenic activities, metals with $5 < EF < 100$ as moderate enriched, and metals with $EF > 100$ as metals with a high degree of anthropogenic influence. In Fig. 2, we present EF values in box plots for all analyzed metals. Non-enriched metals (Ce, La, Co, Sm, Mn) are clearly attributed to geogenic sources; moderate enrichment metals ($EF \leq 20$ V, Ni, Mo, Cr, Pb,) are suspected to be emitted from anthropogenic activities. Cu, Cd, and Sb are strongly anthropogenic enriched, with, $EF > 100$. This is consistent with the fact that Sb has been pointed out as an emission from vehicle break wearing (Cheng

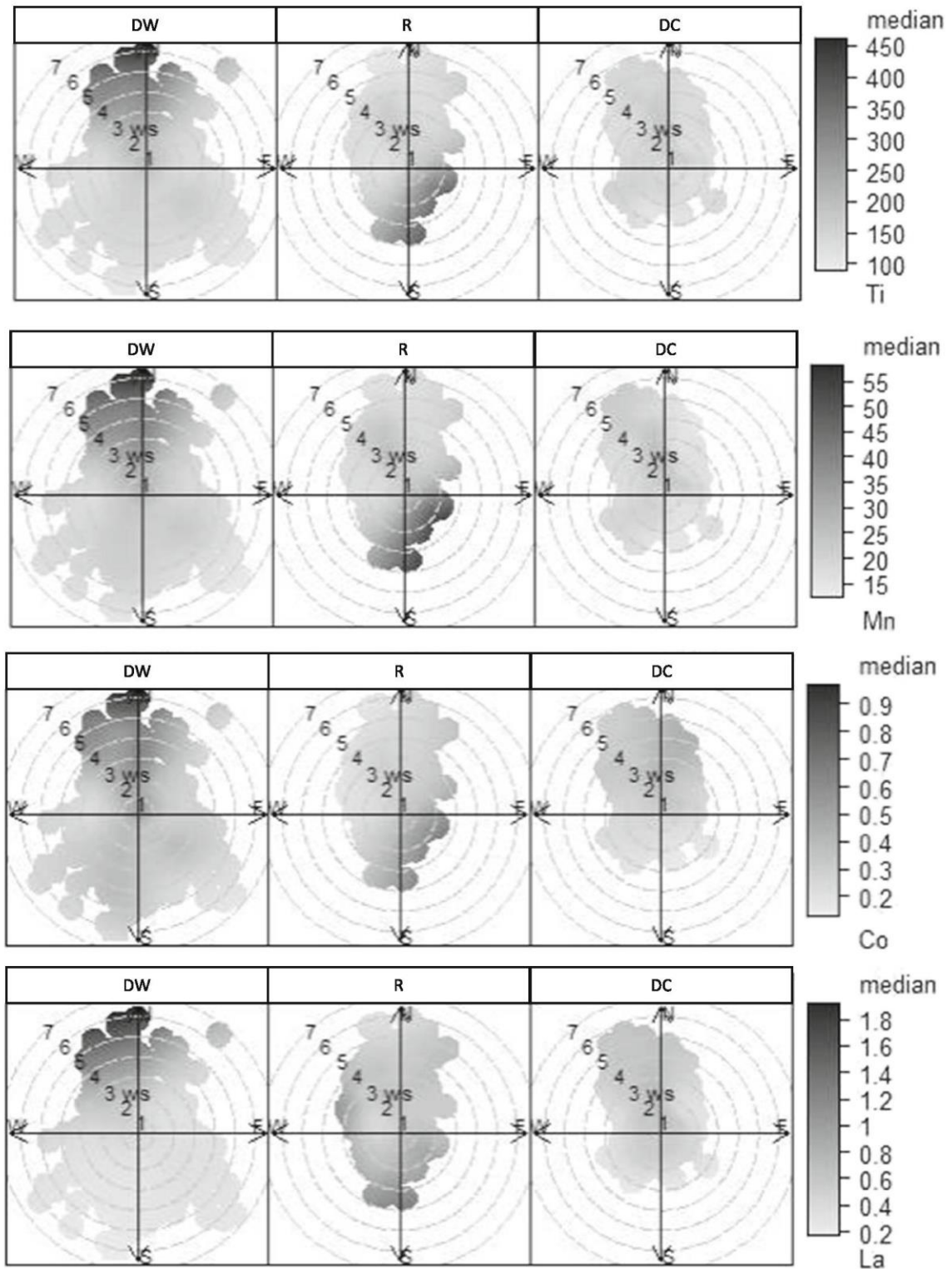


Fig. 3 Seasonally computed wind plots for metal concentrations in collected PM_{2.5}

et al. 2010) and that Cu and Cd are associated with industrial and metallurgic actives (Alleman et al. 2010; Zhai et al. 2014).

There is a high seasonal variability of EF values for some metals (Table 8). The significant seasonal changes of V and Ni allow us to determine that these

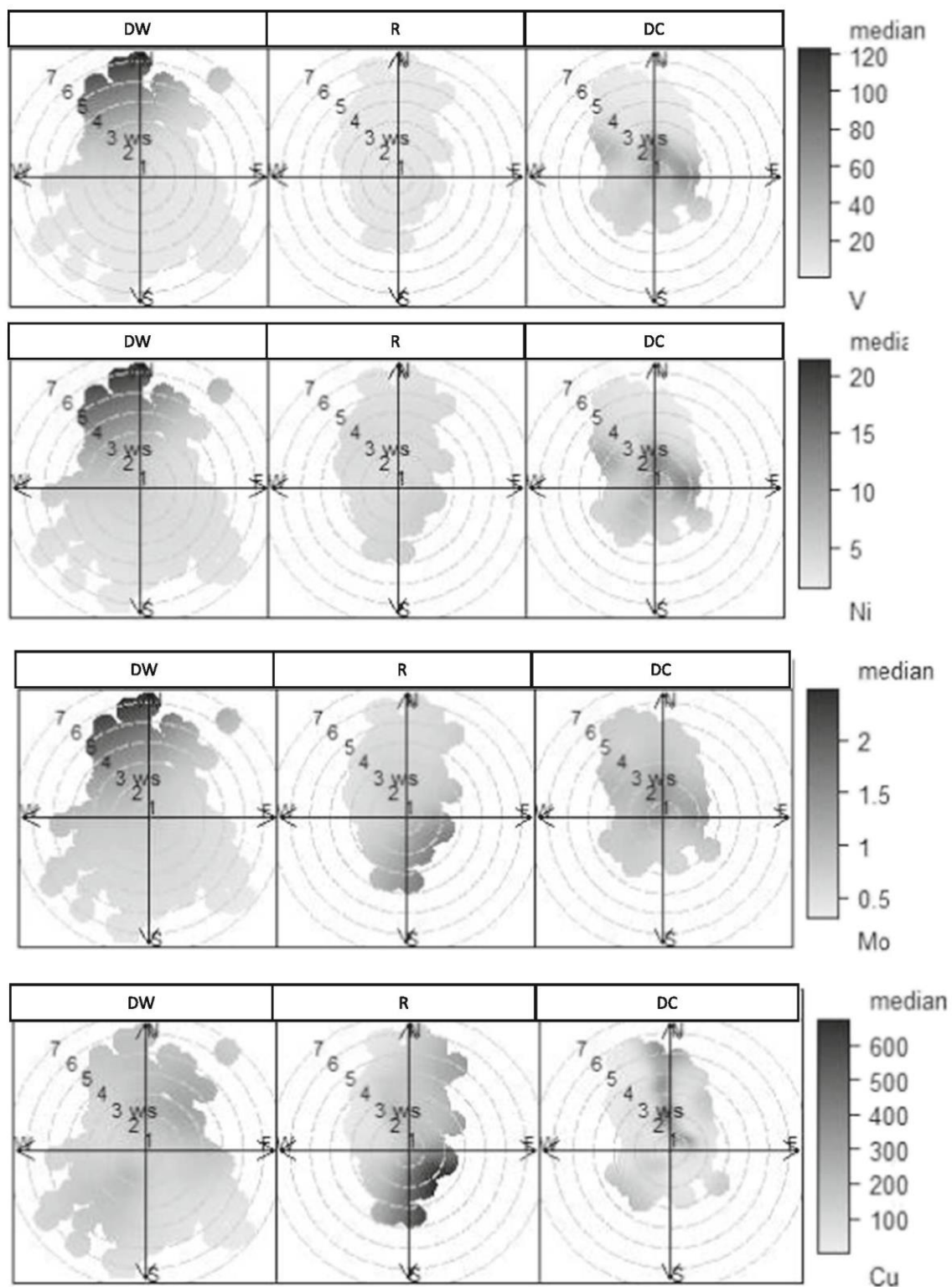


Fig. 3 (continued)

elements come from the sum of geogenic and anthropogenic sources, mixed in different relative amounts. For V, Ni, and Mo, elements correlated as shown in Table 7, and the geogenic contribution

during R is evident, suggesting a decrease on the impact of anthropogenic sources during this season. Conversely, the high EF ($p < 0.05$) values during DC reveal the addition of the anthropogenic

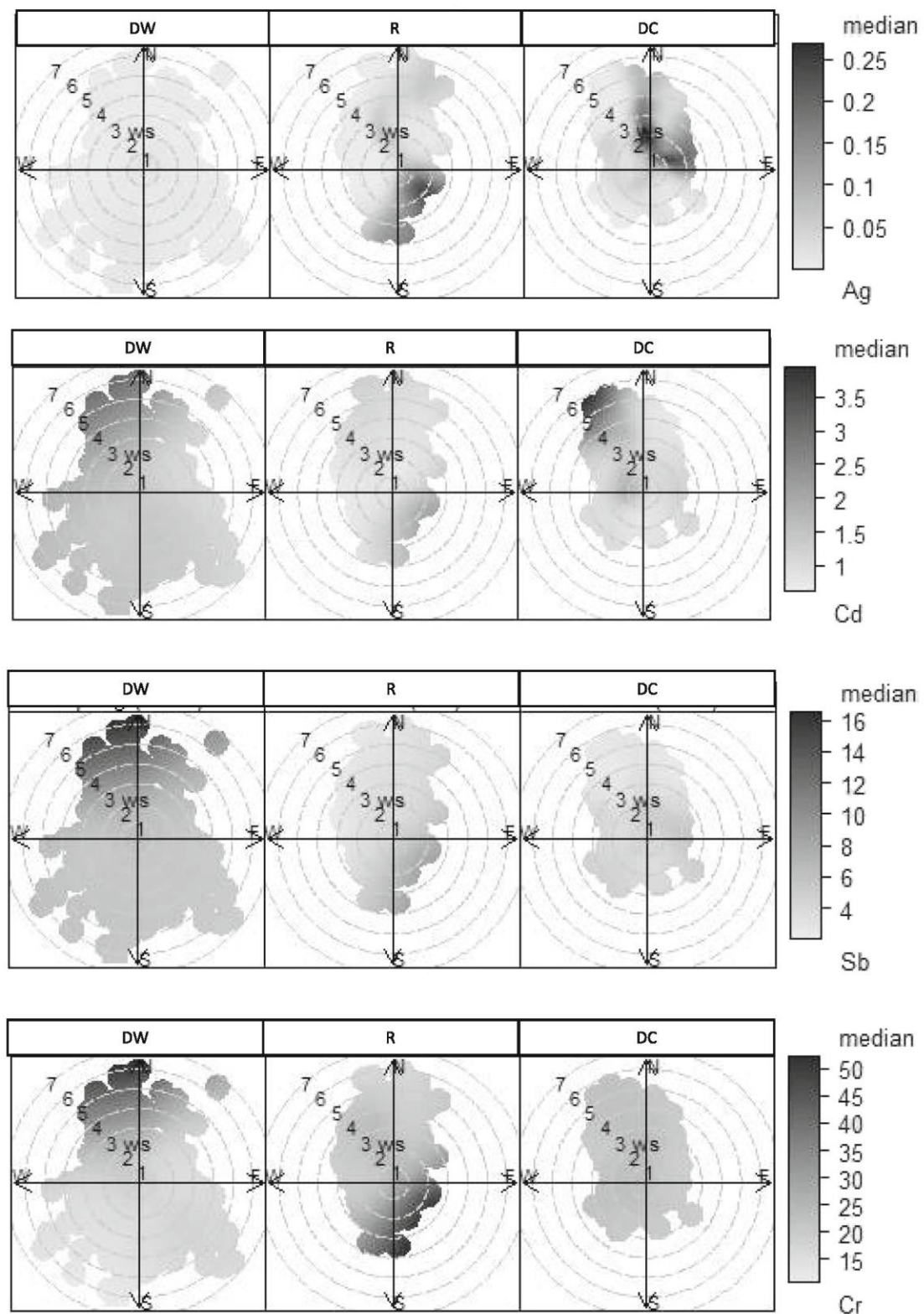


Fig. 3 (continued)

contribution. This is further supported by the Ni/V median ratio of 0.64, which is discrepant with the Ni/V ratio of samples associated with anthropogenic

oil fuel combustion. Other researchers have reported Ni/V values between 2.0 and 3.5 (Yuan et al. 2006; Alleman et al. 2010; Pandolfi et al. 2011; and

Ledoux et al. 2017). Moreover, Miranda et al. 2005 found values of Ni/V ratio lower than 0.3 for the studied area, suggesting that the increase we found for this ratio may indicate an anthropogenic input.

PCA

The application of principal component analysis (PCA) (Table 9) indicated that six factors explain 89% of the total variance.

Factor 1 includes La, Sm, Eu, and Ce and explains 43.0% of total variance. This confirms the importance of geogenic sources of PM_{2.5} in MCMA, as pointed by Morton-Bermea et al. 2018. It is evident that NW and NE sites presented the higher concentrations of these elements as described previously. The provenance of the geological material carrying these metals was already discussed.

Factor 2 explains 17.5% of total variance and includes Ni, V, and Mo. As previously discussed (“Correlations and enrichment factors of metals in PM_{2.5}” section), their origin is related to the sum of geogenic and anthropogenic sources.

Factor 3 is formed by Ti, Mn, and Co related to geogenic sources, attributed to resuspension from local soil. The percentage of total variance explained by this factor is 12.2%.

Factor 4, explaining 7.6% of total variance, involves Cu and Ag and is related to anthropogenic activities based on EF values (Table 5). This is consistent with the spatial behavior of Cu, showing that emissions of this metal are mainly located at SW and NW sites (Fig. 1), and this former characterized mainly as an industrial area, in accordance with the industrial origin of this metal (Johnson et al. 2006).

Cadmium comprises Factor 5, while Pb Factor 6. They explain 4.5% and 4.2% of total variance, respectively. These metals are attributed to anthropogenic sources related to either industrial activities or vehicular traffic.

Relationship between metal concentration and wind patterns

Wind patterns play an important role in the metal concentration variability. An assessment of wind

patterns (wind flow and intensity) shows significant differences during the sampling seasons (Fig. S1). An analysis of the metal behavior by sectors, northward winds (45°–315°), eastward winds (315°–225°), southward winds (225°–135°), and westward winds (134°–45°), provides valuable information that enhances the identification of the origin of the metals as well as to the understanding of their distribution in the study area. The assessment of metal concentrations of the sectors mentioned above by means of *U* test shows that, for all sites, the concentrations of Cr, La, Sm, Ce, and Eu are significantly higher ($p < 0.05$) when southward wind occurred than those when northward winds occurred. This observation enhances the reported effects of wind patterns to some pollutants (O₃, SO₄, NO_x) described by De Foy et al. (2005); however, they observed a decrease of pollutant levels when northward wind occurred. Moreover, Cd and Sb concentrations were higher ($p < 0.05$) at all sites when northward winds occurred. This finding encloses reliable information to source identification for those metals.

A deeper analysis of metal concentration dependence on wind patterns is obtained through polar plots, computed by means of Openair package in R. This allows to analyze not only the effect of wind directions but also the effect of speed (intensity) on metal concentrations. In Fig. 3, polar plots are presented seasonally for the analyzed metals. The wind patterns used to be light wind (US Weather Bureau description) with an average speed of 2.3 m s⁻¹ (Fig. S1). However, the impact assessment of strong wind episodes exceeding 5 m s⁻¹, recorded during the afternoon on April 10, April 16, May 4, and August 2 at NW, NE, and SE provides interesting information. The maximum concentrations for Ti, Mn, Co, La, Eu, Sm, and Ce occurred during these episodes. The above provides evidence suggesting that wind intensity is responsible for carrying geogenic material, in spite of wind direction.

On the other hand, during DC, there were conditions of atmospheric stability with calm winds and low temperature, which resulted in an accumulation of metals from local sources. It was also possible to identify that during this season, the highest concentrations of V, Ni, and Mo occurred when the wind blew from the SE, suggesting that the corresponding anthropogenic component of these metals can be

differentiated only during DC. These statements highlight the importance of meteorological conditions to the impact and distribution of metals in PM_{2.5} in MCMA.

Conclusion

According to previous information of metals contained in PM_{2.5} in the atmospheric environment of the MCMA, the geochemical data generated in this study were used to verify previous information of the metal concentration ranges and their spatial and temporal behavior as well as to recognize the sources of emission in the area. Furthermore, the use of statistical tools to the geochemical and meteorological data highlighted the importance of wind intensity to the impact of emission sources.

The 17% increase in PM_{2.5} mass concentrations observed from 2011 to 2013 is attributable to differences in the impact of geogenic sources. This is consistent with changes in wind intensity. The mechanism by which the geogenic sources have been highly impacted was revealed by means of wind plots. This allowed us to conclude that high-speed episodes (5 m s^{-1}) are responsible for raising geogenic metal concentrations rather than wind direction. Despite these differences in metal concentrations, the spatial distribution is consistent with the 2011 observations.

The identification of the emission sources was inferred from the information obtained from EF and PCA. The seasonal evaluation of EF revealed changes in the behavior of the ratios of geogenic and anthropogenic sources for metals associated to mixed sources (Ni and V), as a consequence of meteorological changes during DC season.

Improved metal concentration analysis, identification of source emissions, and distribution patterns in PM_{2.5} may result in the development of reliable public policies, based on the potential risk of toxicological effects of breathable particulate matter since the MCMA houses more than 20 million inhabitants.

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Material suplementario de “Spatial and temporal distribution of metals in PM_{2.5} during 2013: assessment of wind patterns to the impact of geogenic and anthropogenic sources

Este material junto con los diagramas de cajas y bigotes en el Anexo 1 de esta tesis fueron inicialmente desarrollados con la base de datos del muestreo de 2013. Estos mismos análisis se ejecutaron posteriormente para el muestreo del 2011, así las observaciones vistas en esta base de datos pudieron ser cotejadas, dando paso con eso, a la posibilidad de realizar la publicación Morton-Bermea et al. 2018

Tablas del supporting information. (SI)

Table S1. Statistical comparison of annual median concentration at each site.

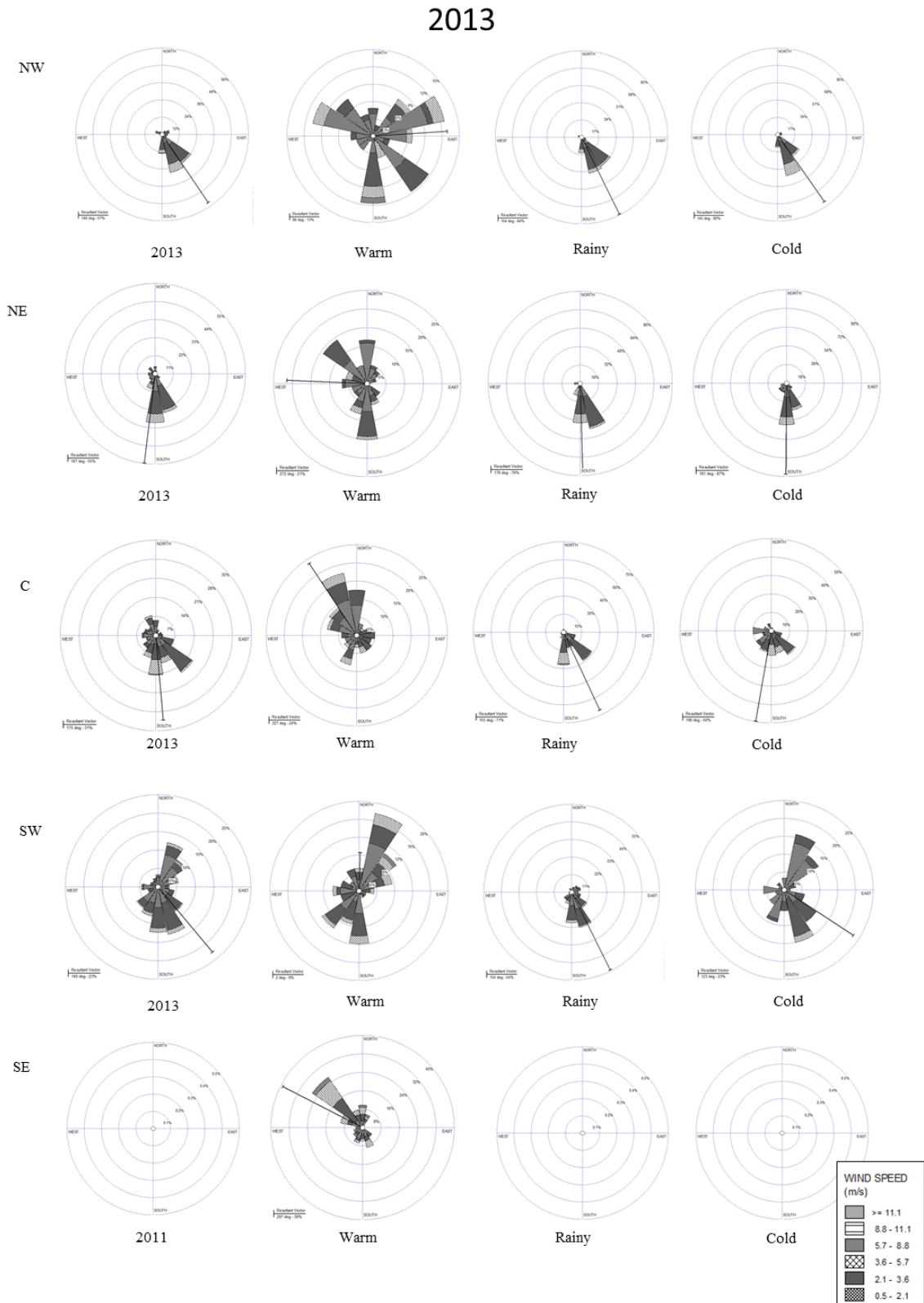
Locations comparison		Ti	Mn	Co	Cu	Cr	Ni	V	Cd	Sb	Pb	Se	Mo	Ag
NW	NE	NE	NE	NE	NE	=	=	=	=	=	=	NW	=	NE
NW	C	=	=	=	C	=	=	=	=	=	=	NW	=	=
NW	SW	=	=	=	SW	=	=	=	NW	=	=	NW	=	=
NW	SE	=	=	=	SE	=	=	=	=	=	=	NW	=	=
NE	Vs	C	NE	NE	NE	NE	=	NE	=	=	=	NE	=	NE
NE		SW	NE	NE	NE	NE	=	=	=	=	=	NE	=	NE
NE		SE	NE	NE	NE	NE	=	=	=	=	=	=	NE	NE
C	SW	=	SW	=	SW	=	=	=	=	=	=	=	=	=
C	SE	=	=	=	=	=	=	=	=	=	=	=	=	=
SW	SE	=	=	=	SW	=	=	=	=	=	=	=	=	=

Table S2. Statistical comparison of medians for each site among seasons.

Seasons comparison		Ti	Mn	Co	Cu	Cr	Ni	V	Cd	Sb	Pb	Se	Mo	Ag
DW	R	=	=	=	DW	R	=	DW	DW	=	=	=	=	=
DW	Vs	DC	=	=	DW	DC	DW	=	=	=	=	DC	DC	=
R		DC	=	=	=	=	R	DC	=	=	=	=	DC	=

Figura del supporting information

Fig. S1. Wind Roses for each sampling sites during the year, and the three sampling season in MCMA



Platinum concentration in PM_{2.5} in the Mexico City Metropolitan Area: relationship to meteorological conditions

En esta publicación se muestran los resultados de la evaluación de Pt en el PM_{2.5} colectado durante 2013. El Pt se diferencia del resto de los metales por ser un contaminante bien identificado con emisiones vehiculares. El Pt se encuentra en los convertidores catalíticos de vehículos. Los convertidores catalíticos se emplean para disminuir emisiones de hidrocarburos no combustionados, óxidos nitrosos (NO_x) y también oxidar monóxido de carbono (CO) en dióxido de carbono (CO₂). El Pt se emite tras el deterioro de los convertidores catalíticos y la emisión varía con la edad del vehículo y algunos factores asociados con los operarios de los vehículos. Sus implicaciones a la salud son nicho de estudio por toxicólogos y epidemiólogos.

La concentración de durante 2013 para el platino fue de $55 \text{ pg m}^{-3} \pm 15 \text{ pg m}^{-3}$. Se observó una diferencia temporal significativa ($p < 0.05$): DC > R > DW; no se encontró diferencia significativa en relación a la distribución espacial (Figuras 2 del artículo). El Pt ha aumentado 19.6% en relación con la última evaluación de Pt en la zona (Morton-Bermea, et al., 2014). Esto se relaciona con el crecimiento de la flota vehicular.

Se observaron concentraciones mayores al 90 percentil durante los días del *regreso a clases*, caracterizado por altos niveles de congestionamiento vehicular. Estas altas concentraciones ocurrieron durante el periodo de lluvias. Apoyado con el análisis de distribución de vientos con diagramas polares (Figura 4 del artículo) se concluye que la intensidad del viento tiene más importancia en el comportamiento de estas concentraciones que los efectos de lavado de la atmosfera.

La implementación de convertidores catalíticos en vehículos para disminuir las emisiones CO han sido exitosas (Figura 5 del artículo) sin embargo, el incremento de las concentraciones de Pt ponen en manifiesto que la mejora de la calidad del aire debe ser rediseñada. Ya que se ha creado un nuevo problema ambiental buscando solucionar otro.



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Platinum concentration in PM_{2.5} in the Mexico City Metropolitan Area: relationship to meteorological conditions

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ABSTRACT

Platinum (Pt) concentrations in PM_{2.5} were evaluated by means of inductively coupled plasma mass spectrometry (ICP-MS) to evaluate the spatial and temporal behavior and to assess trends. Samples were taken from five representative sites in the Mexico City Metropolitan Area (MCMA): Tlalnepantla-northwest (NW), San Agustín-northeast (NE), La Merced -center (C), Coyoacán-southwest (SW), and Universidad Autónoma Metropolitana Iztapalapa-southeast (SE). Under three weather conditions: dry warm (DW-April), rainy (R-August), and dry cold (DC-November) in 2013. We found that the PM_{2.5} median mass concentration was $24 \mu\text{g m}^{-3} \pm 15 \mu\text{g m}^{-3}$ while Pt concentration was $55 \text{pg m}^{-3} \pm 15 \text{pg m}^{-3}$ (median, interquartile range). Seasonal trend was identified: the concentrations decreased significantly in the following order DC > R > DW. No spatial distribution was observed. Interestingly, among other meteorologically parameters, wind intensity resulted to be the major factor for the dispersion of Pt in PM_{2.5} in MCMA. Furthermore, we found that Pt concentrations increased significantly by 19.6% between 2011 and 2013. Regardless of the increase in Pt, carbon monoxide (CO) levels decreased opposite to a rise in vehicular fleet. These results urge for environment public policies that address the upward tendency of Pt levels especially in urban areas.

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Introduction

In past decades, several courses of action have been adopted to enhance air quality in urban centers. One of them is the implementation of catalytic converters in motor vehicles. These devices transform harmful exhaust gas emissions to less toxic forms by leveraging catalytic properties of the platinum group elements (PGE): including

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platinum (Pt), palladium (Pd), and rhodium (Rh). The introduction of vehicle catalytic converters in the United States since the 1970s, the 1980s in Europe, and in the 1990s in Mexico has enabled successful reduction of nitrogen oxides (NO_x), carbon monoxide (CO), and hydrocarbon (HC) emissions into the atmosphere.

In spite of the aforementioned statement, catalytic converters spread metals into the air including PGE. These emissions result from abrasion processes inside catalytic converters associated with wear, heat, aging, and operating vehicle conditions. For this reason, motor vehicles are considered the largest source of anthropogenic PGE emissions in urban areas (Schäfer *et al.* 1999; Zereini *et al.* 2001; Zimmermann and Sures 2004; Rauch *et al.* 2005; Pino *et al.* 2010; Sen *et al.* 2016). High levels of Pt have been reported in ambient samples close to heavy traffic roadways (Morton *et al.* 2001; Nash III *et al.* 2003; Whiteley and Murray 2003; Abdou *et al.* 2016; Qi *et al.* 2011; Zereini and Alt 2012; Sievers and Schuster 2015; Morton-Bermea *et al.* 2016; Cortés *et al.* 2017).

The metallic Pt emitted from vehicles can be transformed into the environment into more toxic forms such as its halide salts (Gomez *et al.* 2001; Ravindra *et al.* 2004; Hooda *et al.* 2008). Some epidemiological research are concerned with chronic exposure to particulate matter (PM), which has been associated with increased morbidity and mortality (Singer *et al.* 2005; Puls *et al.* 2012; Wiseman and Zereini 2010; Merget and Rosner 2001).

Up till now, hardly any Pt research has been conducted in Mexico City (CDMX) or the Mexico City Metropolitan Area (MCMA) although about eight million automobiles with catalytic converters are presently running in the area (INEGI 2014). In 2001, Morton *et al.* (2001) reported the first evidence of PGE found in topsoil. Furthermore, Rauch *et al.* (2006) reported of Pt in PM_{10} , he observed an increase in Pt concentrations in PM_{10} during 1991–2003. Morton-Bermea *et al.* (2014) reported the concentrations of Pt in $\text{PM}_{2.5}$; and examined spatial and temporal variations, Pt distribution patterns were surprising. The rainy season and the southwest location were the most affected by the high concentrations of Pt. Additional research is needed to confirm the previous assessment.

This study reports the Pt in MCMA including the spatial and temporal variation, trends and the influence of meteorological parameters such as wind patterns on the distribution and dispersion of the Pt in $\text{PM}_{2.5}$. The comparison of this Pt data with previous studies facilitates evaluation of the trend of Pt emissions in MCMA. To reach this goal, our research group has developed an inductively coupled plasma mass spectrometry (ICP-MS) validated analytical protocol, which can be implemented routinely during monitoring programs.

Experimental methods

Sampling and analytical treatment

PM_{2.5} sampling campaign

In 2013, a $\text{PM}_{2.5}$ sampling campaign was carried out simultaneously at five locations within MCMA (Tlalnepantla-northwest (NW); San Agustín-northeast (NE), La Merced-center (C), Coyoacán-southwest (SW), Universidad Autónoma Metropolitana Iztapalapa-southeast (SE) (Figure 1). In Table 1, we list the main characteristics of each site.

Mexico City Metropolitan Area (MCMA)

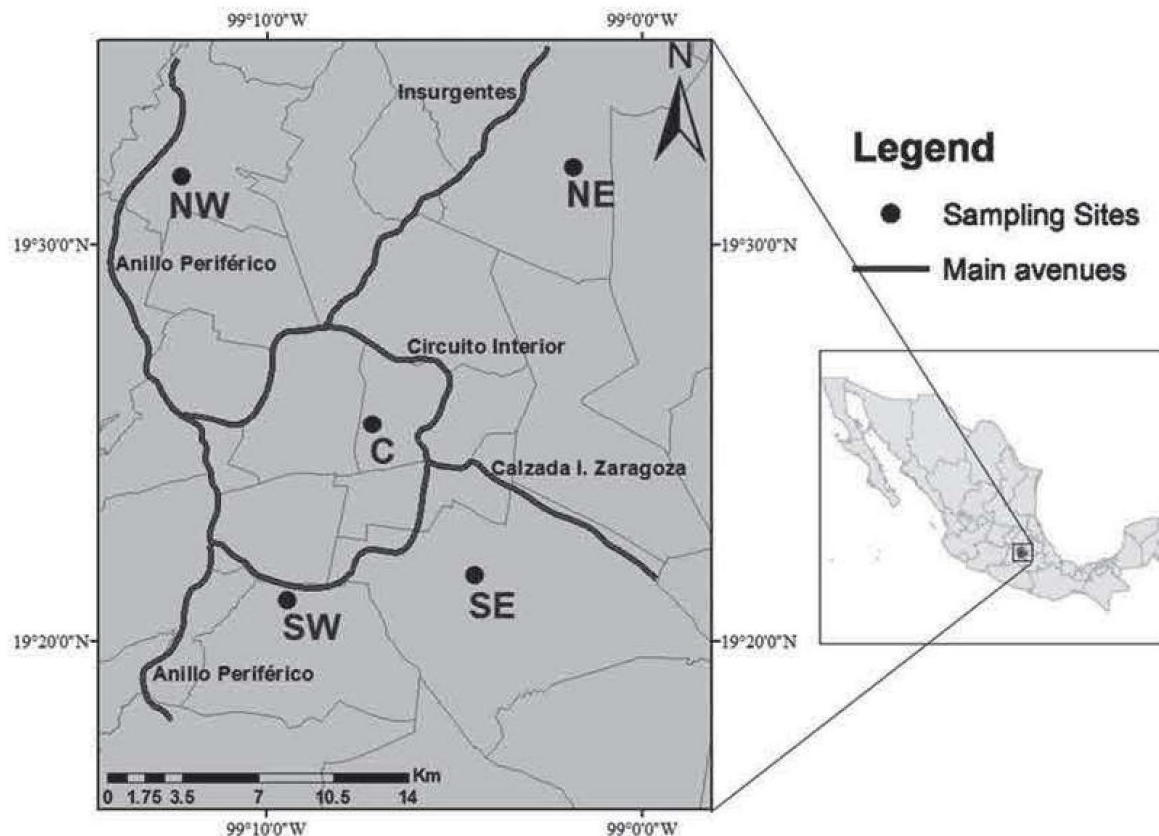


Figure 1. Location of sampling sites in MCMA.

Table 1. Main features of the sampling sites monitoring during this camping sampling.

Site name	Position in MCMA	Main characteristics
Tlalnepantla	Northwest, NW	Residential and commercial area with industrial settlement and traffic avenues
San Agustín	Northeast, NE	Residential and commercial area with few industrial settlement and avenues
Merced	Central, C	Commercial and residential zone with vehicular avenues
Coyoacán	Southwest, SW	Residential zone and vehicular avenue
Universidad Autónoma Metropolitana-Iztapalapa	Southeast, SE	Residential zone and vehicular avenue with small manufactories

The sampling period includes three different seasons: dry warm (DW-April), rainy (R-August), and dry cold (DC-November). 24-h integrated samples were obtained every 6 days employing glass fiber filter impregnated with Teflon (20.4 cm × 25.2 cm; TIGF, Pallflex). Filters were previously baked at 280 °C. High volume samplers (Tisch and Andersen General Metal Works) were employed with a flow rate of $1.13 \pm 10\% \text{ m}^3 \text{ min}^{-1}$, calibrated according to Federal Register (1987). A total of 75 samples were collected as described. Field blanks were obtained by manipulating filters as samples without exposing them on sites and on each sampling date. No Pt contamination was found on the field blanks. After collection, filters were enveloped in aluminum foil, kept in zip-lock bags, and transported at 4 °C to the laboratory.

All meteorological parameters were obtained from Automatic Monitoring Network (RAMA) from the Mexico City Environmental Ministry (<http://www.aire.cdmx.gob.mx/default.php?opc='aKBhnmI'&opcion=Zw>).

Analysis and quality control

The detailed analytic method and digestion procedure employed are described by Morton-Bermea *et al.* (2014). Briefly, a tenth of each filter undergoes acid digestion (aqua regia and HF) assisted by microwaves (Ethos One, Milestone). The digestion program started from room temperature to 220 °C and kept 20 min on SK-10 liners (Milestone). After cooling, samples were taken to almost dryness and then added with HNO₃ to ensure removal of HF, the final volume was taken to 25 mL with HNO₃ 2% (v/v). To ensure the quality of the results, filter field blanks and reagents blanks were prepared under the same procedure. The standard reference material, urban road dust BCR-723 (Standards, Measurements and Testing Program, of the European Union) was employed to validate the analytical procedure. All measures were performed using ICP-MS (iCAP Q, Thermo Scientific, Germany), the spectral interferences were managed by the application of kinetic energy discrimination and a collision cell. An internal standard of ¹¹⁵In (stock solution; Merck, Germany) was employed to correct instrumental drift. Limits of detection (LOD) were calculated as three times the standard deviation of Pt concentrations in 15 blank filters.

Statistical treatment

Statistica Software V 10.0 (StatSoft Inc, Tulsa, Ok, USA) was employed for all statistical analysis including median, mean, standard deviation, and Mann-Whitney U-test to assess spatial and temporal variability. Wind plots were computed by means of the open-source software R and the open air package (Carslaw and Ropkins 2012). Spearman correlation was used to evaluate the association between PM mass concentration and Pt variables. Open-source R and Openair package were employed to draw wind plots.

Results and discussion

Quality controls

The analytical procedure employed for the quantification of Pt in PM_{2.5} samples was validated by means of recovery rates using the BCR-723 reference material. The average recovery rate found was 70.4% and the coefficient variation 10.8% ($n=15$). LOD was 3.3 pg m⁻³, all reported concentrations are above the LOD.

PM_{2.5} mass concentration

The median PM_{2.5} mass concentration found in this study was 24 μg m⁻³ ± 15 μg m⁻³. No significant difference ($p < .05$, U-test) were found among the five sampling sites; however, seasonal variability was found following the significant trend: DW > DC > R

Table 2. Spatial and seasonal distribution of Pt concentrations.

Pt	n	Mean	Median	Percentile 10	Percentile 90	SD	Quartile range
MCMA	75	59	55	40	87	20	25
Spatial distribution							
Site				pg m ⁻³			
NW	15	58	58	35	87	22	32
NE	15	61	54	40	87	23	24
C	15	54	53	40	68	18	13
SW	15	60	50	40	90	19	33
SE	15	64	59	40	100	22	30
Seasonal distribution							
Season				pg m ⁻³			
DW	25	49	44	37	68	14	14
R	25	61	51	40	106	25	17
DC	25	68	68	43	84	16	15

NW: Northwest; NE: Northeast; C: Central; SW: Southwest; SE: Southeast; DW: dry warm; R: rainy; DC: dry cold; SD: standard deviation.

Bold-marked values were found significantly higher ($p > .05$) via Mann-Whitney U-test.

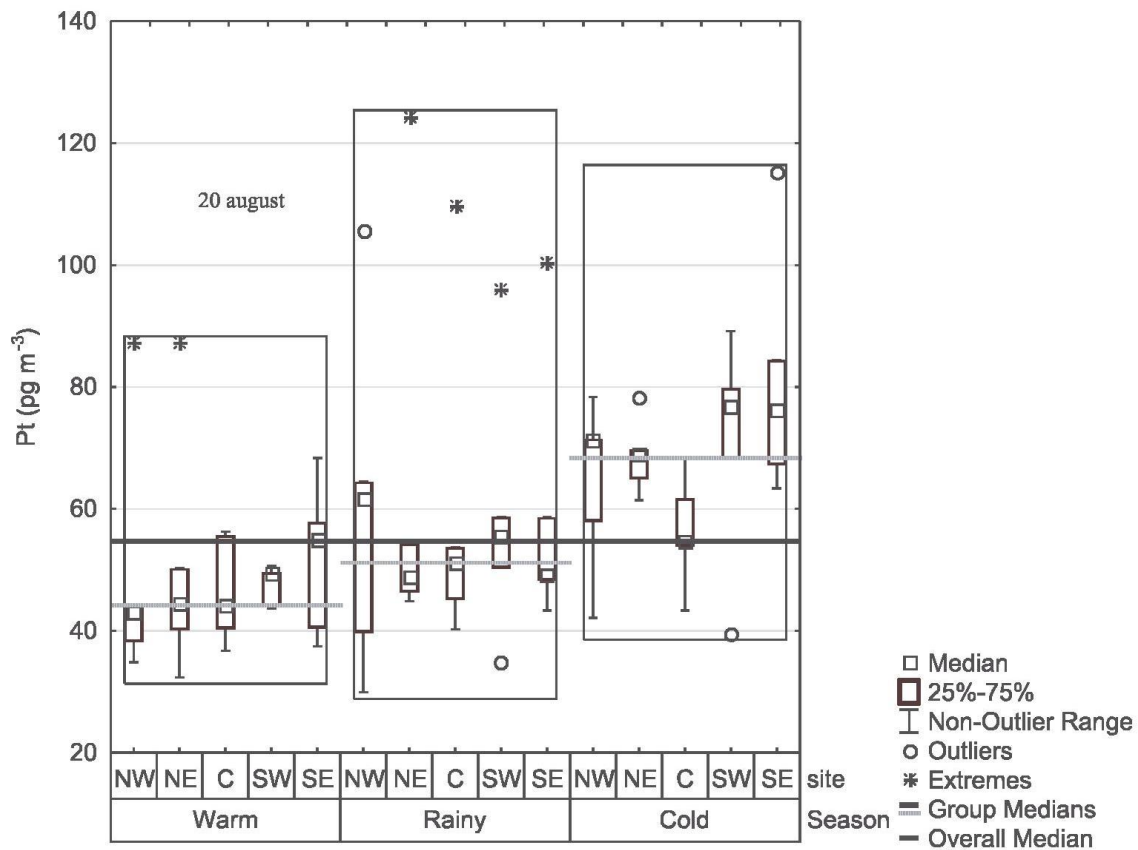


Figure 2. Box plot concentrations of Pt found in MCMA during 2013 sampling campaign.

($38 \mu\text{g m}^{-3} > 25 \mu\text{g m}^{-3} > 16 \mu\text{g m}^{-3}$; $p < .05$). These findings are in agreement with the temporality of PM_{2.5} reported in the study area by Morton-Bermea *et al.* (2018).

Pt in PM_{2.5} spatial and seasonal variations

Pt median and mean concentration at the five sampling sites during the three samplings seasons are shown in Table 2 and Figure 2. The median concentration for all samples

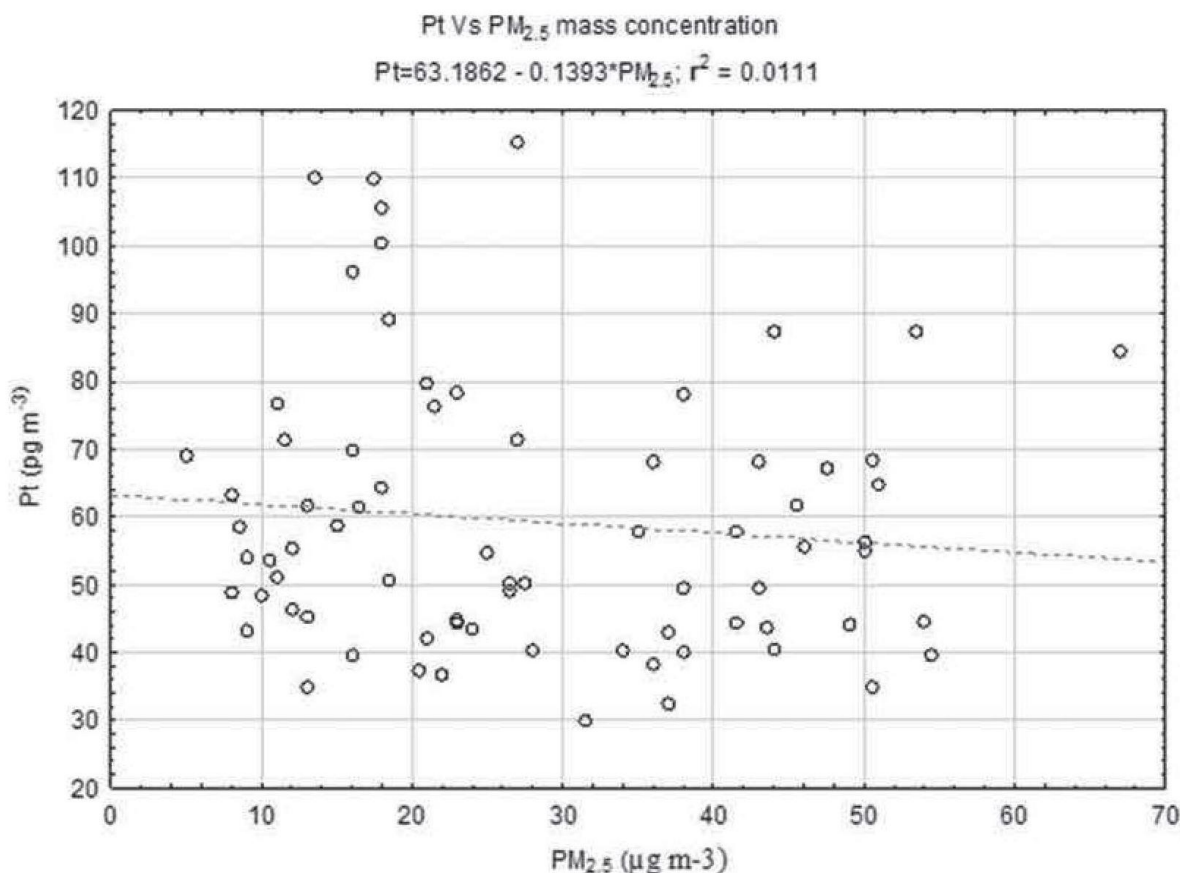


Figure 3. Relationship between $PM_{2.5}$ mass concentration vs Pt collected in $PM_{2.5}$.

found was $55 \text{ pg m}^{-3} \pm 26 \text{ pg m}^{-3}$. The statistical assessment of these data shows a lack of correlation between $PM_{2.5}$ mass concentrations and Pt concentrations (Spearman rank correlation -0.11 , $p < .05$; Figure 3) which implies that source of Pt in ambient air has no significant impact on $PM_{2.5}$ mass concentration.

Pt median concentrations showed the following seasonal trend $DC > R > DW$ ($68 \text{ pg m}^{-3} > 51 \text{ pg m}^{-3} > 44 \text{ pg m}^{-3}$, $p < .05$) (Figure 2). This is consistent with the metal behavior reported for other metals (derived from anthropogenic sources) during the cold season in other urban areas (Moreno *et al.* 2006; Dongarrá *et al.* 2010). Since Pt in atmospheric environment is well known to be related to emission from vehicles and the number of these may not shift radically during seasons; these data suggested us that the significant differences in Pt concentrations among the season had to be controlled and governed by additional factors. On the other hand, the spatial distribution showed no significant difference ($p < .05$) among the sampling sites during each season. Thus, to clarify the spatiotemporal behavior, an assessment by mean of wind plots versus Pt concentration during the three seasons was performed (Figure 4).

The significantly highest concentration levels of Pt in $PM_{2.5}$ registered during DC were attributed to the combined effect of low temperature, which causes a decrease in the layer of inversion, and minor variability of wind direction and low intensity (Figure 4). Conversely, during R, the Pt concentrations were significantly lower than during DC as the expected effect of atmospheric washout typical of rainy season (Figure 4). Unexpectedly, concentrations in R were still higher than those registered in DW (Figure 4), suggesting that the associated washout may not be sufficient to reverse

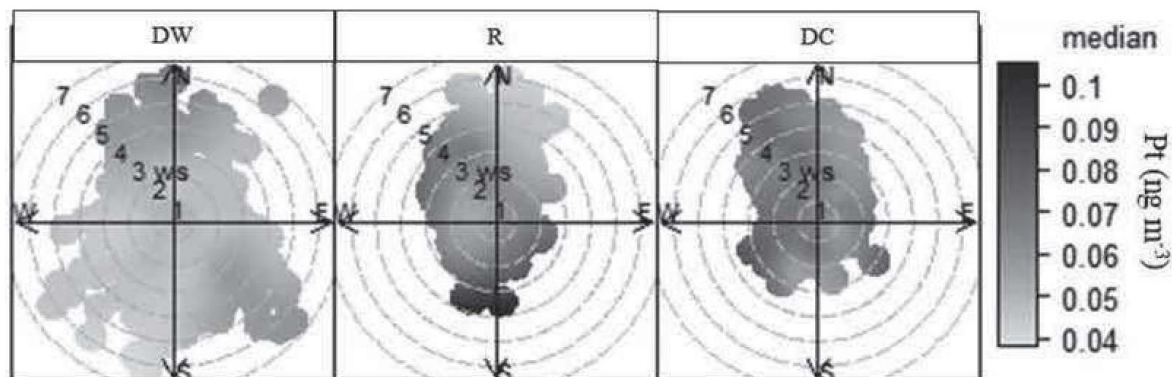


Figure 4. Pt concentration in $PM_{2.5}$ shown in wind plot.

the increment in Pt levels. During DW, the occurrence of wind intense episodes with wide range of directions, which include the northward winds, caused a *dilution effect* to Pt concentration. These observations are in line with the wind patterns identified by de Foy *et al.* (2005) within the MCMA Basin.

Nevertheless, the combination of unfavorable meteorological condition (low intensity and southward winds) along with intense traffic conditions resulted in an unexpected phenomena on 20th August 2013 (R season): Pt concentrations in all sites were found above the 90th percentile, raising the value of median concentration for the season (Figure 2). This is consistent with the fact that on 19th August the scholar summer vacations ended, resulting in one of the busiest traffic periods due to the high demanding transportation needs and consequent traffic congestion. Therefore, these results suggest that atmospheric processes dispersion due to winds have a bigger effect in the resultant concentration in $PM_{2.5}$ of Pt than the atmospheric washout.

Comparison with previous studies and other urban areas

The Pt in $PM_{2.5}$ median comparison shows an increment of 19.6% between 2011 and 2013 ($46 \text{ pg m}^{-3} \pm 17 \text{ pg m}^{-3}$ and $55 \text{ pg m}^{-3} \pm 26 \text{ pg m}^{-3}$, respectively) compared with those obtained from the 2011 sampling campaign (Morton-Bermea *et al.* 2014). Both campaigns were carried out under the same sampling sites, seasons, and collected particle size as a part of routine monitoring program. Therefore, the increment found is related, certainly, to the introduction of new vehicles since the Pt emissions from new automotive catalysts are higher than old ones. Artelt *et al.* (1999) demonstrated a downward trend of platinum emission with increasing converter age. However, regarding the data available from government agencies in terms of the number of vehicle in the studied area are discrepant. In one hand, the *Vehicle Verification Program of Mexico City* (SEDEMA 2014) reports 4.9 million and 5.2 million vehicles for 2011 and 2013, respectively, resulting an increase in the 6.1% of the vehicular fleet. In the other hand, the *Motor Vehicles Registered in Circulation* (VMRC; INEGI 2014) reports 7 million for 2011 and 8.2 million for 2013, resulting and increase in 17.1% of vehicular fleet. The trend that we found in Pt concentration is more likely to fit with the number of vehicles reported by INEGI (2014), since this takes into account all vehicle registered in the metropolitan area in contrast with SEDEMA.

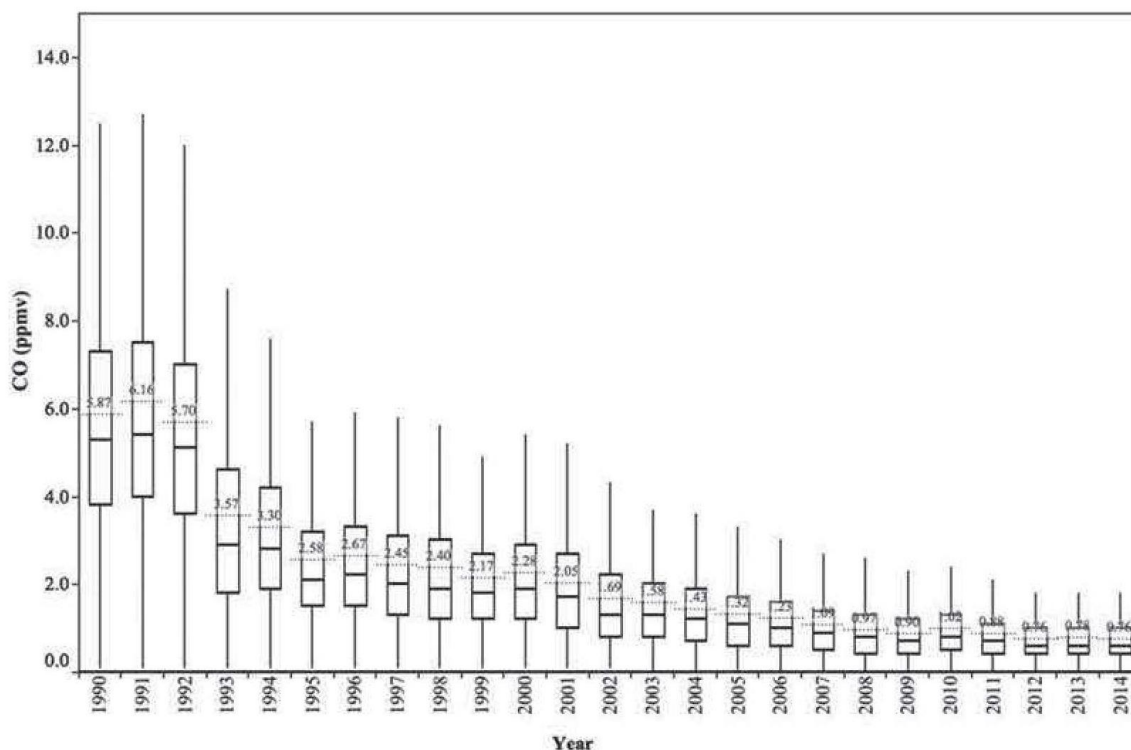


Figure 5. Distribution of carbon monoxide concentration between 1990 and 2014.

Table 3. Comparative chart of Pt concentration in $PM_{2.5}$ with available data from other urban areas.

City, country	Campaign sampling	Pt concentration in $PM_{2.5}$ ($\mu\text{g m}^{-3}$)	Traffic (vehicles/d)	Reference
MCMA	5 urban sites, 2013	Median: 55 ± 26	~ 8 millions*	This study
Kolkata, India	Traffic junctions, winter and monsoon seasons of 2013–2014	860–12,300	Not reported	Diong et al. (2016)
		Industrial sites		
Houston, Texas	Tunnel ventilation air supply, November and December 2012	4.5	$\sim 20,000$	Bozlaker et al. (2013)
		Washburn Tunnel		
Frankfurt, Germany	2008–2010	9.4 (2–23.6)	32,500	Zereini et al. (2012)
Vienna, Austria	2007	12 (8.5–22)	30–52,000	Limbeck et al. (2007)
Goteborg, Sweden	1999	5.4	70,000	Rauch et al. (2001)

A similar upward trend in Pt concentrations was found in PM_{10} by Rauch and colleagues (2006) from samples analyzed between 1991 and 2003. Furthermore, these authors suggested an additional local source of Pt in PM_{10} in NW from the surrounding area due to atypical value; however, the increase in Pt in PM_{10} could also be explained by an artifact of wind pattern in this site.

It is worth mention that despite the concern of Pt upward trend in the atmospheric environment of Mexico City, the implementation of catalytic converters in vehicles back in 1991 has had a positive impact on air quality due to CO reduction (Figure 5).

Table 3 shows the comparison of Pt in $PM_{2.5}$ between our results with those reported for other urban areas. The information available for this particle size fraction is quite scarce. As pointed by Morton-Bermea *et al* (2014), the results in MCMA are much

higher (500–1100 times) to those reported in European cities (Rauch *et al.* 2001; Limbeck *et al.* 2007; Zereini *et al.* 2012) as well as the Texas tunnel in the United States (Spada *et al.* 2012; Bozlaker *et al.* 2013). These differences are related, primarily to the quantity of the vehicles, but other factors at each urban area can be taken into account such as average speed, time of delay in traffic jams and as well the vehicles operational conditions. However, the levels of Pt concentration are yet far from the case of Kolkata city (Diong *et al.* 2016) where industrial sources have been also identified.

Conclusion

The main contribution of this work is based on the information generated from the comparison of the years sampled, which facilitate the evaluation of the trend of the Pt in the atmospheric environment in MCMA; thus, this trend allows us to match tendency of the increase in vehicle fleet reported. On the other hand, the evaluation of the differences during the seasons of 2013 allowed us to recognize the meteorological factors that control the behavior and distribution of the Pt as atmospheric pollutant. This study shows that the effects of low concentration during R are determined by wash out; however, a more prominent dilution effect in DW is explained due to the dependence of intensity and direction of the winds that cause Pt dispersion within of the MCMA Basin. Additionally, the hard traffic conditions are key factor to the accumulation of Pt pollution as shown in the episode of high Pt levels found in entire MCMA due to traffic jams from the back-to-school period. The comparison of the values obtained in this study against those from other cities in the world allows us to understand the dimension of the problem implicated in anthropogenic activities in an extensive and complex city such as MCMA. Although the use of automotive catalysts in the MCMA has brought a decrease in atmospheric CO, the increase in Pt in the environment represents a new concern, especially in episodes of excessive traffic.

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En esta publicación se muestran los resultados de la evaluación de Hg contenido en PM_{2.5} de la colecta de 2013. Es importante conocer la concentración de Hg por sus implicaciones como contaminante (Driscoll, et al., 2013). En este artículo se reporta la concentración promedio, mediana y desviación estándar para el Hg en PM_{2.5}: 120.3 pg m⁻³, 50.6 pg m⁻³ y 223.3 pg m⁻³ respectivamente.

La gran variabilidad en la concentración de Hg se observa en la distribución espacial y temporal (Figura 1 del artículo). Las mayores concentraciones ocurrieron al noroeste (NE) y durante la temporada fría (DC). Esto debido a que el NE es la zona más industrializada en la ZMCM y la temporada fría es la de mayor estabilidad atmosférica.

Son escasos los trabajos que reportan Hg en el tamaño de partícula PM 2.5 en la ZMCM. Sin embargo la comparación de las concentraciones de este artículo con las disponibles previamente (Rutter, et al., 2009) indican que las concentraciones de este contaminante pueden estar disminuyendo. Se requieren de más estudios para corroborar esta tendencia.

La evaluación continua de Hg cobra relevancia desde que en 2013 México firmó el convenio de Minamata y que se promulgó en el diario oficial de la federación en 2017 (Diario Oficial de la Federación, 2017). La conformación de una base de datos en el ambiente atmosférico de ZMCM es referente para el cumplimiento de este compromiso internacional.



Atmospheric PM_{2.5} Mercury in the Metropolitan Area of Mexico City

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Abstract

In this study, atmospheric mercury concentration in airborne particulate matter with an aerodynamic diameter $\leq 2.5 \mu\text{m}$ (PM_{2.5}) was analyzed by ICP-MS. Samples were collected in the Mexico City Metropolitan Area (MCMA), during 2013, in five locations, Northwest, Northeast (NE), Central, Southwest and Southeast, along three seasons: dry warm, rainy, and dry cold (DC). It can be observed that NE shows the highest mercury concentration ($p < 0.05$), where pollution events were identified. The seasonal distribution shows that samples collected during DC present the highest concentration ($p < 0.05$). These results are in agreement with the distribution of important mercury industrial sources located in the northern urban area as well with the temperature and wind conditions during 2013. The comparison of data obtained in this work with those of similar previous studies clearly indicates a decrease, between 2006 and 2013, of mercury content in PM_{2.5} collected in MCMA.

Keywords Mercury · PM_{2.5} · Atmospheric pollution · Spatial distribution pattern · Seasonal distribution pattern · Minamata convention

Even though the implementation of international programs to reduce mercury emissions (Pacyna et al. 2006) there is sufficient evidence of high concentrations found in remote areas. The identification of pollution sources and the understanding of their chemical transformations have attracted considerable attention in recent years. Different works have demonstrated that the atmosphere is the dominant medium for mercury's transportation in the environment. Generally, mercury in the environment exists in inorganic forms, which do not constitute a direct health risk; however, they can be transformed into forms which can cause adverse health effects in humans (Clarkson 1993).

Atmospheric mercury generally has three different phases, with different physical and chemical properties: elemental mercury (GEM-Hg⁰), reactive gaseous mercury (RGM-Hg²⁺) and particulate mercury (PHg). Elemental mercury has a long atmospheric lifetime (0.5–2 years) due to its low solubility and represents the most predominant form of total gaseous mercury, over 95% (Fu et al. 2011). Reactive gaseous mercury and particulate mercury have atmospheric lifetimes of days to weeks, and although they make up only a few percent of the total atmospheric mercury, they are more important due to their large dry and wet deposition velocities (Schroeder and Munthe 1998).

Measurements of atmospheric GEM, RGM and PHg levels in urban areas generally fell in the range of 2.0–5.8 ng m⁻³, 5–10 pg m⁻³ and 10–100 pg m⁻³, respectively (Fu et al. 2011). Mercury quantification in particulate matter $\leq 2.5 \mu\text{m}$ (PM_{2.5}) is of special relevance given that it represents the breathable fraction, and can be removed from the air environment by wet and dry deposition, with an atmospheric life time of days or even weeks. Many studies have focused on the determination of mercury PM_{2.5} (Moreno et al. 2005; Poissant et al. 2005; Yatavelli et al. 2006; Liu et al. 2007; Kim et al. 2009; Xu et al. 2013; Pyta and Rogula-Kozłowska 2016; Qin et al. 2016).

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In Mexico, data of atmospheric mercury are quite scarce. Total gaseous mercury was measured by De la Rosa et al. (2006) in five sites, including the Mexico City Metropolitan Area (MCMA). They reported Total GM (TGM) concentration between 2.8 and 34.2 ng m⁻³ in samples collected in the urban area. Ruttel et al. (2009) conducted high-time resolution measurements of atmospheric mercury to identify local emissions in and around Mexico City. They reported an average PHg of 187 ± 300 pg m⁻³. However, there is not a systematic report of the behavior of particulate mercury considering the whole MCMA, as well as the influence of meteorological conditions.

The aim of the present research is to study the spatial and temporal distribution of Hg in PM_{2.5}, analyzing samples collected at five sites within the MCMA in three different seasons. Statistical assessment of these results will provide useful information not only to evaluate the Hg content in PM_{2.5}, but also to make a comparison with the previously reported data for this area, in order to assess the mercury contamination trend.

In addition, of information obtained from the spatial evaluation will allow to recognize important sources of mercury contamination in the studied area. The above could be the basis to establish a local monitoring program for mercury pollution, which is relevant given the commitments of Mexico with the Minamata Convention.

Materials and Methods

Five samples sites within MCMA were chosen based on their urban characteristics (different pollution sources, traffic density and urban activities): Northwest (NW, Tlalnepantla), Northeast (NE, San Agustín), Central (C, Merced), Southwest (SW, Coyoacán) and Southeast (SE, Universidad Autónoma Metropolitana-Iztapalapa), in 2013 during April (dry-warm season, DW), August (rainy season, R) and November (dry-cold season, DC). PM_{2.5} was collected for 24 h every sixth day, making a total of 75 samples. The sampling equipment was a high volume sampler with an inlet for particles ≤ 2.5 μm (PM_{2.5}) (Tisch and Andersen General Metal Works) previously calibrated according to Federal Pollutant Release and Transfer Register (1987). A flow rate of 1.13% ± 10% m³ min⁻¹ was used. The particles are deposited onto Teflon impregnated glass fiber filter (20.4 × 25.2 cm) (TIGF, Pallflex), previously baked at 280 °C for 24 h. Filters were wrapped in aluminum foil and then kept in Zip-lock bags to be transported. The analysis of unexposed filter papers processed in parallel with field samples were used for monitoring background contamination.

The samples digestion was carried out by means of microwave assisted digestion procedure (Ethos One, Milestone). Around 0.1 g filter material were weighed accurately and

placed in Teflon vessels where acid mixture of 8 mL aqua regia, 1 mL HF and 2 mL HCl was added. The mixture was left to stand overnight. Per carousel, two blanks filters were handled identically to the samples. Temperature program was ramped from room temperature to 120 °C in 20 min, and then maintained for 20 min. After digestion and cooling, the samples were transferred to a Teflon vessel (100 mL) and taken to dryness. To ensure full removal of HF, 3 mL of HCl were added and evaporated to dryness (twice). The digested samples were diluted to 10 mL with 2% HNO₃ (v/v).

Mercury measurements were carried out using an inductively coupled plasma mass spectrometer iCAP Q ICP-MS (Thermo Scientific, Germany) at the Instituto de Geofísica, Universidad Nacional Autónoma de México. Drift correction was achieved by continuous online mixing of an internal standard solution during sample introduction (10 mg L⁻¹, ¹¹⁵In and 2% HNO₃), Au solution at 1 ppm was added to avoid possible instrumental memory effects. The analytical quality of the procedure was determined by analyzing 12 aliquots of Standard Reference Material (SRM) 1648a (Particulate Matter, National Institute for Standard and Technology), prepared and analyzed in the same way as filter samples. Detection limits were calculated as three times the standard deviation of 10 replicates of the procedural blank. For the analytical determination, a calibration curve was built with 12 points (from 0 to 2.5 ppb). Statistical Analysis of data was performed with “Statistica” Software version 8.0 (Statsoft, USA).

Results and Discussion

Recovery percentages were 81.3%. Precision was 7.1%, calculated from ICP-MS mercury analysis of 12 replicate measurements of SRM1648a, loaded in Teflon coated glass fiber filters. Detection limit was 0.008 μg L⁻¹. Mercury concentration in all samples was above the instrumental detection limit. Regression coefficient of the calibration curve was 0.995.

Spatial and seasonal distribution patterns of mercury in PM_{2.5} collected at five sampling sites in the MCMA during three seasons in 2013, are reported in Table 1 and depicted in box plots (Fig. 1). Mercury concentration ranged from 51 to 3841 pg m⁻³. NE and dry cold showed the highest mercury concentration ($p < 0.05$).

The highest concentration ($p < 0.05$) at NE suggests the impact of large mercury industrial sources located in the northern urban area, such as agrochemical, pulp and paper, pigments/dyes and building materials manufacturing industries. This is in agree with Rutter et al. (2009), who identified as strong mercury source from industrial facilities located in and around the MCMA. A full list of such industrial facilities is included in the 2013 Federal Pollutant Release and

Table 1 Spatial and seasonal analysis of mercury concentration (pg m^{-3}) obtained in the MCMA

Hg	n	Mean	Median	Min	Max	SD	% CV
MCMA	223.3	120.3	50.6	3840.7	466.1	223.3	185.6
Spatial distribution							
Site							
NW	15	206.3	111.2	64.6	1314.8	314.0	152.2
NE	15	530.3	213.2	107.3	3840.7	949.7	179.1
C	15	113.7	104.0	52.7	177.3	46.2	40.6
SW	15	138.2	135.2	67.6	252.5	59.9	43.3
SE	15	128.1	96.8	50.6	447.7	101.6	79.3
Seasonal distribution							
Seasons							
DW	25	164.3	112.6	53.5	1314.8	245.4	149.4
R	25	270.4	96.8	50.9	3840.7	746.3	276.0
DC	25	235.2	166.9	60.9	1090.6	215.8	91.8

SD Standard deviation

Higher values are bolded ($p < 0.05$)

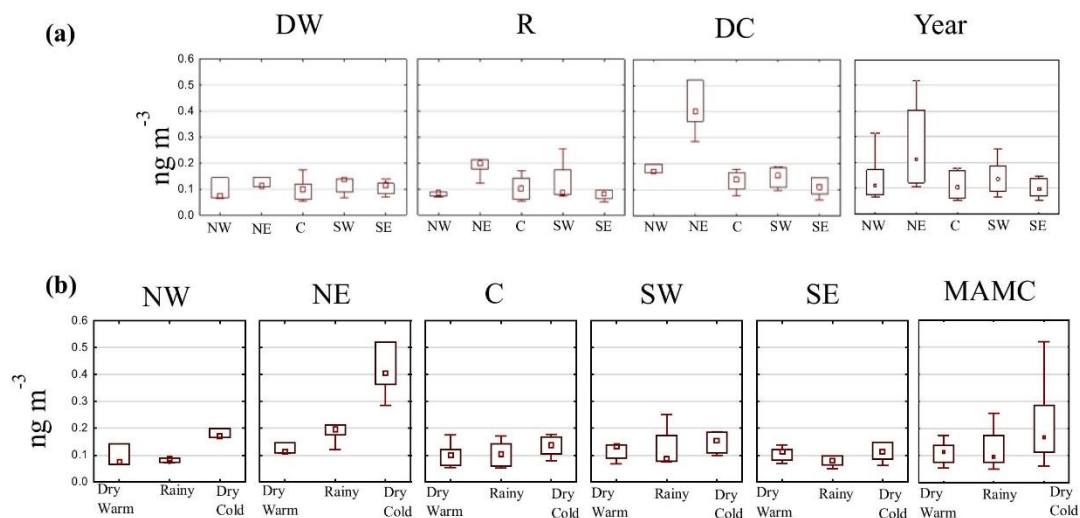


Fig. 1 Seasonal (a) and spatial (b) distribution pattern of mercury in $\text{PM}_{2.5}$. Middle square median, box – 25th and 75th percentiles and bars – 10 and 90 percentiles

Transfer Register (<http://apps1.semarnat.gob.mx/retc/retc/index.php>), confirming that NE is the most industrialized area.

The prevailing wind direction in the MCMA during 2013 was from North to South (<http://www.aire.cdmx.gob.mx/default.php?opc='aKBhnmI='&opcion=Zw>).

The highest variability of % CV values of $\text{PM}_{2.5}$ mercury levels found in NW and NE (152.2 and 179.1 respectability) is the result of the combined influence of the proximity to sources emissions and the wind directions. Table 2 compares

mercury levels in $\text{PM}_{2.5}$ for each season, their meteorological parameters, $\text{PM}_{2.5}$ mass concentration as well as the results of u-test trend.

The highest mercury levels in $\text{PM}_{2.5}$ occurred during DC, the resulted u-test trend is $\text{DC} > \text{DW} > \text{R}$. Conversely, the lowest Hg levels in $\text{PM}_{2.5}$ occurred when % RH is the highest (R). Highest mercury in DC ($p < 0.05$) is in agreement with the lowest T registered (13.9°C) ($p < 0.05$).

The recognition of the effect of cold season in the increase of mercury concentration in the atmospheric environment

Table 2 Seasonal comparison between mercury concentration in PM_{2.5} (Hg in PM_{2.5}), PM_{2.5} mass concentration and meteorological parameters

2013	DW			R			DC			u-TEST TREND
	Mean	Median	Std.Dev.	Mean	Median	Std.Dev.	Mean	Median	Std.Dev.	
Hg in PM _{2.5} (pg m ⁻³)	165	113	245	270	97	746	235	167	216	DC>DW>R
PM _{2.5} (µg m ⁻³)	40.0	38.0	17.4	17.9	16.0	11.1	31.5	25.0	23.3	DW>DC>R
RH (%)	28.9	25.0	16.5	65.0	68.0	19.7	61.5	65.0	18.4	R>DC>DW
T (°C)	21.1	21.3	4.6	17.1	16.1	3.7	14.4	13.9	4.3	DW>R>DC

(<http://www.aire.cdmx.gob.mx/default.php?opc='aKBhml='&opcion=Zw>). The highest values are bolded ($p < 0.05$)

has been previously reported in several parts of the world (Yatavelli et al. 2006; Pyta and Rogula-Kozłowska 2016; Qin et al. 2016).

The identification of mercury pollution events could give information related to possible hotspots to support the spatial pattern. There is a lack of linear correlation between mercury data in PM_{2.5} versus PM_{2.5} mass concentration that suggests a differences in their sources ($r^2 = 0.0129$). Mercury pollution events were defined as those included above percentile 90% of the values for the mercury PM_{2.5}/PM_{2.5} mass concentration ratios. In this way, 11 events, most of them occurring in the north (NE and NW), mainly during DC they were identified.

Although there are many studies related to the evaluation of mercury in the atmospheric environment, the reported results differ in PM size distribution. Data related to mercury in PM_{2.5} are scarce. A comparison between the results of this work with those of similar studies in other parts of the world is presented in Table 3. Mercury concentrations found in this study are comparable to those reported for other megacities, while they are far higher than those found in remote and/or rural areas.

The mercury atmospheric pollution trend can be evaluated by comparing these results with previously reported

data in the same area. There is only one published work including an average mercury concentrations in PM_{2.5} of 187 pg m⁻³ for samples collected at a downtown site in Mexico City during 17 days in March 2006 (Rutter et al. 2009). Considering the median of all data generated in this study (120 pg m⁻³) it can be interpreted that the mercury concentration in the atmospheric environment in the MCMA has decreased considerably between 2006 and 2013. The same interpretation is reached when comparing with partial data obtained from this study. The median concentration obtained for the C site (La Merced), the nearest to the site considered by Rutter et al. 2009, is 104 pg m⁻³. On the other hand, the median of the data obtained during DW, same sampling season considered by Rutter et al. 2009, is 113 pg m⁻³ (Table 3). This comparison suggests that PM_{2.5}-Hg levels in this part of Mexico City have decreased between 2006 and 2013. However, additional and longer time series data at more sites would be required to verify this decrease as a general trend for the MCMA.

This is the first systematic report of spatial and temporal behavior of particulate mercury considering the whole urban area of Mexico City. Due to the small concentration of mercury in airborne particulate matter, its accurate analytical

Table 3 Comparison of data obtained in this study with those reported for other areas

Location	Classification	Hg in PM _{2.5} concentration (pg m ⁻³)	Time	Reference
This work	Urban	51–3841 (mean 223; median 120)	Apr, Aug and Nov 2013	
Mexico City (site: North of the urban area)	Urban	187 ± 300 (mean)	March 2006	Rutter et al. 2009
Seoul, Korea	Urban	6.9–148.3 (mean 23.9)	Feb 2005–2006	Kim et al. (2009)
Guiyang, China	Urban	8–8407 (mean 368)	Aug–Dec 2009	Fu et al. (2011)
Detroit, USA	Urban	mean 20.8	2003	Liu et al. (2007)
Southeast coastal cities, China	Urban	7.6–956.5 (mean 141.2)	Nov 2010, Jan, Apr and Aug 2011	Xu et al. (2013)
	Rural	5.6–89.4 (mean 37.0)		
	Remote	3.2–59.9 (mean 24.0)		
East China Sea	Remote	16.6 (average)	Oct 2011–Aug 2012	Qin et al. (2016)
Mt. Changbai	Remote	0–1001 (mean 77)	Aug. 2005–Jul 2006	Wan et al. (2009)
Ohio River Valley	Rural	0–76.82 (mean 5.29)	July 2004–July 2005	Yatavelli et al. (2006)
Quebec, Canada	Rural	mean 26	1 Jan–12 Dec 2003	Poissant et al. (2005)

determination represents an important challenge. The analytical quality of the results obtained in this study, validated by the analysis of certificated reference material, allowed us to assess the scale of pollution of mercury in atmospheric environment of the MCMA and to determine its spatial and temporal behavior.

Data evaluation indicates higher mercury concentrations during DC in NE. This temporal distribution is in agreement with the meteorological conditions (flow direction and temperature) during the sampling days. Further, the spatial distribution is in agreement with the location of important industrial facilities in the northern urban area, such as agrochemical, pulp and paper, pigments/dyes and building materials manufacturing industries. This was strengthened by the identification of mercury pollution events mainly in the NE y NW during DC.

The fact that Hg concentrations in $PM_{2.5}$ found in this study are of the same order of magnitude to those reported for urban areas in Asia, considered the largest emitters of mercury worldwide, is worrying. However, the fact that there is a decreasing concentration behaviour when comparing our results to the previous study in the studied area, is somehow reassuring, although future research is needed to confirm this.

These results provide the first mercury data in the atmosphere of the MCMA area applying a systematic methodology, concerning the spatial and temporal behavior of Hg in $PM_{2.5}$, as well as the influence of meteorological parameters. However this information and the relation to the impact of large mercury industrial sources in the northern urban area, must be confirmed with further studies, in order to establish public policies. These findings become of relevance considering the international commitments due to Minamata Convention.

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Conclusiones

El protocolo experimental propuesto para la determinación de elementos trazas (metales, Pt y Hg) contenidos en PM_{2.5} atmosférico mediante ICP-MS ha resultado satisfactorio en términos de los porcentajes de recobro de los elementos reportados en materiales estándar de referencia: NIST 1648, BCR-723 y MCR-2709. Los resultados son el producto de la combinación óptima de un procedimiento de digestión y las condiciones instrumentales de operación del ICP-MS.

La metodología propuesta puede ser empleada de forma rutinaria para la determinación simultánea de elementos en concentraciones traza en PM cuyos resultados son adecuados para la caracterización de un área urbana.

Se ha mostrado que constituir una base de datos de concentraciones de metales junto con información de parámetros meteorológicos es fundamental para la ejecución de análisis estadísticos que brindó conocimientos relacionados con la distribución, tendencias, variaciones de la emisión de metales en zonas urbanas aplicadas a la ZMCM.

Se estudiaron las causas de variabilidad en las concentraciones de los metales. La evaluación de las mismas permitió identificar las fuentes de los metales y también permitió *prorratar* el impacto de las fuentes identificadas de metales en este entorno urbano. En ese sentido cabe resaltar la influencia que han tenido las fuentes naturales geogénicas en el impacto de las concentraciones de metales. Así mismo se puede constatar el impacto de las actividades antropogénicas que aportan metales e identifican fuentes de contaminación.

Las diversas evaluaciones propuestas permitieron identificar en la ZMCM que el aporte de Ni y V proviene tanto de fuentes geogénicas como antropogénicas (fuente mixta): hecho notable comparado con otras zonas urbanas en las que Ni y V son aportados antropogénicamente. Además, mediante factores de enriquecimiento estacionales se logró demostrar que durante la temporada fría la componente antropogénica es predominante.

Se ha identificado al Pt como un metal de origen antropogénico en la zona con crecimiento estrechamente relacionado con el amento del parque vehicular en la metrópoli.

Se han identificado también, emisiones localizadas de Hg en la zona más industrializada de ZMCM. La disminución de este contaminante cobra importancia por los compromisos de México en su cumplimiento con el convenio de Minamata.

El reconocimiento de metales aportados por las diferentes fuentes brinda una sólida guía para el desarrollo estratégico de políticas públicas. De esta forma los tomadores de decisiones en los diferentes sectores de gobierno (salud, protección civil, prevención y monitoreo, etc.) pueden proponer regulaciones a emisiones de metales antropogénicos. Además, los datos vertidos en la presente son parámetros de referencia para la mejora en la calidad de aire, sobre todo partiendo del monitoreo de metales que por su reciente demanda tecnológica representan un peligro para la salud y el ambiente.

Es de suma importancia que la información descrita en la presente investigación sea tomada en cuenta por los actores políticos y tomadores de decisiones para la implementación de

normatividad que repercuta en la mejora en la calidad del aire en la Zona Metropolitana de la Ciudad de México. Así mismo la sociedad civil puede beneficiarse del conocimiento subyacente para la exigencia del cumplimiento de los derechos de salud y calidad del ambiente.

Recomendaciones posteriores:

Se recomienda la conformación de un grupo de trabajo integro y sólido con la capacidad de vincular otras *capacidades* de análisis atmosférico. Las limitaciones en la identificación de fuentes de contaminación serán superadas mediante la integración de base de datos que además de las concentraciones de metales reúnan las concentraciones de óxidos de nitrógeno (NO_x), de azufre (SO_x), iones inorgánicos, carbono elemental, dentro de otros.

La posibilidad de obtener más información referente del origen y evolución del PM puede ser explorado mediante microscopia electrónica de barrido, complementariamente se pueden emplear esta técnica.

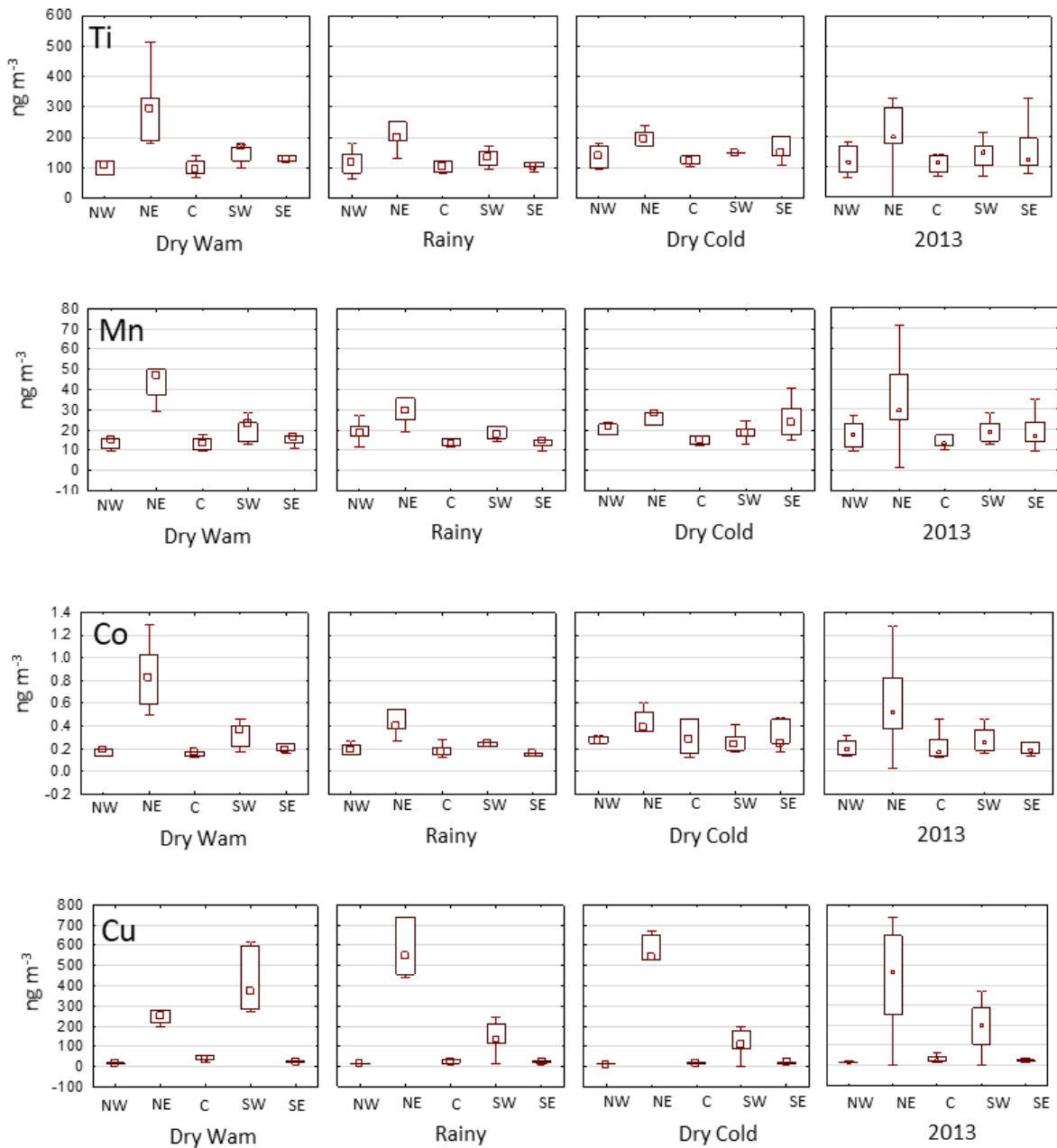
También se recomienda ejecutar campañas de muestreo que puedan contemplar los efectos diurnos y nocturnos en el PM serán valiosos para profundizar en el origen y distribución de los contaminantes. También, estas campañas de muestreo pueden aumentar la frecuencia de los días de colecta. Así mismo se recomienda coleccionar partícula de otros tamaños de diámetro aerodinámico simultáneamente.

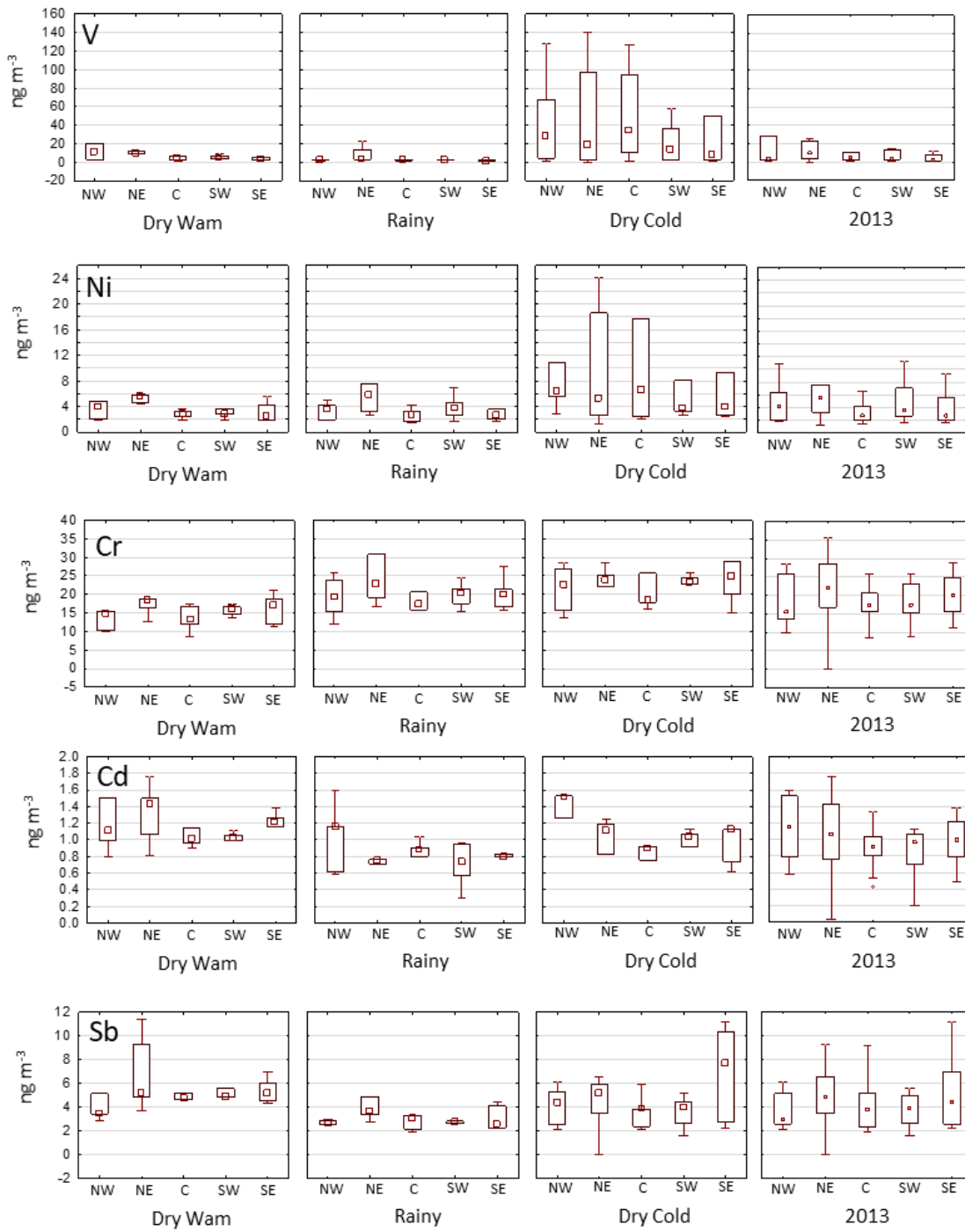
Desarrollar modelos de pronóstico que permitan predecir episodios de contaminación en función de vigilancia de las fuentes ya identificadas y que puedan predecir episodios de contaminación.

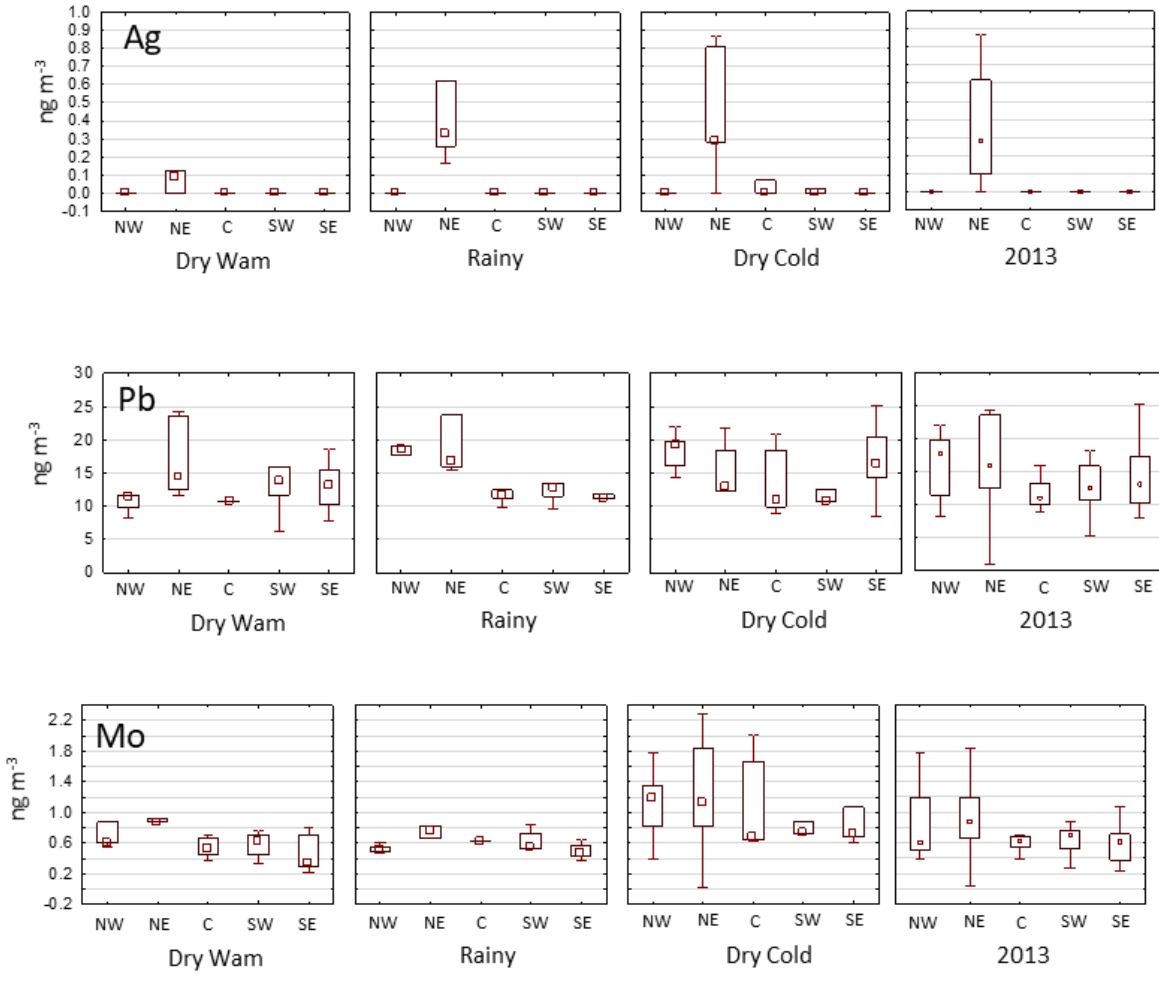
La vinculación con los grupos de trabajo del sector salud en términos epidemiológicos y toxicológicos son de gran importancia para la mejora de la calidad de aire y las repercusiones en la calidad de vida de los habitantes de esta zona urbana.

Anexo 1 Distribución espaciotemporal metales en 2013.

Distribución espaciotemporal a través de diagramas de cajas y bigotes de para las concentraciones de los metales cuantificados en el muestreo atmosférico de 2013. La información obtenida de la formulación de estos gráficos fue posteriormente verificada la base de datos de 2011; los sendos diagramas de estos fueron publicados en (Morton-Bermea, et al., 2018). Se incluyen aquí estos de 2013 con fines comparativos a los publicados de 2011.







Anexo 2 Pláticas de divulgación con resultados de esta investigación.

Los diagramas del Anexo 1 si bien no fueron publicados, sí fueron presentados en pláticas de divulgación antes de la culminación de las publicaciones en la presente tesis:

“¿En lo que respiras hay metales: El aire de la Ciudad de México” realizada el 18 de abril 2016 en el Colegio de Ciencias y Humanidades plantel Sur (CCH sur)



y también “Respirando metales: El aire de la Ciudad de México” el 07 de septiembre 2017 en El Centro Interdisciplinario de Investigación para el Desarrollo Integral Regional, Unidad Oaxaca del Instituto Politécnico Nacional:



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La Técnica al Servicio de la Patria

CIDIIR OAXACA

El Centro Interdisciplinario de Investigación para el Desarrollo Integral Regional, Unidad Oaxaca,
del Instituto Politécnico Nacional otorga el presente:

RECONOCIMIENTO

Al:
M. en C. RODRIGO GARZA GALINDO FLORES

Por haber impartido la Conferencia
“Respirando metales: El aire de la ciudad de México”

Como parte de las actividades del Seminario Institucional, de la Academia de Ingeniería
del Programa de la Maestría en Ciencias en Conservación y Aprovechamiento de Recursos Naturales.

“La Técnica al Servicio de la Patria”



Dr. Salvador Isidro Belmonte Jiménez
Director



CIDIIR OAXACA



**CENTRO INTERDISCIPLINARIO
DE INVESTIGACIÓN PARA EL
DESARROLLO INTEGRAL REGIONAL
CIDIIR
UNIDAD OAXACA
IPN.**

Santa Cruz Xoxocotlán, Oaxaca, México, 07 de septiembre de 2017.

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