Comparison of Organophosphate Flame Retardants Before and During COVID-19 Lockdown and Its Implication on the Human Health

Ali Nadeem[1*], Doha Hantoush[1], Kadi Mohammad[2,] Nazar Ehtisham[3], Summan Ahmed Saleh[1,4], Eqani Syed Ali Musstjab Akbar Shah[5], Govindan Malarvannan[6]

[1] Centre of Excellence in Environmental Studies, King Abdulaziz University, Jeddah 21589, Saudi Arabia, nabahadar@kau.edu.sa
[2] Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia
[3] Department of Environmental Sciences, University of Gujrat, Punjab 50700, Pakistan
[4] Department of Environmental Sciences, King Abdul Aziz University, Jeddah 21589, Saudi Arabia
[5] Public Health and Environment division, Department of Biosciences, COMSATS Institute of Information Technology, Islamabad, Pakistan
[6] Toxicological Center, University of Antwerp, Antwerp 2610, Belgium

1 Introduction

Organohalogenated flame retardants (PFRs) are semi-volatile organic compounds (SVOCs) that are added to the consumer products to meet the regulation of fire hazards[1]. A number of recent studies from different countries indicate that the use of PFRs has been increasing recently, especially after the regulations on the use of penta-, octa-, and decabrominated diphenyl ethers (BDEs) [1]. Instead of chemically bound, these are additives in the host polymer which makes these chemicals prone to leach into the environment during production, use, and recycling[1]. Many studies have reported their presence in the environment and reported the link between exposure to those chemicals and a number of health conditions[2,3]. Humans are getting exposed to these chemicals via contaminated food intake, air inhalation, involuntary dust intake, and dermal uptake[2,4]. High levels of these chemicals are reported in indoor settings of various countries, and involuntary intake of indoor dust is considered as one of the major exposure pathways for these chemicals[2,4].

Many recent studies have reported significantly improved outdoor environmental quality during the lockdowns to limit the spread of COVID-19[5]. Lockdowns were considered the most effective tool to control the human-to-human transmission of COVID-19. These lockdowns resulted in the reduction of industrial activities and traffic, which consequently improved the overall environmental quality of outdoors[5]. Similar to other countries, the Kingdom of Saudi Arabia imposed strict lockdown in the country for many months with restricted movement of the population. With people spending more time at home, increased activities such as cooking, cleaning, and indoor smoking, along with children's activities, might have impacted the indoor air quality[6]. However, studies have not focused on conducting the impact of lockdown on indoor environmental quality. Monitoring indoors is even more important in households with young children and people with compromised health. Therefore, it was important to monitor and understand the dynamics of indoor chemical pollution and study its impact on public health. Considering the knowledge gap, this study was designed to analyze the presence of selected PFRs in floor household dust of Saudi Arabia collected during the COVID-19 related lockdown period. The findings of the study provide a different angle of COVID-19 impact on the environment and people.

2 Materials and Methods

Chemicals, Solvents, and Sampling: The analytical standards for the selected PFRs namely; triethyl phosphate (TEP), tributyl phosphate (TBP), tris(2-chloroethyl) phosphate (TCEP), tri(chloro propyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl)phosphate (TDCPP), triphenyl phosphate (TPhP), tris(2-butoxyethyl) phosphate (TBEP), 2-Ethylhexyl diphenyl phosphate (DPEHP), tris(2-ethylhexyl) phosphate (TEHP), tricresyl phosphate (mixture of isomers) (TCP) and labelled- internal standards were acquired from Restek, Wellington laboratories, and AccuStandard with >99% purity. All solvents used, namely n-hexane (n-Hex), dichloromethane (DCM), iso-octane, toluene, and acetone were purchased from Sigma Aldrich and all these solvents were of analytical grade. Sampling details are provided by Alamri et al.[6]. Briefly, indoor floor dust samples were obtained from different households of Jeddah (N=40) during the months of April-July 2020 when COVID-19 related lockdown was in place. Participant households were asked to collect a fresh dust sample using their vacuum cleaner. The sampled dust was wrapped in the aluminum foil, sealed, labelled, and kept in the freezer until they reached to the lab for the chemical analysis. The samples were pre-treated using 200 um sieving mesh for the homogenized dust samples and were kept at -20°C until analysis.

Sample preparation and analysis*:* Typically ~70 mg was accurately measured and spiked with ISs. Hexane/acetone (4/1, v/v) mixture was added to the test tubes with dust and was kept overnight in the dark to achieve equilibrium. The next day ultrasonication (20 min) was used for chemical extraction. Following ultrasonication, centrifugation (3000 rpm for 10 min) was performed and supernatant was transferred in a pre-cleaned labelled glass tube. The whole extraction method was repeated twice more with leftover dust. The pooled extracts were evaporated using a gentle flow of nitrogen to incipient dryness and were then reconstituted in 1 mL of solvent mixture of hexane/acetone (2:1

v/v). After re-solubilisation, samples were further cleaned on the pre-conditioned 3mL silica (500 mg) BondElut cartridges PFRs were eluted with 8 mL ethyl acetate.
The fraction was evaporated to incipient dryness under a gentle flow of nitrogen and reconstituted in 100 µL of iso-octane. Gas chromatography-mass spectrometry (GCMS) was used for the quantitative analysis. GCMS- QP2010 (Shimadzu) equipped with fused silica capillary column (TR5 30 m x 0.25 mm x 0.25 µm) was used in selected ion monitoring (SIM) mode for the quantitative analysis of PFRs.
Procedural blanks (N=6), dust replica (Na2SO4) (N=4) with known spiked concentration, and standard reference material (SRM) 2585 (N=4) from the National Institute of Standards & Technology (NIST) were part of QA/QC. These were prepared and analyzed alongside the samples. The concentrations of PFRs in SRM 2585 replicates and spiked dust replica were similar (RSD <15%). The levels of PFRs in SRM 2585 were in similar range to previously reported values [21]. To avoid possible photo-degradation, sample preparation was performed in a fume hood with no lights. The final extracts were saved at -20 °C before the quantitative analysis.
To calculate the daily dust intake (DI) via dust ingestion equation was used.

$$\text{Daily dust intake}\left(\frac{\frac{\text{ng}}{\text{kg}\,bw}}{day}\right)=\left(\frac{\text{Cn X IR}}{\text{BW}}\right)\text{Ftime}$$

In this equation Cn represents the concentration of pollutants found in the dust (ng/g). For typical and worst-case case scenarios, median and 90th percentile levels were considered. IR means the rate of dust ingestion; for typical and worst-case scenarios, high and low dust intake (mg/day) for both adults (20 (low) and100 (high) and young children (50 (low) and 200 (high) were considered. F time indicate the amount of time spend by the people in their households, which was 24 hrs for both adults and children during lockdown periods [19]. For many of these chemicals bioaccessibility data is not available, therefore 100% bioaccessibility was assumed for these preliminary estimations. A bodyweight of 70 kg for adults, 25 kg for young children, and 12 kg for toddlers were considered.

3 Results and Discussion

Levels, profile and comparison with earlier studies*:* Among PFRs, TBEP was present at a high median concentration of 5990 ng/g of dust. However, it was found in less than 60% of the analyzed samples. Many other studies have also reported TBEP at higher amounts than other PFRs and brominated flame retardants[7,8]. In some of the analyzed dust samples, TBEP was the most dominant among selected PFRs. This might indicate that those households might have more emission points for TBEP. The TBEP is commonly used in floor polishes, as a solvent in resins, as a viscosity modifier in some plastisols, an antifoam and plasticizer in lacquers, rubber, and plastics[9]. However, no specific information collected on the questionnaire clarified the presence of high TBEP in some samples. Among other PFRs, the order of importance depending on median levels (ng/g) was TCPP (2780), TDCPP (2050), TPhP (925), and TCEP (780). These PFRs were also found more frequently (~90%) in the analyzed samples (Table 1). The more consistent presence of these chemicals at high levels showed a wide range of their applications in indoor consumer products. Three of these chlorinated- PFRs have similar applications as plasticizer and FRs in a wide range of plastics, upholstery furniture, and binding agent in non-woven fabrics, flame resistant paints, unsaturated polyester resins, rigid and flexible polyurethane foam, and etc10. Studies have also reported high persistence and low degradation of chlorinated-PFRs in the environment which consequently help in their environmental buildup over time[10]. TPhP is also used as a plasticizer in lacquers, hydraulic fluids, and varnishes, while in it is used as FRs in Firemaster® 550 (FM 550). FM 550 is a commercial formulation mainly used in polyurethane foam as a substitute for the regulated formulation of Penta-BDE[2]. Other PFRs, namely TEP, TBP, DPEHP, TEHP, and TCP, were found in most dust samples with varying concentrations (Table 1). This is the first study from the region reporting many of these analyzed PFRs and phthalates in indoor dust samples. Therefore, this study highlights the need to include more chemicals for environmental monitoring in the region.
At the start of the Covid-19 pandemic, a strict lockdown was introduced in KSA like the rest of the world to control the spread of infection. Studies from different parts of the world showed improved outdoor environmental quality, while some studies reported that indoor environmental quality was compromised during this period. Recently, a study from KSA showed increased PAHs in indoor dust collected during lockdown[6]. Few studies have previously reported some of the analyzed PFRs and phthalates in indoor household dust from KSA[4,11,12]. Levels obtained in the current study were compared with earlier studies (Figure 1) from the KSA by histogram graphs and using a two-sample t-test. The analyzed PFRs and phthalates were visibly high in the current study than previous studies (figure 1)[4,11,12]. However, no statistically significant differences (P>0.05) were found except for the levels of TCEP and TCPP between the current study and Ali et al.[12]. Levels of TCEP and TCPP were significantly higher (P<0.05) in the current study than Ali et al.[12], this might indicate increased use of these compounds in products used indoors or their slow and gradual build-up in the indoor environment.

Table 1: Descriptive statistics of analyzed PFRs in household indoor dust collected during COVID-19 lockdown. All concentration given are in ng/g of dust.

Chemicals	Abbreviation	Detection %	LOQ	Mean± STD	Median (Mini-Max)
Triethyl phosphate	TEP	67	2	46±44	30 (LOQ - 140)
Tributyl phosphate	TBP	81	3	46±49	220 (LOQ - 220)
Tris(2-chloroethyl) phosphate	TCEP	89	15	1400±1560	780 (LOQ - 7280)
Tri(chloro propyl) phosphate	TCPP	89	15	8880±12890	2780 (LOQ - 52060)
Tris(1,3-dichloro-2-propyl)phosphate	TDCPP	92	15	5710±16600	2050 (LOQ - 102300)
Triphenyl phosphate	TPhP	94	45	4660±12300	925 (LOQ - 59550)
Tris(2-butoxyethyl) phosphate	TBEP	58	15	21915±62000	5990 (LOQ - 369850)
2-Ethylhexyl diphenyl phosphate	DPEHP	94	15	740±805	475 (LOQ - 4800)
Tris(2-ethylhexyl) phosphate	TEHP	81	2	125±175	70 (LOQ - 970)
Tricresyl phosphate (mixture of isomers)	TCP	81	10	260±350	165 (LOQ - 2060)

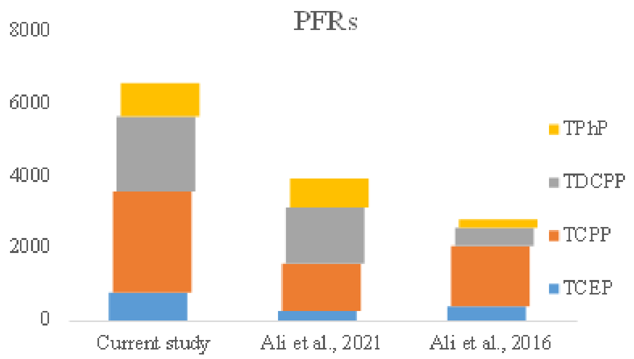

Figure 1: Comparison of median levels (ng/g of dust) of BFRs, PFRs and phthalates with previous studies from the region.

Human risk assessment: Exposure to PFRs is linked with several health problems in lab animals, but limited epidemiological studies are available on indoor exposure to PFRs and health implications[13-15]. Meeker and Stapleton[13] found a negative correlation between levels of TDCPP in house and free thyroxin, but its association was positive with prolactin. While a positive association between the levels of TnBP in floor dust and house-related mucous symptoms, asthma, and rhinitis is reported in literature[13-14]. Likewise, a significant correlation was reported between the levels of TCIPP and TDCPP in floor dust and the prevalence of atopic dermatitis[13]. Therefore to study the impact on population from exposure to PFRs found in indoor dust during lockdown period, daily exposure assessment was calculated. For all selected PFRs, DI was multifold below the reference dose (RfD) values for exposure from the indoor dust.

The calculated health risk assessment showed that Saudi Arabian people were exposed to more chemicals during the COVID-19 lockdown. This was primarily all the activities for both adults and children happened inside the home. Many households reported less cross ventilation during the lockdown period in fear of getting virus inside and increased use of cleaning chemicals to keep the household clean. This whole scenario made an ideal environment for the chemicals to buildup indoors. Even after 20 months, most young children in Saudi Arabia were still getting their education online. Consequently, they still spend most of their time indoors, making them vulnerable to exposure to these chemicals. Although this study is based on a limited number of samples, it still highlighted another aspect of COVID-19 impact on our lives and health. Limited interest and focus have been given to such research, and these findings warrant more studies on indoor environmental monitoring in similar situations.

4 Conclusions

This study analyzed PFRs in household dust collected during the COVID-19 related strict lockdown period in 2020. The analyzed PFRs were visually higher than the previously reported from Jeddah, Saudi Arabia. This finding was in line with the hypothesis that indoor pollution might have increased during lockdown due to the increased indoor activities. The daily exposure to PFRs were below the RfD values. This study also reported some of these chemicals in the region's indoor environment for the first time, highlighting the importance of analyzing more chemicals in the monitoring studies. Although calculated risk was below for most of the chemicals than the respective reference dose, little is known about the synergetic impact of these chemicals on the health of the exposed population. At the same time, this study throws light on another aspect of the COVID-19 in our lives. Limited studies are available on this aspect of COVID-19 lockdown from different parts of the world. More studies are warranted to understand this phenomenon from various regions.

5 Acknowledgements

This work was funded by Deanship of scientific studies, King Abdulaziz University (KAU), Jeddah, under the general program (grant number G -247-249-1441).

6 References

1. Blum A, Behl M, Birnbaum LS, et al. (2019) *Environmental science & technology letters*, *6*(11), 638-649.
2. Stapleton HM, Klosterhaus S, Eagle S, et al. (2009) *Environmental science & technology*, *43*(19), 7490-7495.
3. Bastiaensen M, Gys C, Colles A, et al. (2021) *Environment International*, *147*, 106368.
4. Ali N, Alhakamy NA, Ismail IM, et al. (2021) *International journal of environmental research and public health*, *18*(4), 2125.
5. Mousazadeh M, Paital B, Naghdali Z, et al. (2021) *Environment, Development and Sustainability*, 1-23.
6. Alamri SH, Ali N, Ali Albar HMS, et al. (2021) *International journal of environmental research and public health*, *18*(5), 2743.
7. Dodson RE, Perovich LJ, Covaci A, et al. (2012) *Environmental science & technology*, *46*(24), 13056-13066.
8. Brommer S and Harrad S, (2015) *Environment international*, *83*, 202-207.
9. Van Esch GJ and World Health Organization, (2000) World Health Organization report.
10. Van der Veen I and de Boer J (2012) *Chemosphere*, *88*(10), 1119-1153.
11. Albar HMSA, Ali N, Shahzad K, et al. (2017) *Microchemical Journal*, *132*, 227-232.
12. Ali N, Eqani SAMAS, Ismail IMI, et al. (2016) *Science of the Total Environment*, *569*, 269-277.
13. Araki A, Bamai YA, Bastiaensen M, et al. (2020) *Environmental research*, *183*, 109212.
14. Araki A, Saito I, Kanazawa A, et al. (2014) *Indoor air*, *24*(1), 3-15.
15. Meeker JD and Stapleton HM, et al. (2010) *Environmental health perspectives*, *118*(3), 318-323.