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Phthalate esters on urban airborne particles: Levels in PM_{10} and $PM_{2.5}$ from Mexico City and theoretical assessment of lung exposure

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ABSTRACT

Endocrine disrupting chemicals (EDCs) from the environment are associated with reproductive abnormalities (i.e. decreased sperm concentration; increased endometriosis) and alterations of the cardiovascular system (i.e. increased blood pressure and risk of coronary disease). Some phthalates esters have been identified as EDCs, for which inhalation is considered as one of the routes of exposure. However, only little is known regarding inhalational exposure to EDCs via urban airborne particles. In the present study, we report the monthly concentration of 8 phthalate esters measured in PM_{10} and $PM_{2.5}$ collected and recovered during 7 months in a highly populated area of Mexico City. Using the levels of PM_{10} and $PM_{2.5}$ reported by the automatized network of environmental monitoring of Mexico City for the sampling site, we estimated exposure levels for people of different ages and gender. Two endocrine disrupting compounds, the phthalate esters DEHP and DnBP, were found on the particles in higher concentrations during the warmer months of the year. The highest concentration was reported for DEHP (229.7 μg/g of particles) in $PM_{2.5}$ collected in May 2013. After calculations of the DEHP concentration in the atmosphere, and using the respiratory flow rate, we determined males were potentially exposed to larger quantities of DEHP, reaching up to 18 ng/8 h in April 2013. Despite the concentrations of phthalates seem to be rather small, a comprehensive characterization of its presence is necessary in order to evaluate the overall exposure to these compounds, providing a clear view of exposure on children, adolescents and pregnant women.

1. Introduction

Urban particulate matter (PM) has been linked to adverse health effects and increased mortality in humans (Alfaro-Moreno et al., 2007; Hoek et al., 2013; Fischer et al., 2015). The composition of these PM play an important role regarding the adverse outcomes induced by the particles, but the complexity of the mixture makes it very difficult to assess the participation of each component in relation to different outcomes such as cardiovascular effects, neurological disorders or reproductive abnormalities. The characterization of urban airborne particles has been mainly focused on "the usual suspects" (i.e. transitional metals, polycyclic aromatic hydrocarbons (PAHs), silica, asbestos, among others) but very little is known about the outdoor presence of compounds that despite they are present both outdoors and indoors, are considered as indoor pollutants. Many endocrine disrupting chemicals (EDCs) are among this group of compounds that are usually considered as indoor air pollutants. EDCs are chemicals that can interfere with hormonal pathways, thus altering reproductive capability, sexual development, maturation or the cardiovascular system (Diamanti-Kandarakis et al., 2009; Gore et al., 2015; Mariana et al.,

Abbreviations: DEP, Diethyl phthalate; DiBP, Di-iso-butyl phthalate; DnBP, Di-n-butyl phthalate; BBzP, Benzylbutyl phthalate; Bis, (2-ethylhexyl) phthalate (DEHP); DINP, Di-isononyl phthalate; DIDP, Di-isodecyl phthalate; Di, (2-Propyl heptyl) phthalate (DPHP); RFR, Respiratory flow rate

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2016). The outdoor presence of these pollutants may be due to leaching from indoor environments, as well as the use of some of these chemicals in building materials outdoors.

Phthalate esters are a group of chemicals with possible endocrine disrupting functions, and were originally introduced as plasticizers in polyvinyl chloride (PVC) resins (Rudel and Perovich, 2009). Nowadays they can be found in a wide variety of products including food packaging, building materials, plastics, cleaning products, cosmetics and toys (Bornehag et al., 2005). Outdoor sources of phthalate esters might include construction materials such as pipes, water tanks, coating of cables or wires, amongst others (Rakkestad et al., 2007). As phthalate esters are not covalently bound to the material they can easily leach into the environment (Heudorf et al., 2007; Rakkestad et al., 2007).

Exposure to phthalate esters is mainly related to indoor environments, with phthalate concentrations in indoor air generally higher than in outdoor air (Rakkestad et al., 2007; Rudel and Perovich, 2009). Outdoors, phthalates usually undergo fast degradation (Xie et al., 2007), but they have been found in remote regions due to atmospheric transport and deposition (Xie et al., 2007). DEHP has been detected in isolated regions such as the Amazonian rainforest (Lenoir et al., 2016), the Arctic or the Norwegian Sea (Xie et al., 2007). Finding those EDCs also in big cities might have an impact on human health. The presence of these phthalates indoors and outdoors indicates constant exposure. A study evaluating the exposure to phthalates in a pre-birth cohort of 284 children (8–14 years old) from Mexico City reports an association with changes in the lipid profile (Perng et al., 2017). Mexico City Metropolitan Area (MCMA) is one of the largest and most polluted cities in the world. With more than 20 million inhabitants, many of them spending long periods of time working on streets or moving from one place to another, the exposure to urban particles is of great concern (Rivera-González et al., 2015).

In the present study, we analyzed outdoor particles for phthalate esters that are considered classical indoor pollutants. Particulate matter of two aerodynamic sizes, 10 (PM_{10}) and 2.5 ($PM_{2.5}$) μm, were collected from November 2012 to May 2013, on top of the roof of a health clinic, situated right next to a secondary school. With the concentrations of phthalates that we found, and using the atmospheric concentrations of PM_{10} and $PM_{2.5}$ reported by the authorities, we did a theoretical assessment of the exposure to phthalate esters on people visiting the health clinic and attending the nearby school using respiratory parameters reported for different ages and gender.

2. Methods

2.1. Chemicals

All phthalate ester standards as well as their internal standards (D4-labelled mixture of eight phthalate esters) were purchased by TRC Chemicals, Toronto, Canada. Toluene was purchased from Sigma Aldrich (Sigma Aldrich, Germany).

2.2. Particle sampling

PM_{10} and $PM_{2.5}$ were collected about 3.5 m above ground level, on the roof of a medical clinic neighboring a high school, in the center of Mexico City, in a neighborhood known as “barrio de La Merced” between November 2012 and May 2013. The samples were placed just few meters away from the samplers of the automatized network of air monitoring (RAMA, for its initials in Spanish) of Mexico City. This area in Mexico City is characterized by high population density and heavy traffic. The samples were collected during three days of each week and then recovered following a method previously described (Alfaro-Moreno et al., 2009). Briefly, modified membranes of nitrocellulose were used on high volume samplers, with an air flow of 1.13 m^3/min. After 24 h of sampling, the membranes were collected and stored at 4 °C in a desiccator. To recover the particles, the membranes were independently placed in a previously sterilized (200 °C during 4 h) glass beaker and dry sonicated during 30 min at 40 kHz. Then, the particles were dislodged mechanically and recovered in a glass vial, free of endotoxins. The recovered particles were weighted and stored at 4 °C in a desiccator. The number of patients and students attending the facilities during the weekdays were reported.

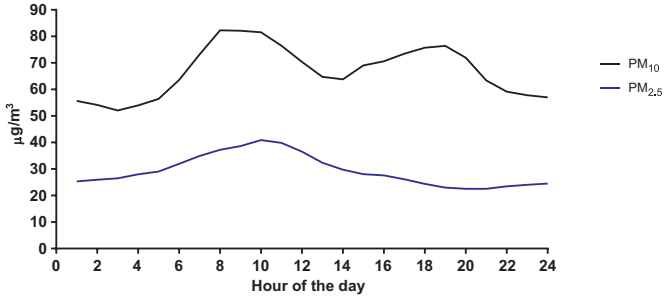

Fig. 1. Average levels of PM_{10} and $PM_{2.5}$ during a day. These averages were calculated using the hourly reports of the RAMA during the 7 months of sampling.

Particles of the same size and same sampling month were pooled and used for further analysis. The hourly levels of PM_{10} and $PM_{2.5}$ for the site where the particles were sampled were taken from reports of the RAMA [http://www.aire.df.gob.mx/], and this data was used to calculate the average, maximum and minimum for each hour of the day, weekday and month of our sampling period.

2.3. GC-MS/MS analysis

Particles were solvent extracted and analyzed by gas chromatography tandem mass spectrometry (GC-MS/MS). The method was modified from Weiss et al., 2016, (manuscript in preparation) for the analysis of the following eight phthalate esters: diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), diisobutyl phthalate (DiBP), benzylbutyl phthalate (BzBP), bis(2-ethylhexyl)phthalate (DEHP), diisononyl phthalate (DiNP), diisododecyl phthalate (DiDP) and bis(2-propylheptyl)phthalate (DPHP). The corresponding D4-labelled phthalate esters were used as internal standards. All standards were purchased from TRC Chemicals, Toronto, Canada.

Briefly, 1–10 mg of particles were weighed into a clean burnt-out glass insert and 500 ng/μL (final concentration) of internal standard (mixture of eight corresponding D4-labelled phthalate esters) was added to all samples. Particles were extracted in 100 μL of clean toluene, followed by 30 min sonication at maximal amplitude. Samples were transferred into glass vials, centrifuged for 10 min at 3000 r/min and 1 μL of the supernatant was injected onto the GC-MS/MS.

2.4. Assessment of PMs and phthalate co-variation

The total amount of phthalates recovered from the samplings for each month was calculated based on their monthly levels in the different particle sizes. The monthly concentration during the sampling days of the seven phthalates founded was calculated from the total amount of recovered phthalates and total volume of air that passed through the high volume sampler during each month. This was then compared to the monthly amount of PM_{10} and $PM_{2.5}$ during the sampling days in order to assess their co-variation over these seven months.

Hourly PM data for the site where the particles were sampled obtained from the RAMA reports from 2012–2013 was used [http://www.aire.df.gob.mx/] to calculate daily variations as well as daily, monthly and weekday average concentrations of PM_{10} and $PM_{2.5}$, respectively.

The total amount of hours sampled each month was calculated together with the monthly total amount of PMs recovered from the previous samplings.

The measured monthly phthalate levels in PMs, expressed as μg/g