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Human Exposure Assessment of Tris (1-chloro-2-propyl) phosphate (TCIPP) via Dermal Contact with Car Dust

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ABSTRACT

Tris (1-chloro-2-propyl) phosphate (TCIPP) synthesis halogenated organophosphate compound that is widely used as flame retardants and plasticizer. The toxicity of TCIPP has led to concern about human exposure. Dermal absorption via indoor dust (particularly cars) represents one of the major human exposure pathways. The present study reports on the investigation of the levels of TCIPP in car dust samples from Basrah Iraq. The samples were collected from 24 private cars in different years of manufacture and countries. After the extraction and purification, samples were analysed by GC-EI/MS. Concentrations of TCIPP in dust samples were between 784 and 29478 ng/g with mean and median concentrations of 5162, 2696 ng/g respectively. Based on the manufactured country, Korean cars were the lowest levels of TCIPP comparing with Chinses,Japanese and the USA manufacture cars. Estimations daily intake via dermal absorptions showed that taxi drivers are more exposed to those of the two age groups (adults and toddlers), with an average of 0.124, 0.493 and 0.842 (ng/kg bw/day) for adults, toddlers and taxi drivers respectively. Those results were several orders of magnitude lower than the corresponding reference dose (RfD values).

1. Introduction

Tris (1-chloro-2-propyl) phosphate (TCIPP), is one of the most important three synthetic chlorinated organophosphate esters (Cl-OPEs) that are primarily used as additive flame retardants and plasticizer in various consumer products [1, 2]. Recently, Cl-OPEs (i.e., TCIPP, tris(2-chloroethyl) phosphate (TCEP) and tris(1,3-dichloro-2-propyl) phosphate (TDCIPP)) have been extensively used as the main alternatives to the restricted brominated flame retardants listed in the Stockholm Convention on persistent organic pollutants (UNEP, 2013). In 2017, it was estimated that the global consumption of Cl-OPEs was 220,000 tons [3]. Asia Pacific (China, Japan, India and South Korea) became the largest regional market, with 55% of global consumption [4], [5]

TCIPP (NIH, 2023) is the most important organophosphate ester flame retardant which represents about 80% of Cl-OPEs in Europe [1]. It has physiochemical properties similar to TDCIPP, but lower cost, and it is preferable for a wide range of applications [6, 7].TCIPP is widely used in rigid and flexible polyurethane foams for building insulation sofas, chairs, vehicle seating,

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and mattresses, as well as in other products such as textiles, paints, coatings, adhesives and electronics [8]. In 2012, the total consumption of TCIPP was approximately 27,000 tons [9].

As semi-volatile organic compound and additive flame retardants, TCIPP can be release into the environment via volatilization, leaching and/or abrasion [10, 11]. It has been detected as an environmentally abundant OPE in indoor and outdoor air, indoor and outdoor dust, water and sediment [11-14]. In addition, it was detected in human serum [15] and human milk [16]. According to the European Commission (EC), 2014, TCIPP is considered as a potential carcinogen chemical. Thus, it has been suggested restrictions in children's supplies (EC, 2014, [9]. In combination with other organophosphorus flame retardants, TCIPP can penetrate the skin quite rapidly [17], which has led to concern about human exposure via dermal absorption.

Inhalation, dermal absorption, dust ingestion, and food ingestion were considered as the main human exposure pathways to indoor continents. Dermal exposure can result from skin contact with contaminated environmental media such as water, soil and indoor dust. Dermal exposure via contact with indoor dust was predicted to be the second most important pathway. However, very limited data are available on human dermal exposure of TCIPP [18]. Globally, a large number of studies have investigated Cl-OPEs in indoor dust reported that the concentrations of TCIPP in cars were the highest comparing with other microenvironments such as, homes, schools and offices [19-25]. This implies that dermal contact of car dust contributes substantially of human exposure to TCIPP, particularly for drivers who spend long time inside the vehicles. Thus, for the first time, this study was designed to determine the concentration of TCIPP in car dust samples from Iraq and to examine human exposure and human health risk assessments of this pollutant via dermal contact.

2. Materials and Methods

2.1 Chemicals

All solvents and reagents (HPLC grade) were obtained from Sigma-Aldrich, (Munich, Germany). Standard of Tris (1-chloro-2-propyl) phosphate (TCIPP) and internal standard d12-tris(2-chloroethyl) phosphate (d12-TCEP) were purchased from Wellington laboratories, (Guelph, ON, Canada). Triamyl phosphate (TAP) as recovery determination standard was purchased from TCI Europe (Zwijndrecht, Belgium). As a reference standard material, indoor dust SRM 2585 was purchased from the US National Institute of Standards and Technology (NIST, Gaithersburg, USA). The purity of all analytical standards was >98%.

2.2 Sampling

24 car dust samples were collected from dashboards and seats from private cars in Basrah, South Iraq between 2021 and 2022, using a vacuum cleaner with a nylon sampling sock placed into the nozzle, according to the standard method [26]. The average age of cars was 8 years ranging between 2 and 27 years. To the best of our knowledge, all cars in Iraq are 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 USA (n=4). After sampling, the sampling socks were closed, sealed in a plastic bag, and stored in the dark at 4˚C. Prior to analysis, all dust samples were sieved using 250 μm mesh testing sieve for 3-5 min, to ensure better sample homogeneity.

2.3 Analysis method

Dust sample (around 75-100 mg) were spiked with 50 ng of d12-TCEP as an internal standard and extracted with 2 x 2 mL 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 procedure was repeated three times and supernatant fluid were collected, evaporated to initial dryness, and resolubilised in 1 mL of hexane. To purify the extract sample, Florisil cartridges were used to fractionate the sample into two fractions. The first fraction was eluted with 8 mL of hexane and the second fraction eluted with 10 mL ethyl acetate. The second fraction was evaporated under a gentle nitrogen stream and then resolubilised in100 mL isooctane containing 0.5 ng/μL of Tri amyl phosphate (TAP) as recovery determination standard. These extraction and clean-up methods were performed at university of Basrah, college of Science, while the instrumental analysis was performed at university of Birmingham, UK using a

gas chromatograph coupled to a mass spectrometer (GC-MS) operated in electron impact ionisation [1, 27].

2.4 QA/QC

For quality assurance and quality control, two method blanks and one standard reference material (SRM 2585) were analysed with each batch of 10 dust samples. Very low concentrations of TCIPP were detected in the blanks. Thus, the results were blank corrected by subtraction of mean blank values from the raw values of TCIPP in the dust samples. SRM 2585 levels were comparable to those from previous studies [22, 27-30]. Average, median, maximum, minimum and STD of internal standard recovery (d_{12}-TCEP) from dust samples were 78.5, 76.0, 130, 45 and 19% respectively.

2.5 Dermal exposure assessment

For dermal contact with dust, the concentration of contaminant contacting the skin is a function of the concentration of that contaminant in the dust and the amount of dust that adheres to the skin per unit surface area. Thus, the average daily intake ((ng/kg bw/day) is calculated as mass of contaminant per unit body weight over a day using the general equation: (USEPA, 2011; [31, 32].

$$ADD = C \times BSA \times DAS \times FA \times IEF / (BW \times 1000) \quad \text{(equation 1)}$$

where DED = dermal estimated dose (ng/kg bw/day), C = concentration of the pollutant in dust (ng/g), BSA = body surface area exposed (1.94 m^2 for adults and 0.6 m^2 for toddlers), DAS = dust adhered to skin (0.01 mg/cm for adults and 0.04 mg/cm for toddlers), FA = fraction absorbed by the skin (4615 cm^2 for adults and 2564 cm^2 for toddlers) , IEF = exposure fraction per day spent in the microenvironment (0.041 for adults and toddlers, and 0.279 for taxi drivers), BW= body weight (kg Assumed mean body weights were 80 kg for adults and 13.8 kg for toddlers (USEPA, 2017; 2011[7].

3.Results and Discussion

3.1 Concentrations of TCIPP in car dust samples.

TCIPP was detected in 100% of dust samples with varied levels among sampled cars. Concentration of TCIPP ranged from 784 to 29478 ng/g, with mean and median concentrations of 5162, 2696 ng/g respectively. This is possibly a result of the global phasing out of brominated flame retardants coupled with wide application and extensive use of TCIPP in cars. The highest concentration of TCIPP was found in a Chines car (C9) manufactured in 2013, while the lowest concentrations was found in a Japanese car (C5) manufactured in 2017. Figure 1 illustrates the concentration of TCIPP in all car dust samples.

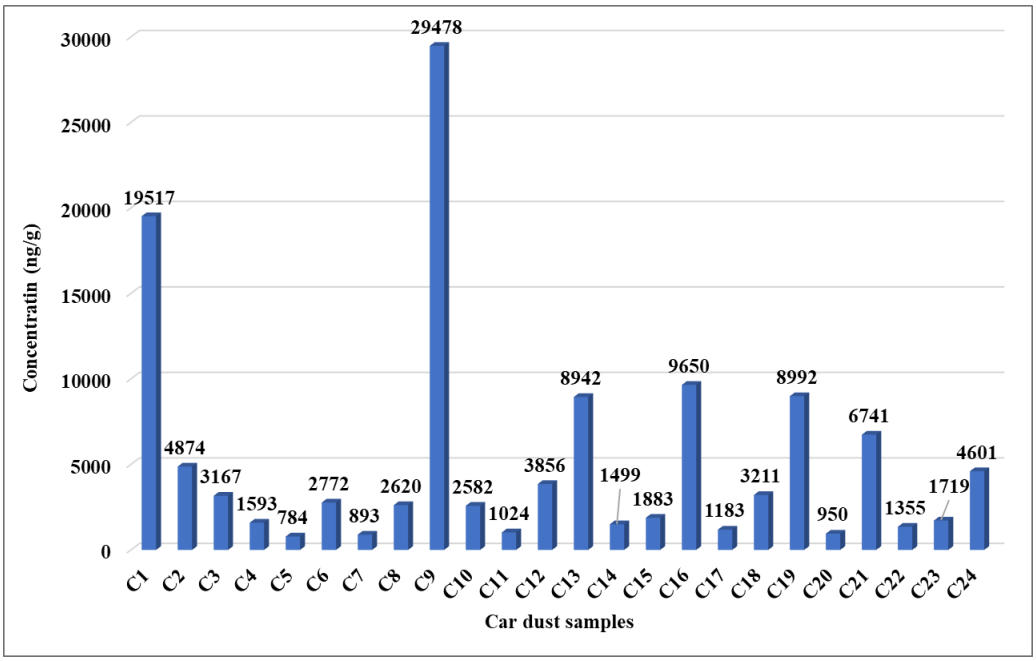

Fig. 1. Concentration of TCIPP (ng/g) in car dust samples

Although TCIPP median concentrations in car dust from Iraq are lower than those from Netherlands [6], South Africa [33], Australia [23], Kuwait [20], Colombia [34] , UK [24], and Germany [35], they are higher than those from Japan [36], Saudi Arabia [37], Egypt [22], and Pakistan [20]. Concentration of TCIPP in this study is comparable with those reported in Greece [7], and Brazil [25]. Figure 2 illustrates a comparison of TCIPP median concentrations in this study and those measured from other studies worldwide in car dust.

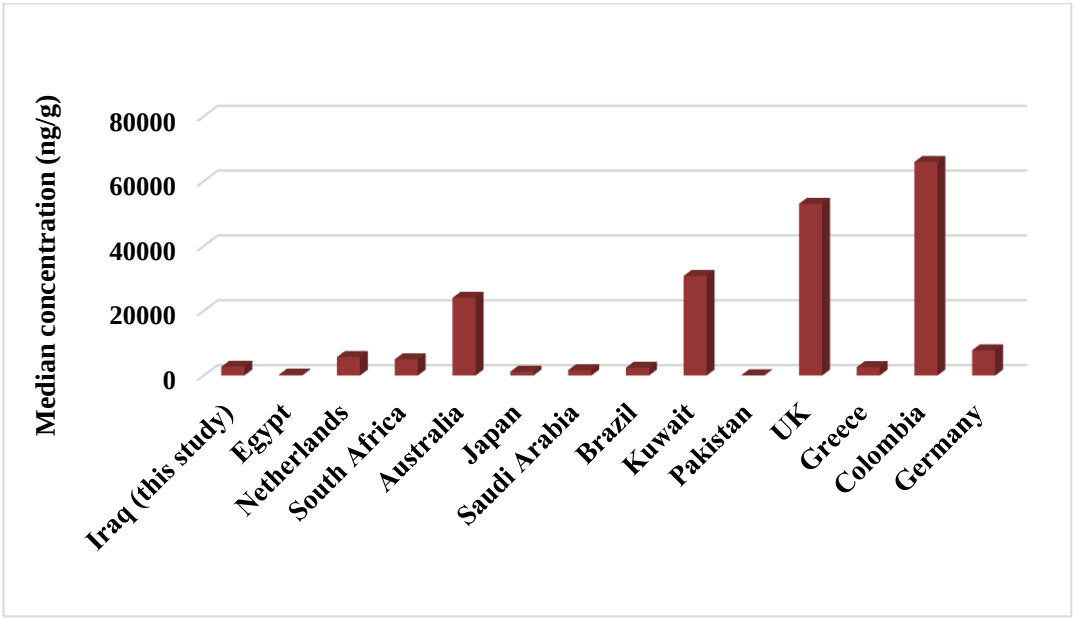

Fig. 2. International comparison of TCIPP in car dust samples from Iraq and those from other countries

3.2 Comparison of TCIPP in car dust based on the manufactured country

Depending on the manufactured region, mean concentrations of TCIPP in Chines and Japanese cars higher than those in USA cars, with mean concentrations of 9492, 6705 and 5374 in Chines, Japanese and USA cars respectively. However, among the studied cars, USA made the highest median concentration (5331 ng/g) in dust samples and Korean cars were the lowest in TCIPP levels. Median concentrations of TCIPP in dust samples from Chines, Japanese and USA cars acceded the median concentration of Korean cars by factors of 2.3, 2.2 and 2.6 respectively. Table 1 shows, mean, median, minimum, maximum and standard deviations (STD) of TCIPP in dust samples depending on the manufacture country.

Table 1. Mean, median, minimum, maximum and standard deviations (STD) of TCIPP in dust samples depending on the manufactured country.

Statistical parameter	Chinese cars (n=5)	Japanese cars (n=5)	Korean cars (n=10)	USA cars (n=4)
Mean	9492	6705	2140	5374
Median	4874	4601	2087	5331
Minimum	950	784	893	1183
Maximum	29478	19517	3856	9650
STD	11554	7531	1002	4544

3.3 Human exposure to TCIPP via dermal absorption

For the two age groups (adults and toddlers), and taxi-drivers, data on concentrations of TCIPP in car dust samples were used to estimate daily dermal (ADD) according to the equation 1. Three exposure scenarios were used: 1) Low-end exposure, in which TCIPP concentration at the 5th percentile; 2) “typical” or average exposure, in which the median concentration of TCIPP was applied, and 3) Hight-end exposure, in which 95th percentile of TCIPP concentration was applied. Table 2 summarises ADD values of TCIPP for adults, toddlers and taxi-drivers using the three exposure scenarios.

Table 2. Estimated daily intake (ng/kg bw/day) of TCIPP for adults, toddlers and taxi-drivers using the three exposure scenarios.

Exposure scenarios	Adults	Toddlers	Taxi drivers
5th %ile (Low-end)	0.041	0.165	0.282
Typical (Average)	0.124	0.493	0.842
95th %ile (Hight-end)	0.828	3.298	5.632

According to the results of the Table 2, the average daily intake (ADD) of TCIPP via dermal absorption for toddlers are higher than those for adults by factor of 4.0. This is likely due to the lower body mass of toddlers and greater assumed dust adhered to skin. In addition, taxi drivers who spend long time inside their vehicles are exposed to the highest levels of TCIPP. ADDs for taxi drivers exceeded those for other adults and toddlers by factor of 6.8 and 1.7 respectively.

According to the manufactured country of the cars, the average daily intake of TCIPP via dermal absorption was in order of Chinese > Japanese > USA > Korean cars. Figure 2 illustrates the average daily intake of TCIPP using the three exposure scenarios via car dust dermal absorption for adults, toddlers and taxi drivers. However, our exposure estimates for the Iraqi population via car dust dermal absorption are several times lower than their RfD values.

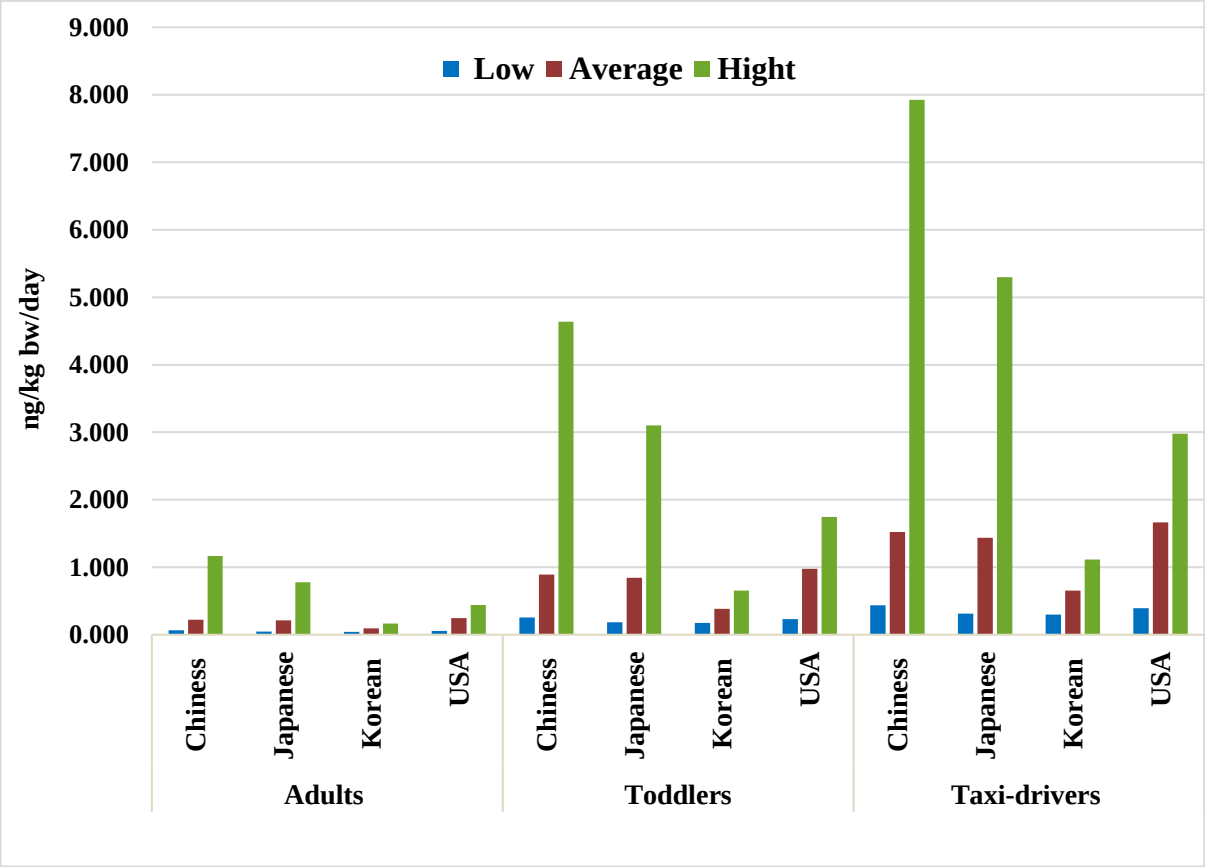

Figure 3. Estimates of Exposure of Adults, Toddlers and Taxi drivers of TCIPP via dermal absorption in Iraq.

4. Conclusion

This study constitutes the first report of concentrations of TCIPP in dust samples from cars in Iraq. In general, the study revealed that the levels of TCIPP were lower than those from Europe countries, Australia and Colombia. Interestingly, the levels of TCIPP in car dust samples were also lower than those from Kuwait which is very closed to Basrah city. This is likely due to the different brands of imported cars in the two countries. Most vehicles imported into Iraq are Korean, while most vehicles imported into Kuwait are made in Japan and USA. Our study revealed that median concentrations of TCIPP in Japanese and USA cars are higher than in Korean cars by factors of 2.2 and 2.5 respectively. Thus, human exposure to TCIPP from car dust is varied based on the country manufactured cars. Among the three investigated groups, taxi drivers are exposed to about seven and two times the level of TCIPP to other adults and young children respectively. While estimated daily intake of TCIPP via dermal absorption for the Iraqi population fall below health-base reference dose value, our study does not account for exposure via dust ingestion. Human exposure via car dust ingestion is recommended.

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تقييم التعرض البشري للفوسفات (1-كلورو-2-بروبيل) (TCIPP) عن طريق ملامسة الجلد لغبار السيارة

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معلومات البحث

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الكلمات المفتاحية

TCIPP ،غبار السيارات ، التعرض البشري ، امتصاص الجلد.

الملخص

تريس (1-كلورو-2-بروبيل) فوسفات (TCIPP) هو مركب فوسفات عضوي مهلجن مُصنّع يستخدم على نطاق واسع كمثبطات للهب وملدنات. أدت سمية TCIPP إلى القلق بشأن تعرض الإنسان. يمثل امتصاص الجلد عن طريق الغبار الداخلي (خاصة السيارات) أحد مسارات التعرض البشري الرئيسية. تشير الدراسة الحالية إلى التحقيق في مستويات TCIPP في عينات غبار السيارات من البصرة في العراق. تم جمع العينات من 24 سيارة خاصة في مختلف سنوات التصنيع والبلدان. بعد الاستخراج والتنقية ، تم تحليل العينات بواسطة GC-EI / MS. تراوحت تراكيز TCIPP في عينات الغبار بين 784 و 29478 نانوغرام / غرام بتراكيز متوسطة ومتوسطة تبلغ 5162 ، 2696 نانوغرام / غرام على التوالي. بناءً على الدولة المصنعة ، كانت السيارات الكورية هي أدنى مستويات TCIPP مقارنة بالسيارات الصينية واليابانية والولايات المتحدة الأمريكية. أظهرت تقديرات المدخول اليومي عن طريق الامتصاص الجلدي أن سائقي سيارات الأجرة أكثر تعرضاً لسائقي سيارات الأجرة للفئات العمرية (الكبار والصغار) بمتوسط 0.124 و 0.493 و 0.842 (نانوغرام / كجم من وزن الجسم / يوم) للبالغين والأطفال الصغار وسائقي سيارات الأجرة على التوالي. كانت تلك النتائج من حيث الحجم أقل من الجرعة المرجعية المقابلة (قيم RfD).

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