Supplementary information for

Development and validation of a GC Orbitrap-MS method for the determination of phthalate esters (PAE) and bis(2-ethylhexyl) adipate (DEHA) in atmospheric particles and its application for screening PM$_{2.5}$ from Curitiba, Brazil

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S1. Washing of pipette tips and 4 mL vials

Pipette tips (i.e., 200 µL, Gilson, PN F161930), and 4 mL vials with screw cap (Fisherbrand, Cat No. 10571013) fitted with PTFE/silicone septa (Chromacol, P/N 13-SC-ST15) were assessed for PAE contamination by analysing the three successive solvent washes for both items in GC-HRMS. Results of the third solvent wash for both pipette tip and 4 mL vial yielded PAE concentrations lower than the method LODs. Hence, the assessed pipette tips and 4 mL vials used in this work were pre-washed thrice with 50:50 DCM: MeOH before use.

S2. Adsorption of PAEs to glassware during sample storage

Adsorption of organic analytes (e.g., PFAS, pharmaceuticals, bisphenols) onto glassware and plasticware surfaces used for sample storage/extraction glassware has been observed in previous studies[1-3], which can affect the accuracy and precision of analytical quantitation. In this work, glassware (i.e., 5 mL glass volumetric flasks, Cole Parmer, Item 34502-78) was used to store prepared PAE and DEHA standard solution mixtures at 4°C. To evaluate if adsorption of PAEs to glassware occurs during sample storage at 4°C, three replicates of a PAE and DEHA standard solution mixture (i.e., 11 pg/µL), that were allowed to equilibrate at RT, were tested at two sample preparation conditions: (1) vortexing for 10-15 seconds, (2) vortexing for 10-15 seconds, then 1-minute sonication. The PAE and DEHA standard solution mixture (at three replicates) that was allowed to equilibrate at RT was tested without undergoing any sample preparation and as a control sample. Recoveries were calculated by dividing the peak area of the target compounds by the peak area of the control at each sample preparation condition. Our results (see Fig. S1) indicate that minimal glassware adsorption occurs for the target compounds. Amount of variation (as expressed through standard deviation) for DBP, DEHA, and DEHP (when vortexed alone) show that vortexing increases measurement variability, while vortexing followed by 1-minute sonication yielded in smaller amount of variations. Based on our results, we used vortexing and 1-minute sonication in succession before transferring PAE and DEHA standard solution mixtures from the volumetric flask to another container (e.g., vials) to mitigate both glassware adsorption and potential measurement precision problems.
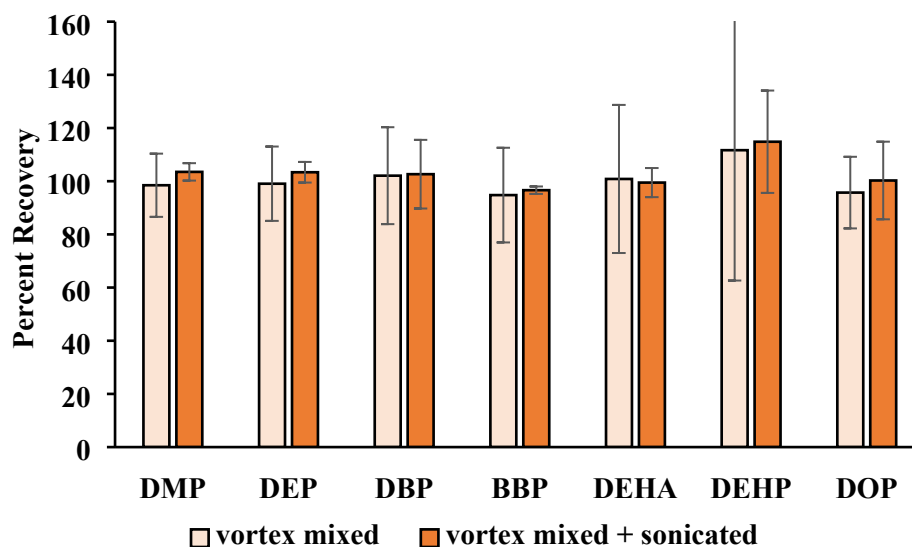
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Fig. S1. Percent recovery of PAEs and DEHA using two sample preparation conditions. (1) the solution was vortexed for 10-15 seconds prior to analysis; and (2) the solution was vortexed for 10-15 seconds and sonicated for 1 minute prior to analysis. Recoveries were calculated for both conditions by dividing the peak area of the target compounds in each condition by the control (i.e., analysed without sample preparation). Standard deviation bars correspond to variations within 3 replicate solution injections at 11.3 pg/µL

S3. Autosampler wash settings

The autosampler (Thermo Scientific TRIPLUS RSH) wash program was designed to mitigate carryover effects between sample injections. A pre-injection and post-injection wash sequence of 100% MeOH, 50:50 DCM: MeOH, 100% DCM, and 50:50 DCM: MeOH was set.

S4. Testing of extraction solvents for PAE contamination

Extraction solvents used in this work (i.e., DCM and MeOH) were tested for potential PAE contaminations and results indicated negligible solvent contamination with target PAEs (i.e., below method LODs).
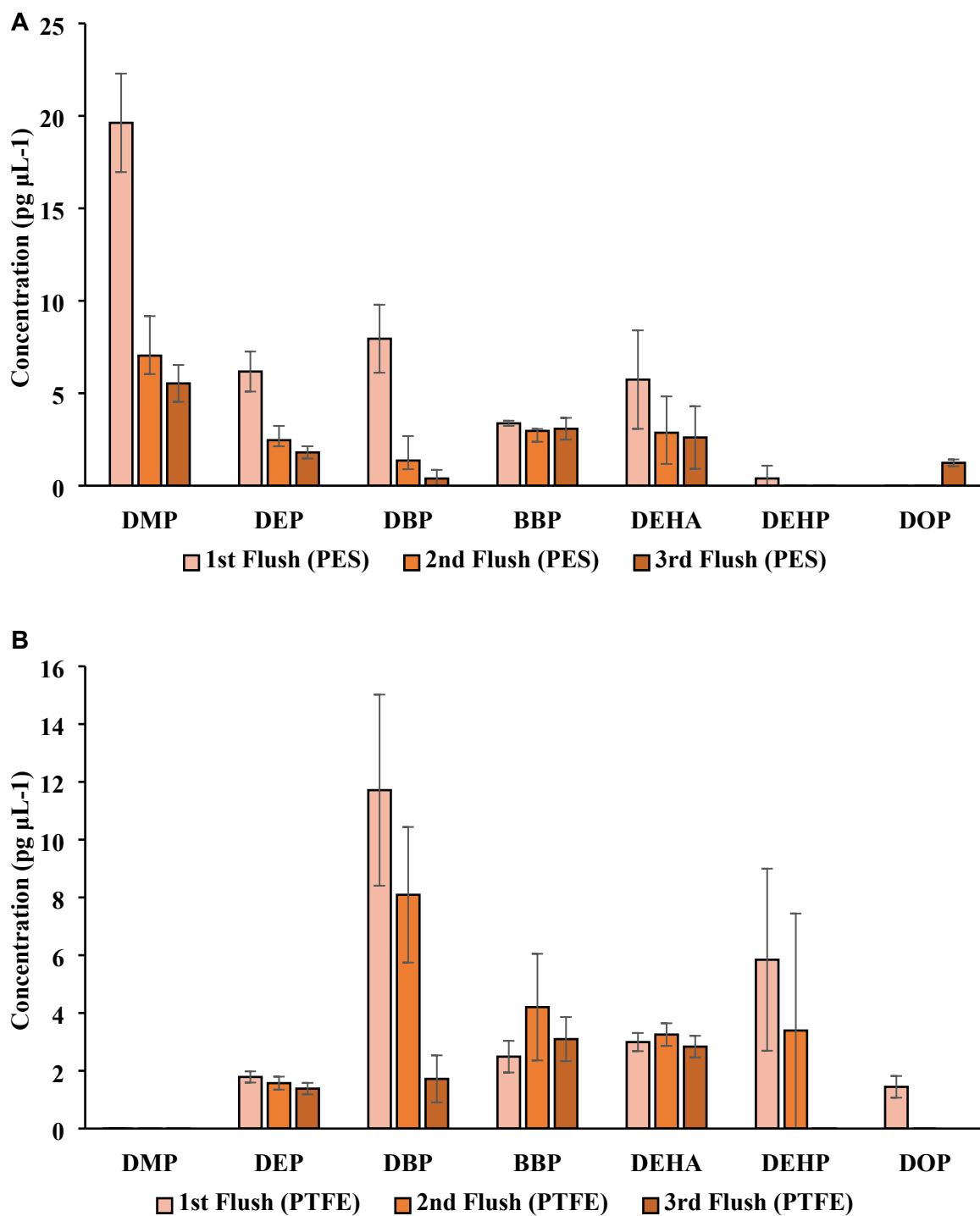
Fig. S2. Results of the PAEs and DEHA leaching test from PES (a) and PTFE (b) syringe filters. Concentrations (pg μL^{-1}) for each analyte are blank-corrected. Standard deviation bars correspond to the concentrations of analytes across five filter replicates. Only DMP in PES (first and second flush), and DBP in PTFE (first flush) were observed above the method LOD. Standard deviation bars correspond to variations within five syringe filters (replicates).
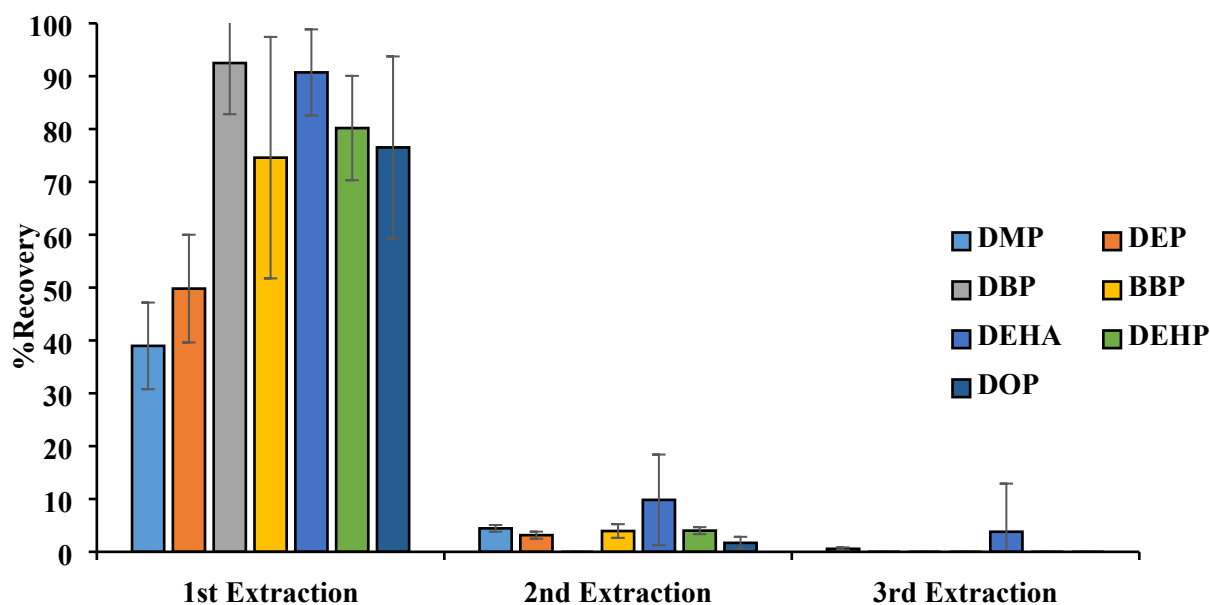
Fig. S3. Percent recovery of PAEs and DEHA from quartz fibre filters after 1st, 2nd and 3rd successive 15-minute ultrasonic agitation steps. Standard deviation bars correspond to the concentrations of target compounds across five analytical replicates.
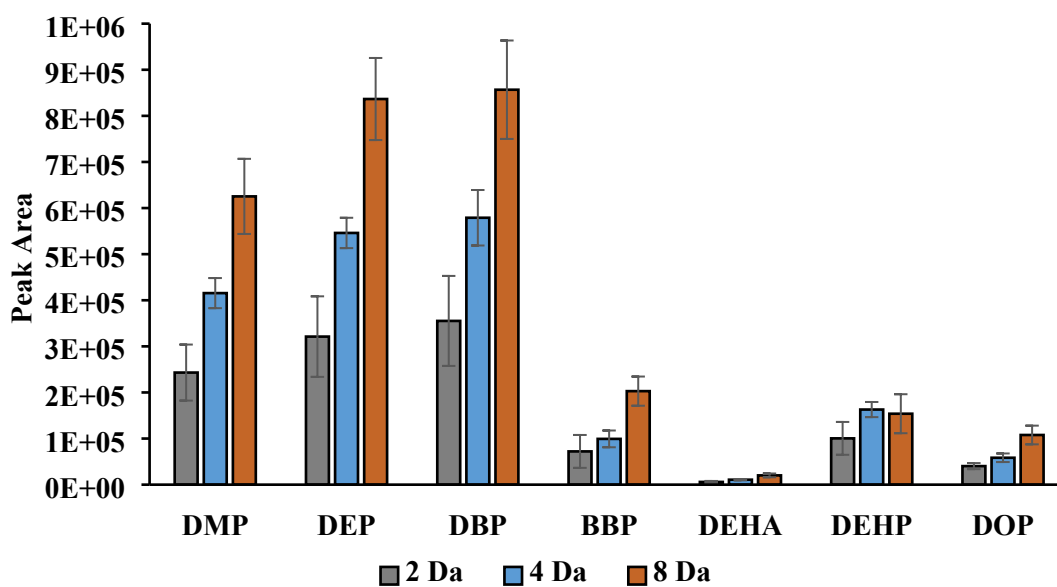

Fig. S4. Effect of increasing the quadrupole isolation window (i.e., 2 Da, 4 Da, and 8 Da) on the peak area of PAEs and DEHA at 11.3 pg μL^{-1}. Standard deviation bars correspond to variations within three replicates.
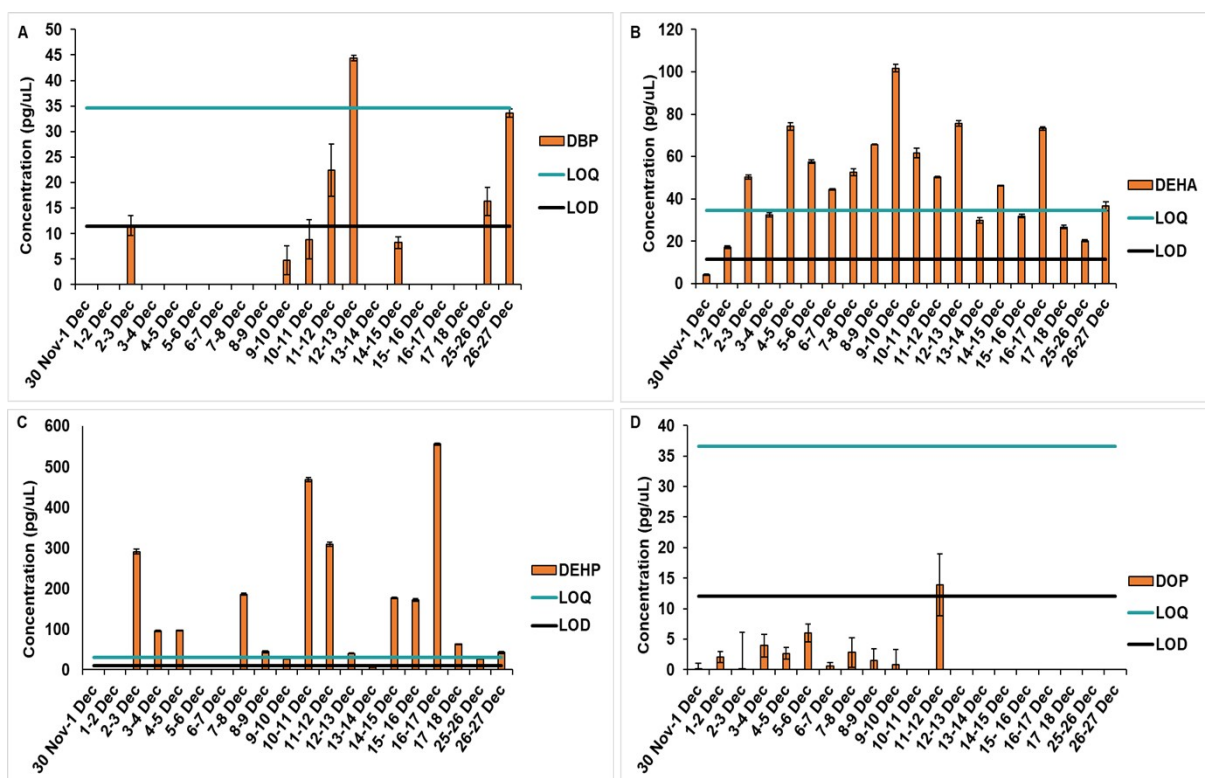
Fig. S5. Concentrations of PAEs and DEHA in PM$_{2.5}$ samples from Curitiba, Brazil in comparison with the LOD (black line) and the LOQ (teal line). Plots for DBP (a), DEHA (b), DEHP(c), and DOP (d) are presented. Standard deviation bars correspond to variations within three replicate sample injections.
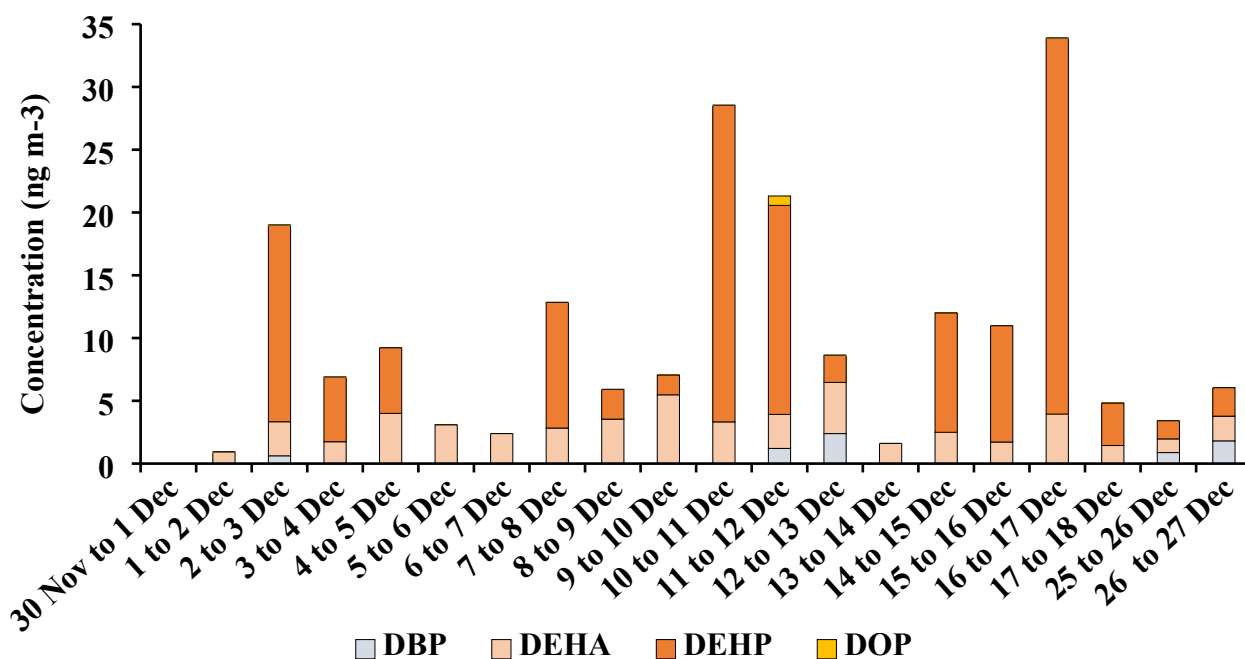

Fig. S6. Distribution of PAEs and DEHA in PM$_{2.5}$ samples collected from 30th November 2020 to 27th December 2020 in Curitiba, Brazil.
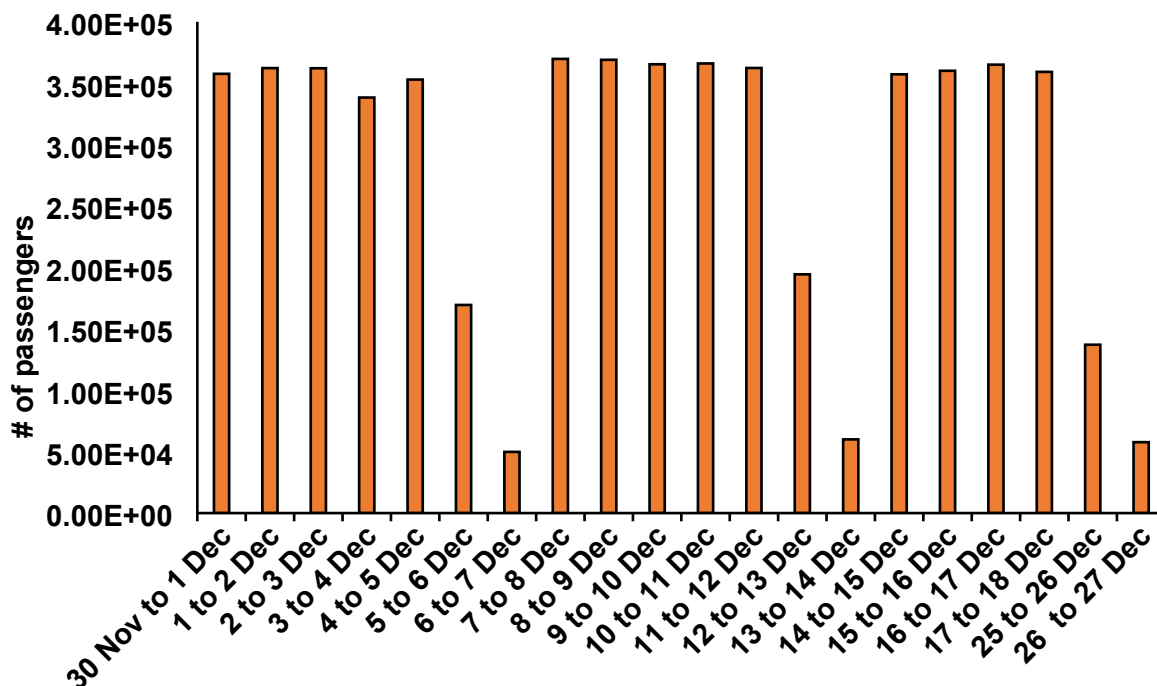
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Fig. S7. Number (#) of public transport passengers (i.e., buses) in Curitiba, Brazil in December 2020[4]
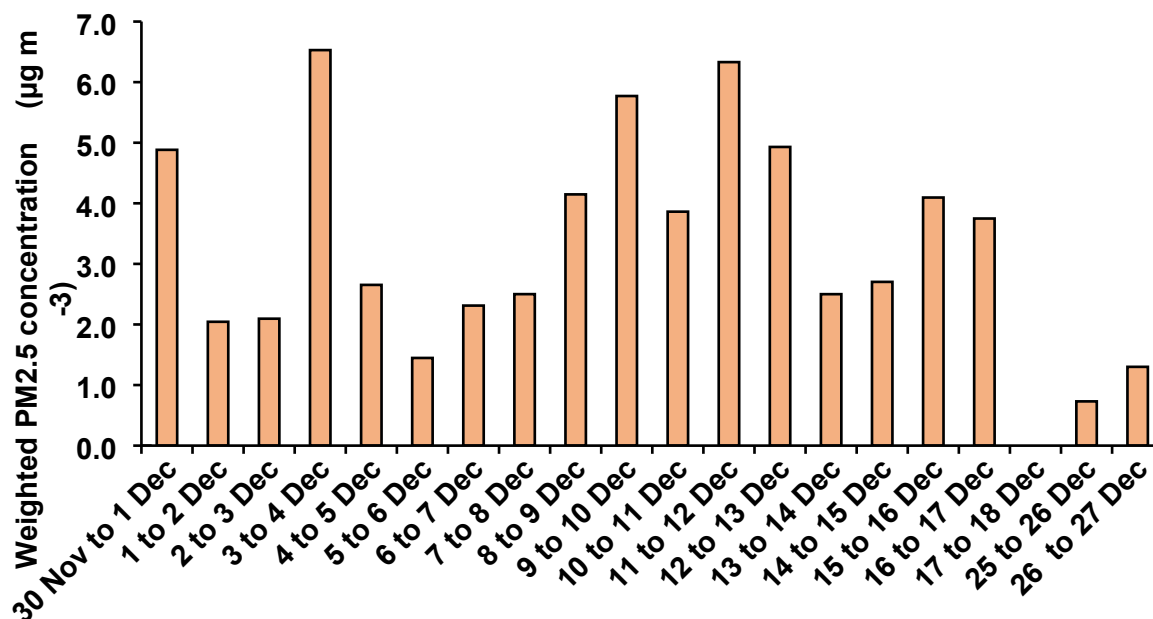

Fig. S8. PM$_{2.5}$ Concentrations in samples collected from Curitiba, Brazil on 30th November to 27th December, 2020.
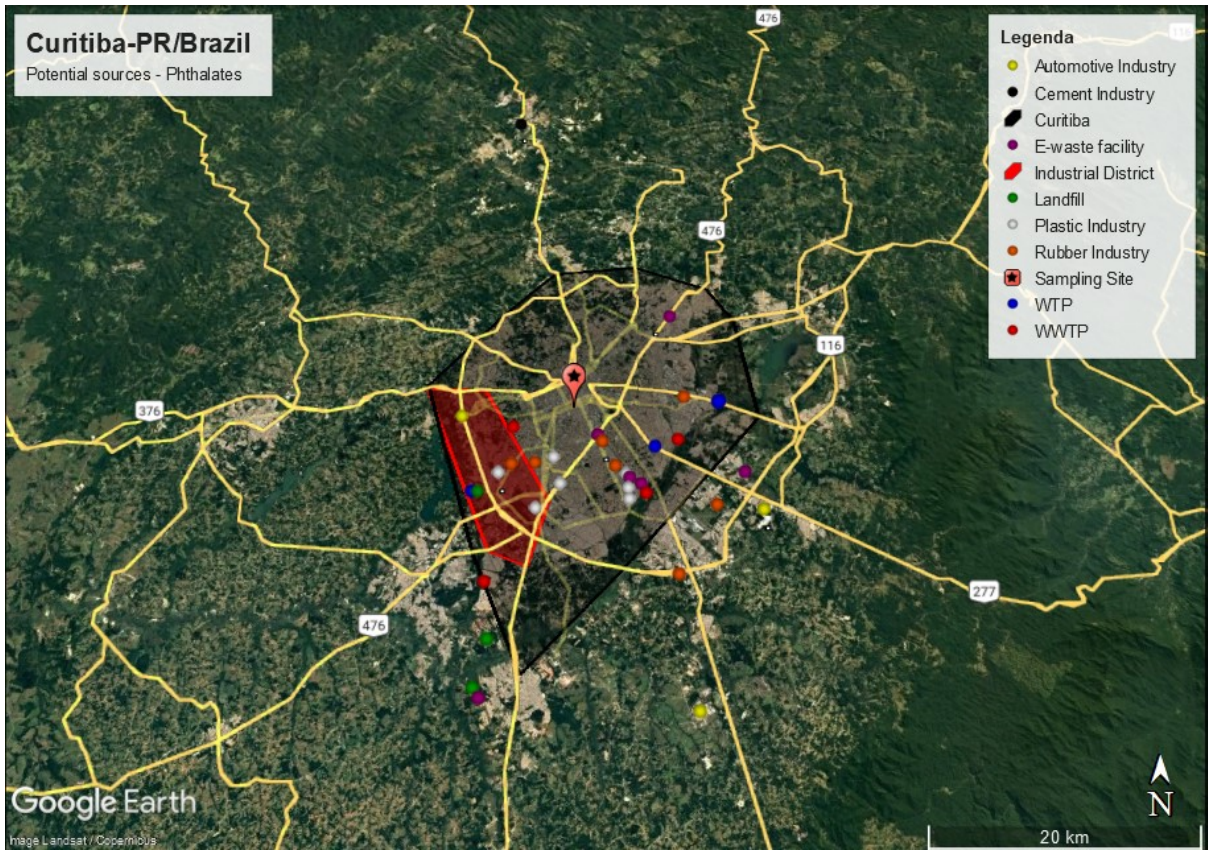
Fig. S9. Location of the sampling site in Curitiba, Brazil and potential sources of PAEs and DEHA in PM$_{2.5}$ (map created using Google Earth)

Table S1. Sampling period, air volume, and PAEs and DEHA concentrations in analysed PM$_{2.5}$ samples from Curitiba, Brazil. Each sample was collected over 24 h periods from 30th November (9:00 AM BRT) to 27th December.

Sample Name	Sampling period				Concentration (ng m^{-3})			
	Start		Finish		DBP	DEHA	DEHP	DOP
	Date	Time	Date	Time				
S-1	30 Nov 2020	9:40	1 Dec 2020	8:41	-	-	-	-
S-2	1 Dec 2020	8:50	2 Dec 2020	8:40	-	0.92	-	-
S-3	2 Dec 2020	8:58	3 Dec 2020	9:20	0.62	2.71	15.67	-
S-4	3 Dec 2020	9:28	4 Dec 2020	9:03	-	1.74	5.15	-
S-5	4 Dec 2020	9:10	5 Dec 2020	9:55	-	4.00	5.23	-
S-6	5 Dec 2020	10:03	6 Dec 2020	9:05	-	3.10	-	-
S-7	6 Dec 2020	9:15	7 Dec 2020	9:04	-	2.39	-	-
S-8	7 Dec 2020	9:17	8 Dec 2020	9:06	-	2.83	10.01	-
S-9	8 Dec 2020	9:18	9 Dec 2020	8:10	-	3.54	2.37	-
S-10	9 Dec 2020	8:17	10 Dec 2020	8:36	-	5.48	1.58	-
S-11	10 Dec 2020	8:44	11 Dec 2020	9:13	-	3.69	25.22	-
S-12	11 Dec 2020	9:21	12 Dec 2020	9:00	1.21	3.07	16.65	0.75
S-13	12 Dec 2020	9:07	13 Dec 2020	9:01	2.39	4.44	2.17	-
S-14	13 Dec 2020	9:18	14 Dec 2020	8:58	-	1.97	-	-
S-15	14 Dec 2020	9:04	15 Dec 2020	8:57	0.45	2.86	9.52	-
S-16	15 Dec 2020	9:02	16 Dec 2020	9:10	-	2.08	9.27	-
S-17	16 Dec 2020	9:16	17 Dec 2020	8:16	-	4.31	29.95	-
S-18	17 Dec 2020	8:22	18 Dec 2020	9:27	-	1.81	3.39	-
S-19	25 Dec 2020	10:04	26 Dec 2020	9:16	-	1.46	1.45	-
S-20	26 Dec 2020	9:25	27 Dec 2020	8:47	-	2.33	2.28	-

Table S2. Comparison of PAEs and DEHA concentration ranges in PM from Curitiba and that of average concentrations reported in the literature.

Study	Sample Type	Study Site	Sampling Period	DBP (ng/m³)	DEHA (ng/m³)	DEHP (ng/m³)	DOP (ng/m³)
This study	$PM_{2.5}$	Curitiba, Brazil	November 2020 to December 2020	0.45-2.39	0.92-5.48	1.45-29.95	0.75
Toro-Heredia et al. (2021)[5]	$PM_{2.5}$	Guayama, Puerto Rico	August-December 2013	23.46	-	59.67	-
Quintana-Belmares et al. (2018)[6]	$PM_{2.5}$	Mexico City, Mexico	November 2012 - May 2013	0.13± 0.15	-	1.07± 0.91	-
Simoneit et al. (2005)[7]	PM_{10}	Santiago, Chile	November 2000	-	-	880	-
Cautreels et al. (1977)[8]		La Paz, Bolivia	-	27.5±8.5	-	18.5±1.5	-
Sánchez-Piñero et al. (2022)[9]	$PM_{2.5}$	Vigo City, Spain	2017	-	-	1.99	-
Patnana et al. (2022)[10]	$PM_{2.5}$	Mohali, India	April 2019 - February 2020	9.16±3.76	1.38±0.71	17.94± 4.35	-
Huang et al. (2022)[11]	$PM_{2.5}$	Guangzhuo, China	June 2017-May 2018	41.85	1.81	76.68	0.52

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