INVESTIGATION OF A NOVEL PERSONAL SAMPLER MATERIAL FOR THE IDENTIFICATION OF HUMAN EXPOSURE TO SEMI-VOLATILE ORGANIC COMPOUNDS

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ABSTRACT

INVESTIGATION OF A NOVEL PERSONAL SAMPLER MATERIAL FOR THE IDENTIFICATION OF HUMAN EXPOSURE TO SEMI-VOLATILE ORGANIC COMPOUNDS

SVOCs are widespread indoors, where they occur at high levels. Humans spend most of their time indoors and are regularly exposed to these compounds. Various methods exist to assess human exposure to SVOCs. However, a novel personal sampler material, i.e. silicone wristband, has been used for the last decade. Due to its commencing use, the uptake capacity of silicone wristbands for SVOCs still needs to be discovered. This study aims to investigate the SVOC uptake rate and equilibrium partitioning coefficients of silicone wristbands. To achieve this aim, an analysis method for determining SVOCs in silicone wristbands was developed and validated with wristbands worn by academic personnel of IZTECH. The results showed that among polycyclic aromatic hydrocarbons (PAHs) acenaphthylene, among organophosphate esters (OPEs), tris (2-butoxyethyl) phosphate and among phthalate esters, di(2-ethylhexl) phthalate were found as the dominant SVOCs in silicone wristbands. Then, the uptake capacity of silicone wristbands for PAHs was investigated by deploying them in a school environment for 36 days, together with polyurethane foam passive air samplers. The uptake rates varied three orders of magnitude for compounds reaching equilibrium, i.e. acenaphthene, acenaphthylene, fluorene, phenanthrene, and anthracene (0.010 – 25.93 m3/day), while for fluoranthene, chrysene, and pyrene uptake rates were close to each other (0.17 – 0.50 m3/day). Furthermore, silicone wristband-air partitioning coefficients were in the range of 5.93 to 7.43 for acenaphthene, acenaphthylene, fluorene, phenanthrene, and anthracene. Lastly, daily and chronic toxic exposures and lifetime cancer risk for school children were assessed using PUF-PAS concentrations, and no significant risk was identified.

ÖZET

YARI-UÇUCU ORGANİK BİLEŞİKLERE MARUZİYETİN BELİRLENMESİNDE YENİ BİR KİŞİSEL ÖRNEKLEYİCİ MALZEMENİN ARAŞTIRILMASI

Yarı uçucu organik bileşikler (YUOB) çevrede geniş bir şekilde dağılmış olup, özellikle iç mekanlarda yüksek konsantrasyonlara rastlanmaktadır. İnsanlar zamanlarının çoğunu iç mekanlarda geçirdikleri için bir dizi YUOB'ye maruz kalırlar. İnsan maruziyetini değerlendirmek için çeşitli yöntemler kullanılabilir. Ancak, son on yıldır kullanılan yeni bir kişisel örnekleyici malzeme olan silikon bilekliklerin YUOB 'ler için alım kapasitesi henüz keşfedilmemiştir. Bu çalışmanın amacı, silikon bilekliklerin YUOB alım hızını ve denge dağılım katsayılarını araştırmaktır. Bu amaca ulaşmak için, silikon bilekliklerdeki YUOB'lerin belirlenmesine yönelik bir analiz yöntemi geliştirilmiş ve İYTE akademik personeli tarafından kullanılan bilekliklerle doğrulanmıştır. Sonuçlar, polisiklik aromatik hidrokarbonlar (PAH'lar) arasında asenaftilenin, organofosfat esterler (OPE'ler) arasında tris (2-butoksi etil) fosfatın ve ftalat esterler arasında di(2-etilhekzil) ftalatın silikon bilekliklerde baskın YUOB 'ler olarak bulunduğunu göstermiştir. Daha sonra, PAH'lar için silikon bilekliklerin alım kapasitesi, poliüretan köpük pasif hava örnekleyicileri ile birlikte 36 gün boyunca bir okul ortamında kullanılarak araştırılmıştır. Dengede olan bileşikler için alım hızları üç basamak olarak değişmiştir, yani asenafilen, asenaftilen, florin, fenanten ve antren (0.010 - 25.93 m^3/gün), floranten, krisen ve piyren için alım hızları birbirine yakındı (0.17 - 0.50 m^3/gün). Ayrıca, silikon bileklik-hava bölünme katsayıları asenafilen, asenaftilen, florin, fenanten ve antren için 5.93 ile 7.43 arasında değişmiştir. Son olarak, okul çocukları için günlük ve kronik toksik maruziyetler ile ömür boyu kanser riski, PUF-PAS konsantrasyonları kullanılarak değerlendirilmiş ve anlamlı bir risk tespit edilmemiştir.

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CHAPTER 1

INTRODUCTION

Synthetic chemicals are widely used in daily products and released to the environment due to human activities. Humans, in a continuous and dynamic interaction with the environment, are exposed to these chemicals. In order to assess human exposure to chemicals, researchers have analyzed samples collected from various environmental media, such as air, water, and soil and estimated the daily dose that human body may intake via main exposure routes, i.e. inhalation, ingestion and dermal contact. Among the various environmental media humans interact with, indoor environments become the most significant source of exposure to chemicals since people spend more than 90% of their time indoors. Indoor air can be considered a mixture of synthetic chemicals that are released from building materials, furniture, electronic equipment, and due to activities like cooking, smoking, cleaning and heating (Lucattini et al., 2018). Hence, monitoring indoor air quality is essential to understand chemical exposure of humans.

To assess life-long environmental exposures and human health effects of chemicals in an integrated approach, personal samplers capable of producing time-integrated environmental data became prominent. Researchers focused on the analysis of biological samples such as blood (Bramwell et al., 2017), human milk and urine (Castorina et al., 2017), enabling them to comprehend chemical exposure on a personal basis. By this way, human health effects of the chemicals and personal exposure can be assessed consecutively. However, biological samples are difficult to analyze due to the lipids and proteins in the matrix, making it even harder to detect low concentrations of the chemicals present in the samples (Mayeux, 2004). Additionally, collecting biological samples includes an intervention to the human body, hence the participants of such studies can hesitate to get included. For this reason, studies can utilize personal sampling equipment, generally in the form of an active sampler in a backpack. The drawback of this sampling equipment is the need for energy for the pump system which

brings a physical burden to the participant and an economic burden to the study (Bohlin et al., 2007).

Silicone wristbands have been used for the last decade as personal passive samplers and shown to be effective to capture an individual's inhalation and dermal exposure (O'Connell et al., 2014; Anderson et al., 2017). It has been shown that silicone wristbands absorb organic compounds with a wide range of octanol-air partitioning coefficients (Anderson et al., 2017), and the concentrations observed in the wristbands correlated well with the biological samples taken from the same person (Hammel et al., 2016; 2018; 2020; Dixon et al., 2018; Nguyen et al., 2020). The studies so far have focused on semi-volatile organic compound (SVOC) exposure of general or vulnerable populations, and occupational exposure assessment using silicone wristbands (O'Connell et al., 2014; Hammel et al., 2020; Wang et al., 2020). However, the uptake characteristics of silicone wristbands including the achievement of equilibrium concentrations with air remained unresolved. A few studies identified the uptake rate of silicone materials not in the wristband form (Sedlackova et al., 2023), and some others investigated the silicone wristbands in specially designed chambers (Tromp et al., 2019). Up to now, there is only one study in which a real indoor environment was used to assess the uptake capacity of silicone wristbands for polychlorinated biphenyls (Frederiksen et al., 2022).

In this context, the aim of this study was to investigate SVOC uptake characteristics of silicone wristbands in a real indoor environment setting. To achieve this aim, sample preparation methods for the quantification of SVOCs in silicone wristbands need to be developed and validated. Hence, a cost-effective and time-efficient analysis method has been developed using laboratory control samples. Method validation was then performed using deployed silicone wristband samples. A personal exposure study using silicone wristbands was conducted with academic personnel of Izmir Institute of Technology living in İzmir, Türkiye, for the first time in the literature. Additionally, silicone wristbands were tested as indoor air samplers in the offices of the participants. For the uptake capacity study, primary school classrooms have been selected as the indoor environment. Indoor air samples were collected using silicone wristbands, passive and active air samplers so that calibration of silicone wristbands were performed using conventional air sampling methods. Sampling was conducted in classrooms with different ventilation types at varying outdoor temperatures, revealing

the potential effects of these variables on SVOC concentrations. Further, a risk assessment for primary school children was conducted for the target SVOCs.

Detailed information on the indoor air pollutants and passive samplers used to detect these pollutants are given in Chapter 2, the materials and methods used in this study are presented in Chapter 3, the results of the study are reported and discussed in Chapter 4 and a conclusion is made in Chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1. Indoor Air Quality

Indoor air quality (IAQ) is the air quality within and around buildings and structures. People mostly spend more than 90% of their time in indoor environments. Therefore, indoor air quality plays a significant role in public health and comfort (US EPA, 2015; US EPA, 2014a). Understanding and controlling indoor air pollutants can help reduce health concerns. Thus, IAQ is related to unique public health and policy issues, regarding hazardous substances such as inorganic compounds and organic contaminants classified with their boiling point range as very volatile (VVOCs), volatile (VOCs), semivolatile (SVOCs) and particulate (POMs) organic compounds.

Inorganic elements like asbestos, radon, and lead represent prominent indoor pollutants. Despite their distinct characteristics, these substances share a mineral or inorganic composition. Exposure to these contaminants may present notable health hazards. For instance, lead is a cause for apprehension due to its prevalence as a surface contaminant within indoor environments. Elevated blood lead levels in children under six often result from contact with lead-contaminated building dust, highlighting the significance of this concern (Godish, 2001). Organic chemical substances known as volatile organic compounds, VOCs, are those whose composition enables them to evaporate under ordinary indoor air conditions of temperature and pressure. This expression for indoor air quality and the standard definition of VOCs used in the scientific literature are synonymous. It is more likely that a chemical will be released into the atmosphere from a product or surface with greater volatility (lower boiling point) (US EPA, 2023). Concerning indoor air quality, primary contributors of VOCs comprise outdoor air, environmental tobacco smoke (ETS), fuel combustion, building materials, furnishings, furniture, carpet adhesives, paints,

solvents, cleaning agents, air fresheners, and cosmetics (Jurvelin, 2003). It is crucial to emphasize that concentrations of VOCs typically present in residential indoor or ambient air are significantly lower than levels, causing immediate health issues in humans. Nevertheless, there have been documented instances of a heightened occurrence of minor yet discomforting diseases, including coughing, sore throat, runny nose, and headaches, particularly in well-regulated indoor settings such as office buildings (Jurvelin, 2003).

SVOCs are synthetic chemicals produced for specific purposes. They are utilized as additives in materials, including floor coverings, furniture, and electronic components, as well as active substances in insecticides, cleaning and personal care products. The common SVOCs in indoor environment are flame retardants (FRs), plasticizers e.g. phthalates (PEs), organophosphate flame retardants (OPFRs), polychlorinated biphenyls (PCBs), pesticides, combustion by-products such as polycyclic aromatic hydrocarbons (PAHs) (Lucattini et al., 2018). SVOCs' presence in an indoor environment gradually causes long-term exposure, affecting human health negatively. According to studies by Yilmaz et al. (2019), Weschler and Nazaroff (2008), Kabir et al. (2015), Giulivo et al. (2016), and Hendryx et al. (2019), polybrominated diphenyl ethers (PBDEs), PAHs, per- and polyfluoroalkyl substances (PFAS), pesticides, PEs, and FRs are all associated with health effects regarding hormonal disruption, adverse reproductive and developmental effects, respiratory symptoms, cardiovascular disease, skin conditions, kidney and liver damage, and diabetes.

2.2. Semi-Volatile Organic Compounds

SVOCs are classified as indoor organic pollutants by the World Health Organization (WHO) and have boiling points between 240 - 260 and 380 - 400 °C (US EPA, 2023). SVOCs enter indoor environment through various mechanisms, including intentional application, such as pesticides; inadvertent generation, as seen with PAHs; and release from products like FRs and plasticizers (Demirtepe et al., 2020). Gaseous chemicals might be associated with particles, leading to their deposition as dust layers

on indoor surfaces (Weschler and Nazaroff 2008). As they are released from consumer products, they can persist in indoor environments through decades due to their slow release rate from sources and tendency to partition into sorbed forms (Weschler and Nazaroff 2008). The most common SVOCs in indoor environments occur as PAHs, PCBs, PBDEs, OPFRs, PEs, pesticides, and synthetic musks.

2.2.1 Polycyclic Aromatic Hydrocarbons

PAHs constitute a subgroup within a category of compounds called polycyclic organic matter (POM), and these compounds are primarily generated through the incomplete combustion of organic materials like coal and wood (US EPA, 2007). Certain PAH compounds have been identified as potential human carcinogens (ATSDR 1995). They are solids that might be colourless, white, or pale yellow-green in their fundamental form (US EPA, 2008). Both anthropogenic activities and natural processes can produce them (Kameda et al., 2005). Human activities such as tobacco smoke, cooking, domestic heating, wood-burning, decorative candle and incense burning have an impact on PAH levels indoors (Kavouras et al., 1998; Castro et al., 2011;Gustafson et al., 2008; Orecchio, 2011). In contrast, PAHs can be transported outdoors to indoors by outdoor anthropogenic activities (e.g. traffic and industrial activities) and natural sources (e.g. volcano eruption, forest fires) (Bayona et al., 1994; Tsapakis and Stephanou 2005; Mantis et al., 2005).

PAHs contain two or more fused benzenoid rings (i.e., benzene-like) that have at least one carbon-carbon bond. figure 2.1 represents some of the chemical structures of PAHs, i.e. naphthalene, pyrene, and benzo(a)pyrene, respectively.

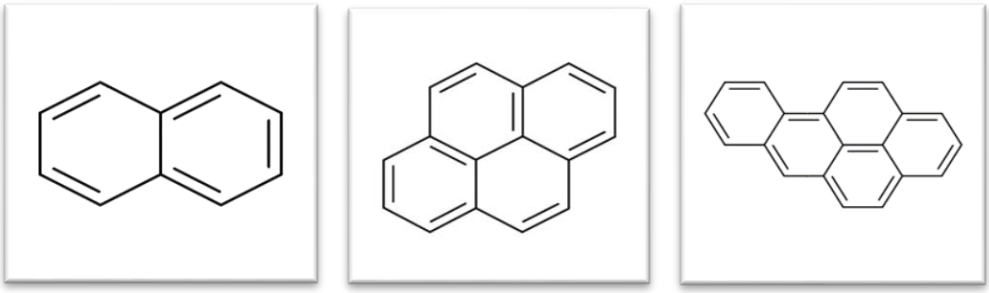

Figure 2.1. The chemical structure of naphthalene (two ring), pyrene (four ring), and benzo(a)pyrene (five ring) (Source: CompTox Chemicals Dashboard from US EPA)

Due to the fusion of benzene rings, nearly a thousand PAH compound is possible. In order to have a reasonable number of PAH compounds to investigate and monitor, US EPA published a list of sixteen priority PAH compounds, and it has been embraced by many scientists to investigate these compounds by utilising existing analytical techniques. Three PAHs were included in the initial "list of 65 toxic pollutants": acenaphthene, naphthalene, and fluoranthene (Keith, 2014). Additionally, there were six PAHs with unidentified isomers, including benzanthracenes, benzopyrenes, benzofluoranthenes, chrysenes, dibenzanthracenes, and indenopyrenes (Keith, 2014). Benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo (a,h)anthracene, and indeno(1,2,3-c,d)pyrene were the seven PAHs chosen since an analytical standard was available and no alkyl-substituted isomers were chosen (Keith, 2014). Benzo(ghi)perylene is typical of a 6-membered ring PAH, and pyrene is a common PAH obtained from coal tar, is produced under a wide range of combustion conditions, and is used as a chemical intermediate for dyes, etc (Keith, 2014). Anthracene was chosen because it is a common PAH obtained from coal tar and is frequently used as a chemical intermediate for dyes and other fine chemicals (Keith, 2014).

PAHs were commonly grouped according to their molecular weights. The lower molecular weight PAH compounds have less than four rings, and the higher molecular weight PAH compounds have four and more than four rings. Moreover, each of the PAH compounds has unique and different physical-chemical properties due to their chemical structure. The physical and chemical properties of 16 PAH compounds are given in Table 2.1, which includes the chemical formula, average molecular weight,

Henry's Law constant, boiling point, octanol-air partitioning coefficient (LogKoa), octanol-water partitioning coefficient (LogKow), and vapour pressure.

Table 2.1. The physicochemical properties of PAHs (Source: CompTox Chemicals Dashboard from US EPA, 2023)

CAS Number	Compoud Name	Chemical Formula	Average Molecular Weight (g/mol)	Experimental Average					
				Henry's Law (atm-m3/mole)	Melting Point (°C)	Boiling Point (°C)	$LogK_{oa}$	$LogK_{ow}$	Vapor Pressure (mmHg)
83-32-9	Acenaphthene	$C_{12}H_{10}$	154.21	1.84E-04	93.9	279	6.31	3.92	2.15E-03
208-96-8	Acenaphthylene	$C_{12}H_{8}$	152.20	1.14E-04	90	280	-	3.94	6.68E-03
191-24-2	Benzo(g,h,i)perylene	$C_{22}H_{12}$	276.34	3.31E-07	277	500	-	6.63	1.00E-10
53-70-3	Dibenz[a,h]anthracene	$C_{22}H_{14}$	278.35	-	268	524	-	6.63	9.55E-10
193-39-5	Indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	276.34	3.48E-07	164	536	-	-	-
86-73-7	Fluorene	$C_{13}H_{10}$	166.22	9.62E-05	115	295	6.79	4.18	6.00E-04
85-01-8	Phenanthrene	$C_{14}H_{10}$	178.23	4.23E-05	99.2	339	7.57	4.46	1.21E-04
120-12-7	Anthracene	$C_{14}H_{10}$	178.23	5.56E-05	215	340	7.55	4.45	6.53E-06
206-44-0	Fluoranthene	$C_{16}H_{10}$	202.26	8.86E-06	108	380	8.88	5.16	9.22E-06
129-00-0	Pyrene	$C_{16}H_{10}$	202.26	1.19E-05	150	399	8.8	4.88	4.50E-06
56-55-3	Benzo(a)anthracene	$C_{18}H_{12}$	228.29	1.20E-05	159	437	-	5.6	2.10E-07
218-01-9	Chrysene	$C_{18}H_{12}$	228.29	5.23E-06	255	448	-	5.81	6.23E-09
205-99-2	Benzo(b)fluoranthene	$C_{20}H_{12}$	252.32	6.57E-07	166	-	-	5.78	5.00E-07
207-08-9	Benzo(k)fluoranthene	$C_{20}H_{12}$	252.32	5.84E-07	217	480	-	6.11	9.65E-10
50-32-8	Benzo[a]pyrene	$C_{20}H_{12}$	252.32	4.57E-07	177	495	-	6.13	5.49E-09
91-20-3	Naphthalene	$C_{10}H_{8}$	128.17	4.40E-04	80.3	218	5.19	3.3	8.50E-02

People are generally exposed to PAHs in indoor and outdoor air by inhalation, and dermal contact. Furthermore, the sources of exposure to PAHs are smoking tobacco products, drinking and consuming food grown in contaminated soil and water, or consuming grilled meat or other kinds of foods (US EPA, 2023). PAH levels can accumulate in human tissues like the ovaries, spleen, kidney, liver and fat (Moon et al., 2012), and long-term exposure to them can have adverse health effects. The possible effects on human health include reproductive, immune system and developmental disorders (Agency for Toxic Substances and Disease Registry (ATSDR), 1995). As studied by Kim et al. (2013), these effects can cause kidney damage, skin, lung, gastrointestinal tract cancers, and eye and skin irritation. According to epidemiological research, there is a high correlation between PAH exposure levels and adverse effects on the respiratory and cardiovascular systems, such as reduced lung function, asthma, heart attack, skin and prostate cancer, and all-cause mortality (Bostrom et al., 2002). Children's inhalation rates are higher than adults because of their size, physiology, and level of activity, and they also inhale more oxygen and have higher resting metabolic rates per unit of body weight (Salvi, 2007).

2.2.2 Organophosphate Esters

OPEs are organic esters of phosphoric acid that contain either alkyl chains or aryl groups, and also they may be halogenated or nonhalogenated. Organophosphate ester flame retardants were used more frequently as alternative to restricted PBDEs, and the class of organohalogen flame retardants (flame retardants containing carbon and halogen elements, most frequently bromine or chlorine) are being phased out as a result of regulatory action and manufacturers' voluntary actions (Blum et al., 2019). Between 1995 and 2001, the world's consumption of OPEs grew from 108,000 to 186,000 tonnes (Van der Veen and De Boer, 2012). BCC Research (2022) reported that the worldwide utilization of flame retardant chemicals that contained phosphorus in 2021 reached an approximate volume of 1.6 billion pounds. Anticipated figures suggested an increase to nearly 1.7 billion pounds in 2022 and a further surge to surpass 2 billion by 2027. This trajectory signifies a compound annual growth rate (CAGR) of 3.7% from 2022 to

2027. Hence, their presence in the consumer products and occurrence in the environment is anticipated to continue in the following decades.

OPEs can be categorised into three groups based on their substituents: halogenated, alkyl, and aryl OPEs (Mingshan Dou & Lijun Wang, 2023). Alkyl chains can be linear or branched and are formed by carbon and hydrogen atoms. Aryl groups are formed of aromatic ring structures, identified by a stable and planar structure of carbon atoms connected with alternating single and double bonds. Alkyl and aryl groups' physical characteristics, such as solubility and volatility, as well as their compatibility with various materials, can impact the chemical structure of OPEs. Halogen-based flame retardants function in the gas phase by radical quenching, which involves breaking the radical chain mechanism that causes the flame during combustion (European Chemical Agency (ECHA), 2023).

Halogens like bromine (Br) or chlorine (Cl) are combined into the molecules of halogenated OPEs. Flame retardants that contain bromine and chlorine are the most effective (ECHA, 2023). Figure 2.2 represents some of the chemical structures of alkyl, aryl and halogenated OPEs: Triethyl phosphate (TEP), Triphenyl phosphate (TPhP), and Tris(2-chloroethyl phosphate) (TCEP), respectively. Moreover, the physicochemical properties of common OPE compounds are given in Table 2.2, which includes the chemical formula, average molecular weight, Henry's Law, boiling point, LogKoa, LogKow, and vapour pressure.

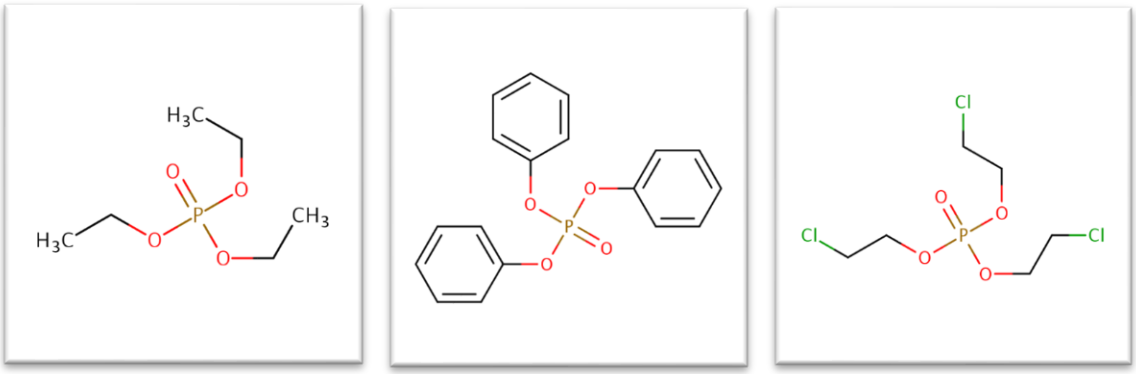

Figure 2.2. The chemical structure of TEP (Alkyl OPE), TPhP (Aryl OPE), and TCEP (Halogenated OPE) (Source: CompTox Chemicals Dashboard from US EPA)

Table 2.2. The physicochemical properties of OPEs (Source: CompTox Chemicals Dashboard | US EPA, 2023)

CAS Number	Compound Name	Abbreviation	Chemical Formula	Average Molecular Weight (g/mol)	Experimental Average					
					Henry's Law (atm-m3/mole)	Melting Point (°C)	Boiling Point (°C)	$LogK_{oa}$	$LogK_{ow}$	Vapor Pressure (mmHg)
115-86-6	Triphenyl Phosphate	TPHP	$C_{18}H_{15}O_4P$	326.288	-	50.1	289	-	4.59	6.28E-06
115-96-8	Tris(2-chloroethyl) phosphate	TCEP	$C_6H_{12}Cl_3O_4P$	285.48	-	-45	330	-	1.44	6.13E-02
13674-84-5	Tris(2-chloro isopropyl) phosphate	TCPP	$C_9H_{18}Cl_3O_4P$	327.56	-	-40	-	-	2.59	-
78-51-3	Tris(2-butoxyethyl) phosphate	TBEP	$C_{18}H_{39}O_7P$	398.477	-	-70	-	-	3.75	-
1241-94-7	2-ethylhexyl diphenyl phosphate	EHDPP	$C_{20}H_{27}O_4P$	362.406	5.42E-05	-54	375	-	5.73	5.00E-05
13674-87-8	Tris(1,3-dichloro-2-propyl) phosphate	TDCPP	$C_9H_{15}Cl_6O_4P$	430.89	-	27	-	-	3.65	-
126-73-8	tri(n-butyl) phosphate	TNBP	$C_{12}H_{27}O_4P$	266.318	-	-79.6	236	-	4	1.13E-03
78-42-2	Tris(2-ethylhexyl) phosphate	TEHP	$C_{24}H_{51}O_4P$	434.642	-	-72.7	216	-	-	8.25E-08
78-40-0	Triethyl phosphate	TEP	$C_6H_{15}O_4P$	182.156	3.60E-08	-56.2	215	-	0.8	0.393

OPEs typically used extensively as plasticisers and flame retardants (Levasseur et al., 2022). For instance, TPHP can be found in various commercial flame retardant mixtures used in furniture. Nevertheless, it has also been used in personal care products (as well as nail polish), industrial electronic equipment as a plasticiser, in products made of artificial leather, in varnishes, and as a phthalate substitute (Stapleton et al., 2012a; Stapleton et al., 2012b; Bergh et al., 2011; Marklund et al., 2005). Additionally, EHDPP and TCEP have been linked with food packaging and insulation materials, respectively (Li et al., 2019). As additive FRs, OPEs are not chemically bonded to the products, and they can easily be released into the environment through volatilisation, dissolution, leaching, and abrasion during the production and consumption of consumer and commercial products (van der Veen and de Boer, 2012). As a result, they are frequently observed in typical sources of human exposure (Blum et al., 2019).

OPEs can negatively impact human health by entering human bodies through ingestion, inhalation, and skin contact (M. Dou and L. Wang, 2023). Chlorinated-OPEs (Cl-OPEs) such as TCEP, TCPP, and TDCPP have shown carcinogenic properties, and they may build up in livers and testis, thereby inducing tumours (Hou et al., 2016; Van der Veen and De Boer, 2012). TPhP, TnBP, and TCEP have all been linked to neurotoxic effects (Wei et al., 2015), and TPhP has also been associated with skin allergies and effects on fertility.

2.2.3 Phthalate Esters

A class of industrial compounds known as phthalates are 1,2-benzene dicarboxylic acid dialkyl or alkyl aryl esters. Pure phthalates are often transparent liquids with lightly pleasant odours and lightly yellow hues (ATSDR, 2002, 1997, 1995; NTP-CERHR 2007). The general structure of phthalate esters (dialkyl ortho-phthalates) is shown in Figure 2.3. R, R' groups can be cyclic rings, linear, branched, or linear/branched substituents (US EPA, 2012). The isomeric forms of phthalic acid are classified as ortho, meta, and para, depending on how the carboxylic acids connect (Kumari and Pulimi, 2023). Nevertheless, the ortho form of benzene dicarboxylic acid, which is produced when a particular alcohol combines with phthalic

acid to make the ideal ester, is primarily utilised as a plasticiser and accounts for a significant amount of all phthalate esters produced globally (Kumari and Pulimi, 2023). According to Seyoum and Pradhan (2019), there were 6 to 8 million tonnes of PEs produced annually to use by various industrial enterprises.

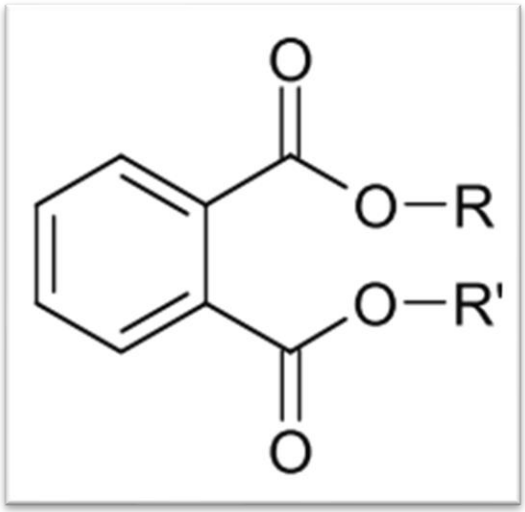

Figure 2.3 The general chemical structure of PE (Source: PEs from US EPA)

The most commonly utilised PEs in consumer products are dimethyl phthalate (DMP), diethyl phthalate (DEP), di-isobutyl phthalate (DiBP), di-n-butyl phthalate (DnBP), benzyl butyl phthalate (BBP), di-cyclohexyl phthalate (DcHP), di-n-hexyl phthalate (DnHP), bis (2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DnOP) and di-isononyl phthalate (DiNP) (Wang Y. et al., 2019; Dutta et al., 2020). The physicochemical properties of common PE compounds are given in Table 2.3, which includes the chemical formula, average molecular weight, Henry's Law, boiling point, LogKoa, LogKow and vapour pressure.

Table 2.3. The physicochemical properties of PEs (Source: CompTox Chemicals Dashboard from US EPA, 2023)

CAS Number	Compound Name	Abbreviation	Chemical Formula	Average Molecular Weight (g/mol)	Experimental Average					
					Henry's Law (atm-m3/mole)	Melting Point (°C)	Boiling Point (°C)	$LogK_{oa}$	$LogK_{ow}$	Vapor Pressure (mmHg)
117-84-0	di-n-octyl phthalate	DnOP	$C_{24}H_{38}O_4$	390.564	-	-25.7	381	-	8.1	1.00E-07
84-74-2	Di-n-butyl phthalate	DnBP	$C_{16}H_{32}O_4$	278.348	1.81E-06	-35	340	-	-	2.01E-05
84-66-2	Diethyl phthalate	DEP	$C_{16}H_{14}O_4$	222.24	-	-39.9	296	-	2.45	2.10E-03
85-68-7	Benzyl butyl phthalate	BBP	$C_{19}H_{20}O_4$	312.365	-	230	370	-	4.82	8.25E-06
605-54-9	Bis(2-ethoxyethyl) phthalate	DEEP	$C_{16}H_{22}O_6$	310.346	-	34	345	-	-	-
117-81-7	Di-2-Ethylhexyl Phthalate	DEHP	$C_{24}H_{38}O_4$	390.564	-	-53.3	308	-	7.53	1.42E-07
84-61-7	Di-cyclohexyl phthalate	DcHP	$C_{20}H_{26}O_4$	330.424	-	65	-	-	-	8.69E-07
84-75-3	Di-n-hexyl phthalate	DnHP	$C_{20}H_{30}O_4$	334.456	-	-58	186	-	6.82	1.40E-05
84-69-5	Diisobutyl phthalate	DiBP	$C_{16}H_{22}O_4$	278.348	-	-64	317	-	4.11	-
131-11-3	Dimethyl phthalate	DMP	$C_{10}H_{10}O_4$	194.186	-	4.44	284	-	1.58	3.08E-03
117-82-8	Bis(2-methoxyethyl)phthalate	DMEP	$C_{14}H_{18}O_6$	282.292	-	-45	340	-	-	-
131-18-0	Dipentyl phthalate	DPP	$C_{18}H_{26}O_4$	306.402	-	-55	342	-	5.62	-
84-76-4	Dinonyl phthalate	DNP	$C_{26}H_{42}O_4$	418.618	-	-	-	-	-	-
84-62-8	Diphenyl phthalate	DPP	$C_{20}H_{14}O_4$	318.328	-	74.2	403	-	-	-
117-83-9	Bis(2-butoxyethyl) phthalate	DBEP	$C_{20}H_{30}O_6$	366.454	-	-55	-	-	-	-

High molecular weight phthalates, such as DEHP, DiNP, and DnOP, are mainly used as plasticisers in producing flexible vinyl, used in consumer goods, flooring and wall coverings, food contact applications, and medical products (ATSDR, 1997; 2002; David et al., 2001). Producers incorporate low-molecular-weight PEs, such as DEP and DnBP, into personal-care items (e.g., perfumes, lotions, cosmetics) for their solvent and plasticizer properties in cellulose acetate. Additionally, these PEs are utilized in producing lacquers, varnishes, and coatings, and they are also utilized in medications to be released gradually over a specific period (ATSDR, 1995, 2001; David et al., 2001).

PEs negatively impact human health since they have been frequently used in various consumer goods and personal care items. Breast milk, regular cow's milk, infant formula, meals packaged in plastic (NTP-CERHR, 2007; Bosnir et al., 2003; Steiner et al., 1998; Wilkinson et al., 1999), toys made of plastic (Steiner et al., 1998; Wilkinson et al., 1999; Bouma, and Schakel, 2002; Stringer et al., 2000), indoor air (Shea, 2003) are all potential exposure sources for kids.

The precise origins and routes of significant phthalate exposure remain unclear due to the widespread use of PEs. Nevertheless, it is possible to assess exposure through four primary pathways: ingestion, parenteral exposure, dermal contact, and inhalation. Even at low doses, PE contamination interacts with various human physiological systems and may exhibit teratogenic, mutagenic, or carcinogenic effects (Gao & Wen 2016).

2.3. Non-Residential Buildings (School and Office Buildings)

Residences, non-residential structures, and other indoor spaces constitute unique characteristics related to IAQ. The building purposes and populations serviced, access and ownership status, building types and construction aspects, building operation and maintenance, occupant density and activities are the components which make up the characteristics of non-residential structures (Godish, 2001). Non-residential structures include private and public spaces, such as buildings used for education, work, healthcare, incarceration, places of worship, and entertainment (Godish, 2001). Hence, IAQ in these spaces relates to various public health concerns, and policy issues.

Workplace buildings significantly impact the indoor exposure of employees (Young et al., 2021). It is commonly known that indoor environmental quality (IEQ) significantly impacts occupants' conditions and is a vital component that may impact health and well-being (Bluyssen et al., 2011). Office workers have reported occupational health complaints, often linked to symptoms of sick building syndrome (SBS) (Burge, 2004). The definition of "sick building syndrome" (SBS) refers to situations in which building occupants suffer from acute health and comfort adverse effects that seem to be associated with time spent in a building; otherwise, no particular diseases or causes can be determined (US EPA, 1991). The prevalence of SBS may vary depending on factors related to the building, such as high indoor temperatures and light intensity, low ventilation of fresh air, higher-than-expected levels of air pollutants, and inadequate cleaning (Burge, 2004).

According to American Society of Heating and Air-Conditioning Engineers (ASHRAE) (2019), IAQ is defined as adequate if most occupants lack the expression of discomfort and no potentially hazardous amounts of chemical or biological contaminants are present. Indoor pollutant sources in office buildings are electronic devices, construction materials and furnishings, occupant activity, and cleaning agents. According to Lucattini et al. (2018) and Mitro et al. (2016), many endocrine-disrupting SVOCs comprise undisclosed constituents that easily release out of materials, thereby exposing occupants through inhalation, accidental dust ingestion and skin absorption.

Education is essential to developing a child's social ability, with children staying in school for extended periods (Oliveira et al., 2019). Primary schools serve children of ages 6 to 14 for approximately five to eight hours per day, thus being the second-most frequent indoor environment after homes (Sofuoglu et al., 2011). This situation indicates how essential schools are regarding exposure's time-based factor (Sofuoglu et al., 2011). Numerous factors, including the use of high-emitting building materials and furnishings, minimal landscaping with poor drainage, HVAC (heating, ventilation, and air conditioning) units, lack of preventative maintenance, crowded conditions, and cleaning products that release chemicals into the air, can be correlated to indoor pollution seen in school buildings (Godwin and Batterman, 2007). Due to the unique characteristics of every school environment, the amount of indoor and outdoor pollutants affects each individual's exposure (Stranger et al., 2007). As stated by Blondeau et al. (2005), other variables that affect the concentration of pollutants are the age and location of school buildings, pollutants that are transported indoors from

outdoors, chemical reactions that occur in indoor air, and heterogeneous processes that occur at the air-solid interfaces. Several studies have linked indoor air pollution to both short- and long-term health problems for students as well as educators in terms of comfort, productivity, and academic performance (Daisey et al., 2003; Shendell et al., 2004; Dijken et al., 2005; Mendell and Health, 2005; Shaughnessy et al., 2006). Compared to adults, children inhale more air (Bennett et al., 2008). Children's lungs may be exposed to higher amounts of air pollutants due to differences in inhalation routes (nasal versus oral) and the nose's ability to filter aerosols (Bennett et al., 2008). Due to their more curious and physically active personalities, which include crawling on the ground, children may also be less tolerant to air pollution (Annesi-Maesano et al., 2013).

2.4. Indoor Air Quality Sampling Methods

Indoor contaminants have been identified to assess possible causal links between disease or disease symptoms and residential and non-residential building environments. Samples from indoor environments are collected to identify airborne biological pollutants, chemicals in building materials, and gas/vapour or particulate-phase chemicals (Godish, 2001). Sampling is an essential part of the air analysis process since air is complex, diverse, and constantly changing in time and location due to human activity (Garcia-Jares et al., 2012). Basic air sampling techniques are required to routinely monitor exposure to organic contaminants in indoor environments (Garcia-Jares et al., 2012). Indoor air sampling requires a very low air volume, making it hard to sample without affecting the tested microenvironments (Garcia-Jares et al., 2012). Because of this, several techniques for gathering outdoor samples are inappropriate for use indoors (Garcia-Jares et al., 2012). The acceptable sampling and analytical techniques must be chosen for the air sampling process, which includes determining the number of samples, the sampling site, time and length, and equipment selection and calibration. Moreover, the organic pollutants monitored in the indoor environments have evolved in the last few years, hence, new methods and procedures have been developed, and the old ones have been modified to monitor the legacy and novel

compounds at the same time (Garcia-Jares et al., 2012). Both passive and active sampling techniques can be used to collect and investigate samples of indoor air (Godish, 2001).

2.4.1 Active Sampling Methods

The most accurate way to measure SVOC air concentrations is presently thought to be utilising active air samplers (AAS), which can collect chemicals in both the gas and particle phases under-regulated flow conditions (Garcia-Jares et al., 2012). Over the past 40 years, this approach has remained mostly constant despite acknowledged sampling artefacts (Bidleman et al., 1984). With respect to the type of sampler (high-, medium-, or low-volume samplers), a defined volume of air is pumped through an adsorbent tube packed with one or more adsorbents during active sampling, where the pollutants are retained at a specific and controlled flow rate, usually ranging from 0.5 to 1400 L min-1 (Garcia-Jares et al., 2012). The flow rate and sample collecting time are the primary factors between AAS's high-volume and low-volume sampler classifications. Flow rates of less than 3 m3/hour are typical for low-volume air samplers (Blanchard et al., 2006; Hayward et al., 2010; Hazrati et al., 2007; Melymuk et al., 2011; Batterman et al., 2009). This frequently leads to small sample volumes (for example, less than 200 m3), however, they may also be utilised for longer deployment durations. For instance, 500–1000 m3 of air can be obtained after 7–14 days of continuous sampling (Hayward et al., 2010; Hazrati et al., 2007; Melymuk et al., 2011). In order to determine the sample volume or flow rate and to compel the sample to pass through the trap, tools, including pumps and flow meters are needed (Garcia-Jares et al., 2012). Thus, the flow meter regulates the flow of a known air volume through the sampler, giving accurate quantitative results (Garcia-Jares et al., 2012). Typically, sampling durations range from a few minutes to many hours (Garcia-Jares et al., 2012). It is also possible to sample the particles after adding quartz or glass filters (Garcia-Jares et al., 2012). Additionally, when sampling, the adsorbent can retain the chemicals that volatilise from the filter (Garcia-Jares et al., 2012). Amberlite XAD-2 and XAD-4, nonionic macro reticular resins or polyurethane foam (PUF), are sorbent materials with

porous polymers (Garcia-Jares et al., 2012). Although it indicates the breakthrough of more volatile molecules, the latter has been used extensively for sampling pesticides, PCBs, polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), PEs, PBDEs, OPEs, or polyfluorinated organic compounds in air (Garcia-Jares et al., 2012). Figure 2.4 shows the active air sampling device and the analytical steps for particle matter (PM) determination.

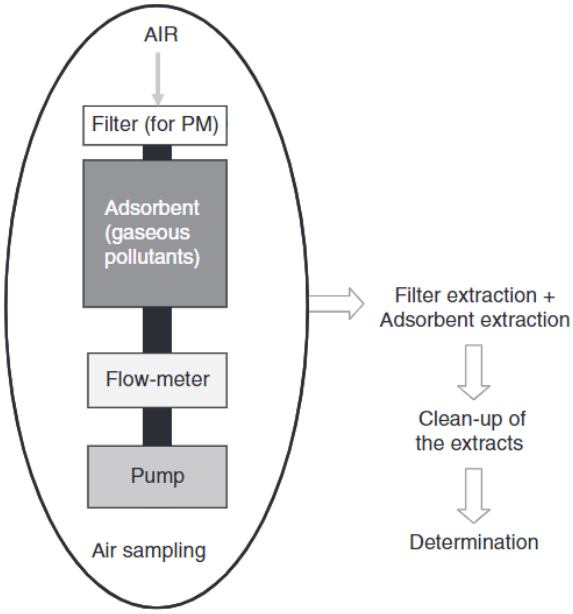

Figure 2.4. The active air sampling device and the analytical steps (Garcia-Jares et al., 2012)

2.4.2 Passive Sampling Methods

In order to improve efficiency and lower the costs associated with SVOC air monitoring, passive air sampling techniques were developed towards the end of the 1990s (Melymuk et al., 2014). Passive samplers (PAS) have several advantages over active samplers, including ease of use, cost-effectiveness, and lack of energy requirement (Nothstein et al., 2000). These benefits make it possible for simultaneous monitoring in several geographically varied regions. Moreover, they are appropriate for

determining indoor air quality because of their silent operation (Hazrati and Harrad, 2007).

Over the past ten to fifteen years, several forms of PAS have been assessed and deployed; some have drawn more attention (Melymuk et al., 2014). Passive sampling methods are immensely beneficial for determining concentrations averaged or integrated across several hours, days, or weeks (Godish, 2001). They are frequently rooted in the idea that pollutants can be absorbed by diffusing onto or into a sorbent material (Godish, 2001). The most used monitoring methods are the XAD-resin-based PAS (Wania et al., 2003) and the disk-shaped PUF-PAS (Harner et al., 2006).

Passive samplers using polyurethane foam (PUF) discs (Tisch TE-1014; 13.97 cm diameter; 1.27 cm thickness; 362.42 cm^2 surface area; 194.66 cm^3 volume; density 0.029 g/cm^3 density) were used for indoor air sampling. Figure 3.8 represents the sampler in additional detail. Passive sampling devices (PSDs), typically constructed using a PUF disc placed between two stainless steel bowls, facilitate the absorption of airborne chemicals into the PUF. Figure 3.9. indicates that the design allows air to flow from the gap between the bowls. It enables the absorbed chemicals to exit through holes in the lower bowl, ensuring the absorption of airborne substances by the PUF.

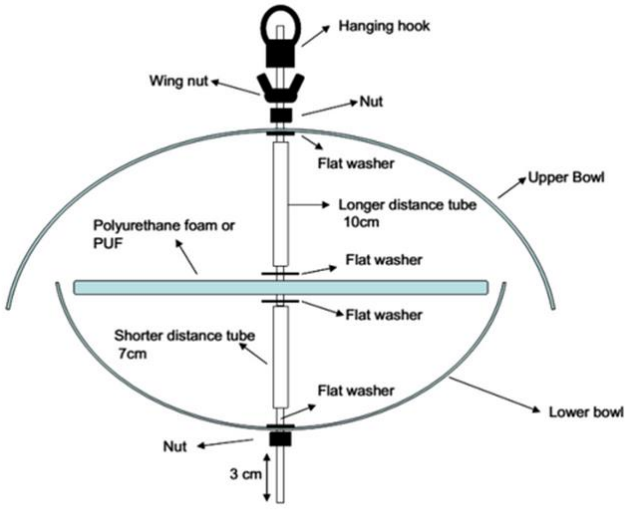

Figure 2.5. Detailed PUF disc as a passive sampler (United Nations Environment Programme, 2017)

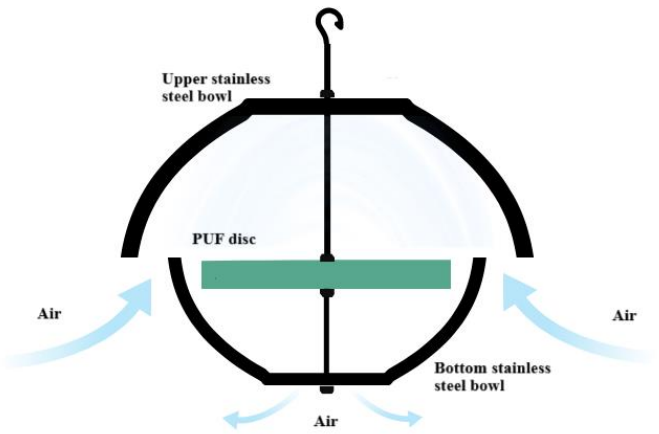

Figure 2.6. Air circulation in stainless steel bowls using PUF disc

Based on differences in the fugacity potentials of a particular compound in the air and sampler media, the diffusion of gaseous phase compound molecules to the sampler medium is achieved (Gorecki and Namiesnik, 2002). Shoeib and Harner (2002), Bartkow et al. (2005), Hazrati and Harrad (2007) described the theoretical knowledge of how chemicals accumulate in a PUF-PAS. The effective concentration gradient between the air and the sampler, represented by the following equation, determines the uptake profile of a chemical from the ambient air into a PUF-PAS (Hazrati and Harrad, 2007).

$$V_{PUF}\left(\frac{dC_{PUF}}{dt}\right) = k_A A_{PUF}\left(C_A - \left(\frac{C_{PUF}}{K_{PUF-A}}\right)\right) \quad (2.1)$$

The air side mass transfer velocities are represented by k_A (cm s^{-1}). The target compound concentration (pg cm^{-3}) in the air being sampled is denoted by C_A, the PUF disc volume (cm^3) by V_{PUF}, and the concentration of compound in the PUF disk (pg cm^{-3}) by C_{PUF}. According to Shoeib and Harner (2002), K_{OA} may be used to calculate K_{PUF-A} or the PUF disk/air partition coefficient. A small "C_{PUF}/K_{PUF-A}" value indicates that uptake is theoretically linear and dependent on k_A, A_{PUF}, and C_A. The passive sampler's chemical absorption and elimination rates are correlated with A_{PUF}, V_{PUF}, and K_{OA}. According to Bartkow et al. (2005), the mass transfer of compounds with a high K_{OA} ($>10^7$) and low atmospheric concentration is governed by the air-side mass transfer rate,

which is $k_O = k_A$. Consequently, the air supply rate to the chamber plays a primary role in controlling this mass transfer.

2.5. Personal Exposure Assessment Tools

Environmental sampling techniques are commonly used to assess human exposure to environmental chemicals. Researchers also perform biomarker analysis from biological matrices, such as blood, urine, or breast milk (Aylward et al., 2014; Dixon et al., 2018). It is noteworthy that biomarker concentrations incorporate all routes of exposure, including ingestion, inhalation, and skin contact (Needham et al., 2005). Nevertheless, biomarkers do not reveal the exposure pathway and route (Paustenbach and Galbraith, 2006). Biomarkers in blood and urine are used by biomonitoring projects, like the U.S. National Health and Nutrition Examination Survey (NHANES), to offer a thorough evaluation of chemical exposures associated with the general U.S. population (U.S. Department of Health and Human Services (HHS), 2017). Several factors affect the quantity of chemical exposure, making it challenging to account for inter- and intra-individual variation when analysing biomarker concentrations (Aylward et al., 2014; Koch et al., 2014). The timing of exposure events and chemical toxicokinetics can also affect biomarker concentrations. Biological samples have to be gathered as soon as possible after exposure due to having short half-lives of nonpersistent compounds of interest (Aylward et al., 2014; Paustenbach and Galbraith, 2006).

Active sampling tools, which include backpacks that monitor air quality, are frequently used by researchers to measure environmental contaminants in an individual's breathing zone (Bohlin et al., 2007; Nethery et al., 2012). Several participants may find the study burdensome, and their behaviour may be influenced by pump noise and carrying a backpack during the study (Bohlin et al., 2007; Cherrie et al., 1994). In order to guarantee accurate calibration, active air monitoring equipment also needs a battery supply and periodic service.

Another well-established technique for determining trace amounts of pollutants is passive sampling, which researchers frequently use to find chemicals in water and air

environments (Huckins et al., 2006; Paulik et al., 2016). The lipophilic membrane of the passive sampling polymer allows organic compounds from the surroundings to permeate through (Huckins et al., 2006). Passive samplers absorb chemicals similar to chemical absorption across an organism's phospholipid membranes, as evidenced by several ecological cases (Paulik et al., 2016; Booij et al., 2006). As a result, they capture the portion of lipophilic organic compounds that are bioavailable (Paulik et al., 2016; Booij et al., 2006). Bohlin et al. (2007) used passive sampling devices to monitor organic pollutant groups such as PAHs and PCBs in the environment. The materials utilised in passive sampling might differ significantly; including sophisticated polymers like silicone and polyethene (Namiesnik et al., 2005) and simple matrices like activated carbon (Tommasino, 1998). For personal SVOC sampling, samplers made of polydimethylsiloxane (silicone) and low-density polyethylene (LDPE) were utilized in the forms of sheets, brooches, wristbands, etc. (Bergmann et al., 2018). The continuous accumulation of chemicals in passive sampling devices over time enhances the sensitivity of analytical detection. This characteristic is the reason why passive sampling devices do not reflect a periodical concentration but rather a time-weighted average (Samon et al., 2022).

2.6. Silicone Wristbands

Silicone wristbands are used as a new passive sampling application to monitor individual chemical exposure (O'Connell et al., 2014; Anderson et al., 2017). They offer a straightforward approach to assessing individual exposure to specific organic compounds in the gaseous phase (Dixon et al., 2018). Silicone wristbands have previously been employed to sample chemicals with log Koa values ranging from 3.3 to 16 (Samon et al., 2022). They contain various compounds, from smaller, more volatile substances like solvents (e.g., toluene) to higher molecular weight compounds such as flame retardants or plasticizers (Bergmann et al., 2018). In their capacity as passive samplers, silicone wristbands enable an ambient pollutant to gradually diffuse (absorb) into the silicone polymer (Kile et al., 2016). This sampling method's non-invasiveness combined with its easy use and affordability present a potential for larger-scale

exposure monitoring studies, particularly in vulnerable groups like children (Romanak et al., 2019; Anderson et al., 2017).

The first study using silicone wristbands (SWs) to assess individual chemical exposures was conducted by O'Connell et al. (2014). Over the past ten years, silicone wristbands have proved useful as personal passive samplers for evaluating the exposure of adults and children to various consumer products and synthetic chemicals (O'Connell et al., 2014; Anderson et al., 2017; Quintana et al., 2019; Dixon et al., 2018; Dixon et al., 2019; Donald et al., 2016; Kile et al., 2016; Hammel et al., 2016; Hammel et al., 2018). Lately, silicone wristbands were utilised to monitor occupational and environmental exposure to PAHs at natural gas production sites (Paulik et al., 2018) to pesticides in underdeveloped nations (Donald et al., 2016; Bergmann et al.,2017), flame retardants in preschoolers (Kile et al., 2016), and PAHs in roofers who work in high-risk environments (O'Connell et al., 2014). Utilizing wristbands in occupational settings offered distinct advantages in efficiently assessing potential acute exposure within a short time frame, such as a single workday, without imposing an excessive burden on workers through multiple sampling tools (e.g., active air sampling packs) (Samon et al., 2022). Correspondingly, wristbands were employed to assess exposure in individuals who might come into contact with environmental pollutants due to closeness (Samon et al., 2022). The exposure assessment contained families of agricultural workers, residents in coal mining communities, individuals residing near natural gas drilling pads, commuters on heavily trafficked roads, and those living close to a natural technological disaster (Oluyomi et al., 2021).

Further demonstrating the efficacy of silicone media as passive samplers, Hammel et al. (2018) also associated the presence of PBDEs, on silicone wristbands, with blood indicators for PBDE exposure (Hammel et al., 2018). Furthermore, several studies have discovered a strong relationship between the chemical buildup levels on the wristband and internal exposure indicators detected in the urine or blood (Dixon et al., 2018; Hammel et al., 2016; Hammel et al., 2018). Lastly, wristbands have been utilized for sampling populations that are more vulnerable to adverse health outcomes, such as children, pregnant women, and individuals with preexisting health conditions (Samon et al., 2022).

Table 2.5 presents the studies conducted using silicone wristbands to assess human exposure to PAHs. In their 2019 study, Wang et al. engaged ten adult participants, comprising three females and seven males, who wore silicone wristbands

on their dominant hand continuously for 72 hours. According to the data presented in Table 2.5, the cumulative median concentration of PAHs, encompassing ten different compounds, reached 263 ng per wristband. Noticeably, Phenanthrene, Benz(a)anthracene and Fluoranthene contributed to the total concentration at 37%, 18%, and 10%, respectively. Romanak et al. (2019) documented the involvement of ten participants, including five non-smoking females and males. These individuals wore wristbands continuously for seven days, ensuring minimal coverage by clothing during daily activities and removing the wristbands solely during swimming in a chlorinated pool. The results presented in Table 2.5 revealed a collective median concentration of 273 ng per wristband for PAHs. Specifically, Phenanthrene, Anthracene, and Fluoranthene demonstrated higher concentrations than other PAHs, with corresponding contributions to the overall concentration of 33%, 24%, and 11%, respectively. A comparison of the contributions to the total PAH concentration between Romanak et al. (2019) and Wang et al. (2019) indicated close similarities in the contributions of Phenanthrene and Fluoranthene. Young et al. (2021) conducted a study employing silicone wristbands among office workers. Participants were instructed to wear SWs for four days to eight hours daily during their shift. The study comprised 251 participants, with a breakdown of sample sizes across different regions: 85 in the United States, 42 in the United Kingdom, 54 in India and 70 in China. According to the findings presented in Table 2.4, Naphthalene, Phenanthrene, Fluoranthene, and Pyrene demonstrated high median concentrations among the PAH compounds.

Table 2.4. PAH concentrations (ng/g wristband) were identified by using SWs in the world

Country	PAH Compound	Test Field	Max (ng/g wristband)	Median (ng/g wristband)	n	Participants	Sampling Duration	Year	Reference
USA-UK-CHINA-INDIA	Acenaphthylene	office buildings	21.7	0.67	251	Office Workers	32 hours	2019	(Young et al., 2021)
	Acenaphthene		32	1.12					
	Anthracene		38.6	1.07					
	Benz[a]anthracene		101	2.1					
	Benzo(g,h,i)perylene		11.9	0.005					
	Benzo(j,b,k)fluoranthene		15.4	0.573					
	Benzo[a]pyrene		16.1	0.585					

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Table 2.4. (cont.)

All Countries USA-UK-CHINA-INDIA	Chrysene	office buildings	83	1.59	251	Office Workers	32 hours	2019	(Young et al., 2021)
All Countries USA-UK-CHINA-INDIA	Dibenz[a,h]anthracene		3.05	0.318					
All Countries USA-UK-CHINA-INDIA	Fluoranthene		185	5.37					
All Countries USA-UK-CHINA-INDIA	Fluorene		41.1	1.35					
All Countries USA-UK-CHINA-INDIA	Indeno(1,2,3-cd)pyrene		13.3	0.223					
All Countries USA-UK-CHINA-INDIA	Naphthalene		1880	28.6					

(cont. on next page)

Table 2.4. (cont.)

All Countries USA-UK-CHINA-INDIA	Perylene	office buildings	<MDL	<MDL	251	Office Workers	32 hours	2019	(Young et al., 2021)
All Countries USA-UK-CHINA-INDIA	Phenanthrene		249	28					
All Countries USA-UK-CHINA-INDIA	Pyrene		193	4.07					
All Countries USA-UK-CHINA-INDIA	Acenaphthylene	office buildings	21.7	0.67	251	Office Workers	7 full days	2019	(Young et al., 2021)
All Countries USA-UK-CHINA-INDIA	Acenaphthene		32	1.12					
All Countries USA-UK-CHINA-INDIA	Anthracene		38.6	1.07					
All Countries USA-UK-CHINA-INDIA	Benz[a]anthracene		101	2.1					
All Countries USA-UK-CHINA-INDIA	Benzo(g,h,i)perylene		11.9	0.005					

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Table 2.4. (cont.)

All Countries USA-UK-CHINA-INDIA	Benzo(j,b,k)fluoranthene	office buildings	15.4	0.573	251	Office Workers	7 full days	2019	(Young et al., 2021)
All Countries USA-UK-CHINA-INDIA	Benzo[a]pyrene		16.1	0.585					
All Countries USA-UK-CHINA-INDIA	Benzo[e]pyrene		19.2	0.772					
All Countries USA-UK-CHINA-INDIA	Chrysene		83	1.59					
All Countries USA-UK-CHINA-INDIA	Dibenz[a,h]anthracene		3.05	0.318					
All Countries USA-UK-CHINA-INDIA	Fluoranthene		185	28.2					
All Countries USA-UK-CHINA-INDIA	Fluorene		41.1	1.35					
All Countries USA-UK-CHINA-INDIA	Indeno(1,2,3-cd)pyrene		13.3	0.223					

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Table 2.4. (cont.)

All Countries USA-UK-CHINA-INDIA	Naphthalene	office buildings	1880	28.6	251	Office Workers	7 full days	2019	(Young et al., 2021)
All Countries USA-UK-CHINA-INDIA	Perylene		<MDL	<MDL					
All Countries USA-UK-CHINA-INDIA	Phenanthrene		249	147					
All Countries USA-UK-CHINA-INDIA	Pyrene		193	21.3					

MDL: method detection limit.
LOQ: limit of quantification.

Table 2.5. PAH concentrations (ng/wristband) were identified by using SWs in the world

Country	PAH Compound	Test field	Min - Max (ng/wristband)	Median (ng/wristband)	n	Participant	Sampling duration	Year	Reference
Bloomington, Indiana, United State	ΣPAHs (10)	home	184 - 2368	263	10	3 female 7 male	72 hours	2018	(Wang et al., 2019)
	Acenaphthylene		1.6 - 10	6.5					
	Acenaphthene		8.5 - 29	13					
	Fluorene		4.8- 36	12					
	Phenanthrene		47- 181	97					
	Anthracene		9.4 - 28	18					
	Fluoranthene		20 - 94	27					
	Pyrene		15 - 75	24					

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Table 2.5. (cont.)

Bloomington, Indiana, United State	Benz(a)anthracene	home	10 - 327	48	10	3 female 7 male	72 hours	2018	(Wang et al., 2019)
Bloomington, Indiana, United State	Chrysene		4.6 - 10	7.1					
Bloomington, Indiana, United State	Benzo(k)fluoranthene		3.7 - 2140	16					
Indiana, United State	ΣPAHs		76.2 - 1240	273	10	5 female 5 male	7 days	2019	(Romanak et al., 2019)
Indiana, United State	Acenaphthylene		2.59 - 7.94	4.46					
Indiana, United State	Acenaphthene		<5.21 - 30.2	10.7					
Indiana, United State	Fluorene		10.8 - 102	24.3					
Indiana, United State	Phenanthrene		21.4 - 336	89.3					
Indiana, United State	Anthracene		<0.57 - 106	64.2					
Indiana, United State	Fluoranthene		9.22 - 198	30					
Indiana, United State	Pyrene		8.46 - 274	29.9					

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Table 2.5. (cont.)

Indiana, United State	Benz(a)anthracene		0.36 - 212	16	10	5 female 5 male	7 days	2019	(Romanak et al., 2019)
Indiana, United State	Chrysene		<2.14 - 143	19.4					

Table 2.6 summarizes the OPE concentrations observed in silicone wristbands. In the study conducted by Wang et al. (2019), TDCPP, TPHP, and TCPP showed highest concentrations among all OPEs with individual contributions of 26%, 22%, and 11%, respectively. On the other hand, deploying the wristbands longer than Wang et al. (2019) study, Romanak et al. (2019) disclosed a higher total OPE concentration per wristband. TBOEP, TDCPP, and TEHP were the dominant OPEs found in the wristbands, contributing 27%, 10%, and 5% to the total concentration, respectively. In Xie et al. (2021) study, a child between the ages of less than 1 to 7 years old, along with the child's mother, wore SWs for two weeks. Throughout this duration, participants were directed to always keep the wristbands on, including during sleep and bathing. For children, TCPP, EHDPP, and TBOEP had higher concentrations than other OPEs, contributing 22%, 12%, and 12% to the overall concentration, respectively. Conversely, the median concentration of total OPEs for mother participants reached 2140 ng per wristband. For mothers, the dominant OPEs were TCPP, TPHP, and TBOEP, with 42%, 9%, and 7% contribution to the overall concentration, respectively. Consequently, a comparative assessment of OPE exposure between child and mother participants indicated a predominance of TCPP in the overall contribution to OPE concentrations, and higher total OPE concentration in mothers' wristbands.

Table 2.6. OPE concentrations (ng/wristband & ng/g wristband) were identified by using SWs in the world

Country	OPE Compounds	Min - Max (ng/wristband)	Median (ng/wristband)	Min - Max (ng/g wristband)	Median (ng/g wristband)	n	Participants	Sampling Duration	Year	Reference
Bloomington, Indiana, United State	**ΣOPEs (7)**	1090 - 10084	1983			10	3 female 7 male	72 hours	2018	(Wang et al., 2019)
	TNBP	45 - 162	61							
	TCEP	26 - 323	75							
	TCPP	76 - 606	212							
	TDCPP	221 - 2179	524							
	TPHP	212 - 1068	441							
	EHDPP	18 - 1367	164							
	TEP	25 - 6978	58							
Indiana, United State	**ΣOPEs**	2440 - 9580	7840			10	5 female 5 male	7 days	2019	(Romanak et al., 2019)
	TEP	<26.7 - 1720	96.7							
	TNBP	<25 - 881	93.1							

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Table 2.6. (cont.)

Indiana, United State	TCEP	27.2 - 348	60.9			10	5 female 5 male	7 days	2019	(Romanak et al., 2019)
	TCIPP	109 - 1050	288							
	TDCIPP	168 - 2060	759							
	TPHP	72.1 - 1360	290							
	TBOEP	878 - 4000	2090							
	EHDPP	<56 - 979	245							
	TEHP	<6.25 - 710	353							
Guangzhou, South China	**Σ_{tri}OPEs**	203 - 16720	2140			47	Mothers	14 days	2018-2019	(Xie et al., 2021)
	EHDPP	1.5 - 1080	103							
	TBOEP	<LOQ - 1960	152							
	TCEP	<LOQ - 910	38.7							
	TCPP	<LOQ - 15920	900							
	TDCPP	<LOQ - 462	37.8							
	TEP	5.4 - 136	26.5							

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Table 2.6. (cont.)

Guangzhou, South China	TNBP	<LOQ - 527	76.5			47	Mothers	14 days	2018-2019	(Xie et al., 2021)
	TPHP	<LOQ - 738	172							
Guangzhou, South China	**Σ_{tri}OPEs**	100 - 3500	1100			47	Children	14 days	2018-2019	(Xie et al., 2021)
	EHDPP	7.3 - 330	132							
	TBOEP	0.5 - 1100	128							
	TCEP	<LOQ - 1490	29.5							
	TCPP	<LOQ - 1730	237							
	TDCPP	<LOQ - 345	35.1							
	TEHP	<LOQ - 197	40							
	TEP	5.8 - 269	35.2							
	TNBP	1.2 - 230	30.5							
	TPHP	8.8 - 359	105							
USA	TDCPP			5 - 1060	163.5	38	Mother	7 days	2015	(Gibson et al., 2019)
	TPHP			0.72 - 2230	399					
	TCPP			5.12 - 929	4.2					
	TCEP			3.27 - 719	108.5					

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Table 2.6. (cont.)

USA	TDCPP			5.85 - 2460	390.5	38	Children	7 days	2015	(Gibson et al., 2019)
	TPHP			0.72 - 3050	440					
	TCPP			6 - 3490	297.5					
	TCEP			3.83 - 656	64.5					
Massachusetts, USA	TCPP			<6.7- 199	39.5	9	Nail salon technicians	≥35 hours per week	2016-2017	(Craig et al., 2019)[a]
	TCEP			all < 30.6	<30.6					
	TDCPP			<6.7 - 35	15.7					
	TPHP			11.8 - 368	132					
	TCPP			<6.7 - 161	40.9	9	Nail salon technicians	≥35 hours per week	2016-2017	(Craig et al., 2019)[b]
	TCEP			<30.6 - 56.2	N/A					
	TDCPP			<1.2 - 27.4	3.3					
	TPHP			<6.1 - 1006	257					
Montevideo, Urugay	**ΣOPEs**			12300	1020	24	Children	7 days	2018	(Travis et al., 2020)
	TBP			0.01 - 510	66.4					
	TCEP			0.02 - 1420	20.8					
	TCPP			0.02 - 4480	208					
	TDCPP			0.01 - 1500	5.1					
	TPHP			0.01 - 8920	85.4					

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Table 2.6. (cont.)

Montevideo, Urugay	EHDPP			0.01 - 4820	290	24	Children	7 days	2018	(Travis et al., 2020)
North Carolina, USA	TCEP				35.8	77	Children	7 days	Aug-15	(Hammel et al., 2020)
	TCPP				55.16					
	TDCPP				179.7					
	EHDPP				73.61					
	TPHP				872.9					
All Countries USA-UK-CHINA-INDIA	EHDPP			<MDL - 6630	14	251	Office Workers	32 hours	2019	(Young et al., 2021)
	TCEP			<MDL - 37.8	0.836					
	TCPP			<MDL - 9260	77.3					
	TDCPP			<MDL - 25500	12.1					
	TEHP			<MDL - 1020	9.62					
	TEP			<MDL - 118	1.14					
	TnBP			<MDL - 54.2	2.1					
	TPHP			<MDL - 1800	35.3					

LOQ: limit of quantification.
(Craig et al., 2019)a: SWs were worn on the wrist
(Craig et al., 2019)b: SWs were pinned to the lapel

Another research conducted with mother-child pairs by Gibson et al. (2019) revealed similar dominant OPEs in the wristbands worn by the pairs, i.e. TPHP, TDCPP, and TCEP for mothers and TPHP, TDCPP, and TCPP for children. It is noteworthy that TPHP and TDCPP exhibited notably elevated concentrations in comparison to the findings from Xie et al. (2021) study, in which the participants were living in China. Hence, country-wise comparison of personal exposure is deemed essential to understanding societal health concerns. Twenty-four children aged 6.0–8.0 years attending first grade in nine elementary schools in different areas of Montevideo, Uruguay, wore SWs on their wrists during all activities throughout seven days (Travis et al., 2020). Among OPEs, EHDPP and TCPP exhibited higher median concentrations, contributing 28% and 20% to the overall concentration, respectively. Another study on children's exposure included 77 children aged 3–6 years, representing 74 different families living in USA (Hammel et al., 2020). After seven days of deployment, TPHP and TDCPP were identified as the dominant OPEs.

OPE exposure of nail-saloon workers was investigated in the study by Craig et al. (2019). Nine female nail salon technicians aged 18 or older, who were non-smokers and employed full-time (≥35 hours per week), utilized silicone wristbands both pinned to their lapels and worn on their wrists. Sample collections were conducted after each participant's work shift, accompanied by a questionnaire containing work-related and nonwork-related inquiries on potential factors contributing to exposure. Both SWs indicated a notable absorption of high concentrations of TPHP and TCPP in the nail salon environment. While TCPP concentrations remained consistent between the two sampling methods using SWs, the concentration of TPHP on lapel-pinned SWs was nearly twice as high as that on wrist-worn SWs. Investigating the work-place exposure across three countries, Young et al. (2021) revealed higher median concentrations for TCPP and TPHP among the OPEs.

PE concentrations detected in SWs so far is presented in Table 2.7. As can be observed from Table 2.7., regardless of the studied groups, all of the studies identified DEHP as the dominant PE compounds measured in SWs. In the nail-saloon workers study, the concentration of DEHP on lapel-pinned SWs was almost six times greater than that on wrist-worn SWs (Craig et al. 2019). In the study by Hammel et al. (2020), the median concentration of DEHP was at least nine times higher than the median concentrations of other PEs, while there was at least one order of magnitude difference between DEHP and other PEs in Young et al. (2021) study. BBP, DnBP and DiBP were

observed to be the dominant PEs following DEHP (Hammel et al., 2020; Young et al. 2021).

Table 2.7. PE concentrations (ng/g wristband) were identified by using SWs in the world

“

Country	PE Compounds	Test Field	Min - Max (ng/g wristband)	Median (ng/g wristband)	n	Participants	Sample Duration	Year	Reference
Massachusetts, USA	BBP	7 Nail salons	<6.7 - 22.3	<6.7	9	Nail salon technicians	7 days	2016-2017	(Craig et al., 2019)[a]
	DnBP		<1120 - 1697	<1120					
	DiBP		<17.6 - 143	<17.6					
	DEP		<31.5 - 967	<31.5					
	DMP		<1.8 - 5.8	<1.8					
	DEHP		<9.3 - 2004	42.4					
Massachusetts, USA	BBP	7 Nail salons	<6.7 - 45.7	N/A	9	Nail salon technicians	7 days	2016-2017	(Craig et al., 2019)[b]
	DnBP		all < 1120	N/A					
	DiBP		<17.6 - 56.1	<17.6					
	DEP		<31.5 - 576	<31.5					

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Table 2.7. (cont.)

Massachusetts, USA	DMP	7 Nail salons	<1.8 - 3.8	<1.8	9	Nail salon technicians	7 days	2016-2017	(Craig et al., 2019)[b]
	DEHP		27 - 3572	251					
USA	DMP	74 homes		22.59	77	Children	7 days	Aug-15	(Hammel et al., 2020)
	DEP			739.1					
	DiBP			976.2					
	DnBP			274.3					
	BBP			1059					
	DEHP			9010					
All Countries USA-UK-CHINA-INDIA	BBP	office buildings	<MDL - 15400	18.3	251	Office Workers	32 hours	2019	(Young et al., 2021)
	DEHP		<MDL - 348000	15100					
	DEP		<MDL - 218000	387					
	DiBP		<MDL - 33300	1660					
	DMP		<MDL - 196	25.3					
	DnBP		<MDL - 31500	1040					

MDL: Method detection limit
Not computed (N/A): The proportion of results below the method detection limit (MDL) was excessively high.
(Craig et al., 2019)[a]: SWs were worn on the wrist
(Craig et al., 2019)[b]: SWs were pinned to the lap

2.7. Uptake Characteristics of Silicone Wristbands

A straightforward approach to conceptualizing the accumulation of chemicals by a passive sampling medium (PSM) is to view it as a uniform, permeable compartment that allows for chemical penetration and dissolution (Shoeib and Harner, 2002). Mass transfer across the interface between the passive sampling medium (PSM) and the air involves the accumulation of resistances within the air boundary layer and the PSM (Shoeib and Harner, 2002). Three stages define the uptake: the curvilinear phase, the equilibrium phase, and the linear uptake phase, also known as the kinetic phase (Shoeib and Harner, 2002). Subsequently, the uptake rate gradually reduces as particular compounds approach equilibrium, entering the curvilinear phase (Samon et al., 2022). According to Shoeib and Harner (2002), sampling at the linear phase, where surface resistance is minimal and the uptake rates are at their highest, is frequently preferred. According to Tromp et al. (2019), silicone samplers have a significantly larger capacity per volume than polyurethane foam (PUF) samplers, which leads to a longer linear uptake phase. In the curvilinear phase, a portion of a compound has already partitioned into the PSD, decreasing the potential for compounds to transfer within the PSD until thermodynamic equilibrium is achieved (Samon et al., 2022). At equilibrium, the potential for a compound to transfer between the PSD and the sampled environmental media becomes equal (Samon et al., 2022).

Anderson et al. (2017) conducted the first investigation on this topic. The PAH concentration in wristbands worn by a participant was compared to the PAH concentration in low-volume active samplers carried by the same person, and the silicone wristband-air distribution coefficient (partitioning coefficient - K_{sa}) was calculated (Anderson et al., 2017). Moreover, Tromp et al. (2019), Donald et al. (2019), and Frederiksen et al. (2022) also assessed the uptake behavior of SWs. To investigate the uptake capacities and distribution coefficients of silicone wristbands, K_{sa} of SVOCs, a specific environment (soccer field) (Donald et al., 2019) or specifically designed chambers (Tromp et al., 2019) were used. However, people spend most of their time indoors, and daily exposure studies adopting silicone wristbands are more closely related to indoor environmental circumstances. The only study conducted in an indoor environment deployed SWs for thirty-one days to test the capacity of silicone

wristbands, and most chemicals failed to reach equilibrium. Therefore, K_{sa} values could not be determined (Frederiksen et al., 2022).

2.8. Motivation and Objectives

In recent years, silicone wristbands, utilised as a novel passive sampler, have yielded substantial results in understanding exposure to SVOCs. Nevertheless, there has been no study conducted in Türkiye to assess human exposure using SWs. Furthermore, critical parameters derived from the data collected using silicone wristbands are required to be established for exposure dose calculations. In essence, this unique research has been conducted to determine the uptake rates of SVOCs by silicone wristbands, the partitioning coefficient between air and silicone, and the concentration levels of SVOCs in indoor environments. Up to now few research has been conducted to determine the uptake characteristics of SWs in indoor environments. As the indoor environment, primary school classrooms were selected to be tested in the present study. The significance of indoor air quality in schools becomes apparent when considering that children spend almost 8 hours a day in school. Moreover, the high number of children in a classroom and insufficient ventilation and cleaning contribute to the decline in indoor air quality. Due to children's metabolic and physical activities, they are more sensitive to environmental pollution than adults, making it crucial to identify chemicals they may be exposed to through inhalation (Ekren et al., 2017).

The objectives of this study were:

i) to use the silicone wristbands to assess personal exposure of academic personnel living in İzmir, Türkiye to SVOCs and also to test SWs as an indoor air sampler in their offices

ii) develop a cost-effective and time-efficient analysis method to determine SVOC levels in silicone wristbands

iii) Estimating the uptake rates in silicone wristbands and air-wristband partitioning coefficients for SVOCs in indoor environments

iv) Determining PAH concentrations in indoor air using PUF PAS in primary school classrooms in İzmir.

iv) Evaluating the exposure of school-age children to PAHs in the classroom and conducting a human health risk assessment for school children.

CHAPTER 3

MATERIALS AND METHODS

3.1. Reagents and Standards

Reagents are crucial elements of laboratory experiments and analyses because chemical reactions rely on them to produce, measure or detect other compounds. In analytical and scientific measures, standards are substances or materials that have known, concentrations, amounts or properties. The accuracy and reliability of experimental data are ensured by using them as standards to calibrate instruments and validate processes.

In order for PAH analyses, a mixture of 16 EPA-PAH compounds, deuterated phenanthrene-d10 and perylene-d12 (surrogate standards), and a para-terphenyl (internal standard) were purchased from Ehrenstorfer (LGC Labor GmbH Augsburg, Germany).For PE analyses, a mixture of 13 PE compounds, deuterated DMP-d4, DnBP-d4 and DEHP-d4 surrogate standards were purchased from AccuStandard (New Haven and CT, USA). To analyse OPEs, nine reference standards that are TPHP, TCEP, TCIPP, TBOEP, EHDPP, TDCIPP, TNBP, TEHP, and TEP, were purchased from AccuStandard (New Haven and CT, USA). Deuterated TCEP-d12 and TPHP-d15 for OPE surrogate standards were purchased from Wellington Laboratories (Guelph, ON, and Canada). Deuterated internal standard benzo(e)pyrene-d12 was purchased from Ehrenstorfer (LGC Labor GmbH Augsburg, Germany) for OPEs and PEs analyses.

3.2. Sampling Sites

3.2.1. Office Environment and Personal Exposure Study

Within the scope of this study, silicone wristbands were initially used to assess human exposure and indoor air quality in offices. The human exposure study participants were the residents of the offices sampled. Within this framework, silicone wristbands were suspended at a height of 2 m above the ground in a total of 13 offices located in the Faculty of Engineering C Building at İzmir Institute of Technology (IZTECH). Figure 3.1 shows the location of offices in the building at IZTECH in İzmir.

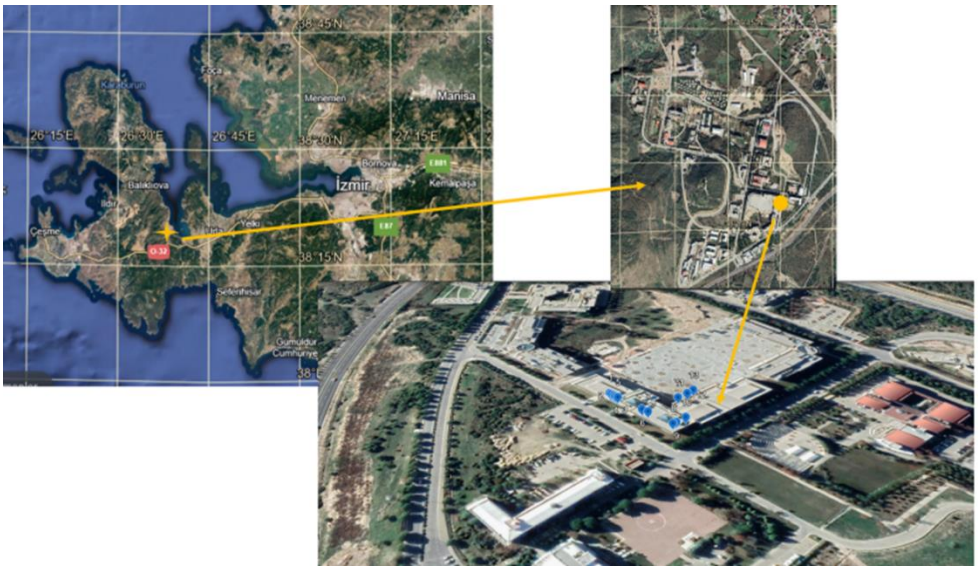

Figure 3.1. The location of the offices in the faculty building

The wristbands were deployed for one month, during September to October 2022. Additionally, four silicone wristbands were deployed in one of the selected offices, and one wristband was collected every week. One silicone wristband was placed in the office using tweezers and hung from the ceiling with pre-cleaned cotton ropes. The collected samples were then stored at -20 °C until analysis.

Thirteen office workers were recruited as full-time, permanent employees (working 40 hours per week) in an office within the university building. Throughout the study, participants were required to continuously wear pre-cleaned silicone wristbands (SWs) on their wrists for a complete seven days while bathing, cooking, sleeping, and performing various daily activities in indoor or outdoor environments. The study aimed to assess the exposure of office workers to SVOCs, concentrating specifically on PAHs, OPEs, and PEs in indoor environments, encompassing both homes and offices. The study took place over one week during the office environment study, i.e. October 2022'. The participants were provided the precleaned SWs with tweezers and asked to wear it themselves. One of the participants exited the study, and one wore the wristband for nine days. After the exposure, SWs were collected in amber glass bottles. The collected samples were then stored at -20 °C until analysis. A concluding questionnaire containing work-related and non-work-related inquiries about potential exposure-contributing factors was administered to the participants. Tables 3.1 and 3.2 show the factors of participants' daily activities, and specific information about their characteristics. The research protocol received approval from the Ethics Committee of İzmir Institute of Technology, ensuring adherence to research ethics standards.

Table 3.1. The factors of participants' daily activities during the study

The Variables of Participant Activities	**Office Workers n = 12**
Avg Times SW Washed in a Day	
3 - 4	1 (9.1%)
4 - 5	1 (9.1%)
7	9 (81.8)
Avg Hours/Day Spent in Office	
7	1 (9.1%)
7 - 8	1 (9.1%)
8	7 (63.6%)
8 - 9	1 (9.1%)
10	1 (9.1%)
Avg Hours/Day Spent in Home	
8 - 10	2 (18.2%)
11	1 (9.1%)
12	2 (18.2%)
12 - 13	1 (9.1%)
13	2 (18.2%)
13 - 14	2 (18.2%)
14 - 15	1 (9.1%)
Avg Mins/Day Spent in Car or Public Transportation	
30	1 (9.1%)

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Table 3.1 (cont.)

60	5 (45.5%)
90	3 (27.3%)
120	1 (9.1%)
240	1 (9.1%)
Avg Mins/Day Spent at Outdoor	
30	1 (9.1%)
60	1 (9.1%)
90	1 (9.1%)
120	6 (54.6%)
150	1 (9.1%)
180	1 (9.1%)

Table 3.2. Specific information about participants characteristics

Characteristics of study based on Participants	**Office Workers n = 12**
Male	6 (55%)
Female	5 (45%)
The Time SW Covered with Clothes	
None	4 (36.4%)
Constantly during one or two days	5 (45.5%)
Daytime hours in every day	2 (18.2%)
Smoking	
None	9 (81.8)
One to three times a day	2 (18.2%)

3.2.2. School Environment and Uptake Rate Study

The second part of this study aimed at estimating the uptake rate of silicone wristbands. To achieve this aim, the school environment was selected as the research focus. Indoor air samples were collected from Nihat Gündüz Primary School, which is governed by the Ministry of National Education, İzmir Provincial Directorate. The school is in İzmir's Işıkkent district, Bornova. There is an intercity bus terminal, cement factories, a personal care product manufacturing plant, and several small to medium-sized enterprises in the vicinity of the school. The school is also located close to the

junction of the İzmir highway. Figure 3.2 demonstrates the school's location, nearby bus terminals, factories, and roads.

Figure 3.2. The location of Nihat Gündüz primary school in İzmir

Sampling was conducted in five classrooms, two having mechanical and three with natural ventilation. The passive samplers used in this study are silicone wristbands and polyurethane Foam (PUF) discs to determine indoor air quality in classrooms and the uptake capacity of silicone wristbands for SVOCs. In each classroom, two PUF-PAS and eight silicone wristbands were used. Thus, forty silicone wristbands and ten PUF samplers were collected in each sampling campaign. Three sampling campaigns were employed: the first sampling campaign represented winter conditions, 17 February – 25 March 2023; the second sampling campaign represented spring weather conditions, 25 March – 29 April 2023; and the third sampling campaign was performed during summer, 20 May – 16 June 2023. The first and third sampling campaigns lasted for 36 days, while the second campaign lasted for 35 days.

The silicone wristbands were placed in each of the five classrooms using tweezers and hung from the ceiling with pre-cleaned cotton ropes in between PUF samplers. Figure 3.3 shows how silicone wristbands were used as passive indoor air samplers in the school and office buildings. Two of the SWs were collected every nine days for the campaigns with a duration of 36 days and every seven days for the 35-day campaign. After collecting all the SW samples with tweezers, they were put into amber

vials and kept in a cool box to transfer to the laboratory. After transportation, they were stored at -20°C at the laboratory until extraction.

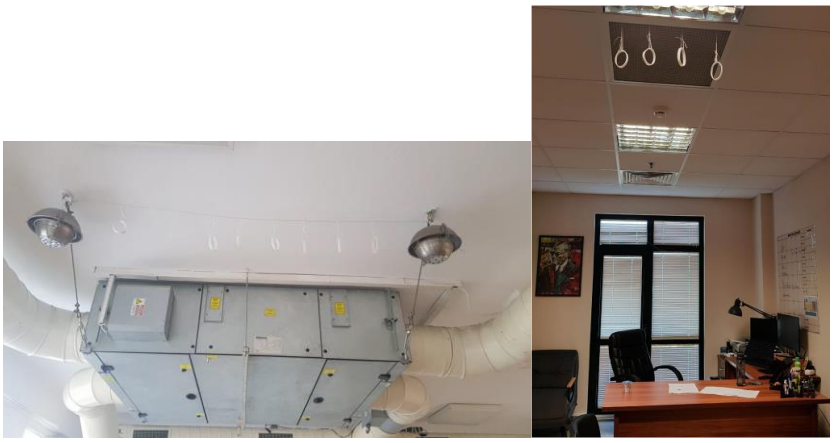

Figure 3.3. The silicone wristband samples as a passive indoor air sampler

One low-volume active sampler was operated in two classrooms with mechanical and natural ventilation to determine the ratio of particulate-phase air concentrations to gas-phase collected in glass fiber filters (gff) and PUF passive samplers, respectively. The methods applied in Genişoğlu et al. (2019) study were used for sampling and sample analysis. Accordingly, PM10 gffs and amberlite adsorbent material (XAD) between PUFs were collected for gas phase active sampling for 24 hours once in two weeks by using low-volume active samplers (Harvard, Air Diagnostics & Engineering Inc.) with flow rates of 10 m^3 d^{-1}. Additionally, meteorological parameters observed close to the sampling area were gathered. Daily averages of wind direction, speed, and temperature data throughout the sampling period were derived from Izmir Bornova/Zeytinlik Research Institute of the General Directorate of Agricultural Research and Policies (TAGEM).

Following the last sampling campaign, a kinetic uptake study was also designed to observe the nine-day accumulation of SVOCs in the SWs. Eight SWs were deployed as in the sampling campaigns and two of them were collected every two days. Then, they were analyzed in the same manner as other deployed SWs.

3.3. Sample Preparation, Extraction and Clean-up

3.3.1 Silicone Wristband Preparation

Silicone wristbands (SW) used in this study were purchased from t-silikon (https://www.t-silikon.com/, İstanbul, Türkiye). They had an average width of 1.1 cm, mean inner diameter of 6.1 cm, average mass of 5.4 g, and average density of 1.3 g/mL.

Previous studies used pre-cleaning procedures to avoid interference in GC-MS analysis so that possible contamination that may arise during the manufacture of silicone wristbands could be removed. Table 3.3 shows the pre-cleaning procedures used in the research studies.

Table 3.3. Some of precleaning method in the literature

Type of Micropollutants	**Precleaning Method (Prior to Deployment)**	**Cleaning solvents, duration and number of repetition**	**Reference**
PAHs, consumer and personal care products, pesticides, PEs, and other industrial compounds	Orbital shaker – 60 rpm	Three times with 800 mL ethyl acetate and hexane mixture (1:1, v:v) for 2.5 h, Two times with ethyl acetate and methanol (1:1, v:v) for 2.5 h	O'Connell et al., 2014
PCBs, PBDEs, OPEs	Orbital shaker – 60 rpm	Three times with 800 mL ethyl acetate and hexane mixture (1:1, v:v) for 2.5 h, Two times with ethyl acetate and methanol (1:1, v:v) for 2.5 h	Travis et al., 2020
PBDEs, OPFRs	Orbital shaker – 60 rpm	Three times with 800 mL ethyl acetate and hexane mixture (1:1, v:v) for 2.5 h, Two times with ethyl acetate and methanol (1:1, v:v) for 2.5 h	Kile et al., 2016
PAHs	Orbital shaker – 120 rpm	One time with 800 mL methanol for 10 min, Three times with 800 mL ethyl acetate and hexane mixture (1:1, v:v) for 1 h, Two times with ethyl acetate and methanol (1:1, v:v) for 1 h	Baum et al., 2020

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Table 3.3. (cont.)

PAHs, Flame retardants, Pesticides, PCBs, VOCs	Vacuum oven – 300 °C	Under vacuum at 0.1 Torr for 180 min. During baking, the vacuum oven was flushed with 99.99% nitrogen at 15, 30, 45, 60, 90, 120, and 180 min intervals.	Anderson et al., 2017
A total of 22 VOC and SVOC chemicals were chosen (Table 1)	Vacuum oven – 300 °C	Under vacuum at 0.1 Torr for 180 min. During baking, the vacuum oven was flushed with 99.99% nitrogen at 15, 30, 45, 60, 90, 120, and 180 min intervals.	O'Connell et al., 2021
PBDEs, Novel brominated flame retardants (nBFRs), PAHs, OPEs	Soxhlet with two different solvent mixtures	One time with a mixture of ethyl acetate and hexane (1:1, v:v) for 24 h, followed by ethyl acetate and methanol mixture (1:1, v:v) for 24 h	Wang et al., 2019
PBDEs, NFRs, OPEs, PAHs	Soxhlet with two different solvent mixtures	One time with a mixture of ethyl acetate and hexane (1:1, v:v) for 18 h, followed by ethyl acetate and methanol mixture (1:1, v:v) for 18 h	Romanak et al., 2019
OPEs,PEs, Nonphthalate, Plasticizers	Soxhlet with two different solvent mixtures	One time with a mixture of ethyl acetate and hexane (1:1, v:v) for 12 h, followed by ethyl acetate and methanol mixture (1:1, v:v) for 12 h	Hammel et al., 2020
Brominated Flame Retardants (BFRs), OPEs, Pesticides, PEs	Soxhlet with two different solvent mixtures	One time with a mixture of ethyl acetate and hexane (1:1, v:v) for 12 h, followed by ethyl acetate and methanol mixture (1:1, v:v) for 12 h	Kassotis et al., 2020
PAHs	Soxhlet with two different solvent mixtures	One time with a mixture of ethyl acetate and hexane (1:1, v:v) for 24 h, followed by ethyl acetate and methanol mixture (1:1, v:v) for 24 h	Hendryx et al., 2020

Three pre-cleaning procedures were tested in this study based on the research reported in Table 3.1. The first approach is vacuum oven cleaning. Three silicone wristbands were baked in a vacuum oven at 200°C for 24 hours, with the oven pressure set to 30 mbar (see Figure 3.4). The silicone wristbands were placed in pre-cleaned amber bottles after baking and kept at 4°C until the extraction procedure. A solvent-based washing procedure was tested as the second pre-cleaning method. The silicone wristbands were put in amber bottles previously cleaned. In the amber bottle, 200 ml of a (1:1, v:v) mixture of n-hexane and ethyl acetate solvent was added. A JSR JSSI-100C model horizontal shaker was used to shake the bottle's contents for one hour at 120 rotations per minute (rpm). Following the completion of the first process, the spent solvent combination was removed as waste, and 200 ml of a 1:1 mixture of ethyl acetate and methanol solvent was added to the wristbands and shaken for one hour at a rate of 120 rpm. After the second solvent mixture was separated as waste, the silicone

wristbands were kept in the amber jar at 4°C. The Soxhlet system was tested as the third pre-cleaning approach. The initial process in this setup was the washing with a mixture of 150 mL of ethyl acetate and 150 mL of n-hexane solvent (1:1, v:v) over 24 hours, with circulating observed 4-6 times per hour. In the second phase, 150 mL of ethyl acetate and 150 mL of methanol solvent were syphoned over 18 hours, with circulating observed 4-6 times per hour (see Figure 3.5). Following each step, solvents were separated as waste. The silicone wristbands were wrapped in aluminium foil and dried overnight in a fume hood. They were then kept at 4°C in an amber jar until extraction.

Figure 3.4. Pre-cleaning with vacuum oven

Figure 3.5. Pre-cleaning with Soxhlet system

The pre-cleaned wristbands were extracted with a mixture of hexane and acetone (1:1, v:v) (30 mL in the first phase and 20 mL in the second step) using the ultrasonic bath for one hour to evaluate the efficacy of the three pre-cleaning processes. The extracts were evaporated to a volume of 1 mL by a rotary evaporator. These samples were analysed in Thermo Trace Ultra gas chromatography (GC) – ISQ single quadrupole mass spectrometry (MS) instrument with EI mode. The full scan procedure began at 90°C and was held for 1 minute, then heated up at a rate of 15°C per minute to 160°C (kept for 1 minute), then 3°C per minute to 210°C (held for 1 minute), and lastly 10°C per minute to 310°C (held for 15 minutes). The range of the mass scan was set at 50-300 amu. The temperature of the MS transfer was 280°C, the temperature of the ion source was 230°C, and the inlet temperature was 250°C. The carrier gas (1.1 mL/min) was helium.

3.3.2 Silicone Wristband Extraction and Clean-up

First, laboratory control samples (LCS) were set up to test the extraction procedures. The method developed by O'Connell et al. (2014) for injecting known quantities of PAH, OPE, and PE chemicals into silicone wristbands was followed. Silicone wristbands cleaned with the selected precleaning process were placed separately in glass beakers, and 75 mL of methanol was added into each beaker to soak the wristbands thoroughly. PAH, OPE, and PE standard solutions were successively injected into the silicone wristbands to achieve 200 ng PAHs and 500 ng of OPEs, and PEs in the wristbands. Due to the risk of cross-contamination, the glass syringe was not allowed to contact with the wristbands throughout the injection procedure. After the injection process had been accomplished, the beakers were lightly covered with aluminium foil and kept in the dark at room temperature for 5 to 7 days to enable all the methanol to evaporate.

Previous research utilised mainly shaker and ultrasonic extraction procedures to determine SVOC concentrations in the SWs. Table 3.4. shows the extraction procedures utilised in these studies.

Table 3.4. Some of the commonly used extraction methods in the literature

Type of Micropollutants	Extraction Method	Extraction Solvents	Extraction Duration and Number of Repetition	Reference
PAHs, consumer and personal care products, pesticides, PEs, and other industrial compounds	Orbital shaker - 60 rpm	100 mL ethyl acetate	Two times for 2 h	O'Connell et al., 2014
PCBs, PBDEs, OPEs Pesticides	Orbital shaker - 60 rpm	25 mL ethyl acetate	Two times for 2 h	Travis et al., 2020

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Table 3.4. (cont.)

PBDEs, OPFRs	Orbital shaker - 60 rpm	25 mL ethyl acetate	Two times for 2 h	Kile et al., 2016
PAHs	Orbital shaker - 120 rpm	30 mL ethyl acetate	Two times for 1 h	Baum et al., 2020
PAHs, Flame retardants, Pesticides, PCBs, VOCs	Orbital shaker - 60 rpm	100 mL ethyl acetate	Two times for 2 h	Anderson et al., 2017
A total of 22 VOC and SVOC chemicals were chosen (Table 1)	Orbital shaker - 60 rpm	100 mL ethyl acetate	Two times for 2 h	O'Connell et al., 2021
PBDEs, Novel brominated flame retardants (nBFRs), PAHs, OPEs	Ultrasonic bath	30 mL a mixture of acetone and hexane (1:1, v:v), followed by 20 mL acetone and methanol mixture (1:1, v:v)	Two times for 2 h (Waited for 17 h after the first extraction process)	Wang et al., 2019
PBDEs, nFRs, OPEs, PAHs	Ultrasonic bath	30 mL a mixture of acetone and hexane (1:1, v:v), followed by 20 mL acetone and methanol mixture (1:1, v:v)	Two times for 2 h (Waited for 17 h after the first extraction process)	Romanak et al., 2019
OPEs, PEs, Nonphthalate Plasticizers	Ultrasonic bath	10 mL a mixture of dicloromethane and hexane (1:1, v:v)		Hammel et al., 2020
Brominated Flame Retardants (BFRs), OPEs, Pesticides, PEs,	Ultrasonic bath	10 mL a mixture of dicloromethane and hexane (1:1, v:v)	Three times for 15 min	Kassotis et al., 2020
PAHs	Ultrasonic bath	30 mL a mixture of acetone and hexane (1:1, v:v), followed by 20 mL acetone and methanol mixture (1:1, v:v)	Two times for 2 h (Waited for 17 h after the first extraction process)	Hendryx et al., 2020

The ultrasonic extraction method was initially tested. First, laboratory control samples were placed in 40 mL amber vials, and 200 ng of phenanthrene-d10 and perylene-d12 for PAH analysis, 200 ng or 500 of Tris(2-chloroethyl) phosphate-d12, Triphenyl phosphate-d15 for OPE analysis, and 200 or 500 ng of Dimethyl phthalate-d4, Di-n-butyl phthalate-d4, Diethylhexyl phthalate-d4 for PE analysis were added to the SWs as surrogate standards. They were first extracted for 2 hours in an ultrasonic bath using a solvent mixture of 30 mL hexane: acetone (1:1, v:v). After the first extraction, silicone wristbands were kept in this solvent mixture overnight. This solvent

mixture was then transferred to clean rotary evaporator flasks. 15 mL of hexane and 11 mL of acetone were added to the glass vials as the next solvent mixture, and they were set in an ultrasonic bath for another 2 hours. The expansion of the wristbands after the first extraction was the reason for using less acetone in the second phase. The solvent mixtures from the two processes were combined and evaporated in a rotary evaporator until their volumes were decreased to 1 mL. The ultrasonic extraction process was also tested using ethyl acetate as a solvent (30 mL, at each step). The extracts were utterly evaporated in the rotary evaporator. Afterwards, a solvent exchange was carried out by injecting 2 mL of hexane into the evaporator flask and vaporising it again to decrease it to 1 mL. The evaporated samples were put into GC vials.

The shaker extraction method was also tested. Laboratory control samples were placed in the cleaned 250 mL amber bottle and spiked with the same amount of surrogate standards with the ultrasonic extraction method. Then, 100 mL of ethyl acetate was added to the bottle. In the first step of the extraction, the shaker was set at 23°C for 2 hours at 60 rpm. After completion of the first step, the solvents were transferred to 500 mL glass flasks previously cleaned with ethyl acetate. Another 100 mL of ethyl acetate was added in the second step. The shaker was set at 23°C for 2 hours at 60 rpm. After completing the second step, they were combined with the first extraction solvents. The same procedure was tested with 1:1 (v:v) n-hexane:acetone solvent mixture.

Following extraction, the purification of extracts is needed to reduce possible interferences in the samples. Generally, 1 mm chromatographic columns were used for purification purposes. Here, a miniature version of a chromatographic column was tested to decrease the amount of adsorbent and solvents used. A small amount of cleaned glass wool (ultrasonic bath for 1 hour using acetone-hexane mixture) was placed at the bottom of the Pasteur pipette. Activated silica gel of 0.5 g (400 °C for 16 hours) was loaded to the Pasteur pipette. On top of silica gel, anhydrous sodium sulphate (400 °C for 4 hours) was added to the Pasteur pipette. 2 mL of dichloromethane (DCM) was eluted from the column for conditioning, and the collected DCM was separated as waste. Once the DCM in the column had been drained, the sample was injected, and the eluate flowing through the column was gathered in a flask. Once the sample was eluted, 2 mL of DCM was added on top of the column. These two elutions were combined as the first fraction in the same flask for PAH

analysis. Following the first fraction, 4 mL of acetone: DCM (7:3) mixture was transferred to the column, and the second fraction was collected in a separate flask for OPE and PE analysis. The first fraction was evaporated in a rotary evaporator until 1 mL. The second fraction was evaporated in the rotary evaporator until the sample evaporated. After the second fraction had been entirely evaporated, 5 mL of n-hexane was added to the flask for solvent exchange. The n-hexane was evaporated to 1 mL and taken to GC vials Before GC-MS analysis, the extracts were spiked with the internal standards p-terphenyl for the first fraction and benzo(e)pyrene-d12 for the second fraction. A similar process to the Pasteur pipette column was carried out for the chromatographic column purification method. Only the amounts of solvent and chemical were altered. 20- and 40-mL DCM were used instead of 2 and 4 mL of solvent, respectively. 5 g silica gel and 2 cm anhydrous sodium sulphate were added to the column instead of 0.5 g and 1 cm, respectively. During the personal exposure study, some OPEs and PEs were identified also in the first fraction, hence the sum of OPEs and PEs detected in two fractions were reported in the results. However, the two fractions were combined in the same flask during the school study.

3.3.3 PUF Extraction

Based on prior research, pre-cleaning procedures for PUFs were used in this study (Lammel et al., 2015; Demirtepe et al., 2019; Genişoğlu et al., 2019). Tisch Environmental 1/2" Tisch TE-1014 PUF discs were cleaned in a Soxhlet system for 8 hours with 300 mL of acetone, followed by another 8 hours with 300 mL of dichloromethane. The solvents were separated as waste after the washing procedures. The cleaned PUF discs were wrapped in clean aluminium foil and dried in a 60°C oven for 16 hours. Once dried, they were stored in sealed zip lock bags at -20°C until ready for use. Two PUFs were placed in each classroom for each sampling campaign. They were collected at the end of the campaigns, wrapped in clean aluminium foil and kept in a cool box during transfer to the laboratory. After transportation, they were stored at -20°C at the laboratory until extraction. Previously developed extraction method for PUFs was validated within the scope of this study (Lammel et al., 2015; Demirtepe et

al., 2019; Genişoğlu et al., 2019). PUF samples were extracted with 350 mL of hexane and acetone mixture (1:1, v:v) using Soxhlet apparatus. The extraction process was completed after 24 hours.

Pre-cleaned glass wool was inserted in a glass chromatography column. After putting in five g of silica gel, it was topped with 2 cm of anhydrous sodium sulphate. The column was conditioned with 20 mL of dichloromethane (DCM). The sample (2-5 mL) was transferred into the column and collected in a rotary evaporator flask. Then, the first 20 mL of DCM was added, followed by a mix of 40 mL acetone: DCM (7:3, v:v) collected in a rotary evaporator flask. The eluate was evaporated in a rotary evaporator to less than 1 mL. The extracts were taken in GC vials. The internal standard p-terphenyl was spiked to the extracts before GC analysis.

3.3.4 Glass fiber filter Extraction

Before sampling, the filters wrapped in aluminium foil were conditioned in a 450 °C oven for 3 hours and weighed before deployment. Then, they were stored in glass Petri dish in a desiccator until deployment. After sampling, gffs were weighed before the extraction. They were placed in 250 mL amber bottle, and 100 ng of phenanthrene-d10 and perylene-d12 for PAH analysis were spiked as surrogate standards. After the injection, a 50 mL acetone-hexane mixture (1:1, v:v) was added to the samples, and they were stored at -20 °C overnight. The gffs were extracted for 30 minutes in an ultrasonic bath. After the extraction, five g of silica gel was put in a glass chromatography column, topped by 2 cm of anhydrous sodium sulphate. The column was conditioned with 20 mL of dichloromethane (DCM). The sample was added to the column and collected in a rotary evaporator flask. Then, 20 mL of DCM was added, followed by a mix of 40 mL Acetone: DCM (7:3, v: v) into the column, and all solvents were collected in one flask. The sample was evaporated in the rotary evaporator, then taken in GC vials. The internal standard p-terphenyl for PAH analysis was spiked to the extracts before GC analysis.

3.3.5 Amberlite adsorbent material (XAD) Extraction

Before deployment, one gram of XAD between PUFs was washed with a 350 mL acetone-hexane mixture (1:1, v:v) using the Soxhlet system. After sampling, XADs were spiked with the same amount of surrogate standards for PAH analysis. The samples were extracted using the Soxhlet system for 24 h, similar to passive PUF samplers. After the extraction, the sample was evaporated in the rotary evaporator to less than 1 mL. The extract was taken in GC vials. The internal standard p-terphenyl for PAH analysis was spiked to the extracts before GC analysis.

3.4. Instrumental Analysis

Thermo Trace gas chromatography (GC)-ISQ mass spectrometry (MS) instrument (Thermo Fisher Scientific Inc.) was used to quantify PAH, OPE, and PE in samples. All target compounds were measured in electron ionisation (EI) mode using a DB5-MS ultra-inert column (Agilent Technologies Inc) (30 m x 0.25 mm x 0.25 m). The oven program used for PAH analysis was begun at 50 °C and held for 1 minute then increased to 200 °C at a rate of 25 °C/minute, then to 300 °C at a rate of 8 °C/minute (3 minutes), and eventually to 320 °C at a rate of 20 °C/minute (1 minute). The injection volume was 2 uL, the temperature of the MS transfer was 280 °C, the temperature of the ion source was 230 °C, and the temperature of the input was 295 °C. Helium was used as the carrier gas at a 1.1 mL/minute flow rate.

The oven programme for OPE and PE analyses begun at 90 °C and held for 1 minute before increasing to 170 °C at a rate of 10 °C/minute (3 minutes), then to 230 °C at a rate of 10 °C/minute (4 minutes), to 260 °C at a rate of 5 °C/minute, and finally to 300 °C at a rate of 10 °C/minute (4 minutes). The injection volume was 2 uL, the temperature of the MS transfer was 300 °C, the temperature of the ion source was 260 °C, and the temperature of the input was 280 °C.

All instrumental studies were initially performed in scan mode to determine the m/z values and retention times. SIM (selective ion monitoring) procedures were developed based on these values, and sample analyses were conducted in SIM mode. Table 3.5 shows the m/z values and retention times of the targeted and surrogate standard compounds.

Table 3.5. The list of SVOCs for GC-MS analysis and their corresponding ion (m/z) and retention time values

Compound Name	Ion (m/z)	Retention time (min)	Compound Name	Ion (m/z)	Retention time (min)	Compound Name	Ion (m/z)	Retention time (min)
Naphthalene	127, 128	5.33	TEP	99, 155, 127	2.65	DMP	77, 133, 163	6.13
acenapthylene	151, 152	6.91	TNBP	99, 155	7.94	DEP	149, 177	8.33
acenaphthene	153, 154	7.09	TCEP-d12 (SS)	261, 263	10.1	DiBP	149, 150, 223	14.55
Fluorene	165, 166	7.66	TCEP	63, 249, 143	10.34	DnBP	149, 150	17.14
Phenanthrene-d10	188, 189	8.95	TCIPP	99, 125, 75	10.99	DMEP	149, 85, 167	20.1
Phenanthrene	177, 178, 179	8.99	TDCPP-d15 (SS)	79, 81	23.14	DEEP	149, 85, 167	20.21
Anthracene	177, 178, 179	9.07	TDCIPP	75, 99	23.4	DPP (DAP)	149, 150	22.01
Fluoranthene	202, 203, 201, 101	11.23	TPHP-d15 (SS)	339, 341	24.42	DnHP	149, 150, 251, 104	25.2
Pyrene	202, 203, 201, 101	11.72	TPHP	77, 325 ,326	24.54	BBP	149, 206, 91	25.29
Benz(a)anthracene	226, 228, 229	14.76	TBOEP	57, 85, 125	24.88	DBEP	149, 85, 101	26.91
Chyresene	226, 228, 230	14.86	EHDPP	250, 251, 362	24.95	DcHP	149, 167	27.4
Benzo(b)fluoranthene	252, 126	17.58	TEHP	99, 113	25.51	DEHP	149, 167	27.66
Benzo(k)fluoranthene	252, 126	17.66	benzoepyrene-d12 (IS)	260, 264	29.56	DnOP	149, 150, 279	29.77
Benzo(a)pyrene	126, 250, 252, 253	18.38				DNP	149, 293	32.07
perylene-d12	264, 260	18.52				DMP-d4	137, 167	6.1
Indeno(123cd)pyrene	138, 276, 277	21.21				DnBP-d4	153, 207	17.09
Dibenzo(ah)anthracene	139, 278, 279	21.34				DEHP-d4	153, 207	27.64
Benzo(ghi)perylene	138, 276, 277	21.95				benzo(e)pyrene-d12	260, 264	31.08
p-terphenyl	230, 231	12.25						

3.5. Quality Assurance Quality Control

Quality control studies are required to assess the performance of chromatographic analyses and extraction procedures for target analytes in samples. In order to check the quality assurance throughout the study, data quality objectives have been developed. These objectives include surrogate standard recovery for all quality control and field samples, analyte recovery for laboratory control samples, and the coefficient of determination (R^2) of the calibration curve obtained for analytes in GC-MS. The United States Environmental Protection Agency (EPA) recommends analyte and surrogate recoveries of 70-130%, a more than 99% coefficient of determination for calibration curves, and a relative standard deviation of less than 20% to differentiate between identical samples (US EPA, 2018). Quality control studies include analysis of laboratory control samples, laboratory and field blank sample analyses, and calculating detection limit values. While the percentage recovery range provided in the US EPA's Method 8000D was 70-130%, the data quality objectives of this study has been established as 50-120%, taking into account literature studies (Young et al., 2021; Wang et al., 2019; Romanak et al., 2019) and our experimental results. The recoveries are considered acceptable if they fit within this range. Additionally, R^2 of >0.99, RSD of <20% were set as the data quality objectives for GC-MS analysis.

An internal calibration with seven points was carried out for each chemical group. The calibration range for PAHs was 2 - 1000 ng/mL, while it was 2 - 400 ng/mL for surrogate standards. A seven-point calibration for OPEs was performed for 9 OPE compounds with concentrations ranging from 20 to 500 ng/mL and two surrogate standards (TCEP-d12 and TPHP-d15) with concentrations ranging from 20 to 500 ng/mL. Calibration for PEs was performed for 13 PE compounds in the range of 20 - 600 ng/mL and surrogate standards (DMP-d4, DnBP-d4, DEHP-d4) in the range of 20 - 500 ng/mL consisting of seven points. R^2 values more than 0.99 were obtained for all analyte compounds and surrogate standards, and RSD values were less than 20%.

Based on the US EPA's Method 8000D, the extraction and elution recoveries' were successfully identified using equations. The response factor (RF) values were computed for each target analyte relative to one of the internal standards using calibration standards, as shown below (US EPA, 2018):

$$\text{RF} = \frac{A_S\, C_{iS}}{A_{iS}\, C_S} \tag{3.1}$$

Where:

A_s = Analyte or surrogate peak response

A_{is} = Internal standard peak response

C_s =Analyte or surrogate mass in the sample aliquot

C_{is} = Internal standard mass in the sample aliquot

RF denotes the line slope between the origin and the given standard response. The linear model is typically representative throughout the range of calibration standards if the relative standard deviation (RSD) of variance in the factors is less than 20%. In order to evaluate the calibration's linearity, the mean RF (internal standard calibration), standard deviation (SD), and RSD (also known as the coefficient of variation, CV) have been computed as follows (US EPA, 2018):

$$\text{SD} = \sqrt{\frac{\sum_{i=1}^{n}(RF_i - RF')^2}{n-1}} \tag{3.2}$$

$$\text{mean RF} = RF' = \frac{\sum_{i=1}^{n} RF_i}{n} \tag{3.3}$$

$$\text{RSD (\%)} = \frac{SD}{RF} \times 100 \tag{3.4}$$

If the RSD is less than 20% over the calibration range, the slopes of the lines for each standard are sufficiently close to one another that the linear model is typically acceptable for the range of standards analysed; RF' may be utilised for estimating sample concentrations. If all of the criteria have been satisfied, the sample amounts were calculated by using the equation (3.5). The units for analyte mass should be the same as the ones utilised for determining RFs.

$$X_s = \frac{A_S}{\text{RF}} \times \frac{C_{iS}}{A_{iS}} \tag{3.5}$$

Where:

Xs = Calculated mass of analyte or surrogate in sample aliquot put into instrument (ng).

As = Analyte or surrogate peak response in the sample

Ais = Internal standard peak response in the sample

Cis = Internal standard mass in sample aliquot introduced into instrument (ng)

RF' = Average RF from the most recent initial calibration.

Laboratory control samples were used to develop silicone wristband analysis procedures as explained in 3.3.2. During school environment study, field blanks were employed for silicone wristbands and PUF-PAS. Cleaned silicone wristbands and PUF disks were taken to the field. During sample collection, they were exposed to the classroom environment in one mechanical and one natural ventilation classroom. Field blank samples were collected approximately 3-5 minutes afterwards, and these samples (6 for PUF and 10 for silicone wristbands) were analysed using the same procedure as the samples. Throughout the study, laboratory blank samples were also analysed. The laboratory blank samples were used to monitor any potential interferences. No blank corrections were employed due to the absence of any identified chemicals in the blank samples.

The method detection limit (MDL) is the lowest analyte concentration that analytical equipment can consistently detect. Determining the MDL before using any analytical procedure for quantitative measurements is critical. In this case, the MDL was measured by GC-MS analysis of the lowest calibration point ten times in sequence. The standard deviation of the concentration values derived from these studies was multiplied by 2.821, the t-test coefficient for ten observations. This value accounts for measurement error, as the US EPA (2016) suggested. The Limit of Quantification (LOQ) values were calculated by multiplying MDL by 3.18. On the other hand, field blank samples were also checked to compute LOQ. The average concentrations of analytes in field blank samples plus three times their standard deviation was used as LOQ, if they exceed the LOQ computed from MDL. Table 3.6 provides MDL and LOQ values used in the analysis of PAHs, OPEs and PEs in office and school studies.

Table 3.6. The method detection limit (MDL) and the limit of quantification (LOQ) values for PAH, OPE, and PE compounds

PAH	MDL	LOQ**	OPE	MDL	LOQ	PE	MDL	LOQ
Ace	1..83	8..00 (9.76)	TEP	10.10	25.43 (69.8)	DMP-d4	3.71	11.79*
Acy	3.25	6.40 (13.9)	TNBP	3.91	12.43* (54.1)	DMP	3.27	28.05 (82.6)
B(ghi)p	4.35	13.83*	TCEP-d12	5.53	17.60*	DEP	3.42	35.61 (100.8)
DbA	1.65	8.63 (1.88)	TCEP	2.82	54.01 (132.2)	DibP	3.21	26.56 (92.9)
Ind(123)pyr	2.37	7.54*	TCIPP	4.29	22.18 (83.9)	DnBP-d4	2.66	8.46*
Flu	1.90	4.76 (65.2)	TDCIPP	8.14	16.03 (41.3)	DnBP	2.57	37.16 (133.2)
Phe	1.87	5.94 (11.2)	TPHP-d15	10.83	34.45*	DEEP+DMEP	11.83	25.00 (67.8)
Ant	0.89	1.68 (1.12)	TPHP	7.18	22.84* (28.5)	DPP	3.30	26.72 (59.3)
Flt	0.19	0.68 (7.14)	TBEP	18.57	59.04*	DnHP	5.54	21.50 (41.9)
Pyr	0.30	0.94 (26.3)	EHDP	3.74	17.04 (36.1)	BBP	6.92	22.02* (65.6)
BaA	0.69	2.19 (0.61)	TEHP	7.90	14.45 (31.5)	DBEP	11.55	25.33
Chr	0.05	1.62 (0.45)				DcHP	5.58	17.74* (28.6)
B(b)F+B(k)F	2.32	7.39* (36.8)				DEHP-d4	14.63	46.51*
BaP	0.82	2.62				DEHP	17.43	55.43*
Nap	19.11	165.4 (67)				DnOP	5.36	17.06*
Phe-d10	15.50	49.29*				DNP	9.60	30.52*
Pery-d12	112.3	357.1						

*These are the determination limit values calculated using the MDLx3.18 method.

** The values given in parentheses are calculated from PUF field blank samples.

3.6. Uptake Rate Calculation

The uptake capacities and wristband-air partitioning coefficients in school environments were determined in this study. Prior studies by Shoieb and Harner (2002), Bartkow et al. (2005), and Hazrati and Harrad (2007) revealed the SVOC uptake behavior of passive samplers.

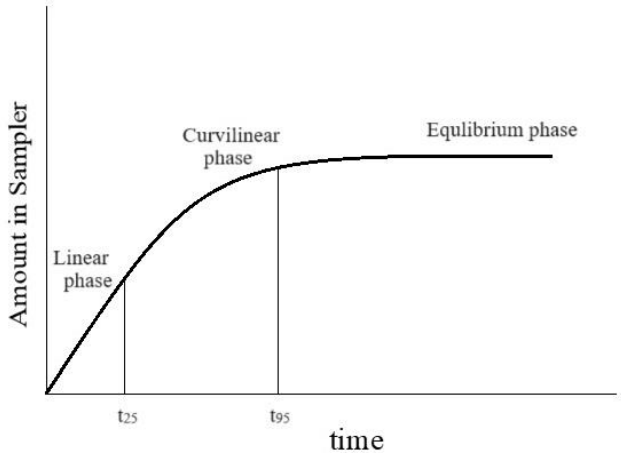

Figure 3.6. The uptake phases of chemicals in a passive sampler (Shoieb and Harner (2002))

For linking mass transfer coefficients to rate constants, the change in concentration in the sampler C_S with time t can be defined as the difference between the uptake and elimination rates by the following equation:

$$V_{SW}\left(\frac{dC_{SW}}{dt}\right) = k_A A_{SW}\left(C_A - \left(\frac{C_{SW}}{K_{S-A}}\right)\right) \quad (3.6)$$

The air side mass transfer velocities are represented by k_A (cm s^{-1}). The target analyte concentration (ng cm^{-3}) in the air being sampled is denoted by C_A, the sampler (SW) volume (cm^3) by V_{SW}, and the concentration of analyte in the sampler SW (ng cm^{-3}) by C_{SW},aAccording to Shoeib and Harner (2002). A small "C_{SW}/K_{S-A}" value indicates that uptake is theoretically linear and dependent on k_A, A_{SW}, and C_A. Equation 3.6 may be solved analytically to obtain a more accurate representation of the uptake profile:

$$C_{SW} = K_{SA}C_A(1 - exp\left(-\left(\frac{A_{SW}}{V_{SW}}\frac{k_A}{K_{SA}}\right)t\right)) \quad (3.7)$$

The equation 3.7 resembles the first-order rate equation:

$$ln\left(\frac{C_{Sw}}{C_0}\right) = -k_u t \quad (3.8)$$

where the uptake rate as a constant k_u (time^{-1}) is $k_u = (A_{SW}/V_{SW})(k_A/K_{S-A})$. The equilibrium concentration of SVOCs which reached the equilibrium phase can then be estimated using the equation 3.9, according to Frederiksen et al. (2022):

$$C = C_\infty (1 - exp(-k_u t) \quad (3.9)$$

where C denotes the concentration [ng/g] in the wristband at a specific moment, t [d]. C_∞ [ng/g] is the equilibrium concentration, and k_u is the rate constant [d-1]. The time it takes the wristband to reach equilibrium was determined as t_{95}, the time it takes to attain 95% of C_∞:

$$t_{95} = \frac{-\ln 0.05}{k_u} \quad (3.10)$$

Shoeib and Harner (2002) arbitrarily determined t_{25} as the upper bound of the linear phase. Hence in this study, it was utilised as an indication of the length of the kinetic phase. Using:

$$t_{25} = \frac{-\ln 0.75}{k_u} \quad (3.11)$$

The sampling rate of the passive sampler may be determined by

$$R = k_u K_{SA} V_{PSM} \quad (3.12)$$

Where R denotes the sampling rate [m^3/d],

For the SVOCs which cannot reach equilibrium and stayed at the uptake phase throughout the sampling period, the concentration in the sampler may follow zero order kinetics, as described by Sedlackova et al.:

$$C = C_0 - kt \quad (3.13)$$

The uptake rate for the compounds following Equation 3.7 can be estimated by calibrating it against the concentration of an active air sample or PUF, where a steady concentration of air was assumed.

$$R = \frac{n_{ps}}{C_{air}\Delta t} \quad (3.14)$$

n_{ps} is the amount of these compounds in the passive sampler, C_{air} is the amount of these compounds in the air detected by active sampling [ng/m^3] or PUF [ng/m^3].

Sampling of SVOCs with $K_{oa} > 10^7$ like PAH, OPE, and Pes on a suitable passive sampler medium in the linear phase is air-side controlled, so the mass transfer coefficient (MTC), also known as the dry gaseous deposition velocity, can be approximated to the air-side mass transfer coefficient, k_a [m/d] (Shoeib and Harner, 2002):

$$MTC \approx k_a = \frac{R}{A_{SW}} \quad (3.15)$$

Where A_{SW} is the sampler's surface area [m^2], involving both the inner and outer surface since both sideswere assumed to collect SVOCs. The sampling rates were estimated separately for each PAH congener on each wristband. Additionally, theresults of kinetic study were utilised to observe the use of varying methods (i.e. Equations 3.9 and 3.13) in uptake rate constant and sampling rate calculations for the PAH compounds reaching equilibrium during the 36-day sampling campaigns.

3.7. Exposure and Health Risk Assessment

The process of determining or assessing the size, frequency, and duration of people's exposure to an agent in the environment is known as exposure assessment (USEPA, 1992). The exposure pathways are inhalation, ingestion, and skin contact. The objective of this investigation focuses on inhalation exposure of SVOCs in the classrooms by schoolchildren.

The exposure by inhalation was assessed using the amounts of chemicals detected and determined using integrated active and passive samplers in indoor environments and using the formula given by the US EPA (US EPA, 2011):

Lifetime daily inhalation exposure:

$$CDI_{inhalation} = \frac{Ci \times IR_{inhal.} \times EF \times ED \times ET}{BW \times AT} \quad (3.16)$$

Table 3.7 demonstrates the exposure assessment parameters and required information, including inhalation rate, exposure time, and body weight depending on age groups and gender, retrieved from the Exposure Factors Handbook (US EPA, 2011), IRIS database for risk factors and toxicological attributes, and literature reviews.

Table 3.7. Exposure parameters and factors used to estimation of exposure, chronic toxic effect, and incremental lifetime cancer risk assessment.

Parameters	**Abbr.**	**Units**	**Variables**	**Reference & Notes**
Exposure frequency	EF	days/year	180	School days in one year
Exposure duration	ED	year	4	Education duration in Turkey
Daily exposure time	ET	h/d	4	Daily class hours
Body weight	BW	kg	15.95 (3^{th}) – 20.65 (50^{th}) – 27.8 (95^{th})	Neyzi et al., 2015
Averaging time	AT	days/year	28287.5	Life expectancy 77.5 years in Turkey (TUIK, 2018)
Inhalation rate	$IR_{inhalation}$	m^3/day	10.08 (5^{th}) – 13.09 (50^{th}) – 17.73 (95^{th})	(US EPA, 2011)
SF (inhalation) of BaP	SF_{BaP}	$(mg/kg\text{-}day)^{-1}$	3.9	US EPA, 2021
Reference concentration (BaP)	RfC	mg/kg-day	2.00E-06	IRIS Database US EPA

The lifetime average daily dose (LADD) of SVOCs to which children are exposed via inhalation were calculated separately for the targeted individual OPE and PE compounds. In contrast, the carcinogenic risk associated with PAH compound exposure were assessed by calculating the equivalent concentration of benzo(a)pyrene (BaP) as the total PAH exposure dose. The BaP equivalent concentrations for PAH

compounds were calculated by multiplying the concentration of each component by the toxic equivalency factors (TEFs) provided by Nisbet and LaGoy (1992). The toxic equivalency coefficients are represented in Table 3.8.

$$BaP_{equi} = \Sigma C_{PAHs} * TEFs \quad (3.17)$$

Table 3.8. Toxic equivalency factors for PAHs (Nisbet and Lagoy, 1992)

PAH Compound	**Toxic equivalency factors (TEF)**	**PAH Compound**	**Toxic equivalency factors (TEF)**
Nap	0.001	BaA	0.1
Ace	0.001	Chr	0.01
Acy	0.001	B(b)f	0.1
Flu	0.001	B(k)f	0.1
Phe	0.001	BaP	1
Ant	0.01	Ind(1,2,3)pyr	0.1
Flt	0.001	B(g,h,i)p	0.01
Pyr	0.001	DbA	5[a]

[a] A TEF of 1 appears acceptable for high DbA doses, while a TEF of 5 is more likely relevant to environmental exposures (chemical-related tumour incidence rate of less than 25%).

Moreover, the carcinogenic risk associated with PAH compound inhalation exposure was determined using the formula in Equation 3.18 (US EPA, 2005).

$$R = LADD \times SF \quad (3.18)$$

Where R is the cancer risk, SF is the slope factor of BaP, and LADD in the units of mg/kg-day. The slope factor for BaP is given in Table 3.7.

3.8. Statistical Analysis

All the data obtained in the study were statistically analysed using Python 3, IBM SPSS 25, and web-based, open-source Jupyter Notebook programs. During the study, Python libraries such as Statsmodel, Numpy, Seaborn, Pandas, SciPy, Matplotlib, and Pingouin were frequently used in conjunction to accomplish extensive data analysis and visualisation tasks in Python. The Shapiro-Wilk test was used to determine the data's normality. Non-parametric tests were performed when the data did not fit a normal distribution, and the correlation between the data was analysed using Spearman. Also, the differences between the data were analysed using the Mann-Whitney U or Kruskal-Wallis test. Differences between dependent variables, such as SVOC air concentrations under ventilation and temperature conditions, were examined using one-way analysis of variance (One-way ANOVA). The correlations and differences were deemed significant if the p-value was less than 0.05.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Method Development

4.1.1 Precleaning Method

To develop the precleaning method three methods, i.e. cleaning using Soxhlet apparatus, vacuum oven, and horizontal shaker, were tested. Full scan analysis of precleaned wristbands in GC-MS yielded chromatograms shown in Figures 4.1, 4.2, and 4.3 for the vacuum oven horizontal shaker Soxhlet apparatus methods, respectively. When the chromatograms were examined, the highest peak ratio in the vacuum oven and horizontal shaker methods were observed as 1one billion, while the highest peak ratio in the Soxhlet method was 120 million. In addition, the number of peaks appearing as contaminants was also less in the Soxhlet method than in the others. Therefore, the Soxhlet precleaning method was selected as the method for cleaning silicone wristbands before use in further studies.

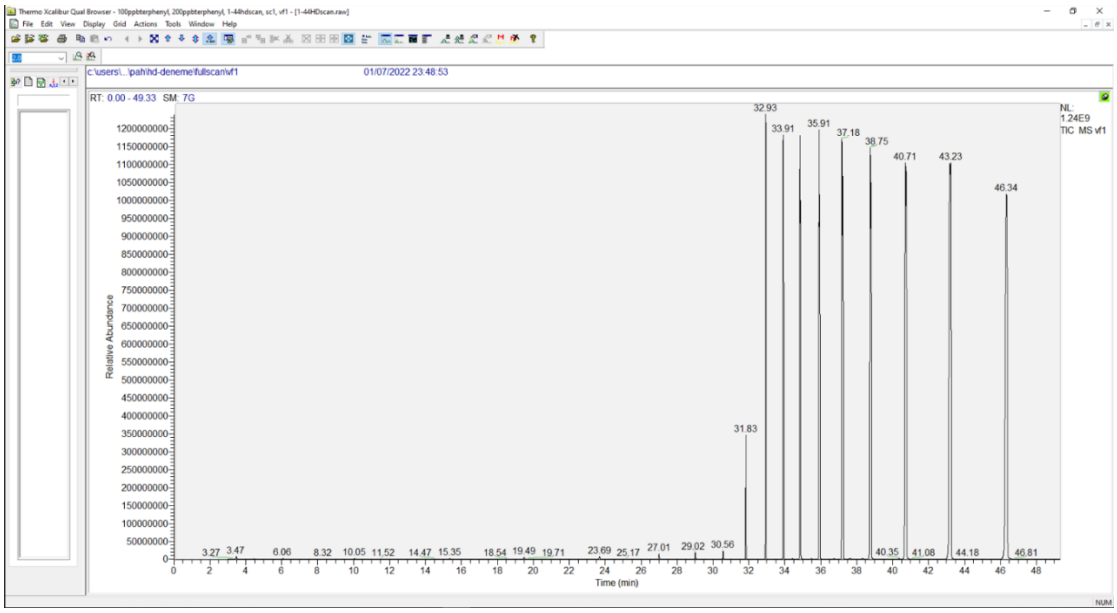

Figure 4.1. The chromatogram of the precleaning method with a vacuum oven

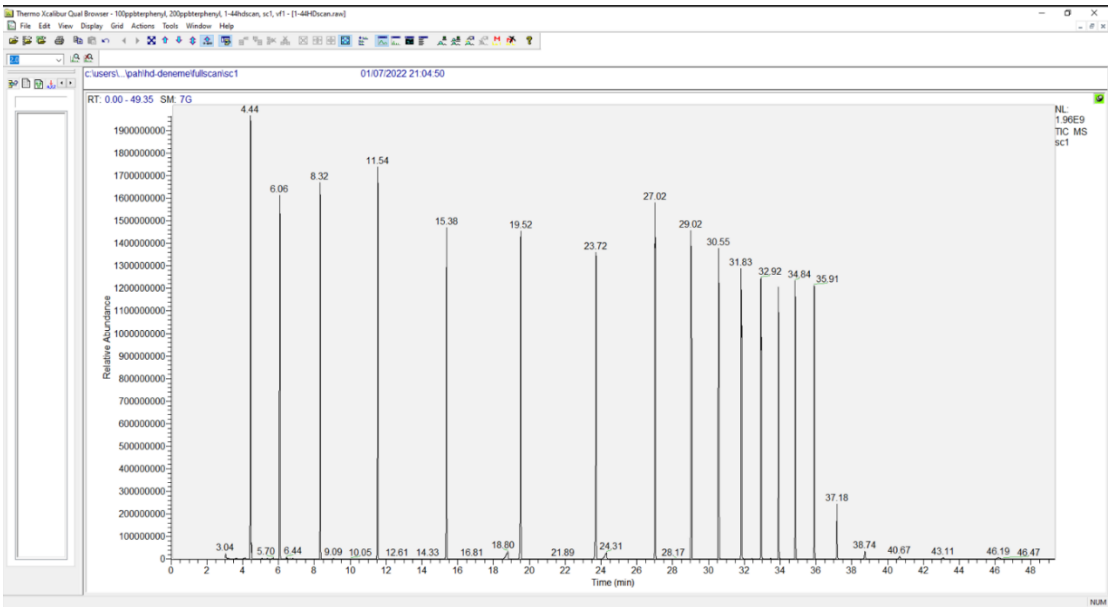

Figure 4.2. The chromatogram of the precleaning method with horizontal shaker

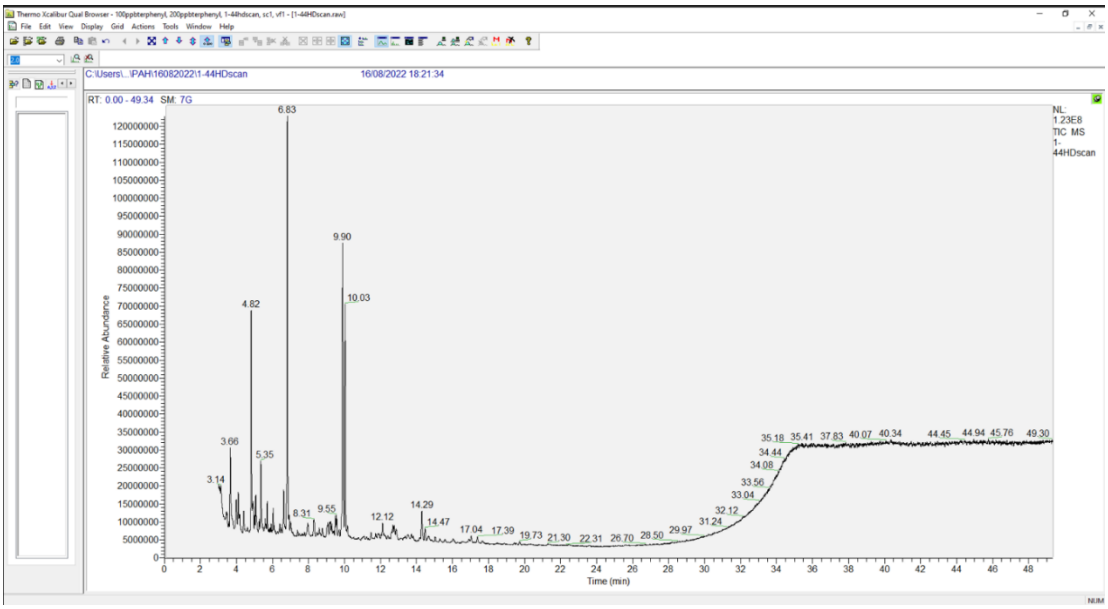

Figure 4.3. The chromatogram of the precleaning method with Soxhlet

4.1.2 Extraction Method

In order to test the extraction methods, laboratory control samples (LCS) were prepared along with solvent blanks and precleaned unspiked silicone wristbands.

The first extraction method tested was the ultrasonic extraction method, which was widely used in many studies (Wang et al., 2019; Hammel et al., 2020; Kassotis et al., 2020; Romanak et al., 2019; Hendryx et al., 2020). The second method was the horizontal shaker method, which has also been used in many studies (O'Connell et al., 2014; Kile et al., 2016; Anderson et al., 2017; Travis et al., 2020; Baum et al., 2020). The results of the tested extraction methods in terms of average per cent recovery are presented in Figure 4.4 and Tables 4.1, 4.2, and 4.3 for PAH, OPE, and PE, respectively. The US EPA recommends a 70-130% recovery range in the 8000D Chromatographic Analysis Method (US EPA, 2018). When all the results were compared, it was found that out of the total 44 chemical compounds determined as target and surrogate standards (SS), 22 showed lower recovery in the ultrasonic bath method, and two PE compounds (DEP and BBP) exceeded the acceptable recovery range at 142% and 140%, respectively. For most of the PAHs, shaker extraction gave better recoveries than ultrasonic extraction, however for OPEs and PEs, shaker extraction resulted in very low

recoveries. Therefore, the ultrasonic bath extraction method was selected for SVOC analysis in SWs. Additionally, differences were observed between the use of hexane: acetone and ethyl acetate solvents. Only 8 out of the 44 measured chemical compounds showed higher recovery using ethyl acetate in the ultrasonic bath method. Therefore, using a hexane and acetone solvent mixture in the ultrasonic bath extraction method resulted in higher recovery than the other tested methods. However, as can be seen from Tables 4.1, 4.2, and 4.3, most compounds were out of the 70-130% recovery range, especially below 70%. For PAHs, this range was found to be between 21.8 – 84.5% (Acy) and 42.9 - 102.4% (BaP), for OPEs between 35 - 41.7% (TEHP) and 3.81 - 151% (TBOEP), and for PEs between 11.8 – 141.6% (DEP). The PAH surrogate standards showed a recovery range between 47.1 - 72.8% (Phe-d10) and 44.9 - 73.5% (Pery-d12). The PE surrogate standards showed a recovery range between 36.2 – 114.4% (DMP-d4), 18 - 70.8% (DnBP-d4) and 20.8 - 78.2% (DEHP-d4). The OPE surrogate standards showed a recovery range between 55.2 – 133.5% (TCEP-d12) and 50.7 – 84.4% (TPHP-d15). Previous studies also observed low recoveries for the same compounds. Using the ultrasonic extraction method, Romanak et al. (2019) obtained recoveries as low as 57±8% (Acy) for PAH compounds, in the LCS analysis. Wang et al. (2019) reported a surrogate standard recovery range of 50-120% for all samples. Furthermore, Acy, TNBP, TCPP, and TEP had recoveries of 58.7%, 47.5%, 52.8%, and 57.8%, respectively, in matrix injection samples (Wang et al., 2019). Compared to the results of similar studies in the literature, it was observed that Acy consistently exhibited low recovery among PAH compounds, and some OPE compounds showed recoveries decreasing to around 50%. Young et al. (2021) utilized the ultrasonic extraction method with a mixture of hexane and dichloromethane solvents. In the study by Young et al. (2021), deuterated surrogate standards for DMP-d4 and DEP-d4 showed recovery of 31±10% and 41±13%, respectively, for all samples. Consequently, the acceptable recovery range was set between 50-120% within the scope of this study.

Table 4.1. The recovery efficiencies of PAH compounds to determine extraction methods by used SW LCS (n=3)

PAH Compound	Ultrasonic Bath Hex:Ace Mixture (%mean ± std.dev)	Ultrasonic Bath Ethyl acetate (%mean ± std.dev)	Horizontal Shaker Hex:Ace Mixture (%mean ± std.dev)	Horizontal Shaker Ethyl acetate (%mean ± std.dev)
Phe-d10	59.5 ± 8.3	52.4±20.0	72.8±5.56	47.1±4.6
Pery-D12	62.9 ± 5.0	60.9±25.6	73.5±3.69	44.9±8.4
Nap	84.4 ± 29.9	69.3±31.4	65.7±14.4	71.8±5.4
Ace	71.2 ± 11.8	61.3±23.3	83.6±9.35	57.1±4.8
Acy	21.8 ± 7.6	29.1±10.9	84.5±13.3	31.9±7.1
Flu	66.0 ± 9.0	57.8±21.5	80.4±9.17	54.0±5.3
Phe	58.3 ± 6.7	51.4±20.7	69.6±5.61	46.2±4.6
Ant	46.6 ± 4.7	40.4±16.6	81.3±4.74	32.7±4.8
Flt	55.0 ± 3.2	49.0±20.3	63.6±1.69	43.4±3.7
Pyr	58.6 ± 2.2	52.2±21.9	59.6±1.79	44.8±3.7
BaA	73.9 ± 5.6	68.3±28.8	56.5±1.99	55.8±4.4
Chr	82.4 ± 5.3	78.6±32.5	63.2±1.73	67.6±6.6
BbF	88.6 ± 9.2	86.4±36.0	99.2±6.00	74.8±8.0
BkF	75.5 ± 6.9	74.1±30.8	84.6±4.00	63.4±6.8
BaP	59.9 ± 4.8	59.3±24.9	102.4±5.1	42.9±5.2
I(123)P	60.4 ± 33.0	76.2±31.2	99.3±6.45	62.6±6.9
B(ghi)P	77.1 ± 5.0	77.9±32.6	60.7±3.55	65.3±6.9
DbA	85.9 ± 9.1	86.5±35.8	95.8±5.95	71.7±7.5

Table 4.2. The recovery efficiencies of OPE compounds to determine extraction methods by used SW LCS (n=3)

OPE Compound	Ultrasonic Bath Hex:Ace Mixture (%mean ± std.dev)	Ultrasonic Bath Ethyl acetate (%mean ± std.dev)	Horizontal Shaker Hex:Ace Mixture (%mean ± std.dev)	Horizontal Shaker Ethyl acetate (%mean ± std.dev)
TCEP-d12	133.5 ± 18.1	118.3±55.1	58.4±2.63	55.2±7.5
TPHP-d15	84.4 ± 4.5	69.8±32.4	69.7±3.4	50.7±2.9
TNBP	117.0 ± 16.8	85.8±48.7	29.4±8.66	57.6±19.2
TCEP	59.9 ± 15.1	6.8±4.5	5.19±2.81	18.0±11.8
TCIPP	69.6 ± 9.2	19.9±17.4	70.7±9.48	27.1±12.1
TDCIPP	57.2 ± 2.8	34.8±20.6	13.8±6.62	35.4±9.5
TPHP	64.3 ± 2.2	41.5±25.9	52.5±15.0	46.9±19.1
TBOEP	82.7 ± 6.6	60.9±40.2	3.81±1.28	151.0±40.0
EHDPP	68.7 ± 4.7	60.2±27.5	58.0±3.54	52.9±12.6
TEHP	41.7 ± 2.1	43.0±15.9	37.9±1.92	35.0±9.1

Table 4.3. The recovery efficiencies of PE compounds to determine extraction methods by used SW LCS (n=3)

PE Compound	Ultrasonic Bath Hex:Ace Mixture (%mean ± std.dev)	Ultrasonic Bath Ethyl acetate (%mean ± std.dev)	Horizontal Shaker Hex:Ace Mixture (%mean ± std.dev)	Horizontal Shaker Ethyl acetate (%mean ± std.dev)
DMP-d4	109.2 ± 17.8	114.4 ± 47.4	87.1±5.26	36.2±0.6
DnBP-d4	60.6 ± 11.3	56.7 ± 16.3	70.8±2.08	18.0±1.2
DEHP-d4	78.2 ± 7.8	68.2 ± 32.1	59.3±2.31	20.8±1.5
DMP	81.5 ± 11.4	63.3 ± 46.3	24.0±13.9	38.6±19.1
DEP	141.6 ± 21.6	93.8 ± 89.1	11.8±10.8	55.2±28.3
DiBP	96.9 ± 16.7	73.7 ± 39.5	92.9±11.8	28.9±6.5
DnBP	74.3 ± 13.7	55 ± 27.5	19.8±6.2	27.6±3.5
DMEP	68.9 ± 11.1	51.6 ± 22.02	29.4±4.7	24.0±5.6
DEEP	56.01 ± 8.76	41.6 ± 17.6	22.3±3.5	18.7±4.4
DPP	64.6 ± 8.88	45.3 ± 18.6	71.8±3.08	19.3±4.8
BBP	139.5 ± 12.6	102 ± 47.1	46.5±5.77	25.4±5.7
DBEP	55.3 ± 9.6	36.3 ± 19.4	36.5±9.51	50.4±9.7
DcHP	67.4 ± 8.35	43.2 ± 16.8	64.3±2.46	22.2±5.6
DEHP	75.35 ± 8.88	49.9 ± 18.03	145.5±4.71	45.1±17.8
DnOP	49.6 ± 2.7	50.2 ± 19.4	67.4±2.54	45.4±12.0
DNP	66.23 ± 3.9	47.8 ± 20.2	103.9±5.78	52.3±13.7

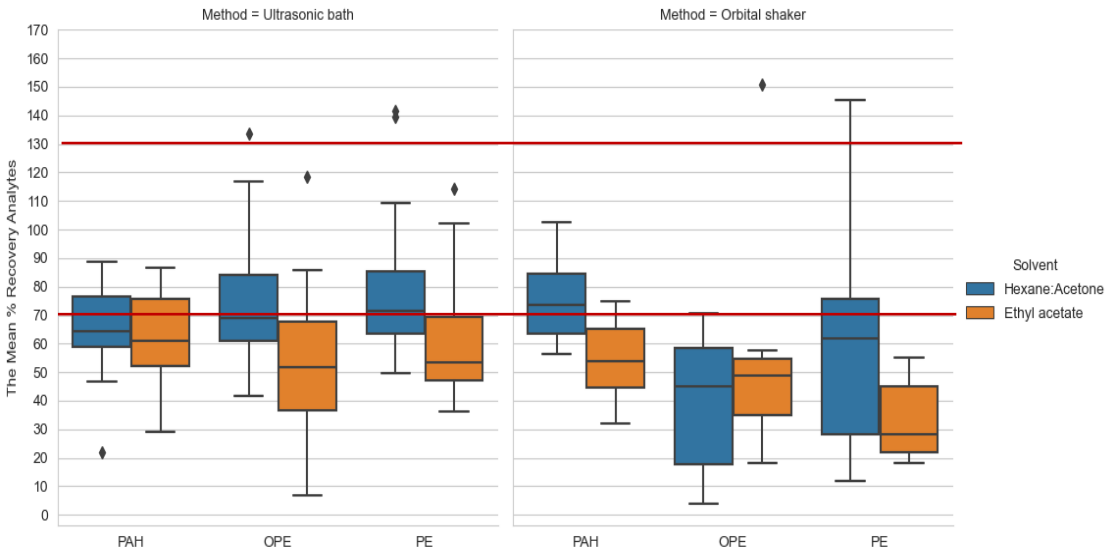

Figure 4.4. The mean recovery efficiencies of PAH, OPE and PE compounds

Purification following extraction is a commonly used method for the targeted chemical compounds. Conventional chromatography columns containing silica gel and Pasteur pipet columns containing silica gel were tested as purification of extracts. The purpose was to develop a more cost-effective method by reducing the amounts of silica gel and elution solvents used in the chromatography column while maintaining similar efficiency. The results of the tested purification methods are presented as mean percentage recovery efficiencies for PAH, OPE, and PE compounds in Figure 4.5 and Tables 4.4, 4.5, and 4.6, respectively. Upon reviewing Table 4.4, it was observed that the mean recoveries for SS are above 80% for both methods. Specifically, PAH compounds showed recovery ranges of 51.6% (B(k)F) to 162.2% (DbA) and 62.3% (DbA) to 86.8% (Nap), for conventional and Pasteur pipette chromatography columns, respectively. Examination of individual compounds revealed that the recoveries for most PAH compounds are comparable between the two methods. Similarly, Table 4.5 indicated that both methods' OPE SS average recoveries were above 70%. The results obtained from the chromatography column ranged from 56.8% (TPHP) to 139.2% (TBOEP), while those from the Pasteur pipette column ranged from 76.9% (TCEP) to 140.9% (TBOEP). Comparable results were obtained for individual OPE compounds as observed in PAHs. Lastly, for PE SS mean recoveries were 42.7% to 84.5% and at 57.9% to 80.3%, for conventional and the Pasteur pipette columns, respectively (Table 4.8). The recoveries of individual PEs ranged from 52% (DNP) to 98.1% (DEP) for conventional column, while the results from the Pasteur pipette column ranged from 61.8% (DEP) to 83.1% (DBEP). Upon comparing individual PE compounds, it was noted that the Pasteur pipette column had better recoveries for some compounds. Overall, the results indicated that recoveries obtained with the Pasteur pipette column, which consumed minor silica gel and sodium sulphate, were comparable with the chromatography column. The Pasteur pipette column occasionally demonstrated higher recoveries for certain OPE and PE compounds. Therefore, the Pasteur pipette purification column method was selected and employed in this study.

Table 4.4. The recovery efficiencies of PAH compounds to determine purification methods

PAH Compound	Purification Recovery with Chromatograph (%mean±std.dev)	Purification Recovery with Pasteur Pipette (%mean±std.dev)
Ace	84.5±7.4	80.1±20.1
Acy	70.0±4.9	77.5±21.3
Bpe	97.5±15.9	67.3±27.3
DbA	162.2±27.0	62.3±22.8
IP	88.4±4.4	65.8±26.9
Fl	90.5±6.9	84.4±17.6
Phe	85.2±10.4	78.0±13.7
Ant	79.2±14.4	71.9±16.2
Fth	72.0±6.7	72.1±16.0
Pyr	72.6±3.5	71.7±15.8
BaA	134.9±8.6	69.9±8.0
Chr	63.8±7.4	72.3±8.9
B(b)F	74.8±6.9	70.5±22.8
B(k)F	51.6±4.9	68.7±19.3
BaP	86.3±9.6	66.3±18.9
Phe-d10 (SS)	94.4±12.2	80.9 ±15.0
Nap	99.2±8.1	86.8±17.9
Pery-d12 (SS)	106.0±10.7	81.1±44.4

Table 4.5. The recovery efficiencies of OPE compounds to determine purification methods

OPE Compound	Purification Recovery with Chromatograph (%mean±std.dev)	Purification Recovery with Pasteur Pipette (%mean±std.dev)
TPHP	56.8±5.0	78.4±1.7
TCEP	82.5±8.8	76.9±1.5
TCIPP	84.1±6.2	84.1±6.6
TBOEP	139.2±52.4	140.9±31.1
EHDPP	80.5±7.4	93.8±2.6
TDCIPP	92.6±7.0	106.4±6.4
TNBP	103.6±7.1	97.0±5.8
TEHP	92.2±4.7	108.4±9.4
TCEP-d12	92.2±9.9	81.2±1.4
TPHP-d15	73.3±9.5	93.2±1.6

Table 4.6. The recovery efficiencies of PE compounds to determine purification methods

PE Compound	Purification Recovery with Chromatograph (%mean±std.dev)	Purification Recovery with Pasteur Pipette (%mean±std.dev)
DMP	81.1±9.6	80.6±2.3
DEP	98.1±13.4	77.8±3.9
DiBP	76.8±8.6	70.1±8.1
DnBP	62.4±9.1	66.3±3.9
DMEP	76.8±6.9	76.8±4.5
DEEP	59.6±5.2	65.7±4.1
DPP (DAP)	56.1±4.3	61.8±3.4
BBP	56.0±4.2	66.7±1.8
DBEP	66.2±2.7	83.1±4.1
DcHP	54.9±3.5	68.3±2.4
DEHP	96.6±48.8	70.7±10.4
DnOP	53.6±19.6	78.7±10.7
DNP	52.0±25.9	76.7±9.0
DMP-d4	84.5±9.4	80.3±3.5
DnBP-d4	60.6±5.9	80.1±17.3
DEHP-d4	42.7±3.8	57.9±10.6

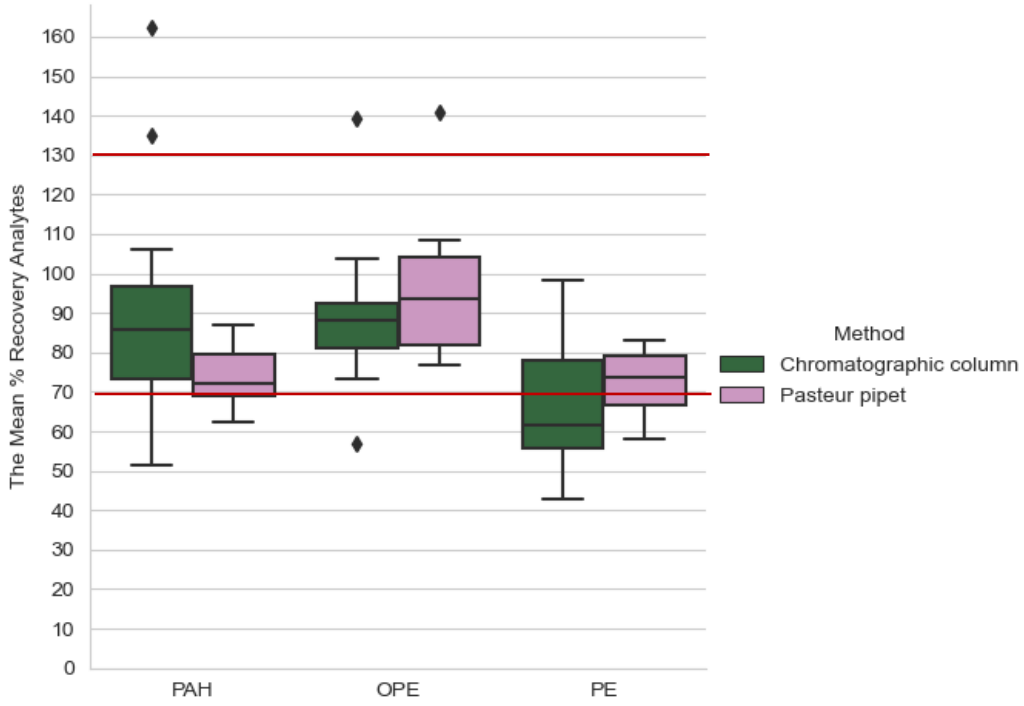

Figure 4.5. The mean recovery efficiencies of PAH, OPE and PE compounds

The last step in method validation was to test the complete extraction procedure. Tables 4.7, 4.8 and Figure 4.6 exhibit the results from extraction of silicone wristband LCSs for PAH, OPE and PE compounds. The result of PAH compounds in Table 4.7 indicated that the average recoveries ranged between 78.8% (Ant) to 104.1% (BbF). Moreover, Phe-d10 and Pery-d12 mean recoveries were 82.1% and 75%, respectively. Table 4.7 indicated that TCEP-d12 and TPHP-d15 average recoveries were 77.3% and 81.9%, respectively, while OPE compounds demonstrated that the mean recoveries ranged between 43.7% (TCPP) to 90.9% (TPHP). Eventually, DMP-d4, DnBP-d4 and DEHP-d4 average recoveries were 112.1%, 49.3% and 50.0%. The mean recoveries of individual PE compounds were in the range of 44.9% (DEEP) to 139.4% (DMP). Figure 4.4 compares the extraction efficiencies of compound groups, all of which lied within the acceptable recovery range of this study.

Table 4.7. The mean recovery efficiencies of PAH compounds for SW LCS (n=3)

PAH	%Recovery ± std.dev	PAH	% Recovery ± std.dev
Phe-d10	82.1 ± 4.5	Pery-d12	75 ± 12.5
Nap	79.8 ± 0.79	BaA	92.3 ± 8.01
Ace	81.9 ± 0.20	Chr	89.7 ± 9.64
Acy	79.6 ± 0.19	B(b)F	104.1 ± 16.46
Flu	93.0 ± 11.01	B(k)F	96.8 ± 23.72
Phe	79.7 ± 10.88	BaP	82.4 ± 4.91
Ant	78.8 ± 5.02	I(1,2,3)p	79.7 ± 7.12
Flt	81.7 ± 6.78	B(g,h,i)p	83.0 ± 5.84
Pyr	85.9 ± 6.89	DbA	86.4 ± 6.10

Table 4.8. The average recovery efficiencies of OPE and PE compounds for SW LCS (n=3)

PE	%Recovery ± std.dev	OPE	% Recovery ± std.dev
DMP-d4	112.1 ± 18.3	TCEP-d12	77.3 ± 18.0
DnBP-d4	49.3 ± 3.2	TPHP-d15	81.9 ± 5.6
DEHP-d4	50.0 ± 1.0	TNBP	47.7 ± 5.3
DMP	139.4 ± 22.2	TCEP	78.1 ± 30.1
DEP	80.9 ± 14.4	TEP	81.4 ± 21.3
DiBP	52.1 ± 6.9	TCIPP	43.7 ± 0.2
DnBP	51.0 ± 23.1	TDCIPP	45.8 ± 3.1
DMEP	62.0 ± 12.6	TPHP	90.9 ± 3.6
DEEP	44.9 ± 3.8	EHDPP	59.8 ± 4.3
DPP	53.1 ± 18.2	TEHP	53.3 ± 2.1
BBP	66.9 ± 7.5		
DHP	84.2 ± 14.3		
DBEP	57.7 ± 18.0		
DcHP	55.8 ± 18.1		
DEHP	54.5 ± 11.1		
DnOP	121.9 ± 12.0		
DNP	76.0 ± 5.3		

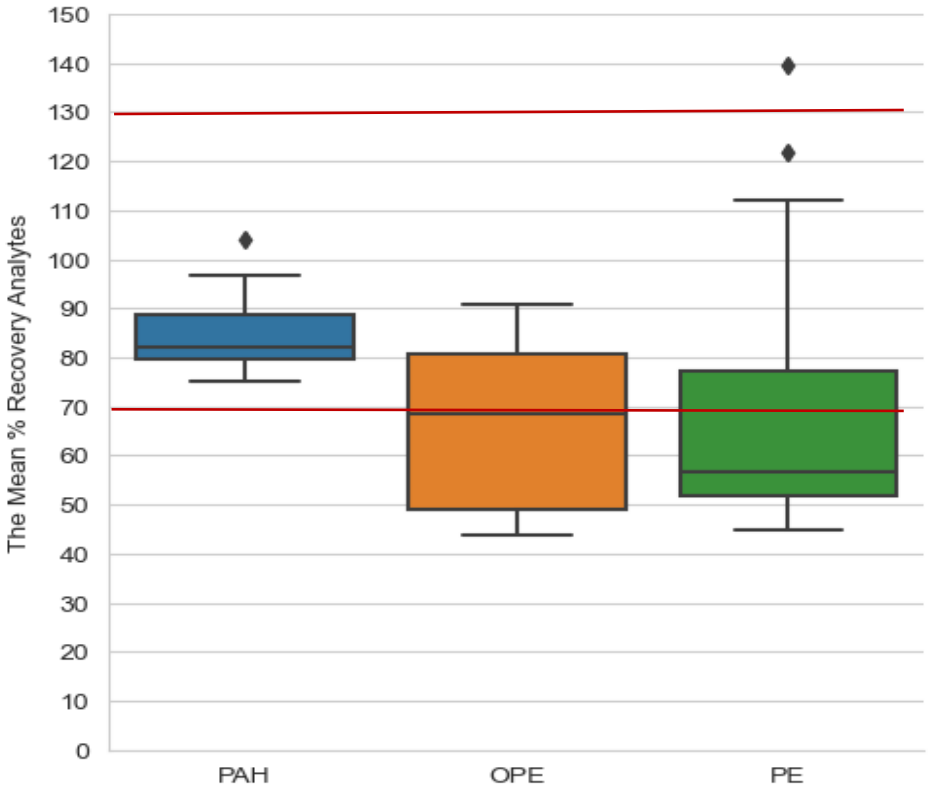

Figure 4.6. The average recovery efficiencies of PAH, OPE and PE compounds for SW LCS (n=3)

4.2. Personal Exposure Study and SVOCs in Office Air

4.2.1 The determination of PAH concentrations in the office environment:

The detected PAH compound concentrations in silicone wristbands, which were hung in offices in the Engineering Faculty C Building of İzmir Institute of Technology (IZTECH), are presented in Table 4.9. Compounds with concentrations below the method detection limit (MDL) and the limit of quantification (LOQ) values provided in Table 3.6 are not reported. PAH compounds falling below the MDL value include Chrysene, Benz(a)anthracene, Benzo(a)pyrene, Benzo(ghi)perylene,

Benzo(b+k)fluoranthene, and Indeno(123cd)pyrene. Consequently, eight PAH compounds exceeding the limit of quantification have been identified (Table 3.6). Low molecular weight PAH compounds (2 and 3 ringed) demonstrate higher concentrations than high molecular weight ones (5 or more ringed). As the molecular weight of PAH compounds increases, it is anticipated that their log Koa values also increase, indicating a lesser preference for the air phase. Therefore, high molecular weight (5 or more ringed) PAH compounds have given results below detection limits.

Table 4. 9. The PAH concentrations in the office environment by using SWs (ng/g wristband)

Office	**Nap**	**Acy**	**Ace**	**Flu**	**Ant**	**Phe**	**Flt**	**Pyr**	**ΣPAH**
B202	3.898	1.787	2.809	5.949	3.806	8.417	1.913	2.475	31.05
B203	<IDL	1.313	4.147	4.445	1.663	8.114	2.179	2.811	25.02
B204	5.046	1.507	6.118	7.623	2.393	14.67	3.229	4.545	45.13
B205	3.587	1.692	4.708	4.434	3.881	12.47	1.752	2.764	35.29
B206	4.355	3.719	8.509	7.076	3.752	14.85	2.540	3.458	48.27
C204	4.372	1.568	3.403	5.163	1.555	11.34	2.035	1.304	30.74
C206	5.534	2.594	4.248	9.297	2.195	17.17	3.720	2.357	47.11
C219	12.74	1.764	4.837	8.246	1.940	12.18	1.772	2.060	45.54
C223	3.978	3.575	3.844	8.106	0.677	8.54	1.662	1.291	31.67
C224	4.356	3.076	3.868	6.816	0.989	9.19	1.464	1.559	31.32
D202	<IDL	<LOQ	1.858	3.162	0.873	6.69	2.100	2.485	17.60
D203	<IDL	<LOQ	2.034	2.338	0.874	6.22	2.424	3.151	17.47
D204	<LOQ	<LOQ	2.437	5.922	1.528	10.89	2.008	2.739	25.96
Mean	3.791	1.756	4.063	6.045	2.010	10.826	2.215	2.538	33.24
Median	3.978	1.692	3.868	5.949	1.663	10.894	2.035	2.485	31.50
Detection Frequency (%)	69	77	100	100	100	100	100	100	

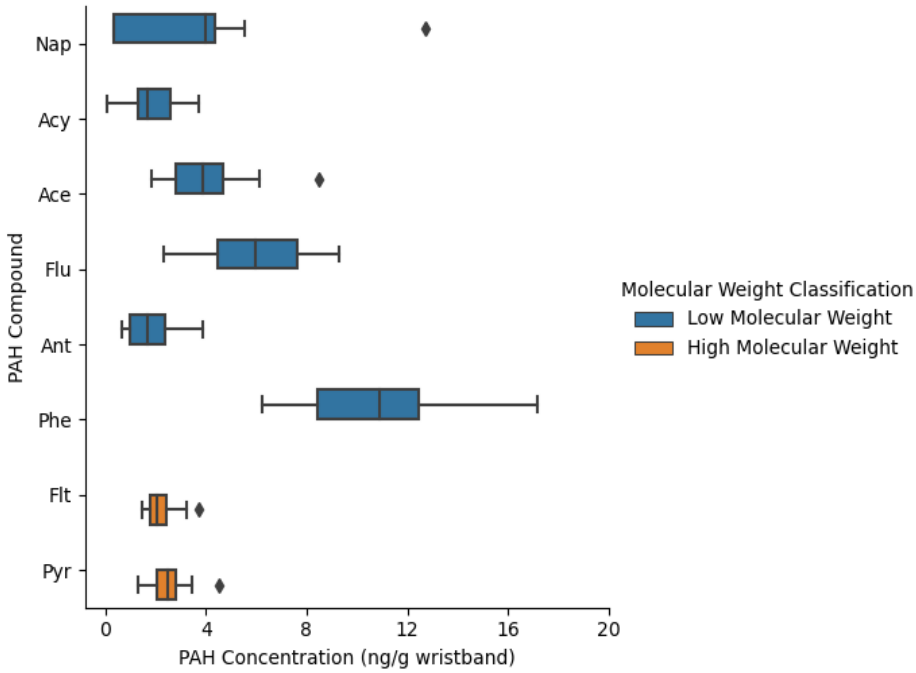

Figure 4.7. The comparison of concentration among PAH compounds in offices

The offices where silicone wristband samplers were placed include offices without a central ventilation system and are ventilated solely through natural ventilation (D-Offices, n=3). Offices B and C have both central and natural ventilation. When examining the statistical relationship between the total concentrations of PAH compounds in the three offices with only natural ventilation and the ten offices with both natural and mechanical ventilation, it was found that the concentrations in the offices with natural ventilation were significantly lower (Kruskal-Wallis test, $p=0.013$, confidence interval $\alpha=0.05$). This finding may also be linked to the orientation of the offices with natural ventilation facing away from traffic flow. Hence, a comparison between the façade directions of the offices was made (Figure 4.8). As can be seen in Figure 4.8, the lowest average concentration was found in offices facing south. While there was no statistically significant difference between the mean concentrations of the offices facing east and north, the difference between the mean concentrations of the offices facing south and the offices facing the other directions was statistically significant (Kruskal Wallis test, test confidence interval $\alpha=0.05$, $p=0.02$). Since traffic emissions are one of the most important sources of PAHs (Dubowsky et al., 1999), the impact of traffic on indoor air quality in north and east facing offices was clearly demonstrated.

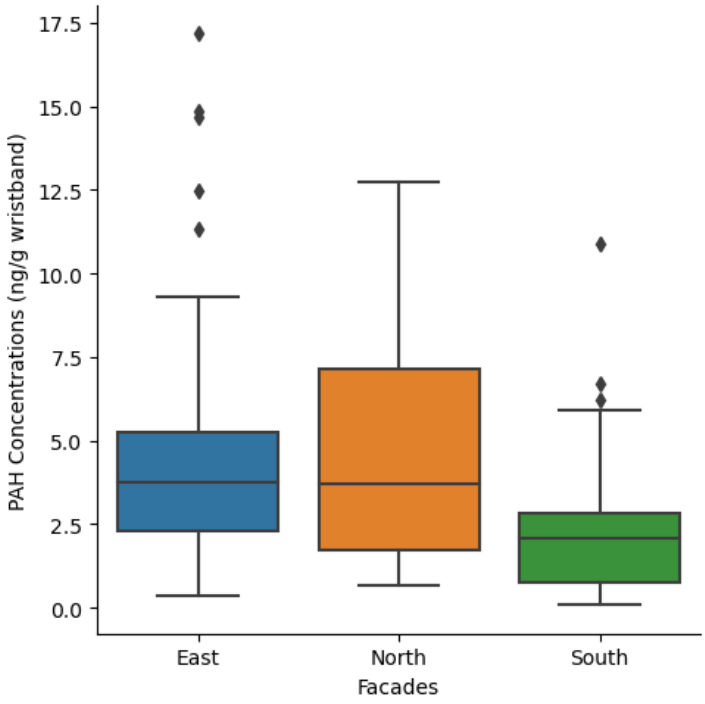

Figure 4.8. The comparison of office PAH compound concentrations with office facades

According to a study, the concentration of 16 PAH compounds emitted from computers ranged from 4296 to 8406 ng/computer (mean = 6466 ng/computer) (Seo et al., 2022). Therefore, the statistical relationship between the number of computers in the offices where samplers were placed, and the concentrations of PAH compounds was examined. It was found that there was no significant correlation between the number of computers and the concentrations of individual or total PAH compounds. Additionally, the average total PAH concentration in offices with two computers (28.67 ng/g wristband) was lower than in offices with one computer (36.10 ng/g wristband). Although this difference was statistically significant (Figure 6, Mann-Whitney U test, p = 0.00001, U-value = 169.0), the hypothesis behind this examination was not verified.

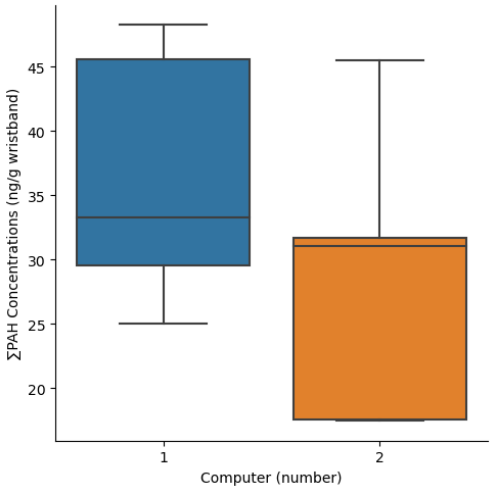

Figure 4.9. The comparison of the total PAH compound concentrations in offices with office computers (laptops + desktops)

In light of these evaluations, the transport of PAH compounds from the external environment to the indoor environment in the offices on our university campus were deemed to have a more significant impact.

4.2.2 The concentrations of OPE compounds in the office environment:

OPE compounds falling below the MDL and LOQ values were not reported. The OPEs below the MDL include TDCPP, TPHP, EHDPP, and TEHP. Consequently, four OPE compounds were identified above the detection limits (Table 4.10).

Table 4.10. The OPE concentrations in the office environment by using SWs (ng/g wristband)

Office	TEP	TNBP	TCEP	TCPP	ΣOPE
B202	138.38	72.42	186.78	287.45	685.03
B203	146.18	56.35	98.46	50.89	351.88
B204	25.44	58.63	81.76	19.25	185.08
B205	22.43	57.07	80.71	199.27	359.48
B206	22.22	55.07	71.09	38.75	187.13
C204	20.09	68.98	89.20	430.92	609.19

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Table 4.10. (cont.)

C206	19.89	59.03	101.71	70.64	251.26
C219	71.74	52.99	60.13	261.97	446.83
C223	64.73	58.70	50.39	54.04	227.85
C224	19.33	49.42	50.69	34.91	154.34
D202	16.22	54.50	34.80	313.34	418.86
D203	13.91	43.28	39.94	475.69	572.81
D204	13.46	248.11	40.29	431.81	733.67
Mean	45.70	71.89	75.84	205.30	398.72
Median	22.22	57.07	71.09	199.27	359.48

As depicted in Figure 4.10, TCPP demonstrates the widest range and highest concentration among the measured OPE compounds in the offices. TEP, on the other hand, has the lowest concentration. The average percentages of TEP, TNBP, TCEP, and TCIPP in the air phase in the office environment, relative to the total OPE compounds, were found to be 11.5%, 18%, 19%, and 51.5%, respectively. Similarly, in offices at the University of Birmingham in the United Kingdom, TCIPP had the highest concentration among airborne OPEs, followed by TCEP and TNBP (Ortiz & Harrad, 2023).

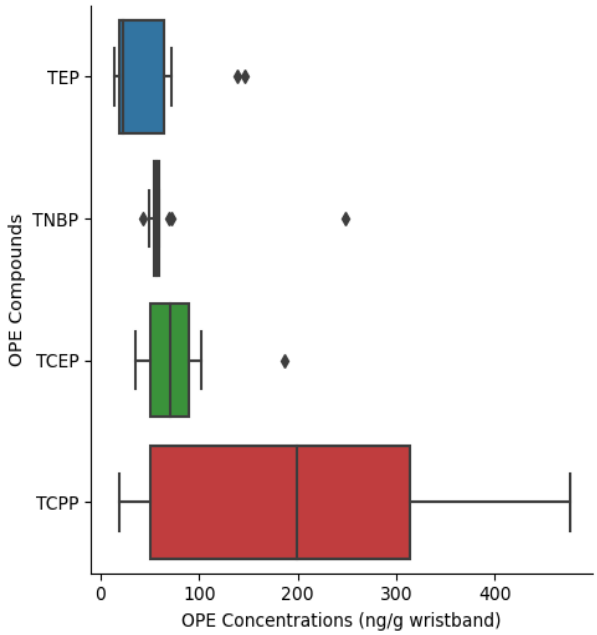

Figure 4.10. The comparison of concentration among OPE compounds in offices

When examining the effect of ventilation type on OPE concentrations in offices, it was observed that the average total OPE concentrations in offices with only natural ventilation (575.1 ng/g wristband) were higher than those in offices with both natural and central ventilation (345.8 ng/g wristband). However, this relationship was not statistically significant (Kruskal Wallis test, $p=0.09$). OPEs detected in indoor environments are generally derived from indoor materials and products rather than outdoor sources. Ventilation with clean air is expected to reduce these compounds' concentrations. Therefore, lower OPE concentrations are expected in naturally and centrally ventilated offices. However, a larger sample size of sampled offices is necessary to reach a more precise conclusion. Office B202 was identified as one of the offices with the highest total OPE concentrations. The elevated OPE levels in office B202 were attributed to four electronic devices (computer, monitor, printer), an average surface area of 19.31 m^2 of suspended ceiling tiles (upper surface PVC vinyl coating), a whiteboard, and five office furniture items.

In offices, electronic devices (laptops, desktop computers, monitors, printers, and photocopiers) could be a source of OPEs. Offices B202, D203, and C219, which have four to five electronic devices, had higher OPE concentrations than other offices. However, no statistically significant relationships were found between the number of electronic devices and OPE concentrations (Kruskal Wallis test, $p>0.05$). Similarly, the relationship between the area of the bookshelf and table, which may contain OPE compounds due to the application of polishing materials, and the number of furniture pieces treated with flame retardants and OPE concentrations were investigated. However, no significant correlations were found (Spearman correlation, $p>0.05$). Finally, the relationship between whiteboards in offices and OPE concentrations was examined. Accordingly, no statistically significant differences were found in the individual OPE compounds and total OPE concentrations between offices with and without whiteboards (Mann-Whitney U test, $p>0.05$). Therefore, it can be speculated that all possible indoor sources collectively affected the OPE levels in the air phase in offices, and increasing the sample size is necessary for meaningful analyses based on a single source.

4.2.3 PE concentrations in the office environment:

The concentrations of PE compounds in the office air environment were assessed by silicone wristbands. The concentrations of PE compounds are presented in Table 4.11. PE compounds falling below the MDL and LOQ values were DMEP, DEEP, DPP, DnHP, DBEP, DcHP, DnOP, and DNP. Subsequently, statistical analyses were conducted based on the concentrations of the 7 PE compounds exceeding the detection limits.

Table 4.11. The concentrations of PE compounds in office environment in SWs (ng/g wristband)

Office	DMP	DEP	DiBP	DnBP	BBP	DEHP	DEHTP	ΣPE
B202	14.20	577.4	431.3	164.6	33.46	23.81	35.44	1280
B203	17.41	169.5	103.1	259.4	28.24	30.45	33.84	642.0
B204	17.53	685.7	358.3	81.24	49.93	35.09	63.78	1292
B205	16.22	483.6	356.2	75.59	31.51	22.36	40.94	1026
B206	15.29	254.0	330.1	73.72	42.00	28.53	28.25	771.9
C204	20.01	502.7	316.2	91.35	10.46	29.96	38.34	1009
C206	15.90	154.9	673.2	80.74	14.97	39.25	32.97	1012
C219	18.09	253.7	542.0	88.73	15.19	51.01	24.50	993.2
C223	20.60	563.0	795.2	98.70	13.69	76.91	21.59	1590
C224	15.69	148.8	454	98.39	7.516	32.92	29.5	787.2
D202	19.85	258.4	453.8	79.33	6.905	133.6	48.05	1000
D203	17.68	209.4	352.7	361.9	8.382	60.71	88.28	1099
D204	22.80	388.0	648.8	99.27	6.099	93.62	36.75	1295
Mean	17.79	357.6	447.3	127.1	20.64	50.64	40.17	1061
Median	17.53	258.4	431.3	91.35	14.97	35.09	35.44	1012

Figure 4.11 illustrates a box plot showing the concentrations of PE compounds measured in offices. DiBP has the highest mean concentration among these compounds, while DMP has the lowest. The compounds DiBP, DEP, and DNBP, which exhibit the highest concentrations, have average occurrence percentages of 42%, 33.7%, and 12% in the office environment, respectively.

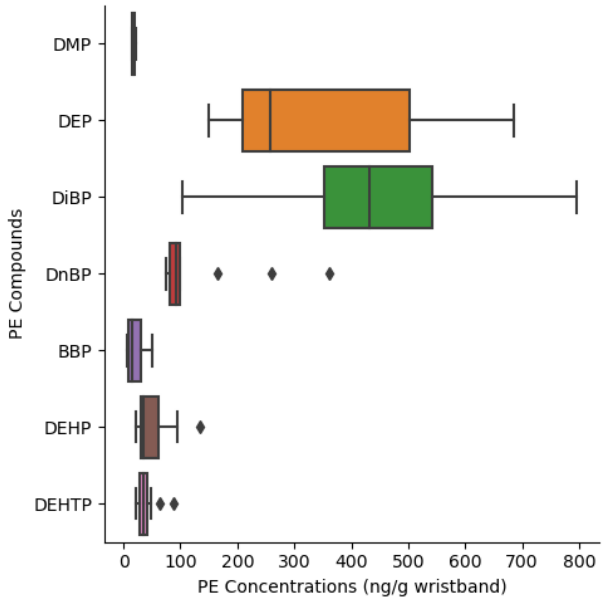

Figure 4.11. The comparison of concentrations among PE compounds in offices

When examining the effect of ventilation type on PE concentrations in offices, it was observed that the average total PE concentrations in offices with natural ventilation only (1131 ng/g wristband) were higher than those in offices with both natural and central ventilation (1040 ng/g wristband). Nevertheless, this relationship was not statistically significant (Kruskal Wallis test, $p > 0.05$). Similar to OPEs, PEs are more likely to originate from indoor materials and products than outdoor sources. These products commonly include PVC-containing plastic items, adhesives, vinyl and tile flooring materials, paints, inks, lacquers, room fragrances, and perfumes (URL1).When comparing PE concentrations in offices, it can be suggested that the intensive use of photocopiers and printers in Office C223, which had the highest concentration, might indicate toner and cartridge use as the primary source, especially considering the presence DiBP in inks (URL1). Office B202, on the other hand, was one of the offices with the highest total PE, particularly DEP, DNBP, and DIBP concentrations. More electronic devices (computers, monitors, printers) continuously used air fresheners, and one carpet in this office suggested that they could be significant sources of indoor pollutants.

All offices are covered with floor tiles. Therefore, the size of the area covered by floor tiles may affect the PE concentrations in office air. When examining the relation between office area and PE concentrations, statistically significant and strong positive

correlations were found between DMP (r=0.69), DEHP (r=0.68), and total PE (r=0.65) concentrations and office area (Spearman correlation, $p<0.05$). Thus, it can be said that tile material is an important factor affecting PE concentrations in offices.

The electronic devices in offices (laptops, desktop computers, monitor, printers, and photocopiers) may be a source of PE due to the plastic materials in their content. However, statistically significant relationships between the number of electronic devices and PE concentrations could not be found (Kruskal-Wallis, $p>0.05$). Only for DNBP concentrations showed an increasing profile with an increase in the number of electronic devices (Figure 4.12). This situation indicated that electronic equipment was one of the significant sources of DNBP. Similarly, the relationship between cupboard area and PE concentrations was investigated due to varnish materials containing PE compounds on the cupboards, but no significant connection was found (Spearman correlation, $p>0.05$). Finally, the relationship between the presence of a whiteboard in offices and PE concentrations was examined. For most individual PE compounds and total PE concentrations, no statistically significant difference was found between offices with and without a whiteboard (Mann-Whitney U test, $p>0.05$). Only for the DEHTP compound, higher concentrations were observed in offices with a whiteboard (n=4) compared to those without (n=9) (Mann-Whitney U test, $p>0.05$). As a result, it has been demonstrated in this study that the presence of PE compounds in the office air phase originated from materials and products used indoors. Increasing the sample size would be necessary to achieve more conclusive results.

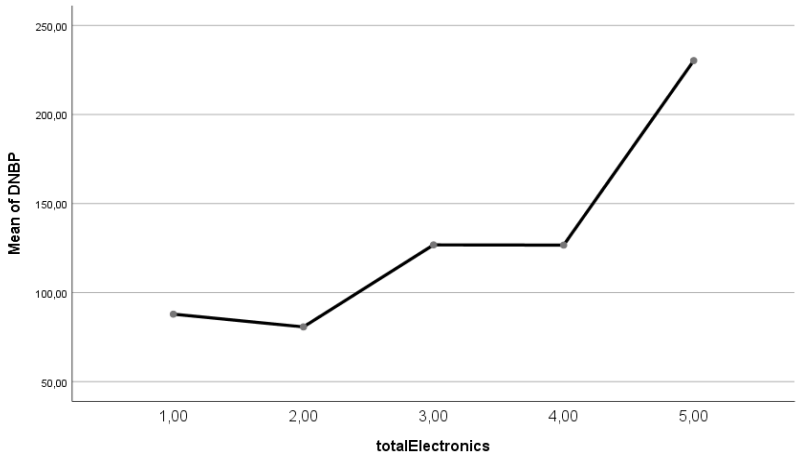

Figure 4.12. The variation in DNBP concentration regarding the number of electronic devices

4.2.4 The determination of PAH concentrations by using SWs as a novel personal passive sampler

The descriptive statistics for the individual PAH concentrations measured in SWs worn by the academic personel, i.e. the residents of the offices presented in Sections 4.2.1 – 4.2.3. are presented in Table 4.12. The highest concentration was observed for Acy, followed by pyrene, and phenanthrene. Correlations among PAH compounds in the worn SW yielded significant relations between Ace and Pyr (r=0.63), Phe and Ant (r=0.62), indicating similar sources for these compounds. Also, a significant correlation between office air and SW concentrations was found for Ace (r=0.59). Hence, it can be speculated that Ace exposure of office workers might be influenced by Ace concentration in the office air. The relations between the PAH concentrations and the participant information were investigated. Accordingly, heating type used in the participants' homes (natural gas, coal, electricity) and location of homes (sub-urban vs urban) were not able to significantly explain the PAH concentrations in the silicone wristbands.

Table 4.12. The descriptive statistics PAH concentrations with SW as a personal sampler (ng/g wristband)

	Mean	**SD**	**Min**	**Median**	**Max**	**Detection frequency (%)**
Nap	12.3	14.4	<LOQ	7.08	50.7	67
Acy	212.8	95.7	92.3	215.4	382.9	100
Ace	6.43	6.62	<MDL	5.11	14.9	50
Flu	4.07	4.21	<LOQ	3.21	16.7	92
Phe	41.8	34.4	2.93	35.6	112.2	100
Ant	39.0	35.1	1.81	28.6	126.2	100
Flt	16.5	19.0	0.81	7.51	59.4	100
Pyr	58.9	46.0	12.6	42.8	154.5	100
BaA	2.97	2.88	<MDL	2.42	9.32	83
Chr	2.22	1.63	0.35	1.70	5.67	100
B(b)f	103.7	90.2	3.45	76.7	239.8	100
B(k)f	101.1	140.3	1.07	47.5	498.6	100
Bap	33.9	22.0	9.68	28.9	66.3	100
IcdPyr	28.7	22.3	<LOQ	19.7	65.7	92
Daant	43.0	51.7	<LOQ	21.6	176.4	75
BghiP	3.31	3.18	<MDL	2.49	9.72	58

When comparing the concentrations of PAH compounds measured in silicone wristbands used as personal samplers over seven days with those reported by Young et al. (2021), it was found that the median concentrations of Ace, Flu, Phe, Ant, Flt, BaA, and Chr were higher than that of the present study.

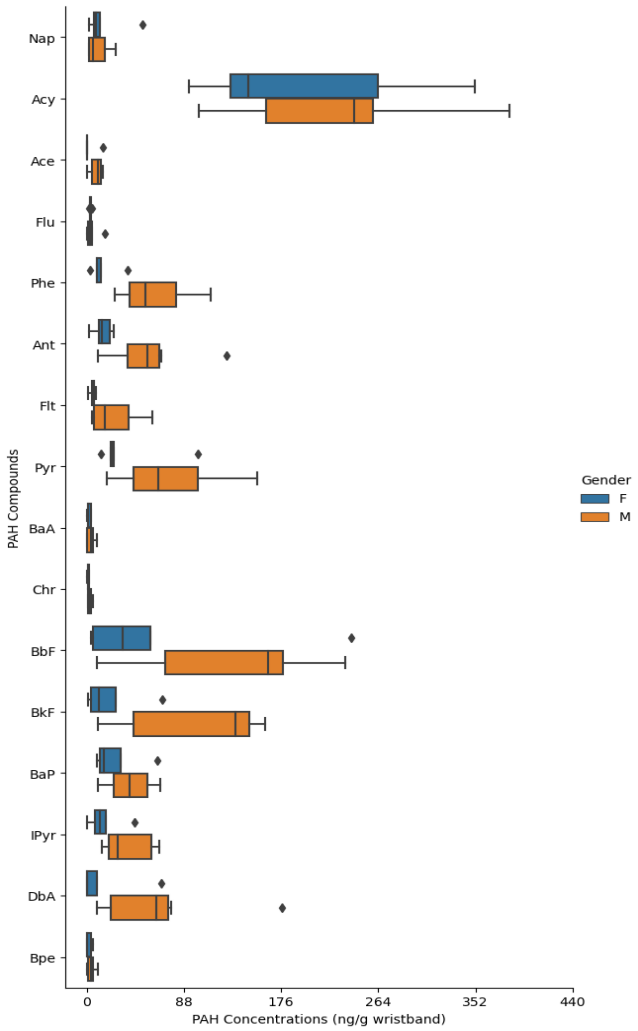

Figure 4.13. The comparison of PAH concentrations in gender with SW as a personal sampler

As shown in Figure 4.13, the median concentration values of Acy, BbF, and BkF for male participants are 242.3, 164.3, and 134.3 ng/g wristband, respectively, with the highest concentration range among these three compounds. For female participants, the median concentration values of Acy, BbF, and Pyr are 146.3, 32.2, and 23.50, respectively, with the highest concentration range among these three compounds.

According to the Mann-Whitney test conducted between the two groups, a statistically significant difference was found (U-value: 5704, p-value: 3.13E-32). However, increasing the sample size is necessary for more accurate results. Statistically, no significant differences were found among the concentrations of PAHs in silicone wristbands (SWs) used as personal samplers and the time spent daily at home, in the office, outdoors, or in public transportation or private vehicles (Kruskal-Wallis test, p-value > 0.05). It is necessary to increase the sample size to obtain more accurate results.

4.2.5 The determination of OPE concentrations using SWs as a novel personal passive sampler

The descriptive statistics detailing the individual OPE concentrations obtained from SWs worn by office occupants are delineated in Table 4.13. TBEP exhibited the highest concentration, succeeded by TCEP and TPHP. Notably, no observable correlation was observed between OPE compounds in the worn SW samples and the indoor air of the office environment. This absence of correlation suggests the potential presence of distinct sources for these compounds.

Table 4.13. The descriptive statistics OPE concentrations with SW as a personal sampler (ng/g wristband)

	Mean	**SD**	**Min**	**Median**	**Max**	**Detection frequency (%)**
EHDP	17.31	20.55	0.4925	13.11	70.7	100
TBEP	921.4	773.9	296.8	599.9	2450	100
TCEP	443.0	157.2	169.0	482.2	658.8	100
TCIPP	49.70	38.36	15.75	32.31	129.4	100
TDCIPP	35.29	34.80	7.503	20.90	115.6	100

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Table 4.13. (cont.)

TEHP	17.64	11.01	6.034	15.62	43.63	100
TNBP	45.66	59.30	3.558	20.91	202.3	100
TPHP	43.28	25.41	12.61	38.80	83.17	100

Upon comparison of the concentrations of OPE compounds measured in silicone wristbands used as personal samplers over seven days with those reported by Gibson et al. (2019), it was observed that the median concentrations of TPHP and TDCPP for mother participants (399 ng/g wristband and 163.5 ng/g wristband, respectively) and for children participants (440 ng/g wristband and 390.5 ng/g wristband, respectively) exceeded those in the present study. Similarly, in the study by Craig et al. (2019), the median concentration values of TPHP were measured at 132 ng/g wristband when worn and 257 ng/g wristband when pinned, surpassing the results of this study. Furthermore, the concentration of TEHP for children was higher than that in the present study. Travis et al. (2020) reported higher median concentration values for EHDPP and TCPP at 290 ng/g wristband and 208 ng/g wristband, respectively, compared to the findings of this study. According to Hammel et al. (2020), concentrations of TPHP, TDCPP, and EHDPP were measured at 872.9 ng/g wristband, 179.7 ng/g wristband, and 73.61 ng/g wristband, respectively. Young et al. (2021) also investigated TCPP, TPHP, and EHDPP concentrations at 406 ng/g wristband, 185 ng/g wristband, and 73.4 ng/g wristband, respectively. In the present study, TBEP, TCEP, and TPHP concentrations were 599 ng/g wristband, 482.2 ng/g wristband, and 38.80 ng/g wristband, respectively. In this study, TBEP, TCEP, and TPHP concentrations were comparatively lower.

From a statistical perspective, no notable variances were detected in the concentrations of OPEs within SWs utilized as personal sampling devices and the duration spent daily at home, in the office, outdoors, or while utilizing public transportation or private vehicles (Kruskal-Wallis test, p-value > 0.05). A larger sample size would be critical to have more precise outcomes.

4.2.6 The PE concentrations using SWs as a novel personal passive sampler

Table 4.14 presents PE concentrations observed in the SWs worn by the participants of this study. DEHP had the highest median concentration, followed by DEP and DiBP. Notable differences occur when comparing the concentrations of DEHP, DiBP, DnBP, and DEP measured in silicone wristbands (SWs) as a personal sampler across different studies. In the study by Young et al. (2021), the concentrations were found to be 79000, 8720, 5470, and 2030 ng/g wristband, respectively. Conversely, Hammel et al. (2020) reported lower concentrations, with 9010 ng/g values for DEHP, 1059 ng/g for BBP and DiBP, and 739.1 ng/g for DEP. Craig et al. (2019) observed 42.4 ng/g concentrations for DEHP worn on the SW and 251 ng/g for DEHP pinned on the lapel where nail saloon workers were the participants. These variations in concentration levels across studies highlighted the importance of considering different methodologies, sampling techniques, and environmental factors when interpreting and comparing results.

Statistically, no significant differences were observed in the concentrations of PEs measured in silicone wristbands (SWs) used as personal sampling devices and the time allocated daily for activities at home, in the office, outdoors, or during the use of public transportation or private vehicles (Kruskal-Wallis test, p-value > 0.05).

Table 4.14. The descriptive statistics PE concentrations with SW as a personal sampler (ng/g wristband)

	Mean	**SD**	**Min**	**Median**	**Max**	**Detection frequency (%)**
BBP	33.07	21.93	14.62	27.21	92.92	100
DBEP	71.30	26.49	41.09	65.49	126.25	100

(cont. on next page)

Table 4.14. (cont.)

DEHP	10494	3181	4143	10696	14057	100
DEP	6312	5020	670.7	5866	17384	100
DMEP	99.74	109	19.76	66.98	418.2	100
DMP	88.72	40.76	24.96	86.33	159.3	100
DNP	62.25	37.22	30.84	51.48	160	100
DPP	15.44	4.107	10.46	14.97	23.54	100
DiBP	1611.34	509.8	641.54	1576	2721	100
DcHP	37.61	12.48	19.53	35.91	58.30	100
DnBP	414.8	657.8	0.7295	103.7	2940	92
DnOP	35.17	22.20	15.09	28.57	92.40	100

4.3. PAHs in Primary School Classroom Air

Indoor air samples were collected from five classrooms of Nihat Gündüz Primary School in Bornova, İzmir, using passive samplers, i.e. PUFs and SWs. The samplers were deployed for around 36 days in each sampling campaign covering winter, spring and summer seasons. Tables 4.15 and 4.16 report the descriptive statistics for the individual PAHs concentrations, while the average concentrations of total PAHs in SWs and PUF samplers are presented in Table 4.18. Moreover, Figures 4.14 and 4.15 compare the average concentrations of each PAH in each campaign collected by SWs and PUF samplers, respectively. Among the 16 PAH compounds, the concentrations of Nap, BaP, B(b)F, B(k)F, Bpe, DbA, and IPyr were not reported as they were either

below the MDL or LOQ values. Consequently, 8 PAH compounds exceeding the quantitation limits were identified in SW and PUF samples from kindergarten and 2B (mechanically ventilated) and 1A, 2A, and 3A (naturally ventilated) classrooms. Given that the log Koa values of PAH compounds increase with molecular weight, it was expected that they did not prefer to be in the air phase. Therefore, results below the detection limits were observed for higher molecular weight (5 or more ringed) PAH compounds. Additionally, differences were noted for individual PAH compounds in SWs and PUFs for mechanically and naturally ventilated classrooms. However, no statistically significant differences were observed for 8 PAH compounds ($p>0.05$). Nevertheless, it can be stated that phenanthrene, fluoranthene, and pyrene levels were higher in the mechanically ventilated classrooms (Figure 4.16).

Among the PAH compounds, phenanthrene exhibited the highest median concentrations of 70.1 ng/g silicone wristband (SW), 34.2 ng/g SW, and 18.1 ng/g SW during the first, second and third sampling campaigns, respectively. Fluorene followed with median concentrations of 19.0, 8.14, and 3.7 ng/g SW, and fluoranthene had the third highest concentration among PAHs observed in SWs. The concentrations of these compounds followed the same order in PUFs as well. The concentration of phenanthrene in PUF were 16.20 ng/m3, 5.22 ng/m3, and 4.04 ng/m3 for the consecutive campaigns. These concentrations were compared with previous studies which reported PAHs in school environments (Table 4.17). The acenaphthene concentrations were found to be below those reported in the USA (Wilson et al 2003). Regarding phenanthrene, the concentration in the first campaign exceeded that reported in France (Raffy et al. 2016). However, it was lower than that in the USA (Wilson et al 2003).

Table 4.15. The PAH concentrations for each sampling campaigns using SW

PAHs	Sampling Campaign	mean	std.dev.	min	50%	max
Acenaphthene	1	2.864	1.053	1.45	2.765	7.75
	2	2.117	0.601	1.03	2.120	4.26
	3	1.875	0.532	0.86	1.845	3.53
Acenaphthylene	1	11.08	4.527	4.86	10.49	20.52
	2	4.549	2.193	0.96	4.075	10.60
	3	1.601	0.664	0.57	1.505	3.02
Anthracene	1	4.403	2.185	0.61	4.650	9.25
	2	3.309	1.721	0.99	2.775	8.21
	3	0.762	0.218	0.20	0.765	1.16
Chyrsene	2	0.841	0.536	0.14	0.780	2.08
	3	0.386	0.209	0.11	0.330	0.87
Fluoranthene	1	16.01	7.488	5.20	15.29	37.51
	2	9.244	4.921	2.26	7.975	22.28
	3	4.883	2.194	1.64	4.900	9.43
Fluorene	1	19.18	4.693	11.48	18.96	32.64
	2	7.831	1.706	3.80	8.14	11.07
	3	4.346	2.020	2.59	3.705	13.32
Phenanthrene	1	67.60	14.63	33.77	70.05	91.84
	2	36.29	11.52	16.00	34.21	61.76
	3	17.48	4.784	9.87	18.11	30.37
Pyrene	1	9.638	4.925	2.87	8.935	24.35
	2	5.329	2.799	1.47	4.37	11.40
	3	2.407	1.635	0.69	2.085	8.89

Table 4.16. The PAH concentrations for each sampling campaigns using PUF

PAHs	Sampling Campaign	mean	std. dev.	min	50%	max
Acenaphthene	**1**	1.280	0.3496	0.89	1.20	1.82
	2	0.350	0.0436	0.30	0.36	0.40
	3	0.450	0.03	0.40	0.46	0.48
Acenaphthylene	**1**	4.918	1.388	2.87	4.84	6.49
	2	0.470	0.175	0.31	0.42	0.67
	3	0.294	0.0344	0.26	0.28	0.34
Anthracene	**1**	1.496	0.2065	1.35	1.43	1.86
	2	0.406	0.1352	0.27	0.37	0.63
	3	0.252	0.0432	0.19	0.26	0.30
Chyrsene	**1**	0.268	0.0853	0.17	0.24	0.38
	2	0.170	0.0464	0.11	0.17	0.22
	3	0.108	0.0259	0.08	0.10	0.14
Fluoranthene	**1**	2.986	0.7853	1.88	3.10	4.07
	2	1.290	0.3798	0.83	1.15	1.81
	3	0.822	0.1964	0.59	0.75	1.06
Fluorene	**1**	6.838	1.295	5.31	6.62	8.88
	2	1.636	0.1665	1.44	1.73	1.78
	3	1.162	0.0844	1.08	1.12	1.28
Phenanthrene	**1**	16.32	2.978	12.91	16.20	19.95
	2	5.170	0.6921	4.18	5.22	5.90
	3	4.048	0.3907	3.51	4.04	4.47
Pyrene	**1**	1.996	0.5435	1.35	1.98	2.85
	2	0.760	0.2188	0.50	0.68	1.03
	3	0.400	0.1037	0.32	0.34	0.56

Table 4.17. The PAH concentrations (ng/m^3) observed in the school environment by previous studies

	Nap	Acy	Ace	Flu	Phe	Ant	Flt	Pyr	Chr	Reference
USA	564	2.96	26	6.09	17.4	0.68	0.71	0.364	0.099	Wilson et al 2003
France			5.5	8.7						Raffy et al. 2016
Algeria			6.8	24	0.53	1.6	1.4	0.22		Boudehane et al 2016
France			1.9	7.2	10.9	0.5	0.7	0.6		Wei et al 2020

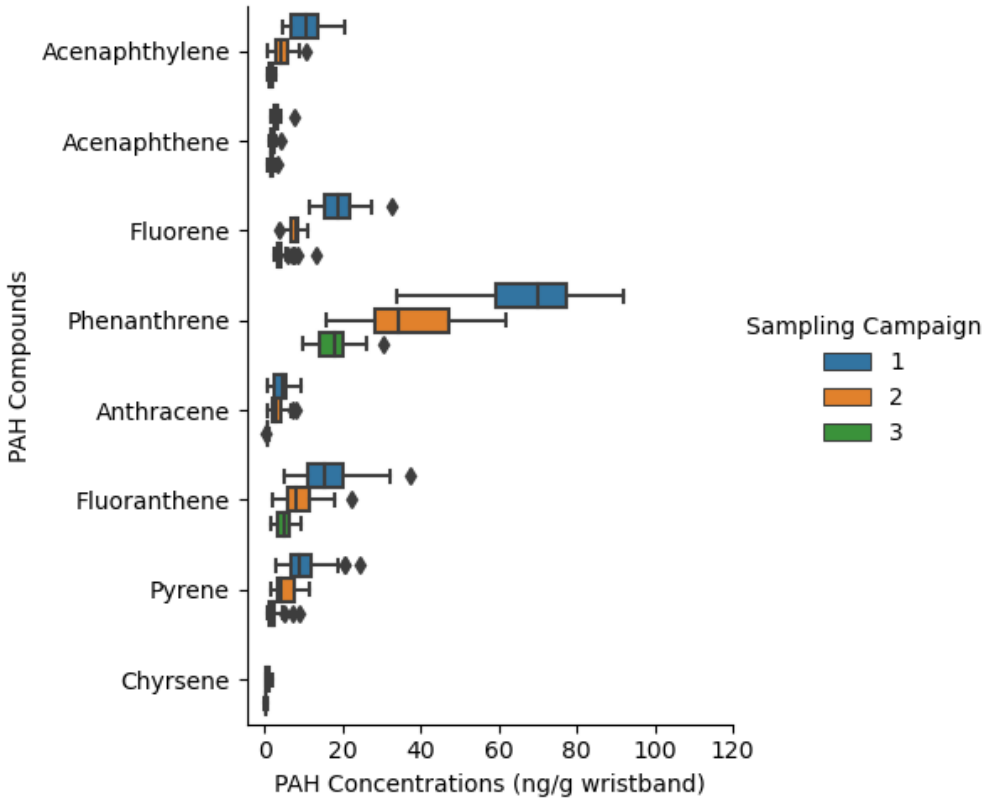


Figure 4.14. The mean PAH concentrations for each sampling campaigns using SW

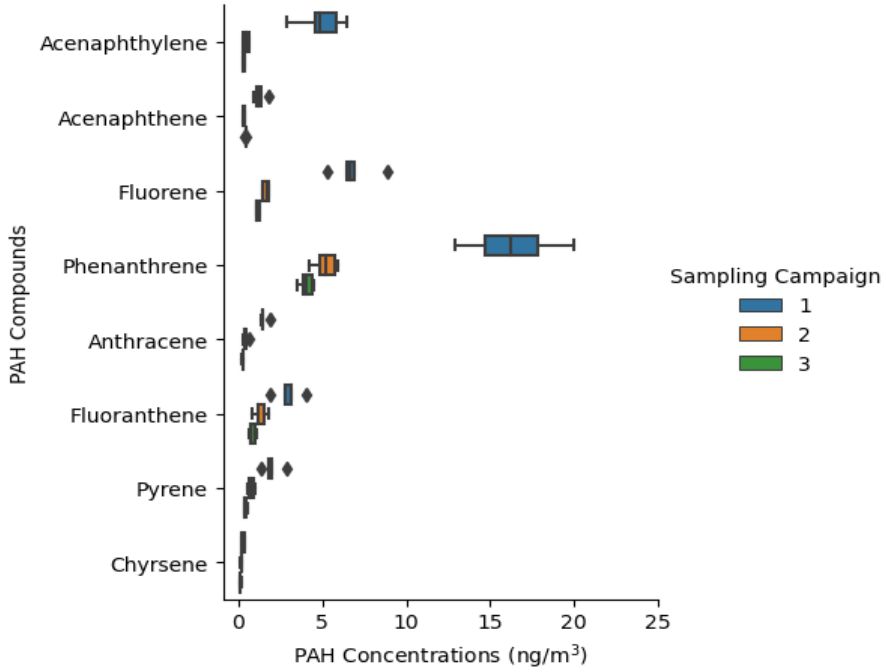


Figure 4.15. The mean PAH concentrations for each sampling campaigns using PUF

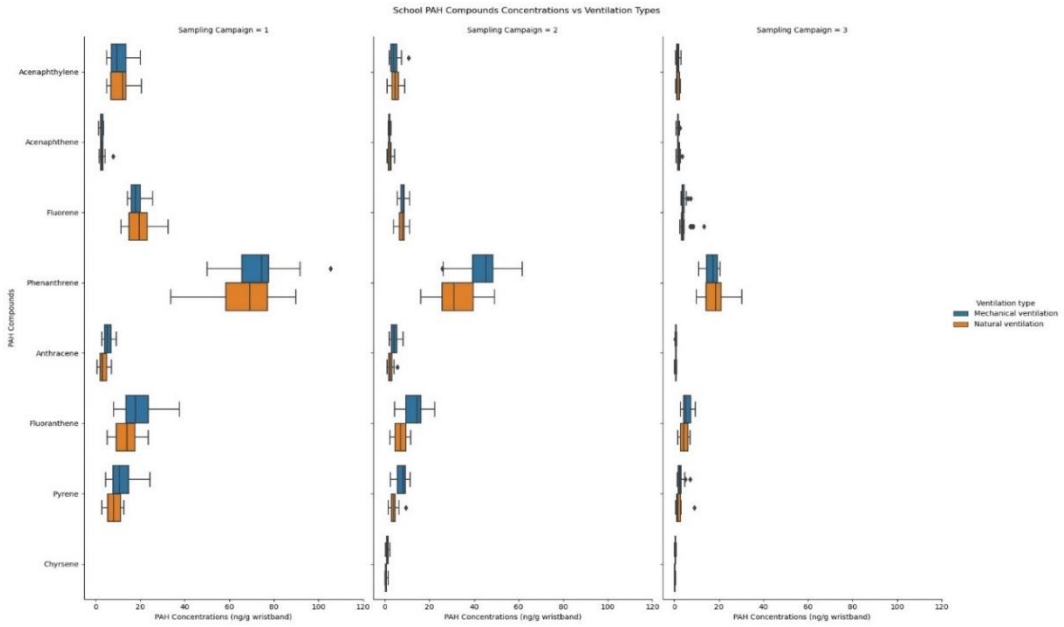


Figure 4.16. The mean PAH concentrations for each sampling campaigns with ventilation type using SW

During the three sampling campaigns, temperatures were recorded, and comparisons were made between the average indoor and outdoor temperatures. The Mann-Whitney U test results indicated that there was no statistically significant

difference between the average indoor and outdoor temperatures for both the first (C1) and second (C2) campaigns, when the heating system was on for approximately six hours (U = 100, p-value = 0.052). Similarly, for the third campaign, when heating system was off, the indoor and outdoor temperatures did not show a statistically significant difference (U = 77, p-value = 0.06). The average outdoor temperatures were 13.1℃, 17.2℃ and 25 ℃ for the consecutive campaigns.

Figure 4.17 shows the accumulation of total PAHs in SW and in PUF at the end of each campaign with respect to the average outdoor temperatures. The concentration levels in SW and PUF across three distinct seasons exhibited a declining trend from winter to summer. This phenomenon was hypothesized to stem from the migration of outdoor pollutants to indoor, largely attributed to the heating systems in winter times. In the vicinity of the school, residential heating included both biomass burning and natural gas systems.

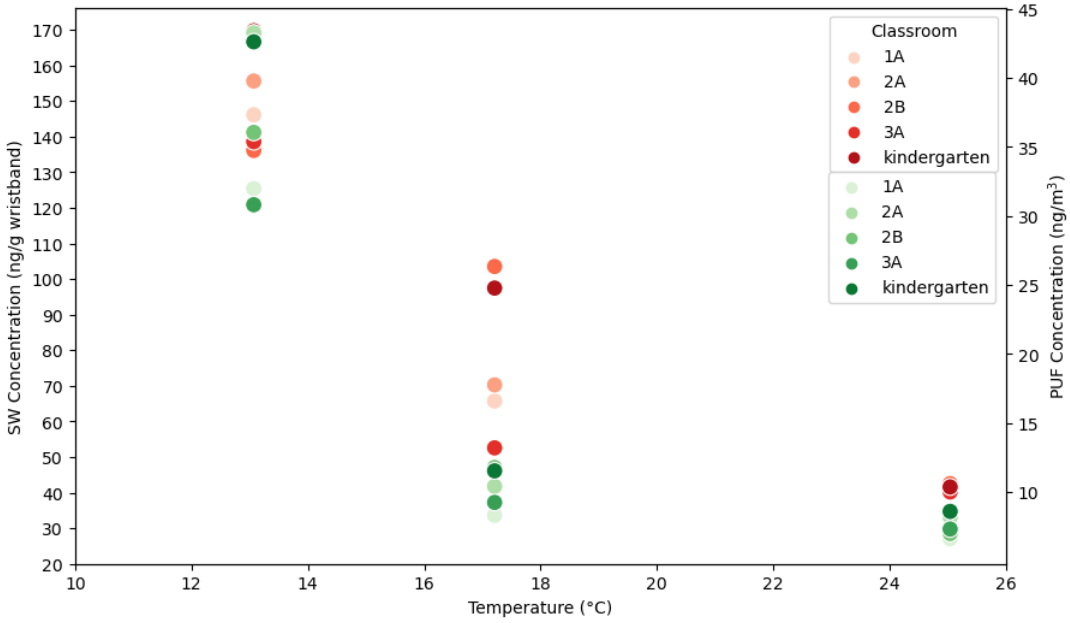


Figure 4.17. The sum of PAH concentrations for each classroom using SW and PUF at three average sampling campaigns' outdoor temperatures

The potential impact of seasonal variations, Koa of the compounds, meteorological parameters, encompassing wind speed and direction, and duration of the sampling on the gas phase concentration of PAHs in the SW was investigated by

employing multiple linear regression (MLR) analysis. To achieve this, three cases were generated and corresponding equations were obtained as shown in Table 4.18. The first case was related to predominant wind direction $(wd, °)$ and speed $(u, m/s)$. The second case included wind direction, speed, and temperature (T, Kelvin) in reciprocal form. The last case considered the wind direction, speed, temperature, ventilation type (VT, categorical data), sample collection duration (t, days), and Log Koa parameters investigate their impact on concentration. As a result, the PAH concentrations in SW explained approximately 56% of the variability using Equation 4.1, and 61% of the variability using equation 4.3. Hence, adding more parameters to the model did not result in a significant increase in the model fit. Hence, Equation 4.1., which included wind speed and wind direction provided a practical and pragmatic approach to explain the PAH concentrations in the school classrooms. The adjusted R-squared values for the equations were slightly lower than the R-squared, which was expected due to the model's moderate complexity. However, given the model's simplicity, the adjusted R-squared values were nearly equivalent to the R-squared. The F-statistic for the model was 588.5, with a probability of 3.78×10^{-165}, indicating a p-value less than 0.05. Consequently, the model demonstrated strong statistical significance, suggesting that the predictors contributed significantly to predicting the response variable beyond random chance.

Table 4.18. The three different cases were corresponding equations and parameters

Equation	m_1	m_2	m_3	m_4	m_5	m_6	R^2
$lnC = m_1 u + m_2 \cos(wd)$ Eqn. 4.1	0.35	0.26					0.56
$lnC = m_1 u + m_2 \cos(wd) + m_3 \frac{1}{T}$ Eqn. 4.2	0.15	-0.48	1184				0.58
$lnC = m_1 u + m_2 \cos(wd) + m_3 \frac{1}{T} + m_4 VT + m_5 LogK_{oa} + m_6 t$ Eqn. 4.3	0.01	-0.63	1799	-0.25	-0.19	0.02	0.61

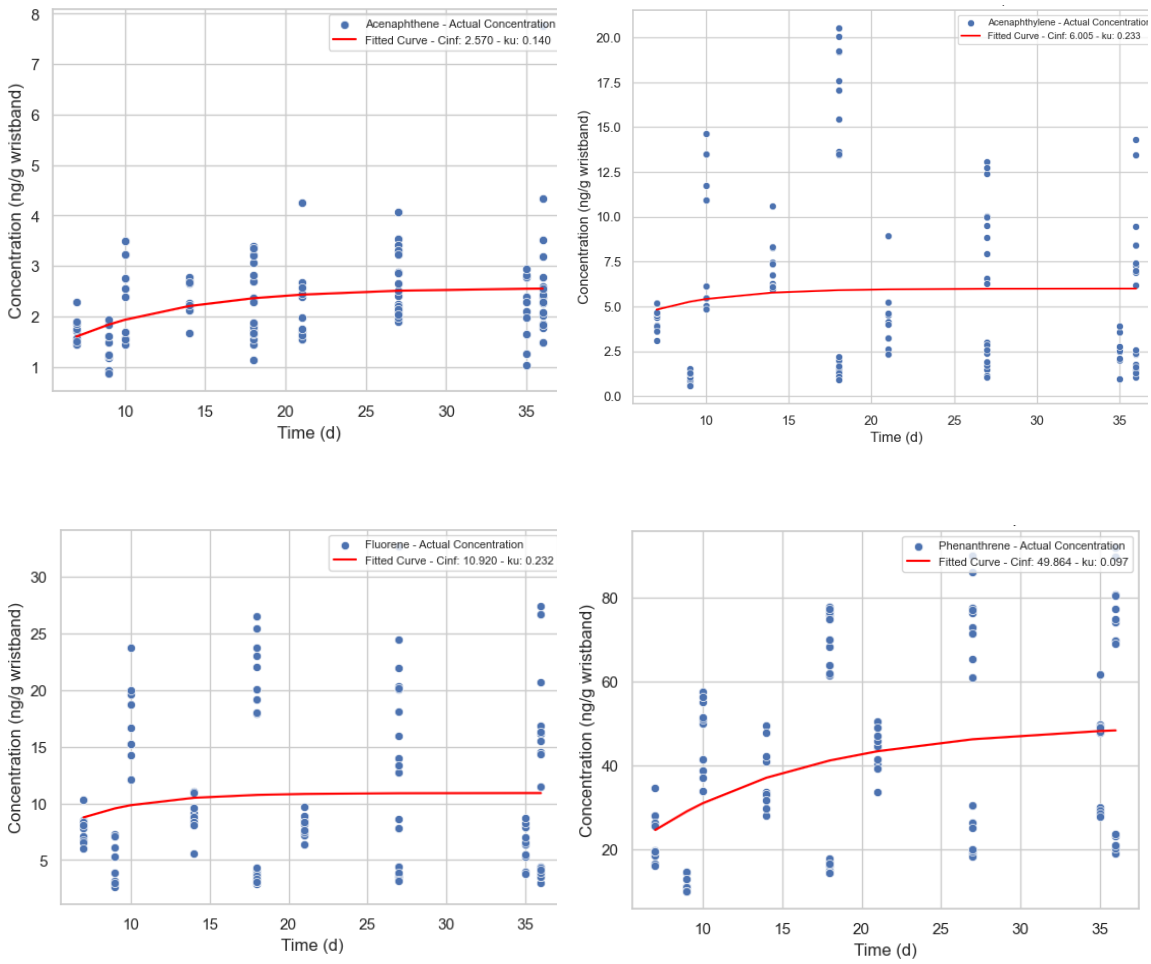
Table 4.19. The sum of PAH concentrations at each classroom using SW and PUF

Classroom	Sampling Campaign	Mean Outdoor Temperature (°C)	ΣPAH SW Concentration (ng/g wristband)	ΣPAH PUF Concentration (ng/m3)
1A	1	13.07	146.16	31.98
2A	1	13.07	155.64	43.27
2B	1	13.07	136.14	36.06
3A	1	13.07	138.6	30.82
Kindergarten	1	13.07	169.77	42.63
1A	2	17.21	65.75	8.31
2A	2	17.21	70.28	10.41
2B	2	17.21	103.55	11.77
3A	2	17.21	52.59	9.24
Kindergarten	2	17.21	97.48	11.53
1A	3	25.04	41.31	6.62
2A	3	25.04	41.51	8.17
2B	3	25.04	42.54	6.99
3A	3	25.04	40.2	7.31
Kindergarten	3	25.04	41.6	8.59

4.4 Uptake Capacity of SW

The daily variation of PAH compounds in silicone wristbands was investigated graphically and through modelling. The individual PAH compounds were analyzed involving all data from the classrooms and the sampling campaigns (Figures 4.18 and 4.19). Figure 4.18 demonstrates that acenaphthene, acenaphthylene, fluorene, phenanthrene, and anthracene exhibited a concentration profile with an initial increase and reaching an equilibrium. Hence, it can be speculated that for a period of 36 days, these compounds achieved to follow the uptake profile in a passive sampler proposed by Shoieb and Harner (2002) (Figure 3.5). The change in concentration with time in SW followed the equation 3.6, and the concentrations can be fitted to equation 3.9 for acenaphthene, acenaphthylene, fluorene, phenanthrene, and anthracene. Using a non-linear regression model, C_∞ (C_{inf}) and k_u were determined (Table 4.20). Using equation 3.10, the time it takes the wristband to reach equilibrium was also determined as t_{95}. It was observed that the t_{95} values of the compounds remained below the 36-day sampling

duration. As a result, equilibrium was reached for the five PAH compounds. However, fluoranthene, chrysene, and pyrene exhibited a continuously increasing profile as observed in Figure 4.18. Hence, for these compounds linear uptake phase was deemed to continue. Then, equation 3.13 was used to estimate k_u, and C_0 (C_{int}) (Table 4.21). These three compounds did not reach equilibrium throughout the sampling period, indicating that their concentration levels varied. Consequently, compounds with lower molecular weights reached equilibrium rapidly, while three-ring PAH compounds such as phenanthrene and anthracene reached equilibrium with an increasing concentration over time starting from the 30th day, and four-ring PAH compounds mostly failed to reach equilibrium during the sampling period.



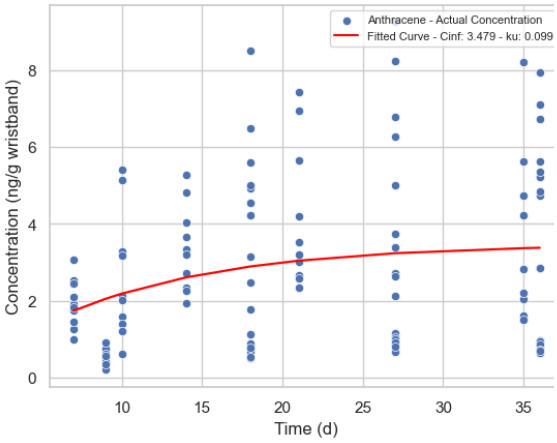


Figure 4.18. The uptake profile for 5 PAHs compounds, which reached equilibrium with used non-linear model

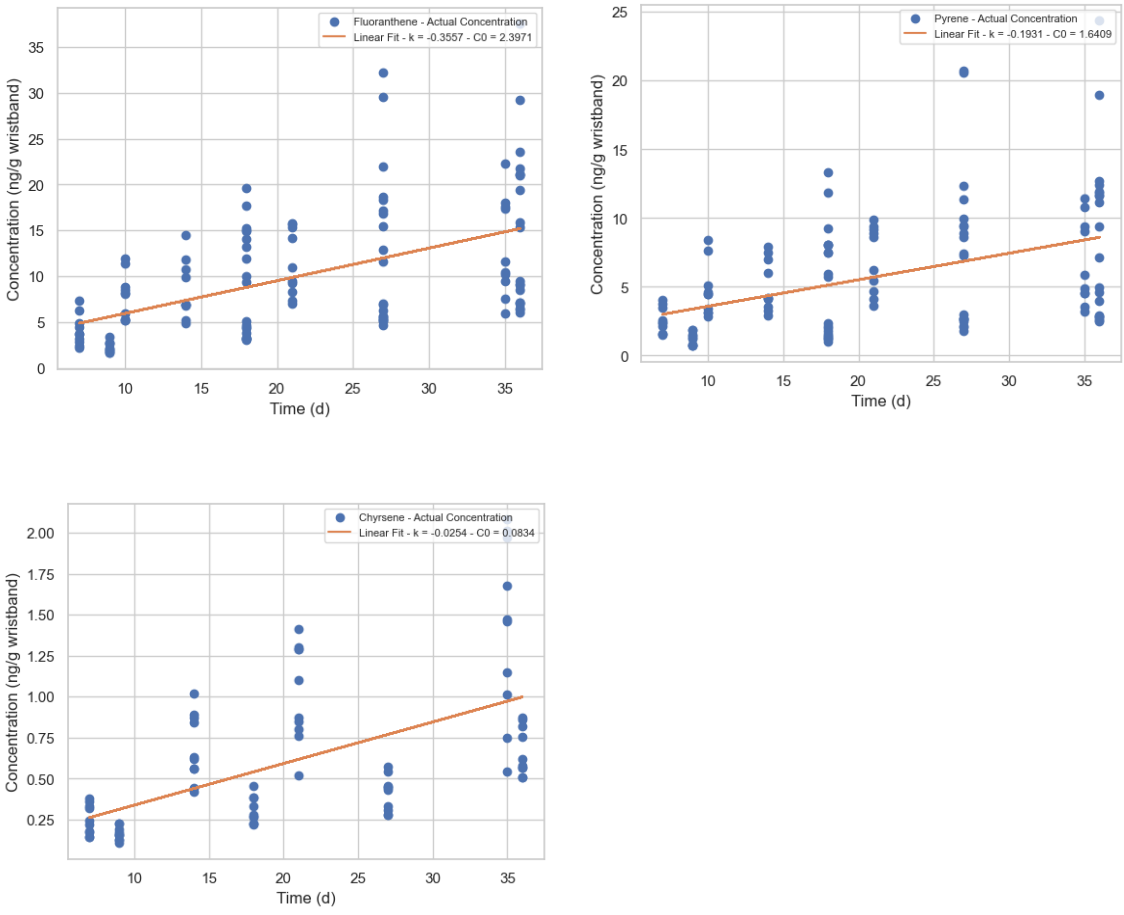


Figure 4.19. The uptake profile for 3 PAHs compounds, which did not reach equilibrium with used linear model

The sampling rates of each PAH compound using silicone wristbands were calculated using two different methods (Equations 3.12 and 3.14) and using PUF and XAD gas phase PAH concentrations (Table 4.12). The sampling rate values calculated according to Sedlackova et al. (2021) using equation 3.12, were higher than those according to Frederiksen et al. (2022) using equation 3.14. Furthermore, the sampling rates calibrated using PUF concentrations were higher than the sampling rate calibrated using XAD. Specifically for Ace, Acy and Flu, the sampling rates differed on one order of magnitude basis. The reason for this observation was the difference between gas phase concentrations measured using PUF and XAD. PUF concentrations represented a 36-day deployment period, while XAD concentrations were calculated considering a 24-hour active sampling. Having higher volatility compared to other PAHs, Acy, Ace and Flu might be affected by the deployment period of the samplers, since for these compounds two-weeks of PUF exposure time was deemed sufficient (Bohlin et al., 2014). Moreover, the Ksa were calculated by calibrating both XAD and PUF concentrations, which fall within the range specified by Tromp et al. (2019), where another type of silicone wristbands was investigated in a chamber experiment. For PAHs that did not reach equilibrium (Table 4.21), both methods used by Sedlackova et al. (2021) and Frederiksen et al. (2022), the sampling rates were found to be close to each other. For these compounds, Ksa values could not be calculated.

A kinetic study was also conducted in a classroom with doors and windows closed for nine days. Due to the short duration of this study, all PAH compounds were in the linear uptake phase of the SW. According to the results of the kinetic study, the sampling rate values calculated using Equations 3.12 and 3.14 were found to be very close to each other, as presented in Table 4.22. There was one order of magnitude difference between PUF and XAD calibrated sampling rates of Ace, Acy and Flu, a similar observation with the sampling campaigns. It was observed that the PUF calibrated sampling rates decreased from compounds with lower molecular weights to those with higher ones.

Table 4.20. The comparison of C∞ (Cinf), k_u, sampling rate and K_{sa} value in the literature by the used non-linear model

Campaign 1-2-3 ($C_t = C_\infty * (1 - \exp(-k_u * t))$)													
	k_u	**t_{25}**	**t_{95}**	**C_∞ (ng/g)**	**$C_{XAD\text{-}air}$ (ng/m3)**	**$C_{PUF\text{-}air}$ (ng/m3)**	**Sampling Rate (R_{XAD}) (m^3/d) (Sedlackova et al., 2021)**	**Sampling Rate (R_{PUF}) (m^3/d) (Sedlackova et al., 2021)**	**Sampling Rate (R_{XAD}) (m^3/d) (Frederiksen et al., 2022)**	**Sampling Rate (R_{PUF}) (m^3/d (Frederiksen et al., 2022)**	**K_{sa} Log(C_∞/ $C_{XAD\text{-}air}$)**	**K_{sa} Log(C_∞/ $C_{PUF\text{-}air}$)**	**K_{sa} Tromp et al., 2019 (mean ± std dev)**
Acy	0.23	1.25	13.02	6.01	5.17	0.29	1.464	25.93	0.010	0.174	6.18	7.43	5.66 ± 1.57
Ace	0.14	2.05	21.40	2.57	3.90	0.45	0.5060	4.394	0.015	0.132	5.93	6.87	5.80 ± 1.34
Flu	0.23	1.25	13.02	10.92	5.18	1.16	2.657	11.84	0.020	0.091	6.44	7.09	6.22 ± 1.41
Phe	0.10	2.97	30.88	49.86	4.61	4.05	5.752	6.550	0.126	0.143	7.15	7.20	6.69 ± 0.46
Ant	0.10	2.88	29.96	3.48	0.69	0.25	2.771	7.497	0.032	0.087	6.82	7.25	7.02 ± 1.62

Table 4.21. The comparison of C_0 (Cint), k, sampling rate and K_{sa} value in the literature by the used linear model

Campaign 1-2-3 ($C = C_0 - kt$)											
	k	**t_{25}**	**t_{95}**	**C_0 (ng/g)**	**$C_{XAD\text{-}air}$ (ng/m3)**	**$C_{PUF\text{-}air}$ (ng/m3)**	**Sampling Rate (R_{XAD}) (m^3/d) (Sedlackova et al., 2021)**	**Sampling Rate (R_{PUF}) (m^3/d) (Sedlackova et al., 2021)**	**Sampling Rate (R_{XAD}) (m^3/d) (Frederiksen et al., 2022)**	**Sampling Rate (R_{PUF}) (m^3/d) (Frederiksen et al., 2022)**	**K_{sa} Tromp et al., 2019 (mean ± std dev)**
Flt	0.36	0.80	8.32	2.40	0.75	0.82	0.48	0.44	0.2834	0.258	7.53 ± 0.34
Pyr	0.20	1.44	14.98	1.64	0.81	0.40	0.25	0.50	0.1267	0.256	7.65 ± 0.27
Chr	0.03	9.59	99.86	0.08	0.06	0.11	0.50	0.28	0.31	0.173	

Table 4.22. The comparison of C_0 (Cint), k, sampling rate and K_{sa} value in the literature by the used linear model

Kinetic Study ($C = C_0 - kt$)										
	k	**t_{25}**	**t_{95}**	**C_0 (ng/g)**	**$C_{XAD\text{-}air}$ (ng/m3)**	**$C_{PUF\text{-}air}$ (ng/m3)**	**Sampling Rate (R_{XAD}) (m^3/d) (Sedlackova et al., 2021)**	**Sampling Rate (R_{PUF}) (m^3/d) (Sedlackova et al., 2021)**	**Sampling Rate (R_{XAD}) (m^3/d) (Frederiksen et al., 2022)**	**Sampling Rate (R_{PUF}) (m^3/d) (Frederiksen et al., 2022)**
Acy	0.12	2.34	24.36	3.56	3.81	0.26	0.032	0.470	0.032	0.468
Ace	0.14	2.12	22.03	0.08	2.55	0.45	0.053	0.303	0.052	0.293

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Table 4.22. (cont.)

Flu	0.31	0.93	9.66	0.18	3.39	1.22	0.092	0.254	0.085	0.237
Phe	1.03	0.28	2.91	0.76	3.08	4.37	0.334	0.236	0.284	0.201
Ant	0.08	3.55	36.98	0.04	0.53	0.30	0.153	0.269	0.132	0.232
Flt	0.20	1.44	14.98	0.36	<LOQ	0.99		0.203		0.150
Pyr	0.04	7.57	78.84	0.06	0.50	0.45	0.08	0.08	0.082	0.090

4.5. Human Exposure Assessment

The issue of indoor air quality in schools poses a significant concern from a social perspective, especially in primary educational institutions where children spend a substantial portion of their day. Children, being more susceptible to pollutants due to higher inhalation rates, are particularly vulnerable. Prior studies have demonstrated that indoor air pollution within school environments, even at low concentrations, can lead to various health issues, reduced productivity, adverse effects on academic performance, and compromised mental well-being among children (Mohai et al., 2011). Given their adverse health effects, especially on young individuals, PAHs emerge as one of the most concerning contaminants in schools. Adolescents, with their higher rates of respiration and increased physical activity, are particularly at risk of exposure to hazardous pollutant compounds compared to adults (Pohl et al., 2005; Pohl and Abadin 2008).

This study used indoor air concentrations in PUF samples to compute daily and chronic toxic exposures and lifetime cancer risk (R) assessments. The study employed three distinct scenarios and adopted a deterministic approach due to the singular school setting, consistent location, and uniform age range. These were associated with the exposure of 15 PAHs, where B(bk)F represented the combined concentrations of Benzo(b)fluoranthene and Benzo(k)fluoranthene through the inhalation pathway. These were undertaken using concentration data collected from each classroom during each sampling campaign, focusing on the 5^{th}, 50^{th}, and 95^{th} percentiles of concentration levels and exposure parameters given in Table 3.7. The 5^{th}, 50^{th} and 95^{th} percentiles constituted the first, second and the third scenarios.

Table 4.23. PAHs concentrations in primary school classrooms for three scenario

PAHs	1. Scenario Concentration (ng/m^3)	2. Scenario Concentration (ng/m^3)	3. Scenario Concentration (ng/m^3)
Nap	0.016	0.571	13.53
Acy	0.194	0.430	5.931
Ace	0.300	0.449	1.532
Flu	1.084	1.716	7.614
Phe	3.496	5.374	20.64
Ant	0.198	0.379	1.754
Fth	0.586	1.179	3.652
Pyr	0.320	0.701	2.413
Chr	0.081	0.163	0.347
BaA	0.023	0.104	0.201
B(bk)F	0.143	0.222	0.404
BaP	0.044	0.052	0.117
IndP	0.002	0.025	0.070
D(ah)A	0.009	0.018	0.033
B(ghi)P	0.007	0.032	0.085

Table 4.24. BaP equivalence and daily exposure for each scenario

PAHs	Scenario 1 BaP equivalence (BaPequi)	Scenario 2 BaP equivalence (BaP_{equi})	Scenario 3 BaP equivalence (BaP_{equi})	Scenario1 Daily Exposure (ng/kg-day)	Scenario2 Daily Exposure (ng/kg-day)	Scenario3 Daily Exposure (ng/kg-day)
Nap	0.00002	0.0006	0.0135	0.00	0.00	0.06
Acy	0.00019	0.0004	0.0059	0.00	0.00	0.03
Ace	0.00030	0.0004	0.0015	0.00	0.00	0.01
Flu	0.00108	0.0017	0.0076	0.00	0.00	0.03
Phe	0.00350	0.0054	0.0206	0.01	0.01	0.09
Ant	0.00198	0.0038	0.0175	0.00	0.01	0.08
Fth	0.00059	0.0012	0.0037	0.00	0.00	0.02
Pyr	0.00032	0.0007	0.0024	0.00	0.00	0.01
Chr	0.00081	0.0016	0.0035	0.00	0.00	0.02
BaA	0.00225	0.0104	0.0201	0.00	0.03	0.09
B(bk)F	0.01434	0.0222	0.0404	0.02	0.06	0.18
BaP	0.04385	0.0520	0.1167	0.06	0.13	0.52
IndP	0.00020	0.0025	0.0070	0.00	0.01	0.03
D(ah)A	0.00895	0.0180	0.0334	0.01	0.05	0.15
B(ghi)P	0.00007	0.0003	0.0008	0.00	0.00	0.00

Table 4.25. Chronic toxic exposure and lifetime cancer risk for each scenario

PAHs	Scenario 1 Chronic Toxic (ng/kg-day)	Scenario 2 Chronic Toxic (ng/kg-day)	Scenario 3 Chronic Toxic (ng/kg-day)	Scenari 1 Lifetime cancer risk (R)	Scenario 2 Lifetime cancer risk (R)	Scenario 3 Lifetime cancer risk (R)
Nap	4.87E-07	2.97E-05	1.24E-03			
Acy	5.78E-06	2.24E-05	5.42E-04			
Ace	8.95E-06	2.34E-05	1.40E-04			
Flu	3.23E-05	8.94E-05	6.96E-04			
Phe	1.04E-04	2.80E-04	1.89E-03			
Ant	5.90E-05	1.97E-04	1.60E-03			
Fth	1.75E-05	6.14E-05	3.34E-04			
Pyr	9.53E-06	3.65E-05	2.21E-04	4.71E-10	1.27E-09	5.42E-09
Chr	2.42E-05	8.49E-05	3.17E-04			
BaA	6.71E-05	5.42E-04	1.84E-03			
B(bk)F	4.27E-04	1.15E-03	3.69E-03			
BaP	1.31E-03	2.71E-03	1.07E-02			
IndP	5.81E-06	1.30E-04	6.38E-04			
D(ah)A	2.67E-04	9.38E-04	3.05E-03			
B(ghi)P	2.18E-06	1.67E-05	7.75E-05			

In three scenarios, the daily exposures to each PAH exceeded the chronic toxic exposure via inhalation by 98%. Lifetime cancer risk was assessed across three scenarios, considering each PAH. Table 4.24 presents the contribution of individual PAHs of BaP_{equi} using the US EPA equation and the estimation of lifetime cancer risks for each scenario. As shown in Table 4.25, the calculated R values for the inhalation route were $4.71x10^{-10}$, $1.27\ x10^{-9}$, and $5.42\ x10^{-9}$, respectively. These findings suggested no significant risk associated with inhalation exposure to PAHs; according to the US EPA, the acceptable risk range falls between 10^{-6} and 10^{-4}, with values above 10^{-4} indicating potential risk. Hence, the results of the three scenarios were below both 10^{-6} and 10^{-4}, indicating negligible risk for schoolchildren in this primary school.

CHAPTER 5

CONCLUSION

SVOCs are ubiquitously used in commercial products, such as electronic equipment, furniture, and building materials. These compounds are applied to the products as additives, hence they can easily leach out of the product and be released to the environment. Additionally, some SVOCs such as PAHs are unintentionally produced during combustion processes. Therefore, SVOCs can be found in indoor environments, even at higher concentrations than outdoor. Spending most of their time in the indoor environments, humans are exposed to a mixture of SVOCs, which might result in various health problems. Hence, assessment of human exposure to SVOCs is a critical issue regarding the health of our societies. A novel personal passive sampler material has been utilized effectively for the past ten years to assess human exposure to various SVOCs. However, this material, i.e. silicone wristband, has never been used by Turkish participants so far. More importantly, the uptake of SVOCs by the silicone wristband is still unclear in terms of the uptake rate and the time needed to reach equilibrium with air concentrations. Hence, the aim of this study was to investigate uptake characteristics of silicone wristbands and to assess the exposure of IZTECH's academic personnel to SVOCs, specifically PAHs, OPEs and PEs.

In order to quantify the SVOCs in silicone wristbands, an effective analysis method is required to be developed. As the first step in precise and accurate analysis, silicone wristbands should be precleaned to eliminate possible interferences in chromatographic analysis. Previously used methods, i.e. Soxhlet apparatus, vacuum oven and horizontal shaker, were tested and Soxhlet apparatus was found to perform better in terms of removing interferences. The second step in developing analysis method was testing various extraction methods. Within the scope of this study, ultrasonic bath and horizontal shaker extraction methods were tested using n-hexane: acetone and ethyl acetate solvents. As a result, ultrasonic extraction using n-hexane: acetone solvents yielded SVOC recoveries that were within the acceptable recovery

range of 50-130%. Although some SVOCs showed recoveries as low as 20%, previous studies also reported low recoveries for similar extraction methods. The third step in analysis was purification of extracts. Purification is generally achieved using one millimetre diameter columns involving approximately five grams of adsorbents, leading to tens of millilitres of solvents being eluted from the column. To minimize the use of these consumables with the same efficiency in terms of SVOC recovery, Pasteur pipette columns were tested using only 0.5 g of adsorbent and less than ten millilitres of solvent. Accordingly, similar or sometimes better SVOC recoveries were obtained using Pasteur pipette columns compared to conventional chromatography columns. The last step in analysis method development is to test the whole method using laboratory control samples. This analysis yielded recoveries in the range 43.7% (TDCPP) to 139.4% (DMP). Despite five SVOCs being outside of the acceptable range, most of the SVOCs complied with the given recovery criteria, hence the developed method was used in further studies.

Silicone wristbands were utilized to assess personal exposure to SVOCs for the first time in Türkiye within the scope of this study. Twelve participants from the academic personnel of IZTECH wore the wristbands for seven days. Additional silicone wristbands were also deployed in the participants' offices as indoor air samplers. As a result, acenaphthylene among PAHs, TBEOP among OPEs and DEHP among PEs were identified as the SVOCs with the highest concentration in the personal SWs worn by the academic personel of IZTECH. The collected information from the participants could not reveal particular sources for these SVOCs, however a combination of sources might have affected the concentrations. For the office environment, PAH sources could be attributed to the outdoor to indoor transport of PAHs, possibly originating from traffic emissions. On the other hand, OPE levels in the office air could not be related to any specific source. Lastly for PEs in the offices, despite absence of a statistical significance, the number of electronic equipment in the offices seemed to affect the DNBP concentrations.

To estimate the uptake rate of silicone wristbands, primary school classrooms were equipped with eight silicone wristbands and two PUF-PAS for 36 days to collect gas phase PAHs. Also, 24-hour active air samplers were operated to differentiate between gas and particle phase concentrations of PAHs in classrooms. Indoor air samples were collected from five classrooms during three sampling periods, representing winter, spring and summer seasons. As a result, PAH concentrations in

both silicone wristbands and PUF-PAS decreased as the outdoor temperatures increased. This observation was expected since PAH formation due to biomass burning levels off at the end of the heating season. Among PAHs, phenanthrene, fluorene and fluoranthene dominated the profiles in every season for almost all classrooms.

The concentration of PAHs in silicone wristbands can be affected by seasonal variations, duration of the sampling period, Koa of the compounds and meteorological parameters related to wind. Hence, multiple linear regression analysis was performed on the data. As a result, the approximately 61% of the variability in PAH concentrations can be explained by taking into account all the mentioned parameters.

The uptake of SVOCs in passive samplers follow an exponential curve reaching a plateau where equilibrium is attained. During 36 days of deployment in each sampling campaign, acenaphthene, acenaphthylene, fluorene, phenanthrene, and anthracene were observed to reach equilibrium, while fluoranthene, chrysene, and pyrene exhibited a continuously increasing profile. Hence, two different models were used to fit the data and calculate the uptake rate of each PAH compound. The sampling rates varied depending on the calculation method used for compounds reaching equilibrium (0.010 – 25.93 m^3/day), while for fluoranthene, chrysene, and pyrene uptake rates were close to each other (0.17 – 0.50 m^3/day). Furthermore, for acenaphthene, acenaphthylene, fluorene, phenanthrene, and anthracene silicone wristband-air partitioning coefficients were in the range 5.93 to 7.43, consistent with the literature reporting values from the chamber experiment.

Lastly, daily and chronic toxic exposures and lifetime cancer risk (R) were assessed using PUF-PAS concentrations. Scenarios generated for 5^{th}, 50^{th}, and 95^{th} percentiles of concentration levels resulted in no significant risk for school children.

The study developed a cost-effective analysis method for SVOCs in silicone wristbands. Personal exposure to SVOCs using silicone wristbands was assessed for the first time in Türkiye and possible exposure sources for the participants were speculated. The study also proposed uptake rates for individual PAH compounds by comparing two calculation methods and two samplers for the calibration of the silicone wristbands. There have been no study revealing uptake rates of silicone material in the form of a wristband for PAH compounds in a real indoor environment.

Further studies are required to identify uptake rates of other SVOC compounds. Longer duration of deployment might allow PAHs more than four rings to reach equilibrium, or at least curvilinear phase of the uptake curve. Although a real

environmental setting produces more reliable data on uptake characteristics of silicone wristbands, controlled environmental conditions can also facilitate the identification of confounding effects on the silicone wristbands.

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