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Levels, distribution profiles and risk assessment of chlorinated organophosphate esters in car and road dust from Basrah, Iraq

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ABSTRACT

The occurrence, concentrations, and distribution profiles of chlorinated organophosphate esters (Cl-OPEs) were investigated in seventy-one car and road dust samples collected from Basrah, southern Iraq. In addition, estimated daily intakes (EDIs) via dust ingestion were assessed for toddlers, regular adults, and taxi drivers. In car dust samples, the concentrations of Σ_3Cl-OPEs ranged from 4120 to 73200 ng/g (median 11700 ng/g) with tris (1,3-dichloroisopropyl) phosphate (TDCIPP) the predominant compound. In road dust samples, the concentrations of Σ_3Cl-OPEs ranged from 269 to 3400 ng/g (median 373 ng/g) and 114–526 ng/g (median 222 ng/g) in urban and rural areas, respectively, with tris (2-chloroisopropyl) phosphate (TCIPP), predominant. Concentrations of Cl-OPEs in urban road dust are significantly higher ($P < 0.05$) than those in rural road dust, suggesting commercial and industrial activity, population density, and heavy traffic may influence the concentrations. The different compositional profiles of Cl-OPEs in car and road dust may be attributed to the physicochemical properties of Cl-OPEs and the pathways through which they can be released into indoor and outdoor environments. EDI values of Cl-OPEs for the Iraqi population via car dust ingestion were in the order: toddlers > taxi drivers > regular adults, exceeding those via road dust by factors of 27 and 40 from urban and rural dust, respectively. For people who work as taxi drivers, EDIs were seven times higher than those of regular adults, implying that people - such as professional drivers - who spend a substantial amount of time in their vehicles may be exposed to hazardous levels of Cl-OPEs. Despite the study showing that the EDIs through dust ingestion for the three population groups were well below the reference dose (RfD) levels, further studies are recommended to assess other pathways, such as inhalation, dietary sources, and dermal absorption.

1. Introduction

Organophosphate esters (OPEs) are a class of manufactured chemicals whose use has increased rapidly due to the bans and restrictions of legacy flame retardants (i.e., polybrominated diphenyl ethers and hexabromocyclododecane). They are generally classified into halogenated (Chlorinated; Cl-OPEs) and non-halogenated compounds. Cl-OPEs are a group of alkyl phosphates that contain both phosphorus and chlorine and are primarily used as flame retardants. The principal Cl-OPEs are tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP) and tris(1,3-dichloroisopropyl) phosphate (TDCIPP) [1,2]. Cl-OPEs are commonly employed in flexible and rigid polyurethane foams, rubber, and polyester resins, that are mainly applied in various products such as building materials, furniture, electronics, and vehicle parts [3,4]. In 2011, the global production of Cl-OPEs was estimated to be180,000 metric tonnes, which was increased by 2017 to about 220,000 metric tonnes [5].

Since they are not chemically bound to the original substance, OPEs can release from the products into the environment via volatilisation, abrasion, and direct contact [6,7]. As a result of these processes and their expanding use, Cl-OPEs have been detected in various environmental and biological samples such as air [8,9], indoor and outdoor dust [10–14], water [15], sediments [16], and soil [17]. Furthermore, the presence of these compounds has been

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identified in the Arctic, indicating their potential for long-range transport [8]. Additionally, biomonitoring research has revealed the existence of Cl-OPEs in various human biological samples, including urine [18], blood [19], and hair [20], indicating their bioaccumulation [21].

Due to their potential negative health effects, human exposure to Cl-OPEs has raised wide concern. Numerous studies have shown various toxicological properties of Cl-OPEs, such as mutagenic, carcinogenic and neurotoxic, and they can accumulate in liver and testis, thereby inducing tumours [22–24]. Human exposure to such chemicals can take place via ingestion, inhalation, and dermal contact. Among these human exposure pathways, dust ingestion has been identified as a major route [24,25]. Investigations into a range of OPEs in dust samples collected from indoor and outdoor environments have identified Cl-OPEs as the dominant chemicals [3,14,26]. For indoor dust, concentrations of Cl-OPEs in car dust exceeded those detected in other microenvironments, such as offices, homes, and schools [14,27–29]. According to one US study [30], concentrations of some organic pollutants, including polybrominated diphenyl ethers (PBDEs) in cars were five to ten times higher than those found in offices and homes. The same study announced that exposure to those pollutants for a 90-min drive was equal to 8 h of office work. It has recently been reported that the physical and chemical characteristics and environmental behaviours of PBDEs and OPEs, are similar [31]. Furthermore, homes and offices are typically designed and maintained at much more moderate and stable temperatures, while cars have windows surrounding the interior, resulting in much higher solar exposure, leading to higher in-vehicle temperatures on occasions with concomitant elevated emissions of more volatile chemicals [30]. This implies that people who spend a large amount of time in their vehicles, such as professional drivers, may be exposed to elevated levels of Cl-OPEs emitted from vehicle components [14].

With respect to outdoor dust, previous studies have reported considerable concentrations of Cl-OPEs in the outdoor environment, such as road and street dust [32]. It has been concluded that vehicles play a significant role in the distribution of Cl-OPEs in the outdoor environment, and that their concentrations in road dust are directly related to traffic density [33]. Out of 14 OPEs, the three Cl-OPEs in road dust were found to be predominant, with their concentrations significantly higher in urban than rural roads [26,34,35]. Of note, road dust significantly contributes to the transportation of pollutants from air to other environmental materials such as groundwater and surface water and may enter the atmosphere by wind or volatilisation [3,36].

To the best of our knowledge, no information is available on the production and use of Cl-OPEs in Iraq. However, our previous study, which was the first report on OPEs in house dust from Iraq [37], revealed elevated concentrations of OPEs with Cl-OPEs the most abundant compounds. In addition, another study that estimated daily intakes (EDIs) of TCIPP via dermal absorptions reported that EDI values for taxi drivers exceeded those for regular adults and toddlers by factors of 6.8 and 1.7, respectively [38]. Nevertheless, there is a large gap in our knowledge about human exposure via inadvertent car and road dust ingestion. Given the extensive use of Cl-OPEs in automobiles, it is anticipated that there will be significant consumption of these chemicals in densely populated urban areas with heavy traffic. Therefore, the main aims of the current study were: (1) to evaluate the levels and distribution profiles of Cl-OPEs in car dust and road dust from urban and rural areas in Basrah, Iraq; (2) to estimate daily intake of Cl-OPEs via car and outdoor dust ingestion to assess health risks associated with Cl-OPEs; (3) to compare these estimates with those previously reported from homes to estimate total daily intake of Cl-OPEs; and (4) to compare the levels and patterns of Cl-OPEs in Iraqi dust with those from other counties.

2. Materials and methods

2.1. Chemicals

Standards of our target Cl-OPEs (tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), and tris(1,3-dichloroisopropyl) phosphate (TDCIPP) (Table S1) and internal standard (d_{12}-TCEP) were purchased from Wellington laboratories (Canada). Triamyl phosphate (TAP) and indoor dust SRM 2585 were obtained from TCI Europe (Belgium) and US National Institute of Standards and Technology (USA), respectively. All solvents (HPLC grade), were purchased from Fisher Scientific (UK).

2.2. Sample collection and analysis method

In total, 71 indoor (cars) and outdoor (roads from urban and rural areas) dust samples were collected from Basrah (Basra) between October 2021 and July 2022. Basrah is an industrial city and the second-largest province in Iraq, considered the commercial capital. Car dust samples (n = 24) were collected using a vacuum cleaner (MODEX VC1040-100W) with a nylon sampling sock according to a previously reported standard method [10]. Additionally, from 23 urban and 24 rural areas, dust samples were collected from roads using a brush (Fig. 1). After sampling, socks were closed with twist ties, placed in plastic bags, and stored at −20 °C. The average age of cars was 8 years, ranging between 2 and 27 years. To the best of our knowledge, at the time of sampling, all cars in Iraq were imported from abroad. According to the country of manufacture, cars were classified into four groups: Chinese (n = 5), Japanese (n = 5), Korean (n = 10), and American (n = 4).

Prior to analysis, dust samples were passed through a 250 μm mesh testing sieve [39]. Information regarding sample extraction, and sample purification were according to the methods previously described [38]. Briefly, in a 10 mL glass centrifuge tube, an accurately weighed aliquot of dust sample (typically 75 mg) was spiked with 50 ng of d_{12}-TCEP as an internal standard. Dust samples were extracted with 2 mL of n-hexane: acetone (3:1 v/v), (vortexed for 2 min, sonicated for 5 min, and centrifuged at 3500 rev/min for 5 min). This extraction process was repeated three times, and after each cycle, the supernatant was separated. The combined extracts were evaporated gently to incipient dryness and resolubilized in 1 mL of n-hexane. The sample extract was purified using the solid-phase extraction (SPE) technique. The extract was fractionated into two fractions using Florisil cartridges. Fraction 1 was achieved by eluting with 8 mL of n-hexane with fraction 2 (containing our target compounds) eluted with 10 mL of ethyl acetate. Fraction 2 was evaporated gently to incipient dryness and resolubilized in 100 μL of isooctane containing TAP as a recovery determination standard. Identification and quantification of Cl-OPEs were conducted at the University of Birmingham, UK, using a gas chromatograph (GC; Trace 1310 Gas Chromatograph) connected to an ISQ quadruple mass spectrometer (MS), both provided by Thermo Fisher Scientific, USA. The MS was operated in EI-selected ion monitoring (SIM) mode, with two characteristic ions monitored for each analyte [40]. Helium was employed at a flow rate of 1.5 mL min-1 as a carrier gas. Figs. S1–S4 show the GC-MS instrumental methods.

2.3. Quality assurance and quality control

For every set of 12 dust samples, an aliquot of SRM 2585 was subjected to analysis. In total, six replicates of SRM 2585 were examined. The results obtained for SRM 2585 were consistent with several values reported in recent literature [13,37,41–44]. Table S2 lists Cl-OPE concentrations detected in SRM-2585 in this study

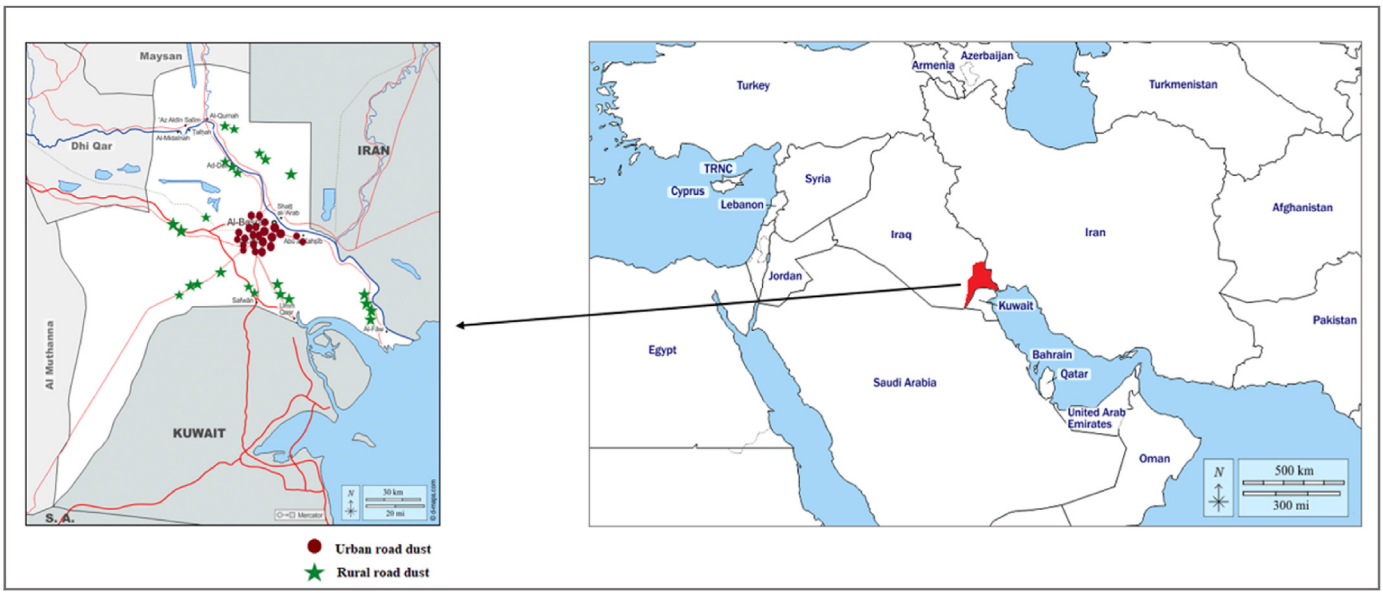

Fig. 1. Location of the study area and dust sampling sites.

compared with certified values and several recently published values. Method blanks (n = 11) and field blanks (n = 6) were conducted. Very low concentrations of TCEP and TCIPP were detected in the blanks. When the concentration of the target compounds ranged from 5.0 % to 11 % of the minimum concentration observed in that batch, the results were adjusted for blanks by subtracting the mean blank values from the raw data of Cl-OPEs detected in the dust samples. The limit of detection (LOD) and limit of quantification (LOQ) were measured as the amount of a target compound that produced signal-to-noise ratios of 3 and 10, respectively. When a target compound was detected in a blank sample, the LOQ was replaced with the Minimum Reported Value (MRV) for that particular compound. The MRV is calculated as the average concentration plus three times the standard deviation of the concentrations observed in the blank sample. Table S3 shows the limits of detection, limits of quantification, and MRV values detected in this study. The mean recoveries of the internal standard (d_{12}-TCEP) in dust samples were 78.5 ± 19 %.

2.4. Estimated daily intakes and health risk assessment

The estimated daily intake (EDI) of Cl-OPEs through dust ingestion was calculated for various population groups based on two recently revised dust ingestion exposure scenarios provided by the United States Environmental Protection Agency (USEPA) [45]. The average "typical" exposure scenario was calculated using the average dust ingestion rate (20 and 50 mg/day for adults and toddlers, respectively) and the median concentrations of the pollutants detected in dust. The high-exposure scenario was estimated using a high dust ingestion rate (60 and 100 mg/day for adults and toddlers, respectively) and the 95th percentile of the concentration detected in dust [43,45]. For the Iraqi population, there are no available data on time-activity patterns and body weight. Thus, our exposure estimates are based pro-rata on typical activity patterns reported previously (the fraction of time spent in a car = 0.041 for regular adults and toddlers and = 0.279 for taxi-drivers, and the fraction of time spent outdoors = 0.047) assuming 100 % absorption of intake [27,45,46]. To calculate the daily exposure to pollutants via dust ingestion:

$$EDI = (C \times IR \times FT)/BW$$

Where EDI is the estimated daily intake via dust ingestion.

C is the concentration of contaminants in dust (ng/g).
IR is the dust ingestion rate (g/day).
FT is the fraction of time spent at the microenvironment (unitless)
BW is the body weight (80 kg for adults and 13.8 kg for toddlers) [45].

2.5. Statistical analysis

IBM SPSS statistics software (V. 20). and Microsoft Excel 2013 were applied. In order to assess the quantitative levels and pattern distribution of Cl-OPEs in dust samples, the mean, median, maximum, and minimum were considered. Due to the skewed nature of the data, all data were log-transformed prior to analysis. The Pearson correlation method was used to look at potential correlations between different factors. Where p values were less than 0.05, results were considered significant.

3. Results and discussion

3.1. Levels and distribution profiles of Cl-OPEs in dust samples

With the exception of TDCIPP in road dust from rural areas, which had a detection frequency of 88 %, the detection frequency of Cl-OPEs in car dust and outdoor dust samples was 100 %. In car dust, TDCIPP was predominant, making an average percentage contribution to Σ_3Cl-OPEs of 45 %, followed by 29 % and 25 % for TCIPP and TCEP, respectively. In road dust, TCIPP was most abundant, with mean contributions of 45 % Σ_3Cl-OPEs, and 57 % followed by TDCIPP of 42 % and 25 %, then TCEP of 13 %, and 19 % in urban and rural areas, respectively. Fig. 2 shows the average percentage contributions to Σ_3Cl-OPEs of individual Cl-OPEs in car dust and road dust from both urban and rural areas.

Concentrations of our target compounds in car and road dust samples analysed in this study are summarised in Table 1, with

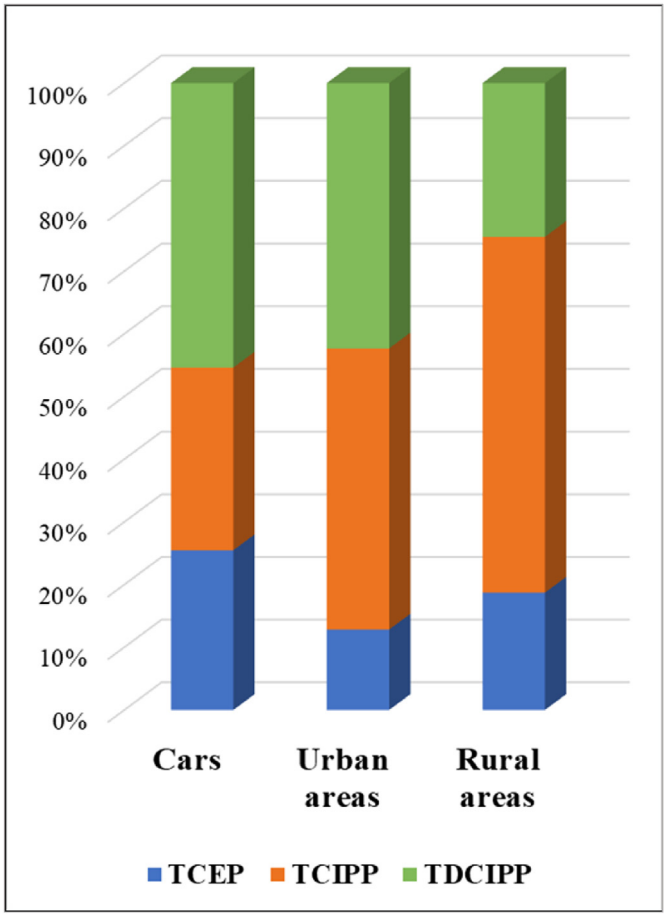

Fig. 2. Average percentage contributions of TCEP, TCIPP, and TCDIPP to Σ_3Cl-OPEs in dust from cars and road dust from urban and rural locations.

concentrations in individual samples provided in Table S4. Concentrations of Σ_3Cl-OPEs ranged from 4120 to 73200 ng/g (average 17720 ng/g), 269–3400 ng/g (average 708 ng/g), and 114–526 ng/g (average 255 ng/g) in car, urban road and rural road dust, respectively. In general, our results revealed that the average concentrations of TCEP, TCIPP, TDCIPP, and Σ_3Cl-OPEs in indoor (car) dust were 50, 16, 27, and 25-fold higher than those in urban road dust and 94, 36, 128, and 69-fold higher than those in rural road dust.

It has been reported that the three Cl-OPEs represent the most commonly used organophosphate flame-retardants in rigid and flexible polyurethane materials, which are extensively applied in vehicles [1]. Moreover, due to its comparatively high cost, TDCIPP is only employed in applications needing a higher degree of flame retardancy, such as textiles in vehicle seating [47,48], which may explain the high average percentage contributions of TDCIPP in car dust. In addition, as semi volatile organic compounds (SVOCs), Cl-OPEs emitted from the interior of a vehicle have the potential to be concentrated due to the limited space. Furthermore, high temperatures in warmer weather, coupled with reduced ventilation, will increase the concentrations of SVOCs in such limited-space environments [29]. Moreover, as seen in Table S1, TCEP has a higher vapour pressure than TCIPP and TDCIPP, suggesting that it may volatilise more easily from treated materials, and is more susceptible to thermal degradation and photolysis outdoors [49]. This may explain the high car/road dust ratio for TCEP. On the other hand, due to its low vapour pressure, TDCIPP may be predominantly emitted from car interior surfaces through abrasion of fabrics or direct contact with dust of fabrics and other TDCIPP-containing material [50]. Our results are consistent with those from Saudi Arabia [29], the Netherlands [47], South Africa [51], Brazil [48], and Colombia [46], in which TDCIPP was the predominant compound in car dust samples.

Table 1
Statistical summary of Cl-OPE concentrations (ng/g) in car dust and road dust from urban and rural locations.

Dust Samples	Parameter	TCEP	TCIPP	TDCIPP	∑Cl-OPEs
Car	Mean	4520	5160	8040	17700
	Median	2520	2700	3510	11700
	Min	653	784	696	4120
	Max	28100	29500	68100	73200
	STD	5740	6700	15200	17500
Urban road dust	Mean	90.7	317	299	708
	Median	65.4	183	109	373
	Min	36.1	126	69.1	269
	Max	441	1620	3130	3400
	STD	84.1	386	651	804
Rural road dust	Mean	47.8	145	62.7	255
	Median	41.0	123	50.9	222
	Min	15.4	61.5	<0.81	114
	Max	165	341	212	526
	STD	34.5	77.7	50.3	116

In road dust samples, paired *t*-test results disclosed that concentrations of Cl-OPEs in urban areas were significantly higher ($p < 0.005$) than those in rural areas. As SVOCs, Cl-OPEs can undergo long-range atmospheric transport from the source via atmospheric particles or in the gaseous phase and can be deposited directly in terrestrial ecosystems [34]. The highest concentrations of OPE emissions were detected at intersections and city centre sites, where traffic is most congested and vehicles frequently stop and start. In comparison, emissions in village and rural areas were notably lower [52]. In addition, our previous study that investigated OPEs in front yard samples revealed that OPE concentrations in dust from front yards are significantly higher when these are used for car parking [37]. This implies that vehicles are significant sources of Cl-OPEs. Furthermore, other studies have indicated that the abundance of brominated flame retardants (BFRs) in road dust declined as traffic density decreased [53]. Cl-OPEs have the same environmental behaviour as BFRs [31]. Our findings agree with the findings of previous studies [26,33,52,54], in which TCIPP was the most abundant Cl-OPE in road and street dust.

With the exception of TCEP and TCIPP in rural areas ($p = 0.013$, $r = 0.512$), no significant correlation was found between our target pollutants from different environments and between individual chemicals from the same environment. This indicates different emission sources of Cl-OPEs in indoor and outdoor environments.

3.2. Comparison of Cl-OPEs in car dust based on the country of manufacture

Although based on a small dataset of cars (Chinese (n = 5), Japanese (n = 5) Korean (n = 10) and American (n = 4)), we compare here Cl-OPE concentrations in car dust based on the country of manufacture. Our results reveal dust from American cars to contain the highest concentrations of Σ_3Cl-OPEs, with mean and median levels of 27000 and 15300 ng/g respectively, while Korean cars were the least contaminated with Σ_3Cl-OPEs, with mean and median concentrations in dust from such cars being 12000 and 8450 ng/g, respectively. Concentrations of Σ_3Cl-OPEs in dust from Chinese and Japanese cars were not dissimilar, with mean and median concentrations of 17200 and 13400 ng/g for Chinese cars and 22200 and 13400 ng/g for Japanese cars respectively. However, different distribution profiles appeared depending on the country of manufacture. For example, as shown in Fig. 3, the highest

concentrations of TCEP were found in Korean cars, contributing 51 % Σ_3Cl-OPEs, while the lowest TCEP concentrations occurred in dust from American cars at 9 % Σ_3Cl-OPEs. Descriptive statistics of the concentrations of Cl-OPEs in car dust depending on the country of manufacture are provided in Table S5.

3.3. Comparison of Cl-OPE levels with other previous studies

Based on information available, there is a lack of prior studies documenting the levels of Cl-OPEs in car dust and road dust in Iraq, and minimal data exists on these pollutants in the Middle East region [27,29,38,55]. Our results revealed that the median concentration of Σ_3Cl-OPEs in car dust from Basrah, Iraq, exceeded generally those reported for car dust from: Saudi Arabia [29], Egypt [27], Pakistan [55], Japan [56], and Greece [48] by factors of 1.6, 18, 43, 1.6, and 1.7, respectively. Conversely, the median Σ_3Cl-OPEs concentration in Iraqi car dust samples was lower than those reported for South Africa [51], the Netherlands [47], Australia [10], Brazil [48], Kuwait [55], the UK [28], and Colombia [46]. Table S6 lists our data for car dust in the context of the available international database, and Fig. 4 illustrates comparisons of the median levels of those studies.

For road dust, Table 2 compares our results with the existing literature. In general, the median concentration of Σ_3Cl-OPEs in urban road dust from Basrah, Iraq, exceeded those from Chengdu [26], Nanjing [54] and Chongqing [52], in China, and in Patna (India) [58] by factors ranging between 4 and 10. However, they were lower than those from New York, USA [11] and Beijing, China [33] by factors of 1.5 and 1.9, respectively. This implies that big cities with traffic congestion are much more contaminated with Cl-OPEs compared with smaller cities, suggesting cars and human activities are the main sources of Cl-OPEs.

3.4. Estimated daily intakes of Cl-OPEs throw dust ingestion

Table 3 lists estimated daily intakes (EDIs) of Cl-OPEs via dust ingestion for regular adults, taxi drivers, and toddlers in the Iraqi population. These EDIs are based on both mean and high dust ingestion rates, using median and high (95th percentile) Cl-OPE concentrations in car and road dust samples. The results revealed that the EDI values of Cl-OPEs for the Iraqi population via car dust ingestion were in the order: toddlers > taxi drivers > regular adults. Under the assumption of mean dust ingestion rates and median concentrations in car dust, the EDIs of Σ_3Cl-OPEs were found to be 0.831, 0.120, and 1.37 ng/kg bw/day for taxi drivers, regular adults, and toddlers, respectively. Under the assumption of high dust ingestion rates and median concentrations, the EDIs of Σ_3Cl-OPEs increased to 3.50, 0.514, and 7.45 ng/kg bw/day for taxi drivers, regular adults, and toddlers, respectively. Assuming the high dust intake and 95th percentile Cl-OPE concentrations (representing worst-case scenarios), the EDIs for taxi drivers, regular adults, and toddlers were found to be 10.5, 1.54, and 14.9 ng/kg bw/day.

For urban and rural road dust, worst-case EDIs of Σ_3Cl-OPEs were 0.089 and 0.017 for adults and 0.834 and 0.162 ng/kg bw/day for toddlers, respectively. A large number of recent studies have reported that the EDIs of OPEs via indoor dust ingestion exceed significantly those arising from ingestion of outdoor dust [12]. Our results revealed that EDIs of Σ_3Cl-OPEs via car dust ingestion exceed those via ingestion of urban and rural road dust by factors of 27 and 40, respectively. The EDI for adults working as drivers (and assumed to spend 8 h in their vehicles daily) was 7 times higher than for regular adults. This implies that long-term exposure to such compounds may be a source of apprehension for professional drivers (Fig. S5).

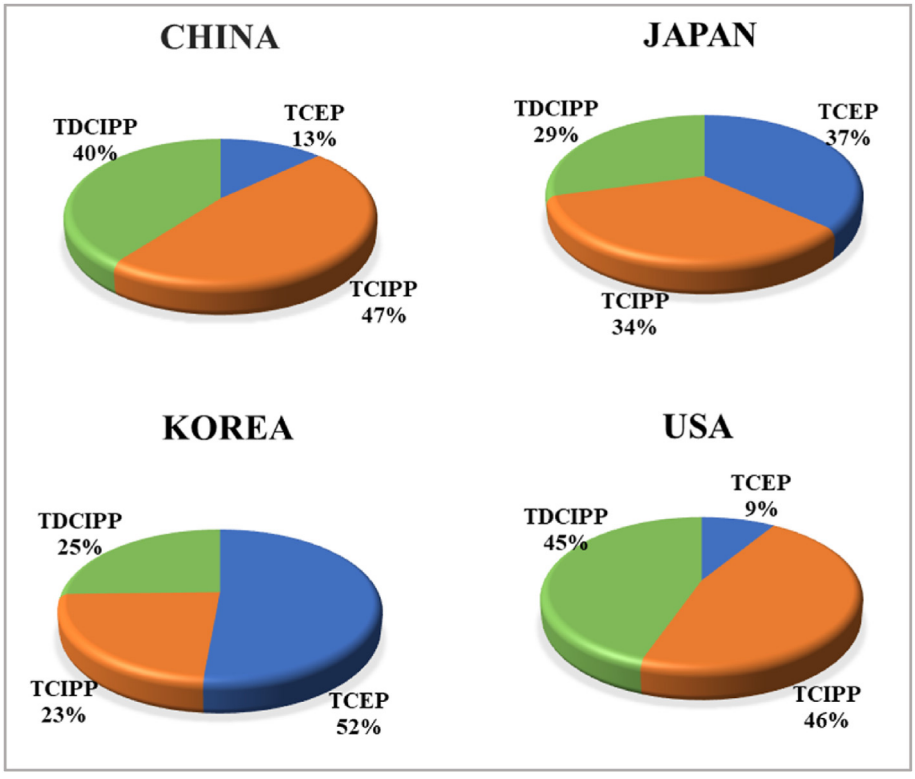

Fig. 3. Distribution profiles of Cl-OPEs in car dust based on the country of manufacture.

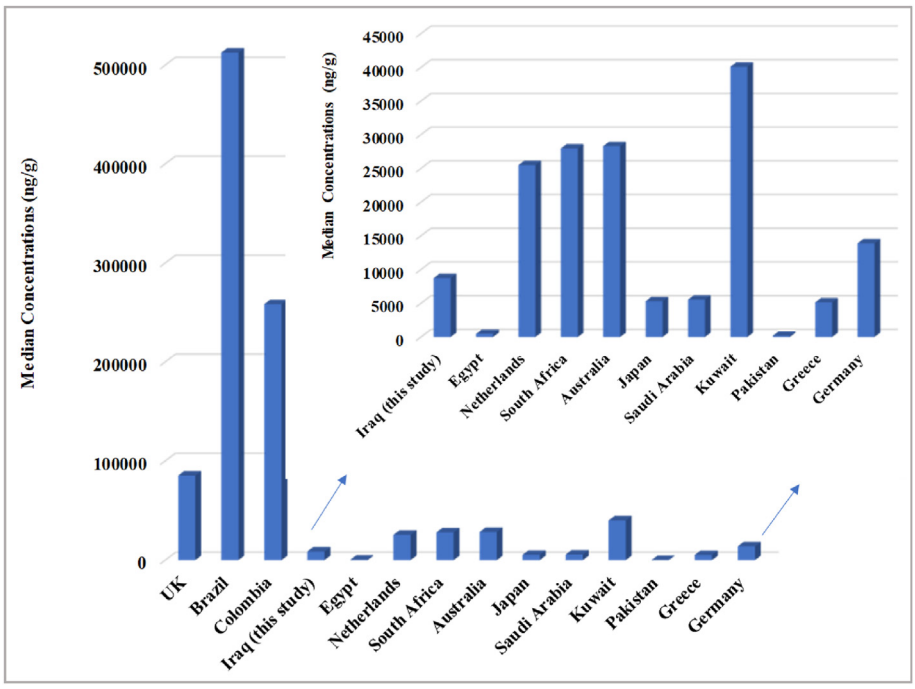

Fig. 4. Comparison of median concentrations of Σ_3Cl-OPEs (ng/g) reported in car dust samples from: UK [28]; Brazil [48]; Colombia [46]; Egypt [27]; Netherlands [47]; South Africa [51]; Australia [10]; Japan [56]; Saudi Arabia [29]; Kuwait [55]; Pakistan [55]; Greece [48]; and Germany [57].

Table 2
Comparison (median concentration (ng/g)) of Cl-OPEs in urban road dust samples from Iraq with those from other countries.

City, Country	Sampling year	No. of samples	TCEP	TCIPP	TDCIPP
Basrah, Iraq (this study)	2022	23	65	183	109
Chengdu, China [26]	2015	8	8.41	21	7.4
Patna, India [58]	2020	16	38.4	34.8	19.8
Nanjing, China [54]	2017	8	6.85	81.99	2.77
New York, USA [11]	2018	5	15.9	262	248
Chongqing, China [52]	2016	37	16.4	26.4	6.59
Beijing, China [33]	2014	65	247	384	30.7

Table 3
Estimates of exposure (ng/kg body weight/day) of adults and toddlers of Cl-OPEs via car and road dust ingestion in Iraq.

OPE	RfD values [59,60]	Car dust						Road dust -Urban area				Road dust -Rural area			
		Taxi drivers		Regular adults		Toddler		Adults		Toddler		Adults		Toddler	
		Median	95th %ile	Median	95th %ile	Median	95th %ile	Median	95th %ile	Median	95th %ile	Median	95th %ile	Median	95th %ile
Mean dust ingestion															
TCEP	22000	0.176	0.711	0.026	0.105	0.375	1.52	0.001	0.002	0.011	0.029	0.000	0.001	0.007	0.019
TCIPP	80000	0.188	1.26	0.028	0.185	0.401	2.68	0.002	0.015	0.031	0.220	0.001	0.004	0.021	0.055
TDCIPP	15000	0.245	2.61	0.036	0.384	0.521	5.56	0.001	0.012	0.019	0.168	0.001	0.001	0.009	0.020
∑Cl-OPEs	–	0.813	3.50	0.120	0.514	1.73	7.45	0.004	0.029	0.064	0.417	0.003	0.006	0.038	0.081
High dust ingestion															
TCEP	22000	0.528	2.13	0.078	0.314	0.750	3.03	0.002	0.006	0.022	0.058	0.001	0.004	0.014	0.037
TCIPP	80000	0.564	3.77	0.083	0.555	0.801	5.36	0.006	0.046	0.062	0.441	0.004	0.011	0.042	0.110
TDCIPP	15000	0.735	7.83	0.108	1.15	1.04	11.12	0.004	0.035	0.037	0.336	0.002	0.004	0.017	0.040
∑Cl-OPEs	–	2.44	10.50	0.359	1.54	3.46	14.90	0.013	0.086	0.127	0.834	0.008	0.017	0.076	0.162

3.5. Total estimated daily intake of Cl-OPEs via dust ingestion

As people spend most of their time in indoor environments (homes, offices, and cars), this has a significant influence on the assessment of exposure to chemicals. In the current study, despite the fact that no data on dust samples from the office was available, we combine previous data on Cl-OPEs in house dust from Basrah [37], with the data of the current study to calculate the total estimated daily intake of Cl-OPEs via dust ingestion. Table S7 shows the total EDI of TCEP, TCIPP and TDCIPP for both adults and toddlers using median and high-end exposure scenarios, and Fig. 5 compares the worst-case (high-end exposure) EDI for Cl-OPEs from Iraqi homes reported by a previous study [37] with those from cars and outdoors from the current study.

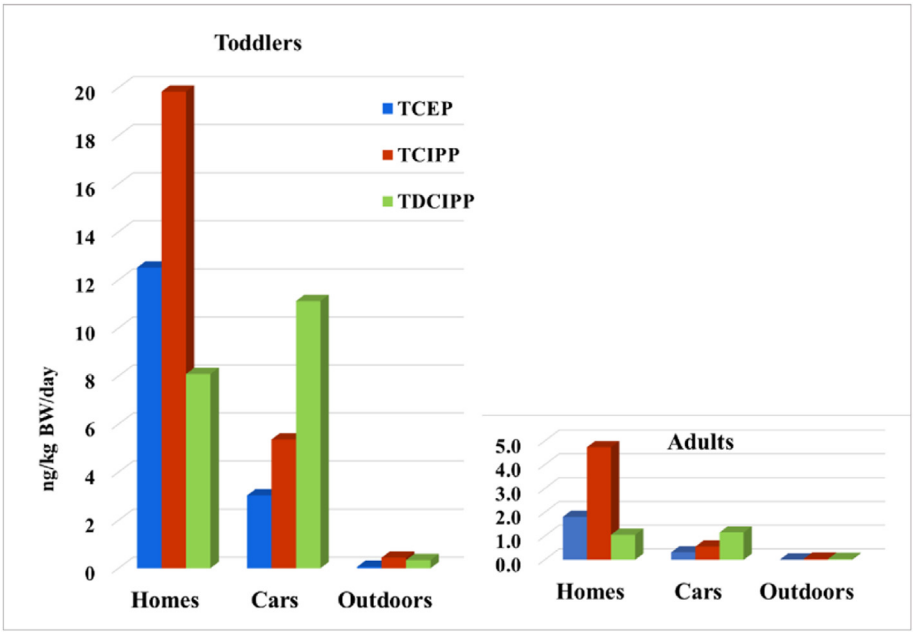

Fig. 5. Estimated daily intakes for adults and toddlers (ng/kg bw/day, under a high-end exposure scenario) for Cl-OPEs via ingestion of dust from Iraqi homes [37] and from car and road dust (outdoors) (current study).

According to the obtained results, the concentrations of Cl-OPEs in car dust were 2–7 times higher than those found in homes. However, under worst-case scenarios and as illustrated in Fig. 5, EDIs of Cl-OPEs via home dust ingestion exceed those via car dust by factors of 6 and 4 for TCEP and 9 and 4 for TCIPP for adults and toddlers, respectively. In contrast, EDIs of TDCIPP via car dust ingestion exceeded those via ingestion of house dust by factors of 1.1 and 1.3 for adults and toddlers, respectively. In general, our results revealed that median exposure to Σ_3Cl-OPEs via ingestion of car and home dust combined was 0.8 and 12.5 ng/day for adults and toddlers, respectively. For individual Cl-OPEs, our results revealed that EDIs of Cl-OPEs via dust ingestion are several orders of magnitude lower than reference dose values [59,60]. However, to obtain a comprehensive health risk assessment, exposure via other pathways such as inhalation, diet, and dermal contact should be considered.

4. Conclusion

For the first time, the investigation of Cl-OPEs in car dust and road dust in Basrah, Iraq, provided insights into their levels, distribution pattern, and estimated daily intakes via dust ingestion. The concentrations of Cl-OPEs in car dust samples were an order of magnitude higher than those from road dust, with TDCIPP being the most abundant in cars and TCIPP being the most abundant in roads. Our results revealed that the country of manufacture may exert an influence on concentrations of Cl-OPEs in car dust, and further investigation of this is recommended. Generally, the concentrations of Cl-OPEs in car dust samples from Iraq were either comparable to or less than those reported in other regions, however, they were higher than those observed in dust samples from Egypt and Pakistan. Considerable concentrations of Cl-OPEs appeared in road dust from both urban and rural areas. Concentrations of Cl-OPEs in urban road dust exceeded significantly those in rural road dust, suggesting that vehicles and human activities may represent important sources to the outdoor environment. Although the estimated exposure levels to our target Cl-OPEs for the Iraqi population through dust ingestion are significantly lower than health-based limited values, this study does not consider exposures via other pathways. Additional studies are recommended to evaluate the potential human exposure to Cl-OPEs via inhalation, ingestion from dietary, and dermal contact with products that contain these chemicals.

CRediT authorship contribution statement

Layla Salih Al-Omran: Writing – review & editing, Writing – original draft, Visualization, Supervision, Software, Resources, Project administration, Methodology, Formal analysis, Conceptualization. **Banan Baqer Hashim:** Validation, Resources, Methodology, Investigation, Formal analysis, Data curation. **William A. Stubbings:** Writing – review & editing, Validation, Software, Resources, Methodology. **Stuart Harrad:** Writing – review & editing, Visualization, Validation, Investigation, Conceptualization.

Conflict of 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

Supplementary data to this article can be found online at https://doi.org/10.1016/j.emcon.2024.100435.

References

[1] G.-L. Wei, D.-Q. Li, M.-N. Zhuo, Y.-S. Liao, Z.-Y. Xie, T.-L. Guo, J.-J. Li, S.-Y. Zhang, Z.-Q. Liang, Organophosphorus flame retardants and plasticizers: sources, occurrence, toxicity and human exposure, Environ. Pollut. 196 (2015) 29–46.

[2] T.G. Bekele, H. Zhao, J. Yang, R.G. Chegen, J. Chen, S. Mekonen, A. Qadeer, A review of environmental occurrence, analysis, bioaccumulation, and toxicity of organophosphate esters, Environ. Sci. Pollut. Control Ser. 28 (36) (2021) 49507–49528.

[3] F. Shi, K. Liang, R. Liu, Q. Dong, Z. He, J. Xu, J. Liu, Elevated occupational exposure to chlorinated phosphate esters at a construction materials manufacturing plant, Environ. Int. 139 (2020) 105653.

[4] X. Han, W. Li, Y. Zhao, Y. Zhuang, Q. Jia, H. Guan, J. Liu, C. Wu, Organophosphate esters in building materials from China: levels, sources, emissions, and preliminary assessment of human exposure, Environ. Sci. Technol. 58 (5) (2024) 2434–2445.

[5] M. Alghamdi, M.A.-E. Abdallah, S. Harrad, The utility of X-Ray fluorescence spectrometry as a tool for monitoring compliance with limits on concentrations of halogenated flame retardants in waste polymers: a critical review, Emerging Contam. 8 (2022) 9–20.

[6] I. Liagkouridis, B. Lazarov, G. Giovanoulis, I.T. Cousins, Mass transfer of an organophosphate flame retardant between product source and dust in direct contact, Emerging Contam. 3 (3) (2017) 115–120.

[7] T.B. Chokwe, O.A. Abafe, S.P. Mbelu, J.O. Okonkwo, L.L. Sibali, A review of sources, fate, levels, toxicity, exposure and transformations of organophosphorus flame-retardants and plasticizers in the environment, Emerging Contam. 6 (2020) 345–366.

[8] J. Li, Z. Xie, W. Mi, S. Lai, C. Tian, K.-C. Emeis, R. Ebinghaus, Organophosphate esters in air, snow, and seawater in the north atlantic and the arctic, Environ. Sci. Technol. 51 (12) (2017) 6887–6896.

[9] Y. Ortiz, S. Harrad, Organophosphate esters in indoor and outdoor air in Birmingham, UK: implications for human exposure, Journal of Environmental Exposure Assessment 2 (3) (2023) 15.

[10] S. Harrad, S. Brommer, J.F. Mueller, Concentrations of organophosphate flame retardants in dust from cars, homes, and offices: an international comparison, Emerging Contam. 2 (2) (2016) 66–72.

[11] W. Li, Y. Wang, K. Kannan, Occurrence, distribution and human exposure to 20 organophosphate esters in air, soil, pine needles, river water, and dust samples collected around an airport in New York state, United States, Environ. Int. 131 (2019) 105054.

[12] Y. Wang, Y. Yao, X. Han, W. Li, H. Zhu, L. Wang, H. Sun, K. Kannan, Organophosphate di- and tri-esters in indoor and outdoor dust from China and its implications for human exposure, Sci. Total Environ. 700 (2020) 134502.

[13] M.R. Gbadamosi, A.L. Ogunneye, L.S. Al-Omran, M.A.-E. Abdallah, S. Harrad, Presence, source attribution, and human exposure to organophosphate esters in indoor dust from various microenvironments in Nigeria, Emerging Contam. 9 (2) (2023) 100208.

[14] L. Wu, X. Li, J. Fan, Y. Bai, Y. Zhang, H. Lu, C. Guo, J. Xu, Distribution characteristics, source attribution, and health risk assessment of organophosphate esters in indoor and outdoor dust from various microenvironments in Beijing, Ecotoxicol. Environ. Saf. 268 (2023) 115713.

[15] J. Huang, Z. Gao, G. Hu, G. Su, Non-target screening and risk assessment of organophosphate esters (OPEs) in drinking water resource water, surface water, groundwater, and seawater, Environ. Int. 168 (2022) 107443.

[16] S. Onoja, M.A.-E. Abdallah, S. Harrad, Concentrations, spatial and seasonal variations of Organophosphate esters in UK freshwater Sediment, Emerging Contam. 9 (3) (2023) 100243.

[17] Q. Zhang, Y. Wang, C. Zhang, Y. Yao, L. Wang, H. Sun, A review of organophosphate esters in soil: implications for the potential source, transfer, and transformation mechanism, Environ. Res. 204 (2022) 112122.

[18] N.K. Jayatilaka, P. Restrepo, L. Williams, M. Ospina, L. Valentin-Blasini, A.M. Calafat, Quantification of three chlorinated dialkyl phosphates, diphenyl phosphate, 2,3,4,5-tetrabromobenzoic acid, and four other organophosphates in human urine by solid phase extraction-high performance liquid chromatography-tandem mass spectrometry, Anal. Bioanal. Chem. 409 (5) (2017) 1323–1332.

[19] M. Hou, Y. Shi, Q. Jin, Y. Cai, Organophosphate esters and their metabolites in paired human whole blood, serum, and urine as biomarkers of exposure, Environ. Int. 139 (2020) 105698.

[20] S. Wang, A. Liu, M. Li, J. Jin, H. Yuan, J. Hu, Y. Wang, J. Jin, Organophosphate esters in tree bark and human hair in Weifang and Yantai, Shandong Province, China: concentrations, profiles and sources, J. Environ. Exposure. Assess 1 (2022) 12.

[21] Y. Gao, L. Wang, X. Zhang, C. Shi, L. Ma, X. Zhang, G. Wang, Similarities and differences among the responses to three chlorinated organophosphate esters in earthworm: evidences from biomarkers, transcriptomics and metabolomics, Sci. Total Environ. 815 (2022) 152853.

[22] R. Hou, Y. Xu, Z. Wang, Review of OPFRs in animals and humans: absorption, bioaccumulation, metabolism, and internal exposure research, Chemosphere 153 (2016) 78–90.

[23] Q. Saquib, A.M. Al-Salem, M.A. Siddiqui, S.M. Ansari, X. Zhang, A.A. Al-Khedhairy, Organophosphorus flame retardant TDCPP displays genotoxic and carcinogenic risks in human liver cells, Cells 11 (2) (2022) 195.

[24] M. Dou, L. Wang, A review on organophosphate esters: physiochemical properties, applications, and toxicities as well as occurrence and human exposure in dust environment, J. Environ. Manag. 325 (2023) 116601.

[25] U.-J. Kim, Y. Wang, W. Li, K. Kannan, Occurrence of and human exposure to organophosphate flame retardants/plasticizers in indoor air and dust from various microenvironments in the United States, Environ. Int. 125 (2019) 342–349.

[26] M. Chen, J. Jiang, Z. Gan, Y. Yan, S. Ding, S. Su, X. Bao, Grain size distribution and exposure evaluation of organophosphorus and brominated flame retardants in indoor and outdoor dust and PM10 from Chengdu, China, J. Hazard Mater. 365 (2019) 280–288.

[27] M.A.-E. Abdallah, A. Covaci, Organophosphate flame retardants in indoor dust from Egypt: implications for human exposure, Environ. Sci. Technol. 48 (9) (2014) 4782–4789.

[28] S. Brommer, S. Harrad, Sources and human exposure implications of concentrations of organophosphate flame retardants in dust from UK cars, classrooms, living rooms, and offices, Environ. Int. 83 (2015) 202–207.

[29] N. Ali, M.W. Kadi, H.M.S. Ali Albar, M.I. Rashid, "Semi-Volatile organic compounds in car dust: a pilot study in jeddah, Saudi Arab. (Quarterly Forecast Rep.) 18 (9) (2021).

[30] J. Gearhart, H. Posselt, D. Dempsey, Toxic at any speed: chemicals in cars and the need for safe alternatives, a report, Ecology Center (2006).

[31] A. Qadeer, S. Mubeen, M. Liu, T.G. Bekele, C.R. Ohoro, A.O. Adeniji, A.M. Alraih, Z. Ajmal, A.S. Alshammari, Y. Al-Hadeethi, D. Archundia, S. Yuan, X. Jiang, S. Wang, X. Li, S. Sauvé, Global environmental and toxicological impacts of polybrominated diphenyl ethers versus organophosphate esters: a comparative analysis and regrettable substitution dilemma, J. Hazard Mater. 466 (2024) 133543.

[32] L. Pang, Z. Huang, H. Yang, R. Pang, M. Wu, B. Jin, A scalable field study using leaves as a novel passive air sampler to evaluate the potential source of organophosphate esters in street dust, Chemosphere 312 (2023) 137248.

[33] W. Li, Y. Shi, L. Gao, C. Wu, J. Liu, Y. Cai, Occurrence, distribution and risk of organophosphate esters in urban road dust in Beijing, China, Environ. Pollut. 241 (2018) 566–575.

[34] H. Yin, D. Wu, J. You, S. Li, X. Deng, Y. Luo, W. Zheng, Occurrence, distribution, and exposure risk of organophosphate esters in street dust from Chengdu, China, Arch. Environ. Contam. Toxicol. 76 (4) (2019) 617–629.

[35] M.J. Fabiańska, B. Kozielska, J. Konieczyński, P. Bielaczyc, Occurrence of organic phosphates in particulate matter of the vehicle exhausts and outdoor environment – a case study, Environ. Pollut. 244 (2019) 351–360.

[36] Y. Wang, M. Bao, F. Tan, Z. Qu, Y. Zhang, J. Chen, Distribution of organophosphate esters between the gas phase and PM2.5 in urban Dalian, China, Environ. Pollut. 259 (2020) 113882.

[37] L.S. Al-Omran, M.R. Gbadamosi, W.A. Stubbings, D.S. Drage, M. Abou-Elwafa Abdallah, S. Harrad, Organophosphate esters in indoor and outdoor dust from Iraq: implications for human exposure, Emerging Contam. 7 (2021) 204–212.

[38] B.B. Hashim, L.S. Al-Omran, Human exposure assessment of tris (1-chloro-2-propyl) phosphate (TCIPP) via dermal contact with car dust, Journal of Basrah Researches (Sciences) 49 (1) (2023) 112–121.

[39] L.S. Al-Omran, S. Harrad, Influence of sampling approach on concentrations of legacy and "novel" brominated flame retardants in indoor dust, Chemosphere 178 (2017) 51–58.

[40] I. van der Veen, J. de Boer, Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis, Chemosphere 88 (10) (2012) 1119–1153.

[41] C. He, X. Wang, P. Thai, J.F. Mueller, C. Gallen, Y. Li, C. Baduel, Development and validation of a multi-residue method for the analysis of brominated and organophosphate flame retardants in indoor dust.", Talanta 164 (2017) 503–510.

[42] J. Persson, T. Wang, J. Hagberg, Organophosphate flame retardants and plasticizers in indoor dust, air and window wipes in newly built low-energy preschools, Sci. Total Environ. 628–629 (2018) 159–168.

[43] A. de la Torre, I. Navarro, P. Sanz, M. de los Ángeles Martínez, Organophosphate compounds, polybrominated diphenyl ethers and novel brominated flame retardants in European indoor house dust: use, evidence for replacements and assessment of human exposure.", J. Hazard Mater. 382 (2020) 121009.

[44] NIST, (National Institute of Standards and Technology), Certificate of analysis standard reference material 2585 organic contaminants in house dust (online) available from: https://tsapps.nist.gov/srmext/certificates/2585.pdf, 2018.

[45] U.S. EPA. US Environmental Protection Agency, Update for chapter 5 of the exposure factors handbook - soil and dust ingestion (online) available from: https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=337521, 2017.

[46] R. Olivero-Verbel, B. Johnson-Restrepo, E. Eljarrat, Human exposure assessment of organophosphate esters (OPEs) through dust ingestion and dermal absorption in Colombian cities, Journal of Environmental Exposure Assessment 1 (2) (2022) 8.

[47] A. Bradman, R. Castorina, F. Gaspar, M. Nishioka, M. Colon, W. Weathers, P.P. Egeghy, R. Maddalena, J. Williams, P.L. Jenkins, T.E. McKone, Flame retardant exposures in California early childhood education environments, Chemosphere 116 (2014) 61.

[48] J. Cristale, T.G. Aragao Bele, S. Lacorte, M.R. Rodrigues de Marchi, Occurrence and human exposure to brominated and organophosphorus flame retardants via indoor dust in a Brazilian city, Environ Pollut 237 (2018) 695–703.

[49] M.U. Khan, J. Li, G. Zhang, R.N. Malik, New insight into the levels, distribution and health risk diagnosis of indoor and outdoor dust-bound FRs in colder,

rural and industrial zones of Pakistan, Environ. Pollut. 216 (2016) 662–674.
[50] Z. Cao, F. Xu, A. Covaci, M. Wu, G. Yu, B. Wang, S. Deng, J. Huang, Differences in the seasonal variation of brominated and phosphorus flame retardants in office dust, Environ. Int. 65 (2014) 100–106.
[51] O.A. Abafe, B.S. Martincigh, Concentrations, sources and human exposure implications of organophosphate esters in indoor dust from South Africa, Chemosphere 230 (2019) 239–247.
[52] M.-J. He, Organophosphate esters in road dust from a suburban area of chongqing, China: characterization of particle size distribution and human exposure, Arch. Environ. Contam. Toxicol. 76 (2019) 630–639.
[53] Z. Cao, L. Zhao, J. Kuang, Q. Chen, G. Zhu, K. Zhang, S. Wang, P. Wu, X. Zhang, X. Wang, S. Harrad, J. Sun, Vehicles as outdoor BFR sources: evidence from an investigation of BFR occurrence in road dust, Chemosphere 179 (2017) 29–36.
[54] Y. Chen, Q. Zhang, T. Luo, L. Xing, H. Xu, Occurrence, distribution and health risk assessment of organophosphate esters in outdoor dust in Nanjing, China: urban vs. rural areas, Chemosphere 231 (2019) 41–50.
[55] N. Ali, L. Ali, T. Mehdi, A.C. Dirtu, F. Al-Shammari, H. Neels, A. Covaci, Levels and profiles of organochlorines and flame retardants in car and house dust from Kuwait and Pakistan: implication for human exposure via dust ingestion, Environ. Int. 55 (2013) 62–70.
[56] M. Tokumura, R. Hatayama, K. Tatsu, T. Naito, T. Takeda, M. Raknuzzaman, M.H. Al-Mamun, S. Masunaga, Organophosphate flame retardants in the indoor air and dust in cars in Japan, Environ. Monit. Assess. 189 (2) (2017) 48.
[57] L. Zhou, M. Hiltscher, W. Püttmann, Occurrence and human exposure assessment of organophosphate flame retardants in indoor dust from various microenvironments of the Rhine/Main region, Germany, Indoor Air 27 (6) (2017) 1113–1127.
[58] I.C. Yadav, N.L. Devi, Legacy and emerging flame retardants in indoor and outdoor dust from Indo-Gangetic Region (Patna) of India: implication for source apportionment and health risk exposure, Environ. Sci. Pollut. Control Ser. 29 (45) (2022) 68216–68231.
[59] D. Cao, K. Lv, W. Gao, J. Fu, J. Wu, J. Fu, Y. Wang, G. Jiang, Presence and human exposure assessment of organophosphate flame retardants (OPEs) in indoor dust and air in Beijing, China, Ecotoxicol. Environ. Saf. 169 (2019) 383–391.
[60] S. Brommer, S. Harrad, N. Van den Eede, A. Covaci, Concentrations of organophosphate esters and brominated flame retardants in German indoor dust samples, J. Environ. Monit. 14 (9) (2012) 2482–2487.