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Organophosphate esters in airborne particles from subway stations

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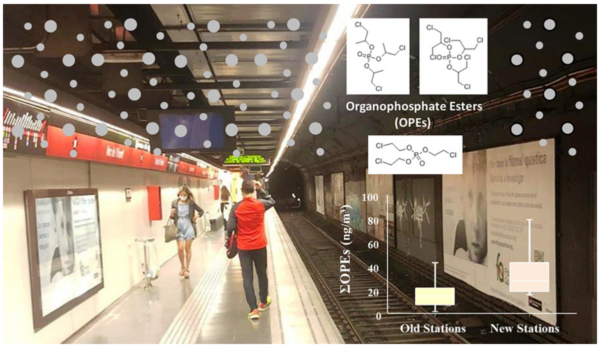
HIGHLIGHTS

- OPEs were detected for the first time in airborne particles from subway stations.
- TDClPP presented the highest values, contributing up to 49% of total OPE levels.
- Materials used for the design of the platforms seem to be related to OPE levels.
- Human exposure to OPEs via inhalation in subway stations was calculated.
- Non-CR and CR risks were much lower than the threshold risk values.

GRAPHICAL ABSTRACT



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ABSTRACT

For the first time, the concentrations of 19 organophosphate esters (OPEs) were measured in airborne fine particulate matter (PM2.5) from subway stations in Barcelona (Spain) to investigate their occurrence, contamination profiles and associated health risks. OPEs were detected in all PM2.5 samples with levels ranging between 1.59 and 202 ng/m^3 (mean value of 39.9 ng/m^3). Seventeen out of 19 tested analytes were detected, with TDClPP, TClPP and TCEP being those presenting the highest concentrations. OPE concentrations are not driven by the same factors that determine the ambient PM2.5 concentrations of other constituents in the subway. Newer stations presented higher OPE levels, probably due to the materials used in the design of the platforms, with greater use of modern plastic materials versus older stations with tiles and stones. Estimated daily intakes via airborne particles inhalation during the time expended in subway stations were calculated, as well as the carcinogenic and non-carcinogenic health risks (CR and non-CR), all being much lower than the threshold risk values. Thus, subway inhalation exposure when standing on the platform to OPE's per se is not considered to be dangerous for commuters.

1. Introduction

Organophosphate esters (OPEs) are high-production-volume chemicals widely used in a variety of industries, including plastics, foams, paints, furniture, building materials and electronics. They are used as plasticizers, as flame retardants, as stabilizers for antifoaming and as additives to floor polishes, lubricants, lacquers and hydraulic fluids. Moreover, OPEs are also used as extreme pressure additives and antiwear agents in hydraulic fluids, lubricants, transmission fluids and motor oils (Du et al., 2019). Their production has increased from 0.3 to 1.0 million tons over the last decade (Israel Chemicals Ltd., 2015).

The occurrence of OPEs in the environment was first reported in the late 1970s (Sheldon and Hites, 1978). Since then OPEs have been

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detected in numerous environmental samples such as in ambient air (Kademoglou et al., 2017), dust (Li et al., 2019a), wastewater effluent (Kim et al., 2017), sediment and biota (Giulivo et al., 2017; Sala et al., 2019), with concentrations ranging from part-per-trillion (ppt) to part-per-million (ppm).

Tris(chloroisopropyl) phosphate (TClPP) and tri-n-butyl phosphate (TNBP) have been observed to disrupt endocrine and reproductive functions, nervous system development and are suspected carcinogens (He et al., 2020). Some epidemiological studies have reported that exposure to TClPP, tris(1,3-dichloro-2-propyl) phosphate (TDClPP) and tris (2-butoxyethyl) phosphate (TBOEP) is associated with decline of semen quality (He et al., 2020). OPEs are also associated with asthma and allergies (Meeker and Stapleton, 2010; Van der Veen and De Boer, 2012). These toxicological data have led to some restrictions: tris (chloroethyl) phosphate (TCEP), TClPP and TDClPP have been banned in children's products and residential upholstered furniture in the EU (EU, 2018).

Due to the increase in the use of OPEs and their reported toxic effects, this group of emerging pollutants has been raising increasing concern. Indoor environments are considered a hotspot for human exposure to OPEs. Humans spend their lives in a variety of microenvironments, such as houses, offices, and cars, and OPEs have been found in all these indoor environments at concentration levels ranging between a few ng/m^3 up to 2 μg/m^3 (Hartmann et al., 2004; Wong et al., 2018; Yadav et al., 2020). However, no information is available about the occurrence of these pollutants in air within public transport microenvironments such as subway stations, where plastic materials are nowadays widely used with different purposes.

In recent years a series of intensive air quality monitoring campaigns have been performed in the Barcelona subway system) within the framework of the METRO and IMPROVE LIFE research projects (Querol et al., 2012; Moreno and de Miguel, 2018 and references therein). The work performed during these campaigns has produced the most detailed publicly available database on rail subway air quality to date, including over 500 inorganic chemical analysis of inhalable particulate matter (PM) collected on underground platforms (Moreno et al., 2017; Minguillón et al., 2018). In addition to this extensive database on the inorganic chemistry of subway PM, measurements also covered several groups of organic components (notable polycyclic aromatic hydrocarbons, van Drooge et al., 2018) and bioaerosols (Triadó-Margarit et al., 2017). In this paper we contribute further to this chemical database on subway air quality by reporting on the presence of OPEs within inhalable PM breathed in the subway environment.

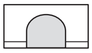
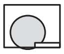
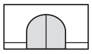
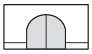
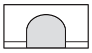
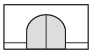
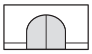
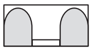
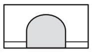
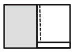
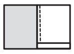
The main objectives of the present study are to evaluate the presence of different OPEs in airborne PM samples from subway stations in Barcelona and to assess the non-dietary human exposure to these compounds through air inhalation for several age groups (infants, children, and adults). To the best of our knowledge, this is the first study to show the occurrence of these plastic additives in PM from the subway environment and to assess human exposure via ambient air inhalation.

2. Materials and methods

2.1. Sampling collection

A total of 30 samples of fine PM (PM2.5 or PM < 2.5 μm) collected between 2013 and 2016 on the platforms of subway stations were selected from the Barcelona Subway database and analysed for OPEs (see Table S1). The sample set includes representatives from all seven of the main Barcelona subway lines (L1: Santa Coloma; L2: Tetuan; L3: Palau Reial, Maria Cristina, Poble Sec, Tarragona; L4: Joanic; L5: Sant Ildefons, Sagrera; L9: Collblanc; L10: Llefià). In addition the database includes samples taken in different times of the year (L1: Santa Coloma in July and October; L2: Tetuan in November/December and May; L10: Llefià in January and June), weekend vs weekday (L3: Maria Cristina; L10: Llefià), from platforms contaminated by ongoing engineering night works (L4: Joanic in November/December; L5: Sagrera; L3: Palau Reial), and from both relatively old (20th century: L1, L2, L3, L4, L5) and new (21st century: L9, L10) lines. A special case chosen was Collblanc (L9) where samples were collected during an experiment designed to test the effect on air quality in a deep station with tunnel ventilators turned off (only piston effect ventilation). The main characteristics of the eleven metro stations where measurements were carried out are presented in Table 1, which includes information on the opening year, depth and station design. The most modern stations (L9-L10) are equipped with platform screen door systems for safety, and air ventilation is produced separately into platform and tunnel.

Table 1
Sampling sites and sampling collection data.

Subway station	Line	Opening year	Depth (m)	Design	Ballast	Trains freq. (weekdays)	Measurement period (different ventilation)	
							Warm	Cold
Santa Coloma	L1	1983	−12,3		No	3′53″	1–30 Jul 2013	1 Oct–2 Nov 2015
Tetuan	L2	1995	−14,8		No	3′55″	2–31 May 2013	25 Nov–20 Dec 2013
Palau Reial	L3	1975	−14,2		Yes	3′43″	1 Apr–14 May 2015	11 Oct–9 Nov 2016
Maria Cristina	L3	1975	−13,7		Yes	3′43″	14 May–10 Jun 2015	
Tarragona	L3	1975	−14,0		Yes	3′43″	10–30 Jun 2015	29 Feb–11 May 2016
Poble Sec	L3	1975	−14,6		Yes	3′43″		19 Sep–11 Oct 2016
Joanic	L4	1973	−7,6		Yes	4′36″	2 Apr–2 May 2013	3 Nov–21 Dec 2015
Sagrera	L5	1959	−10,5		Yes	3′38″		20 Jan–31 Mar 2015
Sant Ildefons	L5	1976	−10,5		Yes	3′38″		3–29 Feb 2016
Collblanc	L9	2016	−60,0		No	6′00″	11 May–26 Jun 2016	
Llefià	L10	2010	−43,6		No	6′00″	31 May–1 Jul 2013	13 Jan–10 Feb 2014

The same sampling protocol was applied on the platform of all eleven selected subway stations during the project. Sampling devices were located at the end of the platform corresponding to the train entry point, behind a light fence for safety protection following the method commonly used for PM collection in this environment (Querol et al., 2012; Martins et al., 2016; Minguillón et al., 2018).

PM2.5 samples were collected on quartz microfiber filters (15 cm diameter) by a high volume sampler (HVS, Model CAV-A/MSb, MCV) at a sampling flow rate of 30 m^3/h over a 19 h period (from 5 a.m. to 12 a.m., subway operating hours) on a daily basis. A field filter blank per period was taken at each station. Filters were stored in aluminium foil at 4 °C in the darkness before chemical analysis, carried out during 2019. Different sections of these filters were used for inorganic major and trace components and total carbon chemical analysis. A quarter of the filter was used for the analysis of OPEs.

2.2. Standards and reagents

A total of nineteen OPEs were analysed in the present study. Analytical standards were purchased from different companies: TBOEP, TCEP, TCIPP, trihexyl phosphate (THP) and tris(2-ethylhexyl) phosphate (TEHP) were obtained from Santa Cruz Biotechnology (SantaCruz, CA, USA); isodecyldiphenyl phosphate (IDPP) and 2-ethylhexyldiphenyl phosphate (EHDPP) were purchased from AccuStandard (New Haven, CT, USA); diphenylcresyl phosphate (DCP), TNBP, triphenyl phosphate (TPHP), triphenylphosphine oxide (TPPO), TDClPP, triethyl phosphate (TEP) and tri-n-propyl phosphate (TnPP) were obtained from Sigma-Aldrich (St. Louis, MO, USA); tricresyl phosphate (TMCP) was purchased from Dr. Ehrenstorfer (Augsburg, Germany); 2-isopropylphenyl diphenyl phosphate (2IPPDPP), 4-isopropylphenyl diphenyl phosphate (4IPPDPP) and bis(4-isopropylphenyl) phenyl phosphate (B4IPPPP) were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada); and, isopropyl phenyl phosphate (IPPP) was purchased from Chiron (Trondheim, Norway). Labelled d_{15}-TDCPP, d_{27}-TNBP, d_{12}-TCEP and $^{13}C_2$-TBOEP were obtained from Wellington Laboratories Inc. (Guelph, ON, Canada). Labelled d_{15}-TPHP was purchased from Cambridge Isotope Laboratories Inc. (Andover, MA, USA).

Acetone and hexane solvents for organic trace analysis were purchased from J.T. Baker (Center Valley, PA, USA). Methanol and water solvent for trace analysis as well as ammonium acetate and formic acid were obtained from Merck (Darmstadt, Germany).

2.3. Inorganic chemical analyses

PM2.5 concentrations were determined gravimetrically weighing the filters before and after sampling after being stabilized for at least 48 h in a conditioned room (20 °C and 50% relative humidity). A microbalance (Model XP105DR, Mettler Toledo) with a sensitivity of ±10 μg was used.

One quarter of each filter sample was acid digested with HNO_3:HF:$HClO_4$ (1:1:1), this treated fraction was then chemically analysed by means of inductively coupled plasma atomic emission spectrometry (ICP-AES: IRIS Advantage TJA Solutions, THERMO) and mass spectrometry (ICP-MS: X Series II, THERMO) to determine major (such as Al, Ca, K, Na, Mg, Pb, Fe, Ni, P, S) and trace elements (Li, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Sb, Ba, La, Ce, Pr, Nd, Hf, W, Pb, Bi, Th, U, among others), respectively, following the standard chemical characterization of PM filters.. A few milligrams of a standard reference material (NIST 1633b) were added to a fraction of a blank filter to check the accuracy of the analysis of the acid digestions. Regarding the precision of the analyses, most of the elements showed an analytical error $< 10\%$, except for P and K which had a 15% error. SiO_2 and CO_3^{2-} were indirectly determined on the basis of empirical factors (Alx1.89 $=$ Al_2O_3, 3xAl_2O_3 $=$ SiO_2 and (1.5xCa) $+$ (2.5xMg) $=$ CO_3^{2-}, see Querol et al., 2001). Blank filters were used for every stock purchased for sampling (one blank filter for each 12 filter stock). A portion of the filter sample (1.5 cm^2) was used to measure total carbon (TC) using the thermal – optical transmittance (TOT) method by means of a laboratory OC–EC Sunset instrument or an elemental C analyzer. Blank filters were analysed in the batches of their respective filter samples and the corresponding blank concentrations were subtracted from each sample in order to calculate the ambient concentrations. Uncertainties were calculated as described by Escrig et al. (2009).

2.4. Sample analysis for OPEs

Throughout all sampling and analysis processes, plastic material was avoided due to potential contamination, as our analytes are used as plasticizers. We try to minimize as much as possible blank signals, i.e., heating all the non-volumetric material at 340 °C and rinsing with ethanol and hexane:acetone (1:1) just before use. For each batch of samples, a blank was included. Blank levels were subtracted from corresponding samples.

Before extraction, filters were spiked with 200 μL of internal standard solution (d_{15}-TDCPP, d_{27}-TNBP, d_{12}-TCEP, $^{13}C_2$-TBOEP and d_{15}-TPHP) at 0.5 ng/μL. Samples were extracted using a pressurized liquid extraction (PLE) system (Giulivo et al., 2016). Filters were loaded into a 30 mL extraction cell filled with hydromatrix, and extracted with hexane:acetone (1:1) at 1600 psi and 50 °C. Extracts were concentrated to incipient dryness and re-dissolved with 500 μL of methanol.

An online sample purification and analysis was performed with a Thermo Scientific TurboFlow™system consisting of a triple quadrupole (QqQ) MS with a heated-electrospray ionisation source (H-ESI), two LC quaternary pumps and three LC columns, two for purification and one for separation. The TurboFlow™ purification columns employed were: Cyclone™-P (0.5x50mm) and C18-XL (0.5 × 50 mm). Chromatographic separation was subsequently achieved using an analytical column: Purosphere Star RP-18 (125 mm × 0.2 mm) with a particle size of 5 μm (Giulivo et al., 2016). Detailed conditions used for purification and chromatographic separation were included in Table S2. Selective reaction monitoring (SRM) mode was used for all compounds with two transitions monitored for each analyte. The most intense transition was used for quantification, while the second provided confirmation. Instrumental working parameters such as retention times, transitions, declustering potential and collision energies were summarized in Table S3.

Instrumental parameters such as recoveries, limits of detection (LODs) and limits of quantification (LOQs) are summarized in Supporting information (Table S4). Our analytical methodology provided recoveries ranging between 53 and 118%, limits of detection (LODs) between 0.8 and 42 ng/g (or between 0.04 and 2.20 pg/m^3), and limits of quantification between 2.7 and 141 ng/g (or between 0.14 and 7.40 pg/m^3).

2.5. Human exposure via inhalation estimates

To evaluate human exposure to OPEs via ambient inhalation, estimated daily intakes ($EDI_{inhalation}$), expressed in ng/kg body weight (bw)/day, were calculated using the following equation: $EDI_{inhalation} =$ Air concentration × Amount of air inhaled per day × Exposure time / Body weight. Different subpopulation groups, classified according to age were considered: infant (1–6 years), children (6–12 years) and adults. The volume of air inhaled per day was assumed to be 6, 11.04 and 19.92 m^3/day for infants, children and adults, respectively (Maceira et al., 2019). Average body weight was assumed to be 16, 29 and 70 kg for infants, children and adults, respectively (Maceira et al., 2019). The calculation assumes that the average exposure time in a subway commuting trip was 15 min (Transports Metropolitans de Barcelona own data) and that 100% of the inhaled chemicals were absorbed in the airways.

2.6. Human risk assessment probabilistic model

Recently, USEPA (2019) updated the oral reference dose (RfD) for some OPEs. Hazard quotients (HQs) were determined using the following equation: $HQ = EDI_{inhalation}/RfD$. $EDI_{inhalation}$ and HQ values were estimated as health risk exposure to OPEs as a single value. However, input values used to calculate them may contain some degrade of uncertainties that come from a varieties of sources. The process of evaluating the uncertain associated with the $EDI_{inhalation}$ and HQ results is often called uncertainty analysis which is often used the Monte Carlo simulation. Monte Carlo simulation uses statistical probabilistic sampling as techniques to approach the solution of the mathematical equation which generating randomly values for estimate uncertain parameters. Monte Carlos probabilistic analysis was performed to estimate the uncertainties using Crystal Ball software, version 11.1.2.4 (Oracle, Inc. Redwood. US). In this study, the number of randomly repetitions for each mathematical equation was set at 25,000.

3. Results

3.1. Occurrence and OPE levels in PM2.5

The mean concentrations of OPEs in PM2.5 samples collected from different subway stations in Barcelona (Spain) are summarized in Table 2 (for individual sample results see Supporting information, Table S5). OPEs were detected in all the analysed samples, indicating widespread contamination by these emerging pollutants, with levels ranging between 1.59 and 202 ng/m^3 (mean value of 39.9 ng/m^3). The concentrations of OPEs measured in PM2.5 varied between subway stations, being the highest values those obtained for Sagrera (147 and 166 ng/m^3) and Collblanc (86.3 and 202 ng/m^3) stations. It must be taken into account that sampling at Sagrera station was carried out at the time they were having night tunnel works. As regards Collblanc station, the highest value was obtained when tunnel ventilation was turned off (202 ng/m^3), showing an increase in the levels of contamination by a factor between 2 and 3 with respect to the sample taken in the same station when ventilation was on (86.3 ng/m^3). These values likely reflect build-up of plasticizers and flame retardants used in this station, which was brand new and so full of newly treated plastic materials. In contrast, the lowest values of OPE concentrations were obtained for Tetuan (from 4.09 to 11.5 ng/m^3) and Joanic (from 1.59 to 12.74 ng/m^3) stations. These two stations are older (Table 1) and are also the smallest of the 11 stations selected in this study.

Seventeen out of nineteen tested analytes were detected. Only IDPP and THP were not detected in any sample. Compounds with highest detection frequencies were TPPO, TPHP, TMCP, TEHP and B4IPPP with 100% of positive samples, followed by TClPP, TDClPP, TNBP and DCP with 97%. As regards concentration levels, the highest values were obtained for TDClPP (mean value of all analysed samples = 14.6 ng/m^3), followed by TClPP (11.0 ng/m^3) and TCEP (9.10 ng/m^3). Fig. 1 shows the percentage contribution of each detected OPE in each sampled station. TDClPP was the most contributing compound, ranging between 23 and 49%, followed by TClPP, with 10–44%. As one of the most commonly used OPEs, since its first use in 1970s, TDClPP has been widely applied in both soft and rigid polyurethane foam (PUF), as well as in plastics, resins, electronics equipment and some fabric backings. TClPP is also used primarily applied to PUF in furniture and building construction (IPCS, 1998).

Some differences in OPE profile have been observed at some stations. For instance, a high contribution (60%) of TCEP was detected in the Sagrera samples, while TCEP contribution was between 2 and 14% in the rest of stations. TNBP contribution reached values of 29, 25 and 20% in Palau Reial, Sant Ildefons and Joanic stations, respectively, whereas the contribution of this compound in the rest of the samples did not exceed 7%. For IPPP, a greater contribution to the rest of the samples was observed in Maria Cristina (16%), Llefià (15%) and Santa Coloma (11%) stations.

Aggregating the OPE results from all subway lines it appears that there is no obvious evidence for a link between OPE concentrations and the major PM2.5 sources in the subway environment (rail and wheel abrasion, outdoor air infiltration, catenary sparkling, ballast, among the major ones), as these sources are mostly related to inorganic components. No correlations were neither observed between OPE and PM2.5 signatures, apart from a possible relationship with the content of carbonaceous aerosol (CA) in which low or absent concentrations of some plasticizers (TEHP, B4IPPP, TBOEP, TPHP and EHDPP) occurred in samples that also contained minimal CA (Fig. S1). However, as will be discussed below, separating the samples into those from different lines does raise at least one such link. A connection, however, does seem to emerge when comparing OPE concentrations with the age of the subway station (Fig. 2). Although there are no significant differences between OPE levels in the new and old stations (Kruskal-Wallis rank

Table 2
OPE levels (mean values expressed in ng/m^3) in PM2.5 samples from subway stations in Barcelona.

	L1	L2	L3				L4	L5		L9	L10
	S. Coloma	*Tetuan*	*Palau Reial*	*M. Cristina*	*Poble Sec*	*Tarragona*	*Joanic*	*S. Ildefons*	*Sagrera*	*Collblanc*	*Llefià*
	n = 4	*n* = 4	*n* = 2	*n* = 2	*n* = 2	*n* = 2	*n* = 4	*n* = 2	*n* = 2	*n* = 2	*n* = 4
TEP	0.02	nd	0.12	0.08	0.04	0.03	0.05	0.04	0.04	0.09	0.37
TCEP	2.42	0.23	1.27	1.39	2.17	0.64	0.21	0.23	94.3	nd	nd
TPPO	0.10	0.05	0.05	0.07	0.18	0.05	0.02	0.15	0.12	0.59	0.76
TClPP	3.11	1.49	20.0	4.42	38.1	8.16	1.24	3.35	15.3	62.7	7.73
TPP	nd	0.12	0.10	nd	0.11	nd	0.12	0.13	0.09	0.18	0.09
TDClPP	6.37	2.67	21.3	4.83	41.1	16.2	2.41	4.50	39.3	66.4	8.20
TPHP	1.02	0.44	0.75	0.64	0.57	0.18	0.36	0.31	0.46	0.46	0.37
TNBP	0.31	0.08	18.5	1.43	1.14	1.70	1.37	3.40	1.55	0.33	1.32
DCP	0.21	0.19	0.34	0.31	0.64	0.16	0.19	0.21	0.44	1.07	2.06
TBOEP	0.06	0.06	0.15	0.26	0.21	0.27	0.01	0.03	0.11	0.05	0.06
2IPPDPP	0.23	0.04	0.06	0.25	0.28	nd	0.02	0.01	0.16	nd	nd
4IPPDPP	0.34	0.16	0.14	0.36	0.39	0.09	0.13	0.14	0.28	nd	0.07
TMCP	0.10	0.11	0.13	0.14	0.14	0.11	0.11	0.13	0.15	0.21	0.11
EHDPP	0.28	0.24	0.17	1.33	0.91	0.66	0.36	0.36	1.07	0.12	0.57
B4IPPP	0.19	0.14	0.14	0.25	0.32	0.13	0.12	0.15	0.21	0.40	0.10
IDPP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
IPPP	1.87	0.41	0.47	3.34	5.87	1.53	0.19	0.30	4.21	10.7	3.97
THP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
TEHP	0.96	0.16	0.24	1.72	2.31	3.13	0.12	0.22	0.72	0.78	0.46
ΣOPEs	17.6	6.47	63.6	20.8	53.4	33.1	6.52	13.5	156	144	26.2

nd = not detected.

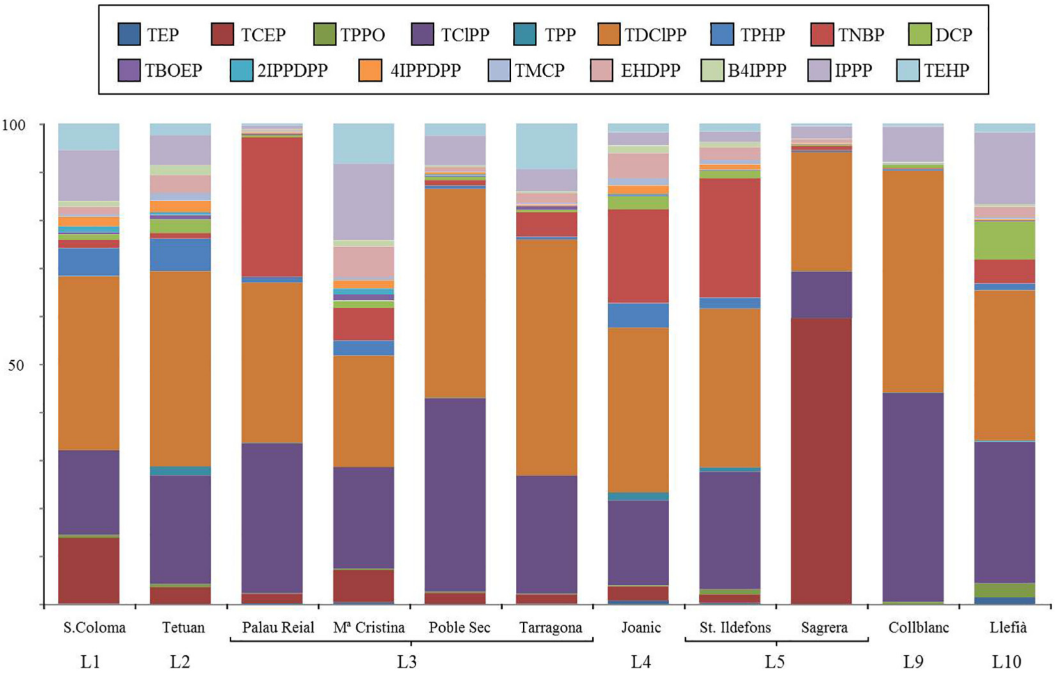


Fig. 1. Percentage contribution of detected OPEs to the total concentration levels in PM2.5 samples from the different subway stations.

sum test: chi-squared = 3.5065, df = 1, *p*-value = 0.06113), there is a marked trend towards higher values in the newer stations. This is likely due to that fact that the newer stations (L9 and L10) are those where plastic materials are more commonly present in the platforms, compared to older stations where cement, tiles and stone were normally utilised. It should be considered that differences may not be so marked by the fact that several old stations have been partially restored, and in these renovations similar plastic materials have also been used. In addition, these new lines (L9, L10) are equipped with a platform screen door system compared to the open system in the older lines. This affects the air quality of the platforms as it inhibits the entrance of PM from the tunnel into the station, but is also likely to increase the concentration of airborne plasticizers in the platform air. A similar observation was also made with regard to polycyclic aromatic hydrocarbon (PAH) concentrations analysed in a L10 station in a previous study (Van Drooge et al., 2018).

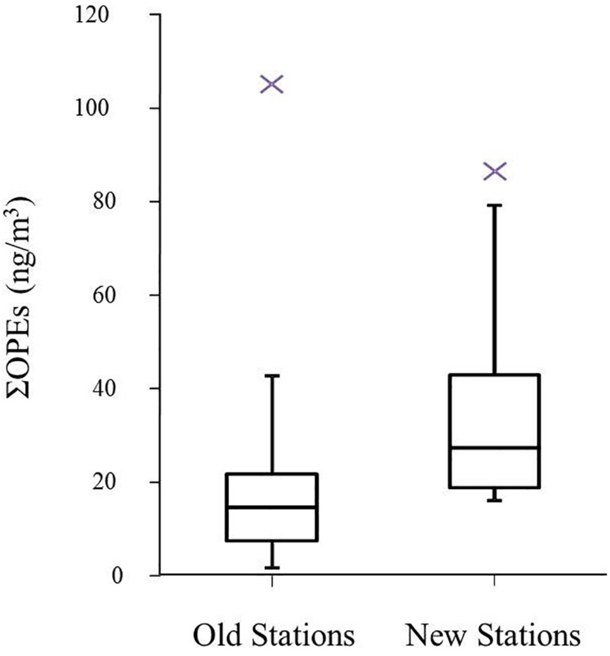


Fig. 2. Comparison between OPE concentrations (ng/m^3) in PM2.5 samples from old (L1, 2, 3, 4 and 5, excluding samples T5239 and T5185 corresponding to samples collected during night tunnel works) and new (L9 and 10, excluding sample T7150 corresponding to sample collected when tunnel ventilation was turned off) subway stations. Outliers (x) are shown.

3.2. Comparison of OPE levels with the literature

Different studies have conducted on OPE occurrence in indoor and outdoor environments (Table 3). Comparison with published data must be carried out with caution because airborne samples were collected using different sampling techniques and analysed with different analytical methods, including different OPEs (from 8 to 19 compounds). One important difference is that some studies only reported OPE concentrations in the particle phase, whereas others reported the sum of gas and PM phase OPEs.

In general, OPE levels in indoor air are one to four orders of magnitude higher than those in outdoor air (Rauert et al., 2018; Wong et al., 2018; Saini et al., 2020), and rural sites have lower concentrations than urban sites (Chen et al., 2020a). OPE contamination in different indoor environments has been published, with most studies focusing on indoor air of houses, workplaces (offices, laboratories, stores, etc.) and schools. Total OPE levels reported in these indoor environments were generally a few ng/m^3 (Li et al., 2019b; Yadav et al., 2020), but in some cases they reached values of up to 467 ng/m^3 (Sakhi et al., 2019; Kim et al., 2019). These values were similar to those obtained in our study, with a mean value of 40 ng/m^3 and a range between 1.59 and 202 ng/m^3.

There are also some works focused on the evaluation of OPE levels inside cars. Hartmann et al. (2004) reported for the first time on OPE levels in indoor air from cars. They found levels of 13 and 42 ng/m^3 in new cars, while concentrations increased to 206 and 270 ng/m^3 in 9 year old cars. Therefore, in both transport modes, cars and subway, OPE levels in air were similar. Later, Tokumura et al. (2017) studied OPE concentrations in the indoor air from 25 cars in Japan. Most OPEs were neither detected nor found at a concentration higher than the method quantification limit. However, high concentrations were found

Table 3
Concentrations (ng/m^3) of OPEs measured in air (gas- and/or PM-phase) samples in different published works.

	Ambient	Matrix	Location	Sampling year	n^{a}	n^{b}	OPE Levels		Reference
							Range	Mean/Median	
OUTDOOR	Urban (megacities)	Gas + PM	Across the Globe	2018	19	18	0.46–15.1	2.83/1.25	Saini et al., 2020
	Rural and urban	PM	Guangzhou and Taiyuan, China	2017–18	72	11	3.10–544	19.5/19.4	Chen et al., 2020a
	Agricultural, rural, urban and polar sites	Gas + PM	Across the Globe	2014	170	18	0.07–7.77	nr	Rauert et al., 2018
	Urban air	Gas + PM	Stockholm, Sweden	2014–15	24	10	0.78–9.10	nr/3.10	Wong et al., 2018
INDOOR	Indoor				23		101–1900	nr/340	
	Residential, office, public building and houses near traffic	Gas	Bihar state, India	2015	15	8	0.09–2.16	0.48/0.35	Yadav et al., 2020
	Indoor environments	Gas	New York state, USA	2018	54	15	<LOQ-170	24.9/8.21	Kim et al., 2019
		PM^{c}			54		2.22–1040	77.5/36.1	
	Homes	Gas	Harbin, China	2013–14	25	9	2.73–18.2	7.43/6.86	Li et al., 2019b
	Homes and schools	Gas + PM	Oslo and Akershus, Norway	2012	54	6	8.6–467	99/55	Sakhi et al., 2019
	Offices, furniture stores, electronics stores, theater and cars	Gas + PM	Zurich, Switzerland	nr	12	8	3.9–270	nr/nr	Hartmann et al., 2004
	Car air filters	PM^{c}	Hanoi, Vietnam	2017	22	10	0.54–13	2.60	Tran et al., 2020
	Cars	Gas	Japan	2013	9	12	<LOQ-1500	nr/nr	Tokumura et al., 2017
	Subway stations	PM	Barcelona, Spain	2013–16	30	19	1.59–202	39.9/26.2	This study
		PM^{c}					19.7–4730	832/288	

nr: not reported.
[a] Number of analysed samples.
[b] Number of OPE compounds analysed;
[c] Particle levels expressed in μg/g.

for TClPP with the highest level of 1500 ng/m^3. Tran et al. (2020) analysed cabin air filters in the air conditioning system of passenger cars and reported mean concentrations of OPEs in the captured dust of 2.60 μg/g, with TCIPP being also the dominant compound. If we compare with our results expressed in g/g of particles, levels in air particles from subway stations were clearly higher, with a mean value of 832 μg/g and samples with levels up to 4730 μg/g. It is important to note that our sampling was programmed to sample PM2.5 over 19 h, whereas the study in cabin air filters included a long-time interval between filter changes. Moreover, air conditioning filters usually collected mainly the coarser PM fractions. Therefore, in order to be able to compare these results, size fractionation of OPEs should be previously evaluated.

Regarding the OPE profile, TCIPP and TNBP were the major contributors to OPE levels in previous published works in indoor air samples (home, offices, school buildings, stores, vehicles, etc.) from different locations around the world (Switzerland, Sweden, Finland, Japan, Norway, China, etc.) (Du et al., 2019). In our study, TClPP was also one of the most contributing OPE in to bulk OPE contents (10 to 44%). However, TNBP contribution was very low, except in some samples where it reached between 25 and 30% of total OPE levels. In contrast, TDClPP was the compound presenting the highest levels in PM2.5 from the subway platforms.

3.3. OPE human exposure assessment and Monte Carlo simulation

Several factors can influence the extent to which humans are exposed via inhalation to air pollutants (in vapour or PM phase), such as ambient concentrations, human breathing rate, duration and frequency of exposure, age, gender and body weight, among others. In this study, we evaluated human exposure to OPEs via airborne PM2.5 inhalation during the time expended in subway platforms. In the Monte Carlo simulation, exposure time was assumed to be a triangular density function where the exposure varied from 10 to 20 min with an average of 15 min. Estimated Daily Intakes by Inhalation ($EDI_{inhalation}$) were calculated following the equation and assumptions described in Section 2.5. Obtained values are summarized in Table 4. $EDI_{inhalation}$ values for ΣOPEs ranged between 0.118 and 0.158 ng/kg bw/day, being values obtained for children and infants similar, and slightly higher than those for adults. This suggests that children may be at higher risk because they are more sensitive during the developmental stage.

Obtained $EDI_{inhalation}$ values are lower than those reported in previous studies for indoor environments. Sakhi et al. (2019) reported an $EDI_{inhalation}$ value of 11 ng/kg bw/day in indoor air from Norwegian homes and schools. Similar values were obtained by He et al. (2018). They estimated that the daily intake corresponding to inhalation for the Australian population was 7.9 ng/kg bw/day. This estimation was based on a fraction of total indoor time of 88% (21.12 h or 1267 min). In contrast, $EDI_{inhalation}$ values for the subway platforms corresponded only to 15 min of exposure. If we refer both estimates to the same exposure time, 15 min, we can deduce that the above exposure values on the subway platforms are higher than that calculated based in indoor environments such as homes and offices (0.094 ng/kg bw/day). Moreover, to assess the complete exposure through the subway ride, it will be necessary to also include the OPE exposure inside the wagons, which have a lot of plastic materials inside.

Recently, USEPA (2019) updated the oral reference dose (RfD) and oral cancer slope factors (SFO) of some OPEs (see Table 4). Some published works also presented RfD values for some other OPEs, such as TEP (Chen et al., 2020b), TPHP (Zhu et al., 2020) and EHDPP (He et al., 2018). However, these reference values have not been agreed by a group of experts, and for our risk assessment study we have only taken into account those agreed by the USEPA. It is important to note that USEPA has not developed inhalation reference concentrations (RfCs) for OPEs because there are insufficient inhalation data from human or animal studies that could be used to derivate these RfCs for OPEs. In the absence of relevant inhalation exposure data, in this study we chose to estimate inhalation RfCs from oral RfDs. It is recognized that it is not an ideal approach but it is the best option when RfCs are missing. Extrapolating from one route of exposure (oral) to another (inhalation) requires specific knowledge about the uptake kinetics into the body by each exposure route, including potential binding to cellular sites. Therefore, it was assumed that all of inhaled compound is deposited in the respiratory tract and completely absorbed into the blood. This approach is justified for conservatively estimating the toxicological risk from exposure to OPEs. Thus, we estimated the HQ or non-carcinogenic (non-CR), and carcinogenic (CR) risks of OPE exposure

Table 4

Estimated daily intakes of OPEs via PM2.5 inhalation ($EDI_{inhalation}$) during the time expended in subway stations (ng/kg bw/day).

	Mean values (ng/m^3)	$EDI_{inhalation}$ Infants		$EDI_{inhalation}$ Children		$EDI_{inhalation}$ Adults		RfD[c]	SFO[c]
		Mean[a]	Uncertainty[b]	Mean	Uncertainty	Mean	Uncertainty		
TNBP	2.31	0.009	0.0271	0.009	0.0251	0.007	0.0141	10,000	0.009
TCEP	9.10	0.036	0.1090	0.036	0.1030	0.027	0.0645	7000	0.020
TEHP	0.84	0.003	0.0044	0.003	0.0046	0.002	0.0024	100,000	0.0032
TClPP	11.0	0.043	0.0774	0.044	0.0768	0.033	0.0432	10,000	–
TDClPP	14.6	0.057	0.0903	0.058	0.0842	0.043	0.0491	20,000	–
TMCP	0.12	0.0005	0.0002	0.0005	0.0002	0.0004	0.0001	20,000	–
ΣOPEs	39.9	0.156	0.2200	0.158	0.2180	0.118	0.5990		

[a] Based on OPE mean values.

[b] Uncertainties were estimated using Monte Carlo Analysis.

[c] Values of RfD (Oral reference dose) expressed in ng/kg bw and day and SFO (Oral cancer slope factor) expressed in mg/kg bw and day, and obtained from USEPA, 2019.

via airborne particle inhalation during the time expended in subway stations (Table 5). The non-CR risk was calculated dividing the obtained $EDI_{inhalation}$ values by the corresponding RfD. It was reported that if the non-CR risk was higher than 1, then a potential non-CR risk to humans might occur. Further analysis was performed through the Monte Carlo probabilistic technique for propagation of full probabilistic distribution providing reliable results for a wider range of estimations $EDI_{inhalation}$ and HQ values reporting the uncertainties associated which giving us a more accurate interpretation of results. Potential risk associate to inhalation of PM2.5 is observed also in the chart bar of the Fig. S2 where the uncertainties represented on the bar error.

The CR risk was calculated multiplying the obtained $EDI_{inhalation}$ values by the corresponding SFO. One cancer incidence case per million people was used as an acceptable level of risk. Hence, if the CR value was greater than 1×10^{-6}, the EDIs exceeded the safe threshold indicating the potential adverse effects. The non-CR and CR values from exposure to OPEs in subway stations were 4–5 and 2–4 orders of magnitude lower than the corresponding threshold level, respectively (Table 5). However, a potential health risk might still exist when considering that OPE exposure also occurs in other indoor environments over the remaining hours of the day. In addition, different studies have suggested that humans are also exposed to OPEs through other routes, such as dermal absorption, dust ingestion and dietary intake. Inhalation is one important OPE adsorption pathway for humans, but previous studies have shown that dust ingestion predominated over dermal absorption and inhalation (Wei et al., 2015; Kim et al., 2019). He et al. (2018) found that EDI through indoor dust (ingestion and dermal contact) was 5.9 ng/kg bw/day, similar to EDI through inhalation (7.9 ng/kg bw/day). Dietary intake is also an important route of exposure. Some studies reported EDI values via foodstuff ingestion, with values of 103 ng/kg bw/day in Belgium (Poma et al., 2018) or 85 ng/kg bw/day in Sweden (Poma et al., 2017).

4. Conclusions

Concentration levels of 19 OPEs were measured for the first time in airborne particles (PM2.5) from subway platforms. Widespread contamination by these emerging pollutants was observed with OPE presence in all samples collected at levels ranging between 1.59 and 202 ng/m^3 (mean value of 39.9 ng/m^3). The most contributing compound to the total OPE levels was TDClPP followed by TClPP and TCEP. Evidences for a link between OPE levels and major PM2.5 sources in the subway environment were not found. However, it seems that newer stations (L9 and L10) presented higher levels of contamination, probably due to the common use of plastic materials in the building of the platforms, compared to older stations.

OPE levels obtained in our study were similar to those previously reported in other indoor environments, such as houses, workplaces and schools. Comparing with other transport modes such as cars, also similar levels were observed. However, our study only focused on the airborne PM2.5 from the subway platforms. To assess the complete transport mode, it will be necessary to also include the study of OPE levels inside the wagons.

Finally, human exposure to OPEs via PM2.5 inhalation during the time expended in subway stations was estimated, obtaining $EDI_{inhalation}$ values up to 0.158 ng/kg bw/day. These values were used to estimate the non-CR and CR risks, being all much lower than the threshold risk values. However, it is important to note that OPE exposure also occurs in other indoor environments, and also by other routes, such as dermal absorption, dust ingestion and dietary intake. The sum of all these exposures can bring the values closer to the established safety limits. Our study suggests that multiple exposure pathways should be considered in a comprehensive exposure assessment of OPEs. In this context, by adopting the precautionary principle it would appear desirable to reduce overall human exposure to OPEs.

CRediT authorship contribution statement

R. Olivero-Verbel: Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **T. Moreno:** Conceptualization, Methodology, Investigation, Resources, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. **J. Fernández-Arribas:** Methodology, Formal

Table 5

Non-carcinogenic and carcinogenic risk of exposure to OPEs by PM2.5 inhalation during the time expended in subway stations.

	Non-carcinogenic risk (Non-CR)						Carcinogenic risk (CR)					
	Infants		Children		Adults		Infants		Children		Adults	
	Mean[a]	Uncertainty[b]	Mean	Uncertainty	Mean	Uncertainty	Mean	Uncertainty	Mean	Uncertainty	Mean	Uncertainty
TNBP	$9.00\ 10^{-7}$	$2.71\ 10^{-6}$	$9.00\ 10^{-7}$	$2.51\ 10^{-6}$	$7.00\ 10^{-7}$	$1.41\ 10^{-6}$	$8.10\ 10^{-11}$	$2.72\ 10^{-8}$	$8.10\ 10^{-11}$	$2.51\ 10^{-8}$	$6.30\ 10^{-11}$	$1.41\ 10^{-8}$
TCEP	$5.14\ 10^{-6}$	$1.55\ 10^{-5}$	$5.14\ 10^{-6}$	$1.46\ 10^{-5}$	$3.86\ 10^{-6}$	$9.23\ 10^{-6}$	$7.20\ 10^{-10}$	$1.09\ 10^{-7}$	$7.20\ 10^{-10}$	$1.03\ 10^{-7}$	$5.40\ 10^{-10}$	$6.47\ 10^{-8}$
TEHP	$3.00\ 10^{-8}$	$4.46\ 10^{-8}$	$3.00\ 10^{-8}$	$4.57\ 10^{-8}$	$2.00\ 10^{-8}$	2.44^{-8}	$9.60\ 10^{-12}$	$4.47\ 10^{-9}$	$9.60\ 10^{-12}$	$4.58\ 10^{-9}$	$6.40\ 10^{-12}$	$2.44\ 10^{-9}$
TClPP	$4.30\ 10^{-6}$	$7.73\ 10^{-6}$	$4.40\ 10^{-6}$	$7.67\ 10^{-6}$	$3.30\ 10^{-6}$	$4.32\ 10^{-6}$	–	–	–	–	–	–
TDClPP	$2.85\ 10^{-6}$	$4.51\ 10^{-6}$	$2.90\ 10^{-6}$	$4.21\ 10^{-6}$	$2.15\ 10^{-6}$	$2.45\ 10^{-6}$	–	–	–	–	–	–
TMCP	$2.50\ 10^{-8}$	$1.19\ 10^{-8}$	$2.50\ 10^{-8}$	$1.09\ 10^{-8}$	$2.00\ 10^{-8}$	$6.64\ 10^{-9}$	–	–	–	–	–	–
ΣOPEs	$1.32\ 10^{-5}$		$1.34\ 10^{-5}$		$1.00\ 10^{-5}$		$8.11\ 10^{-10}$		$8.11\ 10^{-9}$		$6.09\ 10^{-10}$	

[a] Based on OPE mean values.

[b] Uncertainties were estimated using Monte Carlo Analysis.

analysis, Investigation. **C. Reche:** Methodology, Formal analysis, Investigation. **M.C. Minguillón:** Methodology, Formal analysis, Investigation. **V. Martins:** Methodology, Formal analysis, Investigation. **X. Querol:** Investigation, Resources, Writing – original draft, Writing – review & editing. **B. Johnson-Restrepo:** Resources, Investigation, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. **E. Eljarrat:** Conceptualization, Methodology, Validation, Investigation, Resources, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

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

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Appendix A. Supplementary data

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