

**ESTIMATION OF EXPOSURE TO PERSISTENT
ORGANIC POLLUTANTS AND ASSOCIATED
HEALTH RISKS**

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ABSTRACT

ESTIMATION OF EXPOSURE TO PERSISTENT ORGANIC POLLUTANTS AND ASSOCIATED HEALTH RISKS

Persistent Organic Pollutants (POPs) pose significant human health risks due to their global ubiquity, resistance to environmental degradation, long-range transport, and tendency to accumulate in the environment and food chain because of their affinity for organic matter. They partition between gas and particulate, soil and air, and sediment and water, leading to their presence in agricultural products, meat, and marine and freshwater products. This results in exposure through ingestion, inhalation, and dermal contact. Consequently, a comprehensive screening study was designed to investigate as many groups of POPs as possible. Samples of food, indoor and outdoor air, and settled dust were collected from randomly selected homes and schools in Izmir. Additionally, indoor settled dust samples were collected from cafes, bars, and restaurants. Samples were analyzed using GC/MS for target congeners of PAHs, PCBs, PBDEs, NBFRs, and OPFRs. The measured concentrations and collected survey data were used as input variables for USEPA exposure-risk models to simulate ingestion and inhalation exposures (chronic daily intake), as well as associated health risks using the Monte Carlo simulation. Sampling locations were strategically distributed among rural, suburban, urban areas, and areas downwind of an industrial site to assess the impact of urbanization. Within the scope of this thesis work, the most comprehensive dataset has been generated among studies that have entered the global literature, providing information on the levels of such a high number of target POPs analyzed in environmental and food samples.

ÖZET

KALICI ORGANİK KİRLİCİLERE MARUZİYETİN VE İLİŞKİLİ SAĞLIK RİSKLERİNİN DEĞERLENDİRİLMESİ

Kalıcı Organik Kirleticiler (POPs), çevresel bozunmaya karşı dirençli, uzun mesafeler boyunca taşınabilen ve organik maddelere olan yüksek afiniteleri nedeniyle çevresel ortamlarda ve gıda zincirinde biriken, küresel olarak yaygın maddeler oldukları için insan sağlığı açısından önemli riskler oluşturur. Pertikül ve hava, toprak ve hava, sedimen ve su arasında dağıldıkları için tarım ürünlerinde, etlerde ve deniz ve tatlı su ürünlerinde bulunurlar. Bu da yutma, soluma ve deri teması yoluyla maruziyete ve sağlık risklerine yol açar. Sonuç olarak, mümkün olduğunca çok sayıda POP grubunu araştırmak için kapsamlı bir tarama çalışması tasarlanmıştır. İzmir'de rastgele seçilen ev ve okullardan, iç ve dış mekan havasıyla beraber çökelmiş toz ve yemek örnekleri toplanmıştır. Ayrıca, kafe/bar/restoranlardan iç mekan çökelmiş toz örnekleri toplanmıştır. Örnekler hazırlık, ekstraksiyon ve temizleme işleminden geçirildikten sonra, PAH'lar, PCB'ler, PBDE'ler, NBFR'ler ve OPFR'lerin hedef bileşikleri GC/MS cihazıyla analiz edilmiştir. Ölçülen konsantrasyonlar ve toplanan maruziyetle ilgili anket bilgileri, USEPA maruziyet-risk modellerine girdi değişkenleri olarak kullanılarak yutma ve soluma maruziyetlerini (kronik günlük alım) Monte Carlo yöntemi kullanılarak ilgili sağlık riskleri simüle edilmiştir. Örnekleme yerleri, kentleşmenin etkisini araştırmak için kırsal, banliyö, kentsel alanlar ve bir sanayi bölgesinin rüzgaraltı yerleri arasında mekansal olarak dağıtılmıştır. Bu tez çalışması kapsamında, küresel literatüre girmiş çalışmalar arasında çevresel ve gıda örneklerinde analiz edilen bu kadar yüksek sayıda hedef POP bileşiği düzeyleri konusunda bilgi veren en kapsamlı veriseti oluşturulmuştur.

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ABBREVIATIONS

Ace	Acenaphthene
Acy	Acenaphthylene
AFR	Alternative flame retardant
Ant	Anthracene
anti-DP	<i>anti</i> -Dechlorane plus
B(a)A	Benzo[a]anthracene
B(a)P	Benzo[a]pyrene
B(bk)F	Benzo[b,k]fluoranthene
B(ghi)P	Benzo(g,h,i)perylene
BDCIPP	Bis(1,3-dichloro-2-propyl) phosphate
BDE-100	2,2',4,4',6-Pentabromodiphenyl ether
BDE-153	2,2',4,4',5,5'-Hexabromodiphenyl ether
BDE-154	2,2',4,4',5,6'-Hexabromodiphenyl ether
BDE-183	2,2',3,4,4',5',6-Heptabromodiphenyl ether
BDE-209	2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether
BDE-28	2,4,4'-Tribromodiphenyl ether
BDE-47	2,2',4,4'-Tetrabromodiphenyl ether
BDE-77	3,3',4,4'-Tetrabromodiphenyl ether
BDE-99	2,2',4,4',5-Pentabromodiphenyl ether
BEH-TEBP	Bis(2-ethylhexyl)tetrabromophthalat
BTBPE	1,2-bis(2,4,6-tribromophenoxy)ethane
Chr	Chrysene
CR	Cancer Risk
CTR	Chronic Toxic Risk
DB(ah)A	Dibenz(a,h)anthracene
DBE-DBCH	1,2-Dibromo-4-(1,2-dibromoethyl)cyclohexane
DLCB	Dioxin-like PCBs
EHDPP	2-ethylhexyl diphenyl phosphate
EH-TBB	2-Ethylhexyl-2,3,4,5-tetrabromobenzoate
Fla	Fluoranthene

Flu	Fluorene
GC/MS	Gas chromatography/mass spectrometry
HBB	Hexabromobenzene
HBCDD	Hexabromocyclododecane
HM PAH	High molecular weight PAHs (aromatic ring \geq 4)
Ind	Indeno(1,2,3)pyrene
IRIS	Integrated Risk Information System
LM PAH	Low molecular weight PAHs (aromatic ring $<$ 4)
LPG	Liquefied petroleum gas
m-TCP	Tri-m-cresyl phosphate
Nap	Naphthalene
non-DLCB	Non-dioxin like PCBs
OPFR	Organophosphate flame retardants
o-TCP	Tri-o-cresyl phosphate
PAH	Polycyclic aromatic hydrocarbons
PBDE	Polybrominated diphenyl ethers
PC	Principal component
PCA	Principal component analysis
PCB	Polychlorinated biphenyls
Phe	Phenanthrene
POP	Persistent organic pollutant
p-TCP	Tri-p-cresyl phosphate
PTFE	Teflon
PUF	Polyurethane foam
PVC	Polyvinyl chloride
Pyr	Pyrene
syn-DP	<i>syn</i> -Dechlorane plus
T2iPPP	Tris(2-isopropylphenyl) phosphate
TBCO	1,2,5,6-tetrabromocyclooctane
TBOEP	tributoxyethyl phosphate
TBP-DBPE	2,3-Dibromopropyl-2,4,6-tribromophenyl ether
TCEP	Tris(2-chloroethyl) phosphate
TCIPP	Tri(chloropropyl) phosphate
TDCIPP	Tris(1,3-dichloro-2-propyl) phosphate

TEF	Toxicity equivalent factor
TEHP	Tri(2-ethylhexyl) phosphate
TEQ _{B(a)P}	B(a)P equivalent PAH concentration
TNBP	Tributyl phosphate
TPeP	Tripentyl phosphate
TPHP	Triphenyl phosphate
TPrP	Tripropyl phosphate
USEPA	United States Environmental Protection Agency

CHAPTER 1

INTRODUCTION

Since the 1970s; brominated, chlorinated, and organophosphorus flame retardants (FRs) have been heavily used in commercial and household products to reduce fire incidents and slow down the spread of flames. Following the determination of the persistence, long-range atmospheric transport, and toxicological effects on environment and living organisms of polybrominated diphenyl ethers (PBDEs), the most heavily used bromine-based FRs, legislative regulations have led to high demand for new flame retardants (Darnerud, 2003; Marteinson et al., 2021). Among these FRs, while the α and β isomers of DBE-DBCH dominate the isomer profile in technical mixtures, trace amounts of γ and δ isomers can also form during production. Although the current global production volume of DBE-DBCH technical mixture is not precisely known, Albemarle Corporation (USA) has introduced the Saytek BCL-462 technical mixture to the FR market. Additionally, EPA report indicate that annual production had reached 500000 pounds in 2002. Considering that PBDE production had just been banned in the USA at that time, and bans in other countries were not yet under consideration, it can be speculated that present-day BDE-DBCH production may have reached significantly high production volumes.

DP isomers, which have been used for many years as low-production-volume chemicals, were detected to be in air and sediment samples in 2006, indicating their accumulation potential in environmental media (Hoh et al., 2006). The molar concentration ratio of *anti* and *syn* isomers in DP technical mixtures is 3:1 (Sverko et al., 2011). Due to the recommendation of DP as an alternative to Deca-BDE, which has been banned from production and use, intensive effort are underway to establish the literature data for determining whether it accumulates in environmental media (de la Torre et al., 2020, 2018; Drage et al., 2016; Genisoglu et al., 2019; Kurt-Karakus et al., 2017; Lee et al., 2020; Pasecnaja et al., 2021; Someya et al., 2016; Venier et al., 2016; Wang et al., 2020; Yadav et al., 2020).

PBDEs, despite not being used in agriculture, food processing, and packaging processes, are present in unprocessed foods due to their high octanol-air and octanol-water coefficients, as well as their lipophilic structures, resulting in their presence in all environmental systems and food chain. The bioaccumulation of PBDEs in the food chain increases health risks due to the increasing exposure dose as they move up the food chain. Unlike indoor air and dust samples, PBDE levels and congener profiles in foods vary due to tendencies for transformation into lower congeners via atmospheric UV and ozone exposure (Shih and Wang, 2009), as well as microbial and metabolic transformation mechanisms (Luo et al., 2013; Wang et al., 2023). A study on seafood has shown that the cooking process increases PBDE concentration in meals, results in increasing exposure levels (Aznar-Alemany et al., 2017). Consequently, studies conducted on ready-to-eat meals are crucial for modeling exposure levels to reveal health risks.

OPFRs are widely used as alternatives to brominated and chlorinated flame retardants (Yao et al., 2021). OPFRs are semi-volatile and can undergo long-range atmospheric transport, leading to their detection in remote regions such as the Arctic (Chen et al., 2021). Like other flame retardants, they are used in textiles, chemicals, paints, electrical-electronic, and furniture production. Due to their high vapor pressures and short half-lives, it is suggested that the persistence and long-range transport of OPFRs in environmental systems are less than those of PBDEs (Rodgers et al., 2018). However, despite not being expected to accumulate in environmental systems due to their physical and chemical properties, OPFRs have been identified not only in environments where sources are present but also in soil, atmosphere, water sources, and even in Arctic regions in many studies (Cristale et al., 2013; Dodson et al., 2012; He et al., 2018; Khan et al., 2016; Ma et al., 2022; Sakhi et al., 2019; Vasiljevic et al., 2020; Yadav et al., 2020; Yao et al., 2021). Compared to PBDEs, they can be found at levels ten times higher or more (Blum et al., 2019).

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds composed of multiple aromatic rings. These compounds are ubiquitous in the environment, originating from both natural and anthropogenic sources. Their unique structure, characterized by fused benzene rings, imparts specific chemical and physical properties, influencing their behavior in the environment and their interactions with biological systems. PAHs have garnered significant attention due to their persistence, potential for bioaccumulation, and adverse health effects, including carcinogenicity and mutagenicity (ATSDR, 1995; IARC, 2010).

PAHs, emitted into the environment through various natural and anthropogenic processes, pose significant pollution concerns. While natural sources like forest fires and volcanic eruptions contribute, anthropogenic activities are the primary culprits. These activities include incomplete combustion of organic materials like fossil fuels, wood, and biomass, as well as emissions from vehicles, industrial processes, and waste incineration. Additionally, PAHs are present in crude oil and petroleum products, leading to environmental contamination through spills and discharges (Yunker et al., 2002). Certain industrial activities, such as aluminum production and coke manufacturing, also release PAHs into the atmosphere. Furthermore, the use of certain pesticides and herbicides introduces PAHs into agricultural soils and water bodies.

PAHs, categorized under POPs, stem mainly from petroleum and combustion emissions. Formed by incomplete combustion reactions of organic-rich materials, they persist in the environment for extended periods, transported over long distances through atmospheric processes. PAHs with two and three aromatic rings (Nap, Acy, Ace, Flu, Phe, and Ant) are classified as low molecular weight PAHs (LM PAH), while those with ≥ 4 aromatic rings (Fla, Pyr, Chr, B(a)A, B(bk)F, B(a)P, Ind, DB(ah)A, and B(ghi)P) are classified as high molecular weight PAHs (HM PAH) (Tobiszewski and Namieśnik, 2012). Low molecular weight PAHs are associated with petrogenic emissions, while high molecular weight PAHs primarily come from combustion processes. Apart from direct emission from petroleum derivatives, various activities like cooking, fires, smoking, traffic, and industrial processes contribute significantly to PAH emissions (Arfaeinia et al., 2022; De La Torre-Roche et al., 2009; Goto et al., 2021; Kamal et al., 2016; Lim et al., 2007; Lin et al., 2022; Pies et al., 2008; Rostami et al., 2019; Singh et al., 2023; Tobiszewski and Namieśnik, 2012; Zhang et al., 2008). These findings underscore the diverse sources and complex nature of PAH pollution, highlighting the need for comprehensive mitigation strategies.

Polychlorinated biphenyls (PCBs) are a group of man-made organic chemicals consisting of carbon, hydrogen, and chlorine atoms. They were first manufactured in the late 1920s and were widely used due to their non-flammability, chemical stability, high boiling points, and insulating properties. These characteristics made PCBs ideal for use in a variety of industrial and commercial applications, including electrical equipment, heat transfer fluids, and as additives in paints, sealants, and plastics (Erickson and Kaley, 2001).

PCBs are classified as a persistent organic pollutant that consists of 209 individual chlorinated compounds known as congeners. Each congener contains a biphenyl molecule, a structure with two linked benzene rings, and varies in the number and placement of chlorine atoms. The general chemical formula for PCBs is $C_{12}H_{10-n}Cl_n$, where n can range from 1 to 10. The physical and chemical properties of PCBs, such as melting point, boiling point, solubility, and vapor pressure, depend on the degree of chlorination.

PCBs were first synthesized in the late 1920s and gained popularity due to their unique properties, which made them ideal for various industrial applications. By the 1930s, PCBs were commercially produced under trade names such as Aroclor, Clophen, and Kanechlor. Production and use of PCBs peaked in the 1960s and early 1970s, with millions of tons manufactured globally. However, concerns about their environmental and health impacts began to surface, leading to regulatory actions to limit and eventually ban their use (Breivik et al., 2002). Their primary uses included production of electrical equipments, hydraulic fluids and lubricants, plasticizers and sealants, and adhesives and surface coatings. PCBs were widely used as dielectric fluids in transformers, capacitors, and other electrical equipment due to their insulating properties and thermal stability (Breivik et al., 2002). Their chemical stability made PCBs suitable for use in hydraulic systems and as lubricants in machinery (Erickson, 2001). PCBs were added to paints, sealants, and plastics to enhance flexibility and durability. Their resistance to heat and chemicals made them valuable in various coating applications (ATSDR, 2000).

Despite their superior properties such as chemical stability and insulation, PCBs have been found to pose significant environmental and health risks. They are highly persistent in the environment, capable of resisting degradation over long periods. PCBs can bioaccumulate in the fatty tissues of living organisms, leading to higher concentrations at higher levels of the food chain. This bioaccumulation poses severe risks to both wildlife and humans, including immune system suppression, reproductive disorders, developmental problems in children, and increased cancer risk (ATSDR, 2000; IARC, 2016).

Humans can be exposed to PCBs through various pathways, including inhalation of contaminated air, ingestion of contaminated food, and accidental ingestion of contaminated house dust. Each of these exposure routes contributes to the overall body burden of PCBs, making it crucial to understand the distribution and concentration of PCBs in these different media (ATSDR, 2000).

PCBs can enter the atmosphere through volatilization from contaminated soil and water, industrial processes, and the disposal of PCB-containing materials. Once in the air, PCBs can travel long distances from their original source, leading to widespread environmental contamination. Inhalation of PCB-contaminated air is a significant exposure pathway, especially for individuals living near industrial sites or in urban areas with high levels of airborne pollutants (Mackay and Wania, 1995). Indoor environments can act as a sink for PCBs due to their past use in building materials, electrical appliances, and consumer products. House dust can accumulate PCBs from these sources, leading to prolonged exposure, particularly for children who have closer contact with dust through hand-to-mouth activities and playing on floors. The assessment of PCB levels in house dust is critical for evaluating potential health risks.

CHAPTER 2

LITERATURE REVIEW

A study in Turkey determined that the average Σ_5 PBDE levels in raw and packaged milk were 9.51 ng/g-lipid and 6.99 ng/g-lipid, respectively, with BDE-153 and BDE-154 dominant in raw milk, while BDE-47 was dominant in packaged milk (Aydin vd., 2019). In a study conducted on fish in the Iberian region of Spain, it was determined that the Σ_8 PBDE levels reached up to 520 ng/g-lipid levels (Santín et al., 2013), while in a different study conducted in the Valencia region, the average Σ_{12} PBDE level was determined to be 3790 pg/g (ww) (Pardo et al., 2014). In a study conducted in Italy in 2016, average Σ_8 PBDE levels were determined to be 1523, 3749, 2538, 494, 524, 7241 pg/g (ww) in meat, dairy products, eggs, snails, fish, and fish products, respectively (Martellini et al., 2016). In a study conducted in Poland, it was determined that chocolate products containing plastic toys in the form of eggs on the market were contaminated with PBDEs from both the plastic toys and packaging (Śmiełowska et al., 2022). In a study conducted in China, in a region where electronic waste recycling facilities are located, it was determined that the average Σ_{22} PBDE concentration in carp fish reached up to 11400 ng/g (ww) in nine different food products (Chan et al., 2013).

In a study conducted in Norway, indoor air Σ DBE-DBCH levels were determined to be 79.9 pg/m³ in homes and 46.6 pg/m³ in schools (Cequier et al., 2014). Exposure to temperatures above 125°C causes diastereomerization of DBE-DBCH, leading to changes in the isomer profile (Arsenault et al., 2008). Dust-bound DBE-DBCH levels were generally found at relatively low levels. Levels of Σ DBE-DBCH in indoor dust collected from homes were determined to be in the range of 0.073-3.80 ng/g in Sweden, 0.04-0.42 ng/g in Egypt, 2.20-11.0 ng/g in China, 0.90-1.60 ng/g in Canada, 33.7-228 ng/g in Italy, and 0.64-360 ng/g in the United States (Newton et al., 2015; Hassan and Shoeib, 2015; Sun et al., 2018; Fan et al., 2016; Simonetti et al., 2020). While DBE-DBCH levels in outdoor air was variable, α isomer concentrations determined to be in the range of 7.00-130 pg/m³ and β isomer concentrations determined to be in the range of 0.24-2.40 pg/m³ in Sweden (Newton et al., 2015). In a study conducted in England,

outdoor air Σ DBE-DBCH levels were determined to be in the range of 0.14-41 pg/m^3 . A study conducted in the Arctic region of Norway, which also demonstrates long-range transport of DBE-DBCH, determined α isomer concentrations of 29-65 pg/m^3 and β isomer concentrations of 17-46 pg/m^3 (Carlsson et al., 2018).

After the regulations on commercial Penta-BDE mixtures, BEH-TEBP began to be used as a flame retardant additive in the production of polyurethane foam (PUF), polyvinyl chloride (PVC), neoprene rubber, and cable insulation (Niu et al., 2021). In a study conducted in the USA, median concentrations of indoor dust-bound BEH-TEBP and EH-TBB were determined to be 115 and 59.5 ng/g , respectively (Percy et al., 2020). In a study conducted in Norway (Cequier et al., 2014), the average indoor dust-bound concentration of BEH-TEBP was determined to be 85 ng/g , while median concentrations of BEH-TEBP were determined to be 64 ng/g in Iraq (Al-Omran and Harrad, 2016), 58 ng/g in China (Wu et al., 2016), and 2.40 ng/g in Egypt (Hassan and Shoeib, 2015). A relatively high dust-bound BEH-TEBP concentration was determined in USA with a median level of 1246 ng/g (Allgood et al., 2017). In a study conducted in a computer technical service in Turkey (Genisoglu et al., 2019), the median indoor dust-bound concentration of BEH-TEBP was determined to be 173 ng/g , while another study conducted in homes determined to be 0.13 ng/g (Kurt-Karakus et al., 2017). A significant correlation ($R^2 > 0.64$) between the BEH-TEBP and EH-TBB concentrations was determined (Al-Omran et al., 2021). The median indoor dust-bound EH-TBB concentration in computer technical service was determined to be 143 ng/g (Genisoglu et al., 2019). The other study conducted in homes and offices in Turkey determined median dust-bound EH-TBB concentrations in homes were 100, 840, and 150 ng/g at rural, sub-urban, and urban areas, respectively, while those were N.A., 26, and 480 ng/g in offices (Kurt-Karakus et al., 2017).

HBB, synthesized by attaching six bromine atoms to a benzene ring, has been intensively used as FR additive since the 1980s (Venier et al., 2012). The median concentrations of indoor dust-bound HBB in homes were determined to be <DL, 2.70, 580 ng/g in rural, sub-urban, and urban areas of İstanbul-Türkiye, respectively, while those levels in were determined as N.A., 1.30, 190 ng/g , respectively, in offices (Kurt-Karakus et al., 2017). The median indoor dust-bound HBB concentration in computer technical services was 31.4 ng/g (Genisoglu et al., 2019), while the median concentration of TBCO was 50.7 ng/g . The average dust-bound concentration of HBB was determined to be 0.2 ng/g in homes in Egypt (Hassan and Shoeib, 2015). The median dust-bound

concentration of TBP-DBPE in rural, sub-urban, and urban areas were determined to be 2.80, 120, and 2.80 ng/g, respectively, while HBCDD compound was determined to be <MDL, 16, and 0.70 ng/g (Kurt-Karakus et al., 2017). The median dust-bound TBP-DBPE and HBCDD concentrations in offices in urban area of İstanbul were 200 and 240 ng/g, respectively, while in a study conducted in a technical service in Izmir, these values were found to be 17.8 and 718 ng/g (Kurt-Karakus et al., 2017, Genisoglu et al., 2019).

Retrospective analysis of samples taken in 2005 and 2006 resulted in Σ DP concentrations ranging from <MDL to 30 pg/m³, indicating global dispersion of DP into the atmosphere (Schuster et al., 2021). In our previous study conducted in Izmir (Genisoglu et al., 2019), the median dust-bound concentrations of *syn*-DP and *anti*-DP isomers were determined to be 16.7 and 23.6 ng/g, respectively, while another study determined levels of these substances in Egypt (Hassan and Shoeib, 2015) as 1.00 and 0.30 ng/g, respectively. A study in Canada indicated that the average concentrations of *syn*- and *anti*-isomers of DP in dust ranged up to 44 and 98 ng/g (Abbasi et al., 2016). The physical and chemical properties of some flame retardants are shown in Table 2.1.

Due to their persistence and bioaccumulative properties, PBDEs are of significant concern regarding human health such as neurodevelopmental effects, endocrine disruption, reproductivity, cancer, immunotoxicity, metabolic and obesity-related effects. Studies have shown that prenatal and early-life exposure to PBDEs is associated with adverse cognitive and behavioral outcomes. For example, Herbstman et al. (2010) found that children exposed to higher levels of PBDEs in utero had lower scores on tests of neurodevelopment at 4 to 6 years of age. Similarly, other studies have linked PBDE exposure to attention deficit hyperactivity disorder (ADHD) and impaired motor skills (Gascon et al., 2011). PBDEs are known endocrine disruptors, meaning they can interfere with hormone systems in the body. This disruption can lead to various health issues, including thyroid hormone dysregulation. Thyroid hormones are critical for growth and development, and disruptions in their normal levels can have significant consequences. Chevrier et al. (2010) demonstrated a correlation between PBDE exposure and altered thyroid hormone levels in pregnant women, which could impact fetal development. Moreover, exposure to PBDEs has been linked to changes in sex hormone levels and reproductive health issues (Johnson et al., 2013). In humans, there is evidence suggesting that higher PBDE levels are associated with lower semen quality and reduced sperm motility (Meeker et al., 2009).

Table 2.1. Chemical and physical properties of flame retardants

Flame Retardants	CAS Number	Synonyms	Chemical Formula	Molecular Weight (g/mol)	Melting Point (°C)	Boiling Point (°C)	Log Kow	Log Koa
1,2,5,6,9,10-Hexabromocyclododecane	25637-99-4	HBCDD	C ₁₂ H ₁₈ Br ₆	641.7	190	Decomposes	5.62	12.2
Decabromodiphenyl ether	1163-19-5	BDE-209	C ₁₂ H ₂ Br ₁₀ O	959.17	300	Decomposes	10.3	15.4
Octabromodiphenyl ether	32536-52-0	BDE-183	C ₁₂ H ₂ Br ₈ O	801.55	180	Decomposes	8.2	14
Hexabromodiphenyl ether	68631-49-2	BDE-153	C ₁₂ H ₄ Br ₆ O	641.7	160	Decomposes	6.7	12.8
Pentabromodiphenyl ether	60348-60-9	BDE-99	C ₁₂ H ₅ Br ₅ O	564.69	140	Decomposes	6.2	11.6
Dechlorane Plus	13560-89-9	DP	C ₁₈ H ₁₂ Cl ₁₂	653.72	350	Decomposes	9.3	13
Hexabromobenzene	87-82-1	HBB	C ₆ Br ₆	551.5	320	410	6.1	12

Exposure to polybrominated diphenyl ethers (PBDEs) poses multifaceted risks to human health, with neurodevelopmental effects being a prominent concern, particularly in children. Research indicates that prenatal and early-life exposure to PBDEs is linked to adverse cognitive and behavioral outcomes. For instance, Herbstman et al. (2010) observed lower neurodevelopmental test scores in children with higher levels of prenatal PBDE exposure. Additionally, studies have associated PBDE exposure with attention deficit hyperactivity disorder (ADHD) and impaired motor skills (Gascon et al., 2011). PBDEs are recognized endocrine disruptors, capable of interfering with hormone systems in the body, thereby posing risks to various aspects of health, including thyroid hormone dysregulation. Chevrier et al. (2010) demonstrated correlations between PBDE exposure and altered thyroid hormone levels in pregnant women, potentially impacting fetal development. Moreover, PBDE exposure has been implicated in changes to sex hormone levels and reproductive health issues (Johnson et al., 2013). Concerns regarding reproductive health arise from studies demonstrating adverse effects of PBDE exposure on fertility and offspring development in animals (Lilienthal et al., 2006). Human studies also suggest associations between higher PBDE levels and compromised semen quality and sperm motility (Meeker et al., 2009), highlighting potential risks to human reproductive health.

The International Agency for Research on Cancer (IARC) has classified certain PBDE congeners as possible human carcinogens based on animal studies that showed an increase in liver tumors following PBDE exposure (IARC, 2016). While definitive evidence in humans is still lacking, the potential for PBDEs to contribute to cancer risk remains a significant concern, warranting further investigation. PBDE exposure has been linked to immunotoxic effects, including altered immune function. Studies have shown that PBDEs can affect the production and activity of various immune cells, potentially leading to increased susceptibility to infections and autoimmune diseases (Darnerud, 2001). For example, epidemiological studies have found associations between higher PBDE levels and increased incidence of respiratory infections in children (Gascon et al., 2011). Emerging evidence suggests that PBDEs may contribute to metabolic disorders and obesity. Experimental studies on animals have shown that PBDE exposure can lead to changes in lipid metabolism, insulin resistance, and weight gain (Hoppe and Carey, 2007). Human studies have also observed associations between PBDE levels and markers of metabolic syndrome, including increased waist circumference and insulin resistance (Lim et al., 2008). These findings underscore the diverse and complex health risks

associated with PBDE exposure, highlighting the need for continued research and regulatory measures to mitigate potential risks.

PBDEs lipophilic nature facilitates their accumulation in lipid-rich tissues. Major sites of distribution include adipose tissue, liver, and the central nervous system, with varying patterns depending on the specific PBDE congeners (Voorspoels et al., 2006). The liver is the primary site for the metabolism of polybrominated diphenyl ethers (PBDEs). Metabolic processing in the liver involves both Phase I and Phase II reactions. Phase I metabolism primarily involves cytochrome P450 enzymes (CYP450), such as CYP2B6, CYP3A4, and CYP1A1, which oxidize PBDEs to form hydroxylated PBDEs (OH-PBDEs) (Zota et al., 2018; Stapleton et al., 2009). In Phase II metabolism, these OH-PBDEs undergo conjugation reactions to enhance their solubility for excretion. For instance, glucuronidation by UDP-glucuronosyltransferases (UGTs) attaches glucuronic acid to OH-PBDEs (Lai et al., 2012). Sulfation, carried out by sulfotransferases (SULTs), and glutathione conjugation by glutathione S-transferase (GST) further facilitate the excretion of these metabolites through urine and bile (Hakk et al., 2006; Staskal et al., 2006).

Beyond the liver, other tissues also metabolize PBDEs. Adipose tissue, due to its lipophilic nature, acts as a major reservoir for PBDEs, resulting in slow release and prolonged bioavailability (Hakk et al., 2002). The brain, although possessing lower metabolic activity compared to the liver, can accumulate PBDEs, especially those with fewer bromine atoms, indicating some local metabolic activity (Costa and Giordano, 2007). PBDEs can also cross the placental barrier, exposing the fetus. Despite the lower enzymatic activity in fetal tissues, the presence of PBDEs and their metabolites in these tissues suggests active metabolism and potential health risks (Darnerud et al., 2001).

OPFRs, which are expected to have lower levels in soil due to their high vapor pressure compared to PBDEs, might be found at higher levels than PBDEs. The health effects of OPFRs are an emerging area of concern. Some OPFRs have been identified as potential endocrine disruptors, neurotoxins, and carcinogens. Studies have shown that exposure to OPFRs can lead to health problems such as neurotoxicity, carcinogenicity, and disruption of the endocrine system (Yao et al., 2021). OPFRs can interfere with hormone function, potentially leading to reproductive and developmental effects. For example, TCEP and TDCPP have been shown to disrupt thyroid hormone regulation (Meeker and Stapleton, 2010). TCEP has been classified as a potential human carcinogen by the International Agency for Research on Cancer (IARC, 1999). Animal studies

indicate that certain OPFRs, such as TDCPP, can affect neurodevelopment, leading to deficits in learning and memory (Dishaw et al., 2011). Studies suggest that long-term exposure to certain OPFRs may increase cancer risk. Inhalation of OPFRs may lead to respiratory problems and alterations in immune function. Accumulation of OPFRs in tissues varies depending on their structural properties. In a study conducted on mice, it was found that tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) had the highest concentration in muscles, while bis(1,3-dichloro-2-propyl) phosphate (BDCIPP: also, a transformation product of TDCIPP) showed higher accumulation in kidneys (Zhu et al., 2020). The chemical structures and physical properties of the targeted OPFR compounds are shown in Table 2.2.

Among these compounds, TNBP is used in the production of hydraulic oils, plastics, and solvents; TCEP is used in the production of PVC, cellulose, coatings, polyester resins, textiles, and polyurethane foam; TDCIPP is used in the production of plastics, textiles, and polyurethane foam; TBOEP is used in floor coatings, polishes, rubber, and solvent production; TPHP is used in hydraulic oils, PVC, electronic devices, adhesives, thermoplastics, and resin production; EHDPP is used in hydraulic oils, PVC, and food packaging production (Andresen et al., 2004). In a study conducted in Bursa, it was found that the Σ_7 OPFR concentrations in outdoor air ranged from 474 to 19139 pg/m^3 , with alkyl compounds being dominant in the concentration profile ($\Sigma\text{OPFR}_{\text{alkyl}} = 9.20\text{-}18009 \text{ pg}/\text{m}^3$). In the same study, it was determined that the ΣOPFR concentration in the analyzed soil samples ranged from 37 to 468 ng/g . In a study conducted in China, it was determined that the concentration of Σ_{10} OPFR compounds in laboratory and classroom floor dust ranged from 40 to 29200 ng/g (Zhao et al., 2020). In another study conducted in homes, it was determined that the Σ_9 OPFR concentrations were 7.43 ng/m^3 in indoor air, 8250 ng/g in house-dust, and 7999 ng/m^2 in window films (Li et al., 2019).

Regulatory bodies are increasingly scrutinizing OPFRs due to their potential health risks. In the European Union, several OPFRs are listed as substances of very high concern (SVHC) under the REACH regulation. The U.S. Environmental Protection Agency (EPA) is also conducting risk assessments for various OPFRs to determine appropriate regulatory actions (EPA, 2015). Future research is essential to fully understand the long-term health and environmental impacts of OPFRs. There is a pressing need for the development of safer flame retardant alternatives and enhanced regulatory frameworks to manage and mitigate the risks associated with OPFRs.

Table 2.2. Chemical and physical properties of OPFRs

Compound	CAS NO.	Formula	Mw g/mole	log K_{ow}	log K_{oa}	ρ (g/cm ³)	K _{oc} (PH = 7.4)	
<i>Alkyl Compounds</i>								
TPrP	-tripropyl phosphate	513-08-6	C ₉ H ₂₁ O ₄ P	224.2	2.4	6.4	1.0 ± 0.1	528.2
TNBP	-tributyl phosphate	126-73-8	C ₁₂ H ₂₇ O ₄ P	266.3	3.8	9.2	1.0 ± 0.1	2565.3
TBOEP	-tributoxyethyl phosphate	78-51-3	C ₁₈ H ₃₉ O ₇ P	398.5	3	13.1	1.0 ± 0.1	1814.3
TEHP	-tri(2-ethylhexyl) phosphate	78-42-2	C ₂₄ H ₅₁ O ₄ P	434.6	9.5	15	0.9 ± 0.1	1785320
TPeP	-tripentyl phosphate	2528-38-3	C ₁₅ H ₃₃ O ₄ P	308.4	5.3	8.8	1.0 ± 0.1	32.911
<i>Chlorinated Compounds</i>								
TCEP	-tris(2-chloroethyl) phosphate	115-96-8	C ₆ H ₁₂ Cl ₃ O ₄ P	285.5	1.6	7.4	1.4 ± 0.1	140.9
TCIPP	-tris(2-chloroiso-propyl) phosphate -tri(chloropropyl) phosphate -tris (2-chloro-1-methylethyl) phosphate	6145-73-9	C ₉ H ₁₈ Cl ₃ O ₄ P	327.6	2.9	8.5	1.3 ± 0.1	471.8
TDCIPP	-tris(1,3-dichloro-2-propyl) phosphate -tris (2-chloro-1-(chloromethyl) ethyl) phosphate	13674-87-8	C ₉ H ₁₅ Cl ₆ O ₄ P	430.9	3.7	10.6	1.5 ± 0.1	1409.8
<i>Aryl Compounds</i>								
TPHP	-triphenyl phosphate	115-86-6	C ₁₈ H ₁₅ O ₄ P	326.3	4.7	8.5	1.3 ± 0.1	4134.7
EHDPP	-2-ethylhexyl diphenyl phosphate	1241-94-7	C ₂₀ H ₂₇ O ₄ P	362.4	6.3	8.9	1.1 ± 0.1	28924
T2iPP	-tris(2-isopropylphenyl) phosphate	64532-95-2	C ₂₇ H ₃₃ O ₄ P	425.5				
TMPP	-tri-o-cresyl phosphate -tri-m-cresyl phosphate -tri-p-cresyl phosphate	78-30-8 563-04-2 78-32-0	C ₂₁ H ₂₁ O ₄ P	368.4	6.34	9.59	1.25	44000

PAH concentrations in indoor environments vary greatly. The average settled dust-bound Σ_{13} PAH concentrations in homes and hotels in Saudi Arabia were reported to be 3715 and 7063 ng/g, respectively, while those medians were 2289 and 6286 ng/g, respectively (Ali, 2019). While the Phe was the dominant PAH compound in homes, Chr was the dominant in hotels. The average settled dust-bound Σ_{16} PAH concentration in homes was reported to be 160 ng/g in Iran (Mosallaei et al., 2023). In China, homes had an average settled dust-bound Σ_{16} PAH concentration of 53120 ng/g (Wang et al., 2023). A recent study reported the average Σ_{16} PAH concentrations associated with residential indoor air and particulate matter to be 1260 ng/m³ (Soleimani et al., 2024).

Chemical and physical properties of PAHs are shown in Table 2.3. PAHs, which are pollutants that cannot be avoided due to their atmospheric levels and formation during the cooking of foods, are one of the pollutant groups of primary importance for human health. The toxicokinetic of PAHs involves their absorption, distribution, metabolism, and excretion. PAHs are metabolized by various xenobiotic-metabolizing enzymes, including cytochrome P450, epoxide hydrolase, glutathione transferase, UDP-glucuronosyltransferase, sulfotransferase, NAD(P)H quinone oxidoreductase 1, and aldo-keto reductase (Shimada, 2006). Once PAHs enter the body, they are metabolized primarily in the liver through the cytochrome P450 enzyme system. This metabolism can lead to the formation of reactive intermediates, such as diol epoxides, which can bind to DNA and proteins, leading to toxic effects. The liver is the primary organ responsible for PAH metabolism, but other tissues also play a role. This process is divided into Phase I and Phase II reactions, which are essential in determining the toxicological impact of these compounds. PAHs initially undergo oxidation (Phase I metabolism), primarily mediated by cytochrome P450 enzymes, including CYP1A1, CYP1A2, and CYP1B1. These enzymes transform PAHs into epoxides, which are highly reactive intermediates. For instance, benzo[a]pyrene (BaP), a well-studied PAH, is metabolized into benzo[a]pyrene-7,8-epoxide by CYP1A1, which can further be converted into other metabolites (Baird et al., 2005). These epoxides are then hydrolyzed by epoxide hydrolase to form dihydrodiols, such as benzo[a]pyrene-7,8-dihydrodiol, which are generally less toxic and more water-soluble (Shimada and Fujii-Kuriyama, 2004). In Phase II metabolism, dihydrodiols and other hydroxylated metabolites undergo conjugation reactions to enhance their solubility and facilitate excretion. UDP-glucuronosyltransferases (UGTs) catalyze the addition of glucuronic acid to PAH metabolites, forming glucuronides that are easily excreted in urine and bile (Vergara et

al., 2020). Sulfotransferases (SULTs) also contribute by attaching sulfate groups to hydroxylated PAH metabolites, resulting in sulfated conjugates for excretion (Glatt, 2000). Additionally, glutathione S-transferases (GSTs) conjugate glutathione with PAH epoxides, dihydrodiols, and quinones, forming mercapturic acids that are eliminated through the kidneys (Hayes et al., 2005).

Beyond the liver, other tissues such as the lungs and skin also metabolize PAHs, though to a lesser extent. Inhaled PAHs are processed in the lungs where enzymes like CYP1A1 convert them into reactive intermediates, which can cause localized toxicity (Boström et al., 2002). The skin, exposed to PAHs through dermal contact, metabolizes these compounds using similar enzymatic pathways (Shimada and Fujii-Kuriyama, 2004). The gastrointestinal tract, particularly the small intestine, participates in the first-pass metabolism of ingested PAHs, with enzymes in the intestinal mucosa contributing to detoxification and excretion. Additionally, PAHs can cross the placental barrier, exposing the fetus to these compounds. Although fetal tissues have lower metabolic activity, the presence of PAH metabolites indicates some metabolic processing, which raises concerns about developmental toxicity (Lohmann et al., 2007).

Table 2.3. Chemical and physical properties of PAHs

Compounds	CAS no	Chemical Formula	log(K _{aw})	log(K _{oa})	MW (g/mol)
Naphthalene	91-20-3	C ₁₀ H ₈	6.41	3.58	128.17
Acenaphthylene	208-96-8	C ₁₂ H ₈	6.04	3.3	152.21
Acenaphthene	83-32-9	C ₁₂ H ₁₀	5.38	2.57	154.2
Fluorene	-	C ₁₃ H ₁₀	5.56	3.3	166.21
Phenanthrene	85-01-8	C ₁₄ H ₁₀	5.45	2.59	178.23
Anthracene	120-12-7	C ₁₄ H ₁₀	5.15	2.32	178.23
Fluoranthene	206-44-0	C ₁₆ H ₁₀	4.36	1.76	202.25
Pyrene	129-00-0	C ₁₆ H ₁₀	4.04	1.56	202.25
Benz(a)anthracene	56-55-3	C ₁₈ H ₁₂	2.28	0.61	228.29
Chrysene	218-01-9	C ₁₈ H ₁₂	2.23	0.56	228.29
Benzo(b)fluoranthene	205-99-2	C ₂₀ H ₁₂	2.97	0.15	252.31
Benzo(k)fluoranthene	207-08-9	C ₂₀ H ₁₂	2.63	-0.15	252.31
Benzo(a)pyrene	50-32-8	C ₂₀ H ₁₂	2.11	-0.66	252.31
Indeno(1,2,3-cd)pyrene	193-39-5	C ₂₂ H ₁₂	1.65	-0.22	276.33
Dibenz(a,h)anthracene	53-70-3	C ₂₂ H ₁₄	1.45	-0.4	278.34
Benzo(ghi)perylene	191-24-2	C ₂₂ H ₁₂	1.26	-0.52	276.34

In indoor environments, concentrations of persistent organic pollutants vary significantly depending on source intensity. Therefore, concentrations reported in the literature vary widely. The average residential settled dust-bound Σ_{37} PCB concentrations in Guangzhou and Hong Kong were 139 ng/g and 81.8 ng/g, respectively (Wang et al., 2013). In Bangladesh, the settled dust-bound Σ_6 PCB concentrations ranged from 168-3419 ng/g in commercial buildings, 590-4669 ng/g in industrial buildings, 244-2583 ng/g in institutional buildings, and 161-5413 ng/g in residential buildings (Rayhan et al., 2024). In Danish homes, the average settled dust-bound Σ_{15} PCB concentration was reported to be 12000 ng/g (Andersen et al., 2020).

Chemical and physical properties of some PCBs are shown in Table 2.4. Low molecular weight groups (Tri- and Tetra-CBs) have been observed as predominant congeners in indoor air concentrations. In a study, it has been suggested that Di-, Tri-, and Tetra-CBs are associated with unintentionally produced PCBs (Xing et al., 2009). Tetra and Hexa-CBs are found at similar levels indoors. Since Hexa-CBs are reported as intentionally produced PCBs, their presence in homes is thought to be associated with old transformers and electrical equipment (Cui et al., 2017). Additionally, it is estimated that Hexa-CBs may have another source in potentially contaminated soils near sampling locations where PCB usage is commonly reported (Salihoglu et al., 2011). Tri and Tetra-CBs are dominant groups compared to other homolog groups in the atmospheric environment; low molecular weight PCBs and constitute 79% of Aroclor 1016 and 41% to 58% of Aroclor 1232, 1242, and 1248. PCBs, mostly known to be of indoor origin, can also be found at high concentrations in outdoor environments due to industrial activities. A study identified congeners belonging to the Penta-CB group as emitted pollutants in iron-steel and ship dismantling facilities (Kaya et al., 2012).

Exposure to PCBs has been associated with a range of adverse health effects in humans. PCBs are classified as probable human carcinogens by the International Agency for Research on Cancer (IARC), with epidemiological studies linking PCB exposure to an increased risk of various cancers, including liver, biliary tract, and melanoma (IARC, 2016). Additionally, PCBs are known to disrupt endocrine function, leading to reproductive and developmental abnormalities. In utero exposure to PCBs has been linked to low birth weight, reduced cognitive function, and impaired neurodevelopment in children (Grandjean and Landrigan, 2006; Schantz et al., 2003). Furthermore, PCBs have been shown to affect the nervous system, resulting in deficits in cognitive function, learning, and behavior, particularly in children exposed during critical periods of brain

development (Carpenter, 2006). Moreover, PCB exposure has been associated with alterations in immune function, leading to increased susceptibility to infections and autoimmune diseases (Hansen, 1998). These findings underscore the importance of minimizing PCB exposure to protect human health.

The metabolism of polychlorinated biphenyls (PCBs) within the human body is a multifaceted process governed by enzymatic pathways primarily localized in the liver, although other organs such as adipose tissue and the gastrointestinal tract may also contribute. Upon ingestion, inhalation, or dermal absorption, PCBs undergo Phase I metabolism, characterized by the introduction of functional groups, such as hydroxyl or epoxide, by cytochrome P450 enzymes, notably members of the CYP1A and CYP2B families. These enzymatic reactions, including hydroxylation, epoxidation, and dechlorination, generate hydroxylated PCB metabolites (OH-PCBs) and other intermediates, rendering the compounds more water-soluble. Subsequently, Phase II metabolism ensues, involving the conjugation of Phase I metabolites with endogenous compounds like glucuronic acid, sulfate, or glutathione, mediated by transferase enzymes such as UDP-glucuronosyltransferases (UGTs), sulfotransferases (SULTs), and glutathione S-transferases (GSTs). While these metabolic pathways aim to enhance the excretion of PCBs and their metabolites, some metabolites may persist and accumulate in tissues due to their physicochemical properties. For instance, certain hydroxylated PCB metabolites exhibit estrogenic or antiestrogenic activity, potentially contributing to endocrine disruption. PCB metabolites are primarily excreted through urine and feces, with factors such as chlorination degree, metabolic efficiency, and individual variability influencing excretion rates (Grimm et al., 2015).

Although Phase I and Phase II metabolism pathways aim to generate more easily excretable PCB metabolites, certain metabolites produced during these processes may retain persistence and bioaccumulation traits akin to the original compounds. Notably, specific hydroxylated PCB metabolites have demonstrated estrogenic or antiestrogenic activities, potentially contributing to disruptions in endocrine function (Hansen, 1998). Regarding excretion, PCB metabolites are predominantly eliminated through urine and feces, with additional elimination routes including sweat, exhaled air, and breast milk. The efficiency and extent of excretion are influenced by multiple factors such as the degree of chlorination, metabolism efficacy, interindividual variations in enzyme activity, as well as the duration and intensity of exposure (Hansen, 1998).

Table 2.4. Chemical and physical properties of some PCBs

Chemical	CAS Number	Synonyms	Chemical Formula	Log Kow	Log Koa	Molecular Weight (g/mol)	Melting Point (°C)	Boiling Point (°C)	Water Solubility (mg/L)
2,4,4'-Trichlorobiphenyl	7012-37-5	PCB-28	C ₁₂ H ₉ Cl ₃	5.67	8.19	257.54	98	325-326	0.0072
2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	PCB-52	C ₁₂ H ₈ Cl ₄	6	8.41	292	165	365-367	0.0035
2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2	PCB-101	C ₁₂ H ₇ Cl ₅	6.26	8.71	326.43	168	375-377	0.00082
2,3',4,4',5'-Pentachlorobiphenyl	31508-00-6	PCB-118	C ₁₂ H ₆ Cl ₅	6.5	9.04	326.43	179	373-375	0.0009
2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2	PCB-138	C ₁₂ H ₅ Cl ₇	6.83	9.35	360.88	179	415-420	0.0006
2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1	PCB-153	C ₁₂ H ₄ Cl ₇	6.92	9.48	360.88	176	420-423	0.00041
2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3	PCB-180	C ₁₂ H ₃ Cl ₉	7.36	10.13	395.32	185	435-437	0.00019
Decachlorobiphenyl	2051-24-3	PCB-209	C ₁₂ Cl ₁₀	8.18	10.5	498.68	300	535	0.00003

This PhD thesis aims to determine the concentrations of carcinogenic and potential toxic organic compounds, which are classified as persistent organic pollutants, in indoor environments such as homes, schools, and cafes/bars/restaurants, where we spend the most of our time. This study not only focuses on determining the concentrations of these compounds in settled dust and air but also investigates their levels in foods. This study marks the first pioneering effort to monitor both legacy and emerging industrially produced persistent organic pollutants (POPs), as well as globally common combustion by-products like PAHs, in settled dust, air, and food within the same sample population.

Despite regulatory efforts to limit production and use of toxic and potentially toxic POPs, regulatory POPs can remain a significant public health concern due to their persistence in the environment and emission from industrial activities. Monitoring studies are of primary importance in efforts to reduce exposure because they support remediation efforts. Continuing monitoring of environmental contamination and efforts to remediate contaminated sites are essential to reduce human exposure to these harmful chemicals.

Public health mitigation efforts and raising public awareness about emerging persistent organic pollutants are crucial for safeguarding human health and the environment. Implementing mitigation strategies involves measures such as regulatory controls on the production and use of these pollutants, promoting safer alternatives, enhancing monitoring and surveillance systems, and implementing pollution prevention and remediation programs. Concurrently, raising public awareness through research campaigns, community engagement initiatives, and dissemination of information about the health risks associated with these pollutants can empower individuals to make informed decisions to reduce exposure and advocate for policy changes. By combining monitoring of legacy and emerging POPs and associated health risk assessment efforts, this study primarily focused on identifying the levels of priority persistent organic pollutants that could potentially cause public health issues. In this context, this thesis has made significant contributions to the topic of persistent organic pollutants, which has a significant gap in not only local but also global literature, especially in terms of the simultaneous status of legacy and emerging persistent organic pollutants in settled dust, air, and food. Also, this thesis may act as a guide for public health mitigation efforts on POP exposure.

CHAPTER 3

MATERIAL AND METHODS

3.1. Sampling

The main element of the sampling design consists of homes and schools. In İzmir, seven households and schools located in urban, semi-urban, and rural areas, were studied. A school was randomly selected considering distribution among the three urbanization levels and Aliğa industrial area. Then, a household near the school that agreed to voluntary participation was selected, preferably a residence of a student. In each household and a school, one indoor and one passive outdoor air sample were collected, and one sample each of indoor and outdoor settled dust was taken. Dinners consumed (due to being the main meal eaten together by all family members, prepared by combining various foods for consumption, and containing more than one type of food (different plates: main course, side dish/garnish)) on two different days within a week were sampled from each household. One sample was taken from each of the three dishes included in each evening's menu. The sampling in schools also included three lunch samples on different days of a week. Dust samples from indoor and outdoor environments were collected from cafes, bars, and restaurants (located near schools) where students might spend time. According to this sampling design, by monitoring persistent organic pollutants that the household members and the school-attending child could be exposed to at home, school, and in cafes/bars/restaurants, it was possible to determine the concentrations in the places where they spend the most time during the day. These concentration levels were then classified according to the degree of urbanization. The locations of the sampling points on the map are provided in Figure 3.1.

Passive sampling method was used for indoor and outdoor air sampling. Passive sampling devices (double-bowl type) were washed in the laboratory prior to sampling with Alconox and tap water, followed by rinsing with distilled deionized water, acetone and hexane to prevent potential contamination from production or transportation/storage-

related dust. Passive samplers were carefully wrapped with stretch film to prevent particulate matter contamination during transportation to the sampling site. Polyurethane foam (PUF, Tisch TE-1014) substrates used for passive sampling were soaked in an Alconox cleaning solution bath and left for one day. Subsequently, the PUFs were rinsed under tap water followed by distilled deionized water, then soaked in distilled water for one night, and the process of rinsing with distilled water and soaking in distilled water continued until the PUFs were purified from Alconox. The dried PUFs were precleaned using Soxhlet extraction with acetone for 24 hours, followed by an additional 24-hour Soxhlet extraction with a 1:1 mixture of acetone:hexane (v/v) mixture. The PUFs dried under vacuum at 50°C were wrapped in pre-baked aluminum foil and stored in sealed bags. Prepared PUFs were stored in a deep freezer at -20°C until use.

Indoor and outdoor air sampling apparatus were deployed to homes and schools for an average of 30 days. Indoor air samples were taken from the living room where household members spent the most time, while classroom, where educational activities were conducted, preferred in schools. When selecting classrooms, those farthest from potential emission zones such as toilets and canteen, and if available, those not facing the car parking area and traffic, were chosen. Outdoor passive samplers were placed on balconies in homes, while in schools, playgrounds away from benches, seating areas, and traffic were chosen, considering the possibility of individuals entering the school grounds from outside school hours to smoke, as well as locations such as the cafeteria and toilet windows. The details of passive air sampling were also given by Edeballi, 2022. Dust samples were taken at the end of the deployment of air sampler to represent partitioning of targeted analytes between air and dust phases. HEPA-filtered vacuum cleaner was used to collect settled dust samples in indoor environments, while bristle brush was used for outdoor sampling. In schools, samples were collected from areas where fresh dust brought in with shoes was possibly minimized, such as non-stepped areas, while in homes, samples were collected from vacuum cleaning of carpets. To minimize extreme contamination or dilution, the entrance and kitchen-near areas were avoided in settled dust sampling in C/B/Rs. Individual HEPA filters were used for each sampling point, and residual dust on the vacuum cleaner attachments was washed with tap water followed by distilled water between samplings to avoid cross-contamination.

Disposable aluminum food containers were used for collecting food samples. The aluminum containers were pre-baked at 450°C and then placed inside sealed bags. Pre-

cleaned food sample collection containers were left at the sampling points to be collected during the visit after the passive sampling period. For representation of the evening meal, 6 different food samples were collected from homes. Inadequate or spoiled food samples were not processed for analysis. Although the goal was to collect two food samples (targeted sample size was 42) from each school, a total of 37 samples were collected due to the absence of canteens where students could have their meals. In addition to a total of 106 food samples collected from homes, 37 food samples from schools were taken to the laboratory of Adnan Menderes University in cool box containing ice packs for extraction.

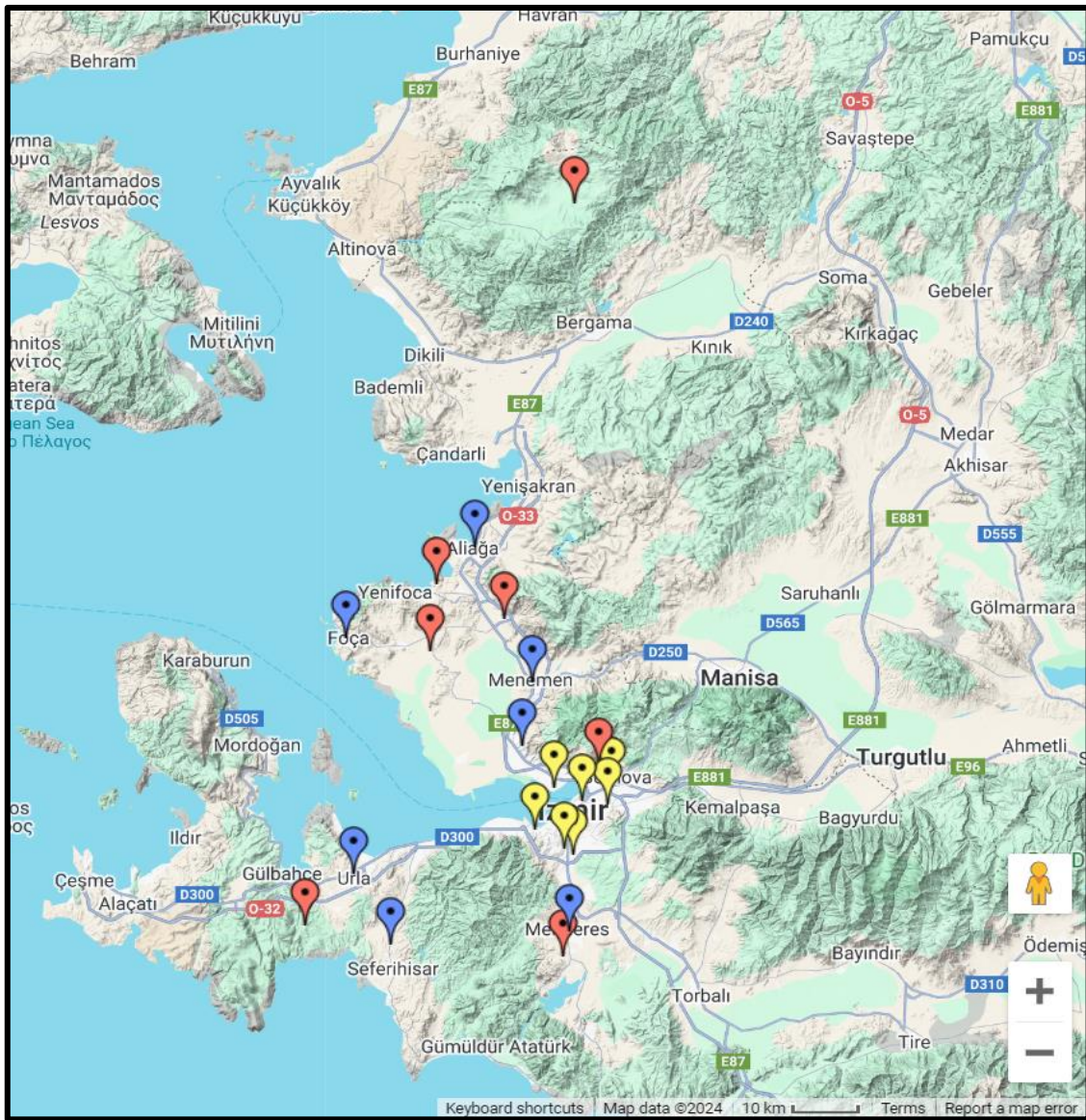


Figure 3.1. Rural (red pins), sub-urban (blue pins), and urban (yellow pins) sampling points in İzmir

3.2. Sample Processing

The classical Soxhlet method was used for the extraction of indoor and outdoor air samples. PUFs were placed into the extraction thimble with a volume of 250 mL, spiked surrogate compounds, and then a mixture of extraction solvent (acetone:hexane; v/v, 1:1) of 350 mL was added to the extraction flask. After setting the heaters to perform a total of 50-60 cycles (approximately 3 cycles per hour), the extraction process was carried out for 20 hours. Following the extraction, the volume of the extract was reduced to approximately 2 mL using rotary evaporator, and then cleaned using silica-bedded solid phase extraction (SPE) cartridges.

The dust samples collected from indoor and outdoor environments were sieved through a 500-micron stainless steel mesh to remove undesired materials such as hair, gravel, paper, pencil residues, and textile fragments. Approximately 0.5 grams of sieved dust sample (precision of 0.0001 gram) were weighed and transferred to amber extraction vials with a volume of 40 mL, and surrogate compounds were spiked. Then, a mixture of 20 mL extraction solvent mixture (acetone:hexane; v/v, 1:1) was added, and the vials were sealed with Teflon-lined cap and left in a dark environment. Dust samples were extracted using ultrasonic extraction (ElmaSonic, 37 kHz) was applied for 15 minutes after the overnight soaking process. Dust particles allowed to settle, and the solvent phase was transferred to clean amber bottles. To prevent possible target compound residues on the dust particles, another 20 mL of extraction solvent was added and followed by another 15-minute ultrasonic extraction. The solvent obtained from the second extraction was combined with obtained from the first extraction, and concentrated using a rotary evaporator until the volume was reduced to around 2 mL. Extracts were cleaned using silica-bedded SPE cartridges.

Silica-bedded SPE cartridges and a vacuum manifold were used for the cleaning of air and dust samples. SPE cartridges were pre-cleaned with 20 mL of acetone, and then the sample was transferred to the cartridge. After elution with 30 mL each of hexane and acetone, the collected phases were combined, and the solvent was evaporated using a rotary evaporator. After reducing the sample volume to around 0.5 mL, solvent was exchanged to an isooctane phase, and the evaporation process was carried out until the volume reached approximately 0.5-0.8 mL. After transferring the samples to gas

chromatography vials, volumetric standards of 25 ng 1,2,3,4,5,6-Hexachlorocyclohexane (epsilon-BHC), 100 ng mirex, and 200 ng terphenyl-D₁₄ were spiked.

Food samples were extracted using QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method (Figure 3.3 and Figure 3.4). Food samples were homogenized using laboratory type homogenizer. A 10 gr homogenized food sample was taken to the 50 mL conical centrifuge tube. Afterward, 10 mL chromatography grade acetonitrile was added and hand-shake for 15 seconds and vortexed for 60 seconds. 4 gr magnesium sulfate and 1 gr anhydrous sodium acetate were added and hand-shake to avoid agglomeration of extraction chemicals and followed with vortex for 120 seconds. Samples were centrifuged for 4 minutes at 4000 rpm to separate solid and liquid phases. The upper liquid phase was taken to a new conical centrifuge tube and 0.6 gr magnesium sulfate, 0.3 gr primary secondary amine (PSA), and 0.015 gr graphitized black carbon (GBC) added and vortexed for 30 seconds. Afterwards, tubes were centrifuged for 4 minutes at 4000 rpm and upper phase were taken. Samples were overnight frizzed at -20 °C and filtered using Teflon syringe filters.

Food samples were cleaned using laboratory prepared chromatography columns with 4 gr deactivated alumina. The clean-up column was pre-cleaned elution of 32 mL hexane. 2 mL food extract was added to chromatography column and eluted with 32 mL hexane and 8 mL dichloromethane. Solvents were evaporated using vacuum concentrator (Labconco) and diluted with isooctane and transferred to the chromatography vials. Samples were kept in freezer at -20 °C until the analysis. Similar amount volumetric standards were spiked to the food samples before the analysis. The target analyte concentrations in food samples were expressed on a wet-weight basis.

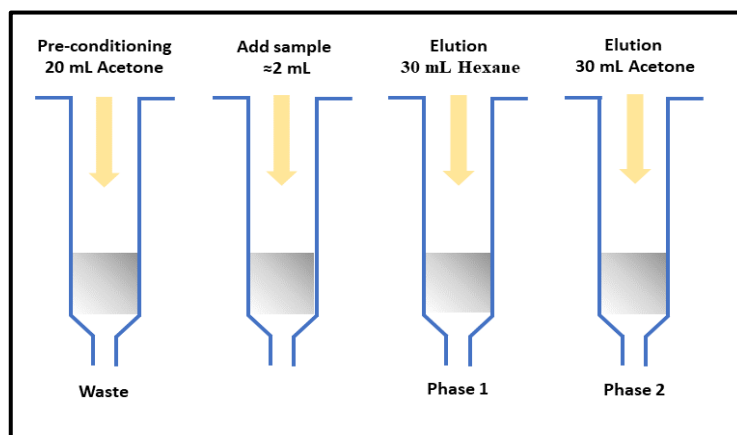


Figure 3.2. Clean-up procedure of dust and air samples



Figure 3.3. Preparation of food samples for the QuEChERS extraction



Figure 3.4. Analytical steps of QuEChERS extraction

3.3. Analysis

3.3.1. PCB Analysis

PCB congeners were analyzed using gas chromatography-electron impact ionization-mass spectroscopy (Thermo Scientific Trace-ISQ, GC-EI-MS) on selective ion monitoring (SIM) mode. Rxi-5MS capillary column (Restek, 60m L, 0.25 mm ID, 0.25 μ m FT) was used for chromatographic separation of PCB congeners. 2 μ L sample injected to GC at 250 $^{\circ}$ C isothermal inlet temperature using surge injection method (130 kPa, 0.30 dk). Oven temperature was programmed as 90 $^{\circ}$ C 1 min isothermal stage, 15 $^{\circ}$ C/min to 160 $^{\circ}$ C, 1 min isothermal stage, 3 $^{\circ}$ C/min to 210 $^{\circ}$ C, 210 $^{\circ}$ C 1 min, 10 $^{\circ}$ C/min to 310 $^{\circ}$ C, 10 dk isothermal stage. SIM parameters of targeted PCB congeners are shown in Table 3.1.

Table 3.1. SIM parameters of PCB analysis

PCB congeners	Ion (<i>m/z</i>)
-4, -10, -6, -7, -8, -5, -14, -19, -12, -18, -17, -15, -27, -24, -26, -34, -29, -31, -25	222, 224, 152, 256, 258, 260
-32, -28, -20, -33, -22, -45, -46, -69, -52, -49, -47, -48, -65, -104, -44, -59, -42, -37, -71	256, 258, 260, 290, 292, 324, 326, 328
-41, -64, -103, -40, -67, -63, -74, -70, -93, -95, -66, -91, -56, -92, -60, -84, -101, -99, -119	290, 292, 220, 324, 326, 328, 254, 256
-83, -97, -87, -115, -85, -128, -110, -77, -82, -134, -135, -136, -147	290, 292, 326, 328, 324, 360, 362
-107, -149, -123, -118, -144, -114, -131, -146, -153, -132, -105, -179, -141, -137, -176, -164, -138, -151, -178, -129, -166, -187, -183, -157, -167, -185	324, 326, 360, 362, 254, 328, 290, 394, 396
-174, -177, -171, -156, -173, -158, -172, -197, -180, -193, -190, -170, -199, -196, -203, -189, -208, -195, -207, -194, -205, -206	394, 396, 360, 362, 426, 428, 462, 392, 237, 272

3.3.2. OPFR Analysis

OPFR compounds were analyzed using gas chromatography-electron impact ionization-mass spectroscopy (Thermo Scientific Trace-ISQ, GC-EI-MS) on SIM mode. OPTIMA-5MS capillary column (Macherey-Nagel, 30m L, 0.25 mm ID, 0.25 μ m FT) was used for chromatographic separation of targeted compounds. 2 μ L sample injected to GC at 265 °C isothermal inlet temperature using surge injection method (90 kPa, 0.30 dk). Oven temperature was programmed as 70 °C without isothermal stage, 25 °C/min to 150 °C, 3 °C/min to 200 °C, 8 °C/min to 290 °C, 3 min isothermal stage, 40 °C/min to 325 °C, 3 dk isothermal stage. SIM parameters of targeted OPFR compounds are shown in Table 3.2.

Table 3.2. SIM parameters of OPFR analysis

Compound	Ion (<i>m/z</i>)
TPrP	99, 141
TBP	99, 155
TCEP	99, 143
TCPP&TCIPP	99, 125
TPeP	99, 169
TDCIPP	77, 99
TPhP	77, 94
TBOEP	85, 125
EHDPP	99, 83
TEHP	99, 112
o-TCP	368, 367
m-TCP	368, 367
p-TCP	368, 367
T2IPPP	118, 452

3.3.3. AFR Analysis

AFR compounds were analyzed using gas chromatography-negative chemical ionization-mass spectroscopy (Thermo Scientific Trace-ISQ, GC-NCI-MS) on SIM mode. TRACE TR-5MS capillary column (Thermo Scientific, 15m L, 0.25 mm ID, 0.10 μ m FT) was used for chromatographic separation of targeted compounds. 2 μ L sample injected to GC at 280 °C isothermal inlet temperature using surge injection method (108 kPa, 0.30 dk). Helium (99.999% purity) was used as a carrier gas with a flow rate of 1.8 mL/min and methane (99.95% purity) was used as a reaction gas with a flow rate of 1 mL/min. Oven temperature was programmed as 80 °C 2 min isothermal stage, 10 °C/min to 150 °C, 3 min isothermal stage, 10 °C/min to 170 °C, 4 min isothermal stage, 10 °C/min to 295 °C, 25 °C/min to 300 °C, 5 min isothermal stage. SIM parameters of targeted AFR compounds are shown in Table 3.3.

Table 3.3. SIM parameters of AFR analysis

Compound	Ion (<i>m/z</i>)
1,2-Dibromo-4-(1,2-dibromoethyl) cyclohexane (α - ve β DBE-DBCH)	81, 160
Bis(2-ethylhexyl) tetrabromophthalat (BEH-TEBP)	79, 81
1,2,5,6-tetrabromocyclooctane (TBCO)	79, 81
Hexabromobenzene (HBB)	79, 81
2,3-Dibromopropyl-2,4,6-tribromophenyl ether (TBP-DBPE)	81, 79
2-Ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB)	79, 81
Hexabromocyclododecane (HBCDD)	79, 81
1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE)	79, 81
<i>syn</i> -Dechlorane plus (<i>syn</i> -DP)	652, 654
<i>anti</i> -Dechlorane plus (<i>anti</i> -DP)	652, 654

3.3.4. PBDE Analysis

PBDE congeners were analyzed using gas chromatography-negative chemical ionization-mass spectroscopy (Thermo Scientific Trace-ISQ, GC-NCI-MS) on SIM mode. TRACE TR-5MS capillary column (Thermo Scientific, 15m L, 0.25 mm ID, 0.10 μ m FT) was used for chromatographic separation of targeted compounds. 2 μ L sample injected to GC at 320 °C isothermal inlet temperature using surge injection method (108 kPa, 1.80 dk). Helium (99.999% purity) was used as a carrier gas with a flow rate of 1.8 mL/min and methane (99.95% purity) was used as a reaction gas with a flow rate of 1 mL/min. Oven temperature was programmed as 90 °C 1 min isothermal stage, 20 °C/min to 320 °C, 5 min isothermal stage. SIM parameters of targeted PBDE congeners are shown in Table 3.4.

Table 3.4. SIM parameters of PBDE analysis

PBDE Congener	Ion (<i>m/z</i>)
2,4,4'-Tribromodiphenyl ether (BDE-28)	79, 81
2,2',4,4'-Tetrabromodiphenyl ether (BDE-47)	79, 81
3,3',4,4'-Tetrabromodiphenyl ether (BDE-77)	79, 81
2,2',4,4',6-Pentabromodiphenyl ether (BDE-100)	79, 81
2,2',4,4',5-Pentabromodiphenyl ether (BDE-99)	79, 81
2,2',4,4',5,6'-Hexabromodiphenyl ether (BDE-154)	79, 81
2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE-153)	79, 81
2,2',3,4,4',5',6-Heptabromodiphenyl ether (BDE-183)	79, 81
2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether (BDE-209)	486.5, 488.5

3.3.5. PAH Analysis

PAH compounds were analyzed using gas chromatography-electron impact ionization-mass spectroscopy (Thermo Scientific Trace-ISQ, GC-EI-MS) on SIM mode. OPTIMA-5MS capillary column (Macherey-Nagel, 30m L, 0.25 mm ID, 0.25 μ m FT) and Rxi-5MS (Restek, 30m L, 0.25 mm ID, 0.25 μ m FT) were used (dependent to availability) for chromatographic separation of targeted compounds. 1 μ L sample injected to GC at 295 °C isothermal inlet temperature. Oven temperature was programmed as 50 °C 1 min isothermal stage, 25 °C/min to 200 °C, 8 °C/min to 300 °C, 7.5 min isothermal stage. SIM parameters of targeted PAH compounds are shown in Table 3.5.

Table 3.5. SIM parameters of PAH analysis

Compounds	Ion (<i>m/z</i>)
Naphthalene	127, 128, 129
Acenaphthylene	151, 152, 153
Acenaphthene	151, 152, 153
Fluorene	165, 166, 167
Phenanthrene	176, 178, 179
Anthracene	176, 178, 179
Carbazole	166, 167, 168
Fluoranthene	200, 202, 203
Pyrene	200, 202, 203
Benzo[a]anthracene	226, 228, 229
Chrysene	226, 228, 229
Benzo[b,k]fluoranthene	125, 252, 253
Benzo[a]pyrene	125, 252, 253
Indeno(1,2,3)pyrene	276, 277
Dibenz(a,h)anthracene	278
Benzo(g,h,i)perylene	276, 277

3.4. Quality Assurance/Quality Control

Prior to the sampling and sampling processing steps all laboratory apparatus and consumables were cleaned and controlled to avoid contamination of samples. All glassware and stainless steel laboratory apparatus were primarily soaked in Alconox® bath and rinsed distilled-deionized water followed by rinsing using acetone-hexane (1:1, v:v) mixture for minimizing potential cross-contamination in sampling and sample processing steps. GC vials were pre-baked at 450 °C for 4 hours and kept in PTFE cap jars. Passive sampling PUFs (TISCH TE-1014) were cleaned by soaking them overnight in an Alconox® bath, followed by sequential Soxhlet® extraction using acetone, hexane, and acetone:hexane (1:1, v:v) mixture, each for 18-24 hr (3 cycle per hr). Pre-cleaned PUFs were wrapped in pre-baked aluminum foil and stored in a ziplock bag at -18 °C until the sampling period.

Before the extraction work package, classical Soxhlet® and automatic Soxhlet® (GERHARDT Soxhterm) extraction methods were validated using targeted analyte fortified PUF samples to ensure the high recovery rates of targeted analytes. Despite some advantages of the automatic extraction system, such as lower solvent consumption and shorter extraction time, the low recovery rates (<50%) made it unsuitable for extracting PUF samples. Classical Soxhlet® method was selected for extraction of PUFs (recoveries of targeted analytes >80%) in the method validation work package.

The importance of ensuring the accuracy and reliability of analytical results is emphasized, particularly in the context of calibration curves. A key indicator of the quality of these calibration curves is the correlation coefficient (R^2), which measures the strength and linearity of the relationship between the concentration of analytes and their corresponding instrument responses. Maintaining a high correlation coefficient is crucial as it directly impacts the precision and validity of the analytical method. The correlation coefficients of all targeted compounds were higher than 0.98. High correlation coefficients show the strong linear relationship between analyte concentration and instrument response and minimizing errors in the quantification of targeted analytes.

The average recoveries of BDE-77 and BDE-181 were 93% and 78% for air samples, while 97% and 93% for dust samples. Also, the recovery rates of PCB-14, PCB-65, and PCB-166 for dust samples were 90%, 82%, and 82%, respectively. The average recovery of BDE-181 was 83% for food samples while PCB-14, -65, and -166 ranged

from 65% to 92%. Isotope dilution was used for PAH analysis utilizing relative response factor of Chrysene-d12. Recoveries of all targeted PAHs were >80%. Procedural dust and PUF blank samples (5 of each) were used to normalize analyte concentrations in field samples by subtracting the average blank concentration (if present) from the field sample concentration.

3.5. Exposure and Risk Assessment

Exposure assessment was conducted by estimation of inhalation and ingestion routes (Equation 4.1 and 4.2). While average daily dose (ADD) levels were estimated considering chronic-toxic health effects, lifetime average daily dose (LADD) levels were estimated for carcinogenic risks. POP concentrations were fitted to the best fitted probability distributions using Crystal Ball software (n=10000 trial, Oracle Inc.) for probabilistic approach. Probability distribution of accidental ingestion rate was taken from Exposure Factors Handbook (USEPA, 2011). Exposure frequency was assumed to be 350 days/yr. Lifetime was assumed to be 75 years. Chronic toxic health risk was estimated based on Reference Dose (RfD) of individual PBDE by using Equation 4.3. A combined probability distribution of females and males body weights was used for simulation of dose (Cetin et. al., 2018). Averaging time was assumed to be equal to exposure duration for CTR and replaced to 30 years for CR.

$$LADD \text{ or } ADD_{ing \text{ and } inh} = \frac{C*IR*EF*ED*CF}{BW*AT} \quad \text{Equation 4.1}$$

$$HQ \text{ or } CTR = \frac{ADD}{RfD} \quad \text{Equation 4.2}$$

$$ILCR \text{ or } CR = LADD \times SF \quad \text{Equation 4.3}$$

where, CDI: chronic daily intake (mg/kg-day), C: concentration (mg/m³), IR: inhalation or ingestion rate (m³/day or mg/day); EF: exposure frequency (day/yr); ED: exposure duration (yr); BW: body weight (kg); AT: averaging time (yr); RfD: reference dose (mg/kg-day); HQ: hazard quotient (unitless).

CHAPTER 4

RESULTS and DISCUSSIONS

4.1. Indoor and Outdoor Settled Dust-Bound PBDE Levels in Living Environments in İzmir-TÜRKIYE

4.1.1. Settled Dust-Bound PBDEs in Schools

The indoor and outdoor settled dust-bound PBDE concentrations in schools located in İzmir-Türkiye were determined. Figure 4.1 and Figure 4.2 show the settled dust-bound concentration levels of targeted PBDE congeners in indoor and outdoor environments of schools. The average settled dust-bound Σ BDE concentrations indoor and outdoor environments schools were determined to be 2393 and 387 ng/g, respectively. The BDE-209 congener predominated both indoor and outdoor environments, with proportions of 89.8% and 95.8% of Σ BDE concentrations, respectively. The average concentration fractions of BDE-47 and BDE-153 in indoor environments of schools were 3.81% and 5.26%, respectively, while the average concentration fraction of BDE-153 in outdoor environments of schools was 4.04%. The average contribution of other congeners to the Σ BDE concentration was less than 1% in samples collected from both indoor and outdoor environments.

The average indoor settled dust-bound BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183, and BDE-209 concentrations in schools were determined to be 0.55, 91.2, 0.63, 11.4, 1.03, 126, 13.3, and 2149 ng/g, respectively. The concentrations of the BDE-209 congener, detected in all indoor dust samples collected from schools, ranged from 435 to 8079 ng/g (median 1679 ng/g). The detection frequencies of BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, and BDE-183 congeners in indoor environment of schools were 6/21, 5/21, 10/21, 14/21, 8/21, 19/21, and 13/21, respectively. The median concentrations of BDE-28, BDE-47, BDE-

100, BDE-99, BDE-154, BDE-153, and BDE-183 in schools were 0.38, 131, 0.48, 11.4, 1.02, 52.9, and 6.82 ng/g, respectively. The coefficient of variation (CV) of PBDE congeners ranged from 0.31 to 1.06. While the CV of settled dust-bound BDE-154 was below 0.5, the CV values of other congeners range from 0.55 to 1.32. The variability in PBDE concentrations could be attributed to factors such as source profiles in indoor environments, ventilation, cleaning frequency, building age, and distance from outdoor sources of PBDEs (Genisoglu et al., 2019).

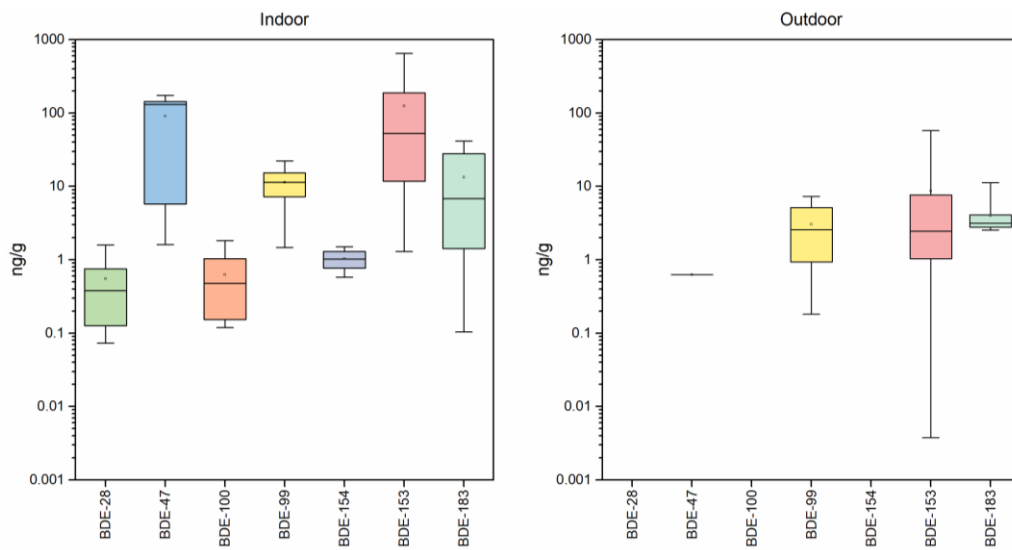


Figure 4.1. Settled dust-bound concentrations of PBDE congeners (wo BDE-209) in schools.

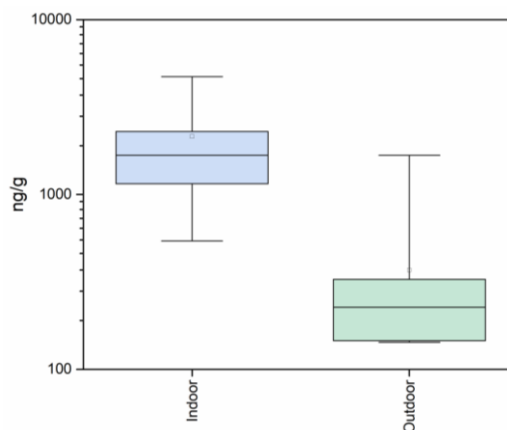


Figure 4.2. Settled dust-bound BDE209 concentrations in schools

Due to the PBDE sources are densely presence in indoor environments, outdoor PBDE levels are lower than that in indoors (Genisoglu et al., 2019; Kurt-Karakuş et al., 2017). The results of the analyses conducted in this study, consistent with the literature, indicate that PBDE concentrations in outdoor settled dust samples collected from schools were lower than those in indoors. While BDE-28, BDE-100, and BDE-154 congeners were not detected in outdoor settled dust, BDE-47 was detected in only one sample at a concentration of 0.63 ng/g. The detection frequencies of other targeted PBDE congeners in outdoor settled dust samples from schools were as follows: BDE-99 was found in 18 out of 21 samples, BDE-153 in 11 out of 21 samples, BDE-183 in 19 out of 21 samples, and BDE-209 in 18 out of 21 samples. The average settled dust-bound BDE-99, BDE-153, BDE-183, and BDE-209 concentrations in outdoors of schools were determined to be 3.04, 8.67, 4.00, and 370 ng/g, respectively. The indoor-to-outdoor (I/O) concentration ratios of BDE-47, BDE-99, BDE-153, BDE-183, and BDE-209 in all dust samples collected from schools were found to be 9.16, 10.3, 806, 2.74, and 8.34, respectively. High I/O ratios indicate that PBDEs in indoor environments are predominantly affected by emissions from indoor sources.

Sampling points were divided into three different classes: urban, sub-urban, and rural areas. The settled dust-bound PBDE concentrations in schools classified according to urbanization levels are shown in Figure 4.3 and Figure 4.4. It was determined that the contribution of BDE-209 congener to Σ BDE concentration in schools located in rural areas was at levels of 92.3%. In rural areas, while the contribution of BDE-153 congener to Σ BDE concentration was at levels of 6.80%, other congeners were below 1%. The mean concentrations of BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183, and BDE-209 in indoor settled dust in schools in rural areas were 0.38, 1.61, 0.76, 9.29, 0.98, 217, 16.3, and 2944 ng/g, respectively. The concentrations of these congeners vary in the ranges of 0.15-0.61, 1.61-1.61, 0.15-1.83, 1.47-15.6, 0.58-1.32, 6.56-650, 1.41-41.5, and 435-8079 ng/g, respectively.

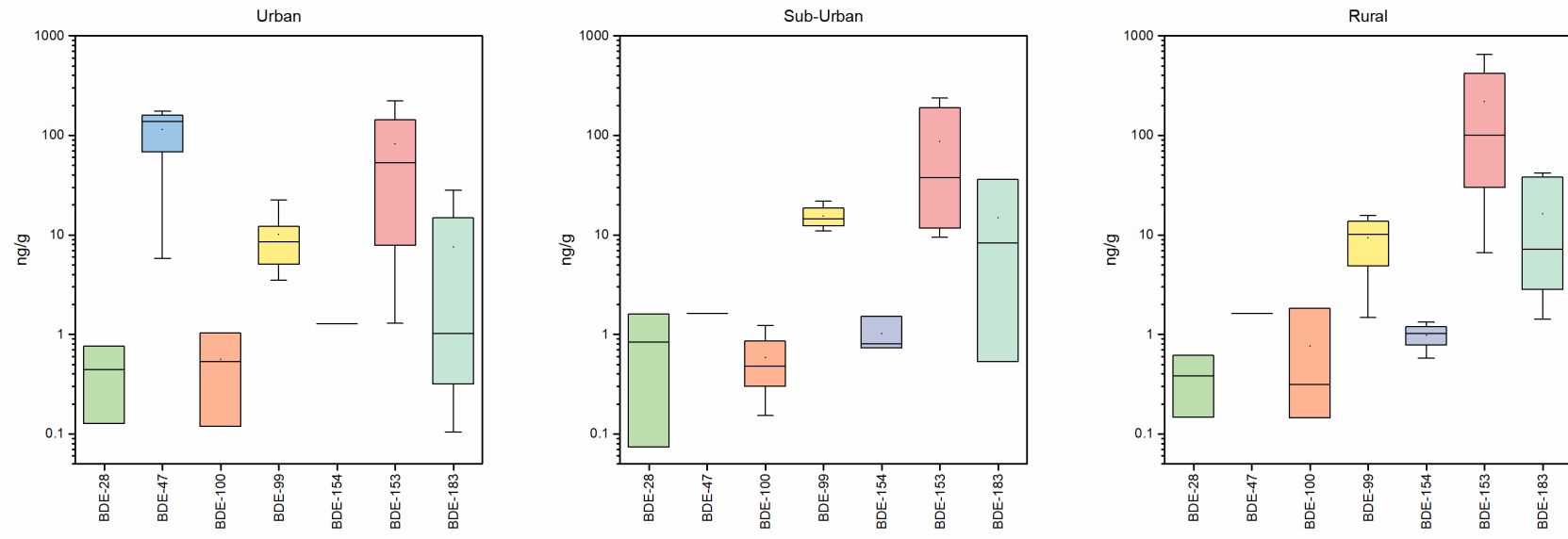


Figure 4.3. Settled dust-bound PBDE (wo BDE-209) concentrations in indoor environments of schools according to the urbanization level

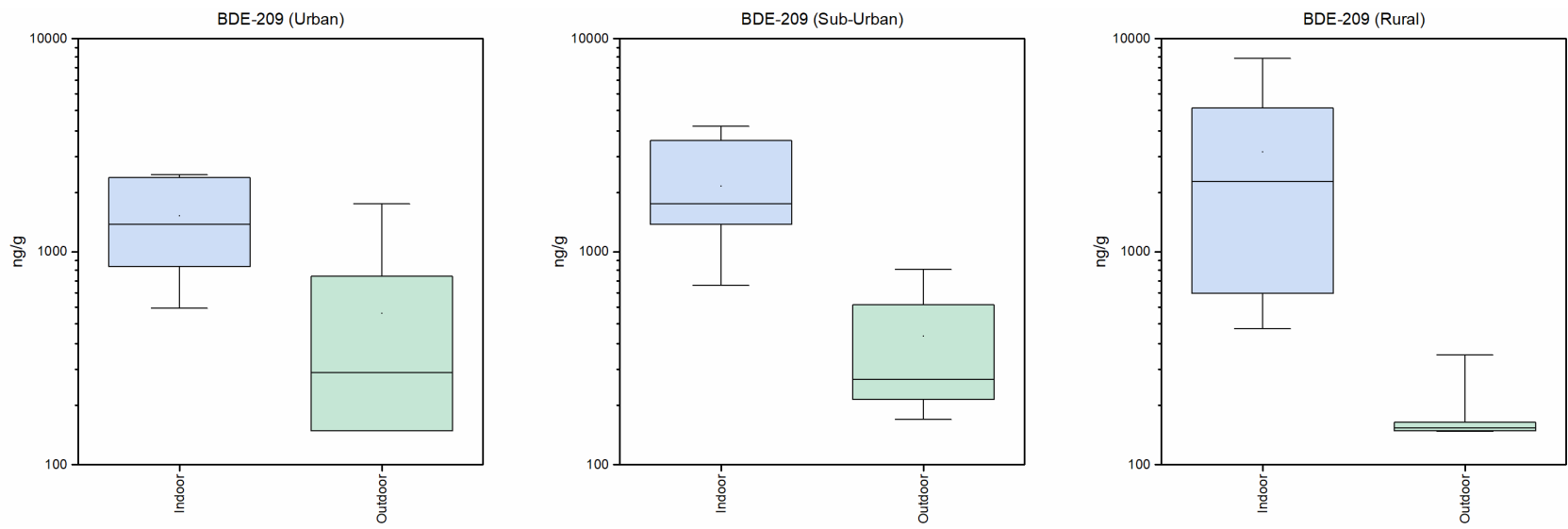


Figure 4.4. Settled dust-bound BDE-209 concentrations in indoor and outdoor environments of schools according to the urbanization level

The BDE-28, BDE-47, BDE-100, and BDE-154 congeners were not detected in outdoor settled dust samples collected from schools in rural areas. The highest settled dust-bound PBDE concentrations in rural areas were detected at a school in Gerenköy, located south of the Aliğa Organized Industrial Site (AOIS), while the settled dust-bound PBDE concentrations in samples collected from a school in Çakmaklı village, the nearest sampling point to AOIS, ranked second. The proximity of the sampling points with the highest PBDE concentrations to AOIS and the prevailing southward wind are considered indicative of the influence of industrial emissions on indoor environments, in addition to emissions from indoor sources. Moreover, relatively old buildings near the industrial area, PBDE sources may still be emits considerable amounts. Additionally, the high PBDE concentrations detected in schools might also be attributed to the use of energy and signal cables openly transmitted between the board-projection-computer in smart board applications due to the lack of appropriate infrastructure, which has been introduced in the last decade. Furthermore, the extension between household cleaning is a known mechanism that increases SVOC levels in indoor environments. It was observed that the amount of dust collected in rural areas during the dust sampling was higher compared to other regions, leading to the conclusion that the cleaning period is longer in these areas.

In commercial penta-PBDE mixtures, the concentration ratio of BDE-47/BDE-99 generally varies between 0.8 and 1.0 (Hazrati et al., 2010; Tian et al., 2010). The BDE-47/BDE-99 concentration ratio was determined to be 0.17. Due to the dominance of the BDE-209 congener and the low concentration ratio of BDE-47/BDE-99 congeners, indicating a low probability of the prevalence of commercial penta-BDE sources and strong probability of the prevalence of commercial deca-BDE sources. In a report published in 2015 concerning commercial deca-BDE mixtures, it was stated that the majority use of commercial deca-BDE mixtures was used in textile and plastic production, with the remaining produced portion extensively used in the production of furniture, plastic casings of electronic equipment, cables, small electronic components, aviation components, electrical, and electronic equipment (SC 2015). The transition to smart board applications in classrooms, coupled with the infrastructure's lack of compatibility with concealed wiring, leading to the implementation of open-channel wiring in many places, could be a factor to consider in terms of students' exposure to flame retardant chemicals. The increase in concentrations observed as samples approach AOIS in rural areas indicates the additional effects of industrial emissions on indoor SVOC pollution. At these sampling points, the I/O concentration ratios of BDE-99, BDE-

153, BDE-183, and BDE-209 congeners determined as 7.34, 26.7, 2.47, and 11.2, respectively, indicate the presence of dominant sources in the indoor environment. However, the BDE-209 congener may undergo atmospheric transport in the particle phase. AOIS, which is a strong PBDE source point for İzmir province due to the iron-steel industry (Odabasi et al., 2009), is considered to have a secondary source of indoor SVOC pollution due to the increase in concentrations observed as approaching Aliğa in this study. The lowest PBDE concentrations were determined in Kuşçular Village, a relatively unaffected by industrial sources. In the sampling conducted in Kozak, located within the boundaries of Bergama province, where the effects of AOSB are thought to be minimal due to predominant wind directions, PBDE concentrations in indoor dust were found to be four times higher than in Kuşçular Village and 10% higher than in outdoor dust at same location. The unexpected high indoor concentrations obtained in Kozak are attributed to the colder temperatures at higher altitudes, resulting in the non-opening of windows for ventilation to prevent heat loss from the indoor environment, thus reducing the expected dilution mechanism through natural ventilation, as well as the emission from PBDE containing building materials may still act.

In indoor settled dust samples collected from sub-urban area schools, the average concentrations of BDE-28, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183, and BDE-209 were determined to be 0.84, 0.58, 15.5, 1.01, 86.7, 14.9, and 2026 ng/g respectively. The highest indoor concentrations were found in two Vocational Technical Anatolian High Schools located in the sampling region. The high PBDE concentrations identified in technical high schools are thought to be associated with the presence of electronic and electrical laboratories within the buildings. In sub-urban schools, the highest BDE-209 concentrations in indoor dust were determined to be 3878 ng/g in Aliğa and 3313 ng/g in Seferihisar, while the lowest BDE-209 level was 695 ng/g in a high school in Urla. In indoor dust samples taken from schools in this region, the contribution of BDE-153 and BDE-209 to the Σ BDE concentration was determined to be 4.04% and 94.4% respectively, while the other congeners were less than 1%. The I/O concentration ratios related to settled dust in sub-urban area schools vary between 6.5 and 27.2. As indicated in the literature, indoor environments are rich in SVOCs sources, which was also observed in this study (Lee et al., 2014). Due to spending time indoors is much higher than outdoors, indoor SVOC levels become important for health risks.

The average indoor settled dust-bound concentrations of BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183, and BDE-209 were determined to be 0.44,

114, 0.56, 10.0, 1.28, 81.6, 7.54, and 1476 ng/g, respectively, in urban schools (Figure 4.3). The BDE-209 congener was dominant with a contribution of 87.3% to the Σ BDE concentration (Figure 4.5). The contributions of BDE-47 and BDE-153 to the Σ BDE concentration were 6.71% and 4.82% respectively, while other congeners were less than 1%. When sampling points are grouped according to urbanization levels, the highest BDE-47 levels in indoor dust were observed in urban areas with an average of 114 ng/g. BDE-47 and BDE-99 congeners were used in the production of commercial Penta-BDE mixtures and before being banned, they accounted for 37% of total consumption (Alcock et al., 2003). Due to its higher vapor pressure, the BDE-47 congener can be relatively easily released from items containing commercial Penta-BDE. The highest indoor BDE-209 concentration (2291 ng/g) in urban areas was again found in an Anatolian Technical and Industrial Vocational High School. The findings indicate that technical high schools are facing significant indoor SVOC pollution. In urban areas, the I/O ratios of BDE-47, BDE-99, BDE-153, BDE-183, and BDE-209 were determined to be 9.16, 10.3, 21.3, 2.74, and 8.34, respectively. Principal Component Analysis (PCA) results of PBDE concentration values associated with dust in schools are given in Figure 4.6 and Figure 4.7. In PCA, it was determined that two components affect PBDE levels. While the BDE-209 component separates from the others in indoor dust, in outdoor dust, the BDE-99 and BDE-209 congeners are separated from BDE-153 and BDE-183.

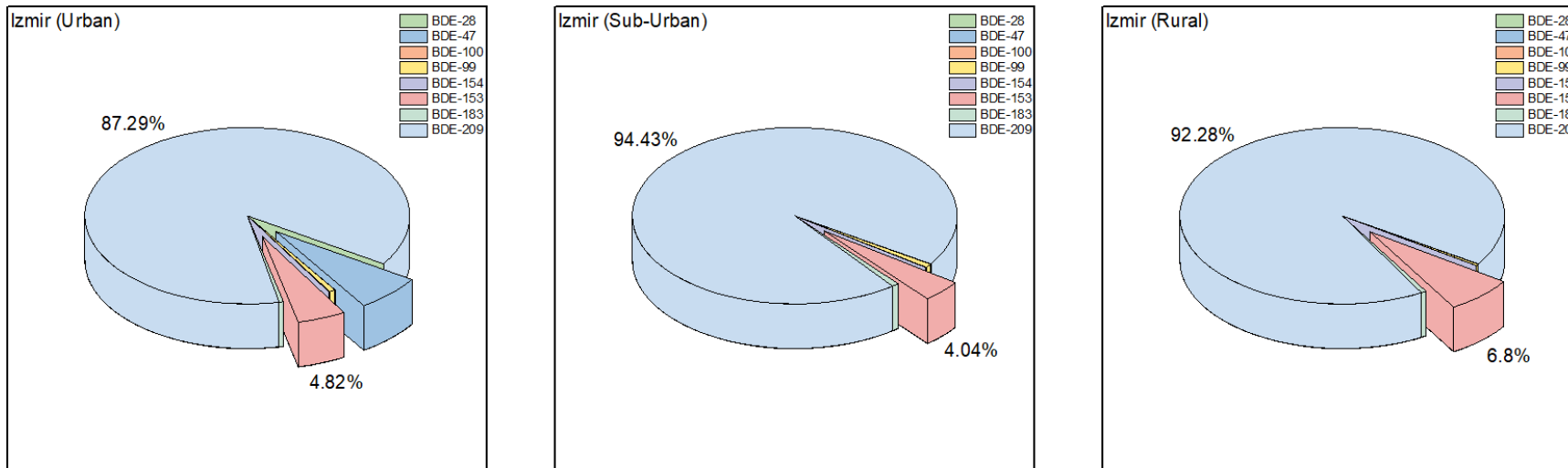


Figure 4.5. Settled dust-bound PBDE concentration compositions in schools

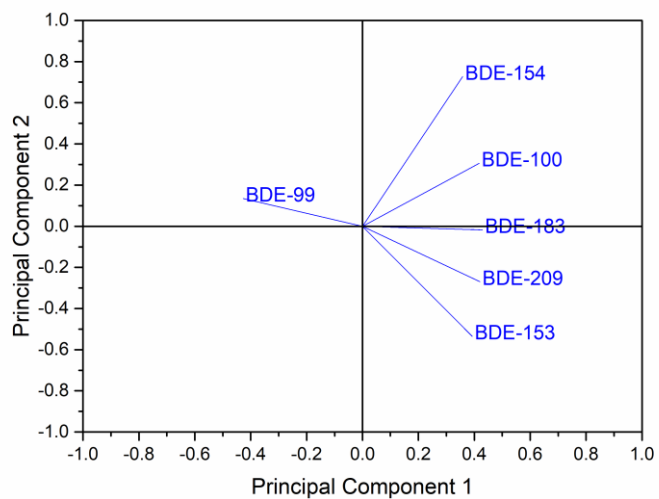


Figure 4.6. Loading plots of indoor settled dust-bound PBDEs in schools

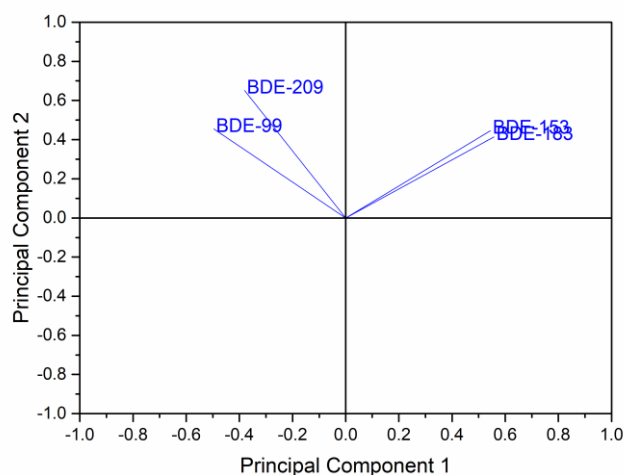


Figure 4.7. Loading plots of outdoor settled dust-bound PBDEs in schools

4.1.2. Settled Dust-Bound PBDEs in Homes

The indoor and outdoor settled dust-bound PBDE levels in homes are shown in Figure 4.8 and Figure 4.9. The average settled dust-bound Σ BDE concentrations in indoor and outdoor environments of homes were determined to be 2038 and 464 ng/g, respectively. The BDE-209 congener dominated the Σ BDE congener concentration profile by 97.8% and 96.6% in indoor and outdoor environments, respectively. Additionally, while BDE-153 contributes to the Σ BDE concentration by 1.09% and 1.53% in indoor and outdoor environments, respectively, the contribution ratios of other PBDE congeners (the contribution ratio of BDE-99 congener in outdoor environment is 1.40%) are less than 1%. The average settled dust-bound concentrations of BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183, and BDE-209 in indoor environment of homes were 1.01, 15.7, 0.81, 3.39, 0.90, 20.1, 4.85, and 1998 ng/g, respectively, while those in outdoor were 0.14, 0.50, 0.63, 7.55, 0.15, 1.53, 0.18, and 433 ng/g, respectively.

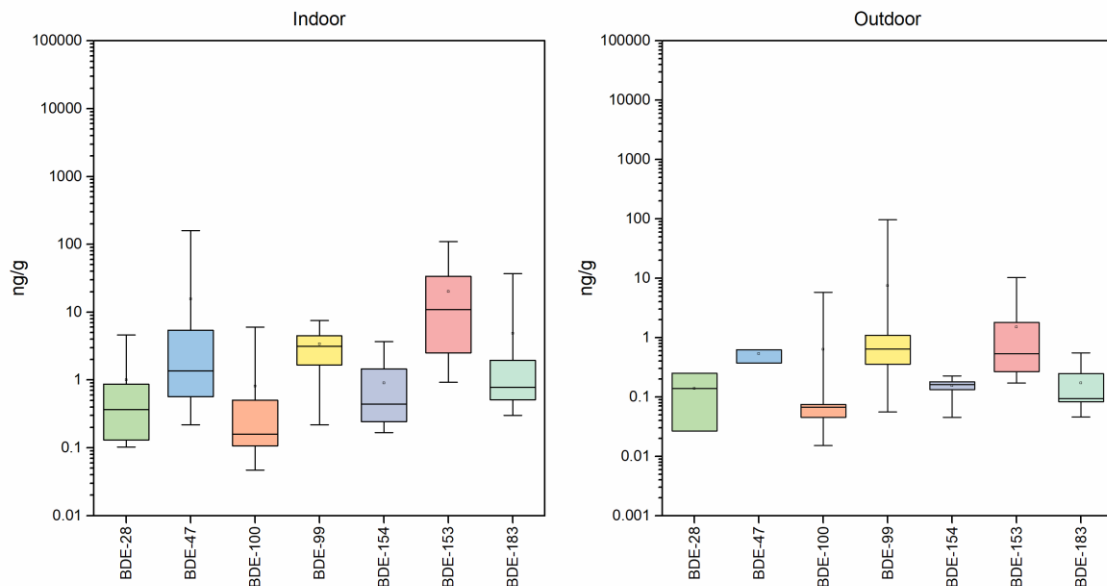


Figure 4.8. Settled dust-bound PBDE (wo BDE-209) concentrations in homes

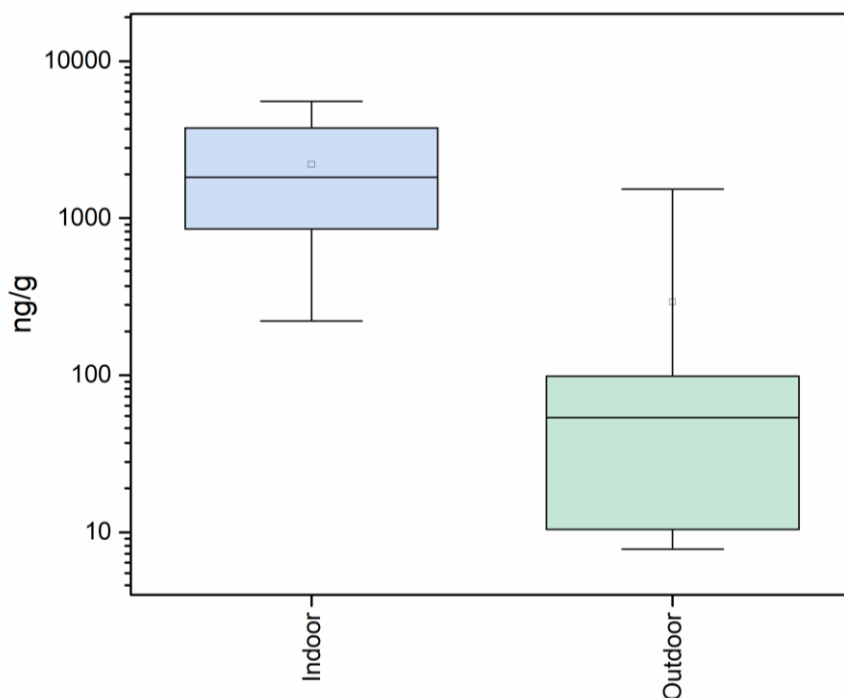


Figure 4.9. Settled dust-bound BDE-209 concentrations in homes

The BDE-183 and BDE-209 congeners were detected in all indoor samples, while the detection frequency of these congeners in outdoor environments dropped to 50% and 85%, respectively. The detection frequency of other PBDE congeners varies between 70% and 95% in indoor samples, while those detection frequency were ranged from 10% to 75% in outdoor samples. While the CV values determined in indoor samples were ranged from 0.64 to 2.98, CV values were 0.29 for BDE-154 and 0.35 for BDE-47, and between 0.90 and 3.43 for other PBDE congeners. The PBDE levels in outdoor dust samples were found to be lower than those in indoor samples, like those in schools. The settled dust-bound I/O concentration ratios in homes were determined to be 4.01, 2.07, 9.19, 2.56, 21.2, 8.06, and 13.8 for BDE-28, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183, and BDE-209, respectively. The loading plots of PCA analysis of indoor and outdoor settled dust-bound PBDE concentrations are given in Figure 4.10 and Figure 4.11. The graph obtained from the analysis using indoor dust concentrations in homes shows that the BDE-153 and BDE-209 congeners separate from each other and from other congeners, while in outdoor dust, the BDE-99 and BDE-100 congeners, along with the BDE-154 congener, separate from the BDE-153, BDE-183, and BDE-209 group.

According to the results of the PCA analysis, there are likely three different sources affecting the levels of indoor dust in homes.

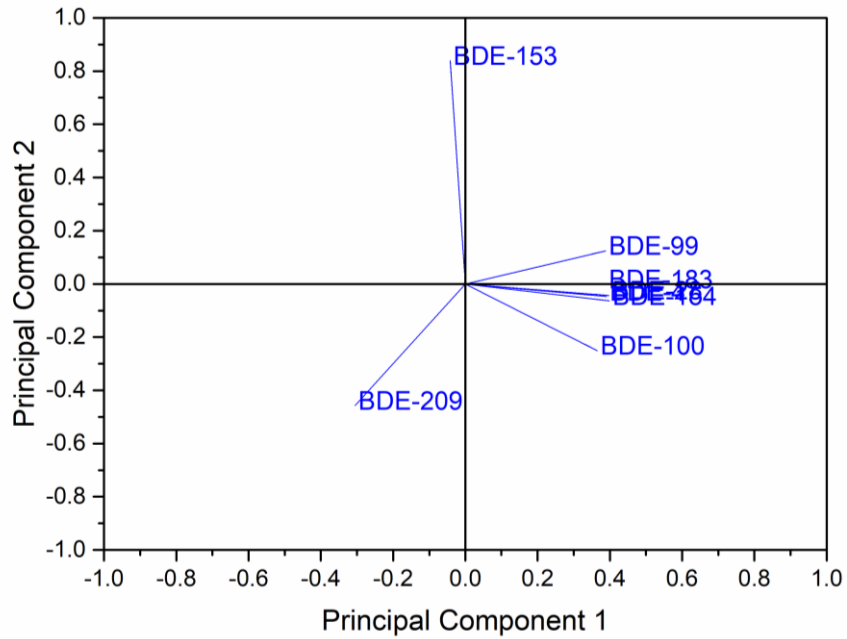


Figure 4.10. Loading plots of indoor settled dust-bound PBDEs in homes

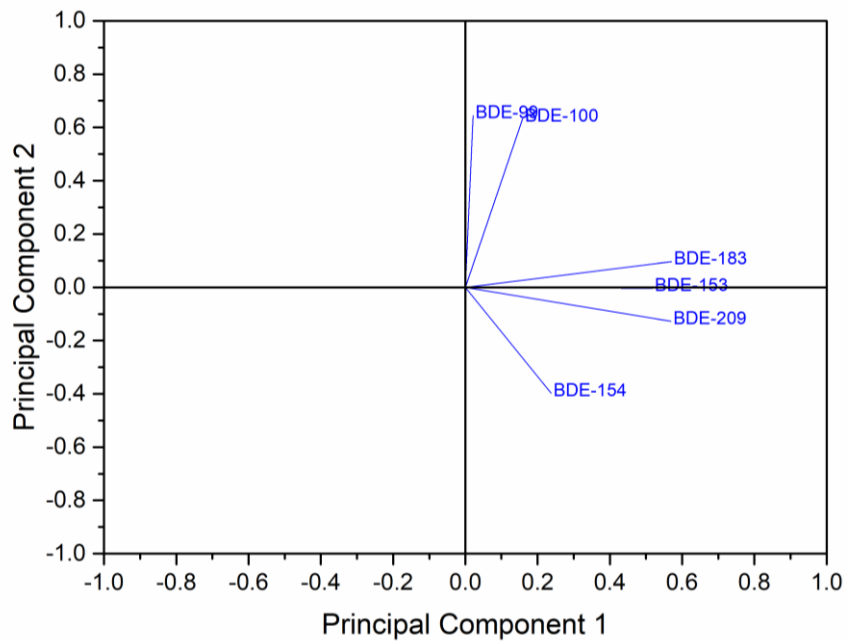


Figure 4.11. Loading plots of outdoor settled dust-bound PBDEs in homes

The urbanization level dependent settled dust-bound PBDE concentrations in homes are shown in Figure 4.12 and Figure 4.13. It was determined that the contribution of the BDE-209 congener to the indoor settled dust-bound Σ BDE concentrations in urban, sub-urban, and rural homes were ranged from 96.3% to 98.9% (Figure 4.14). The contribution of BDE-209 to the Σ BDE concentration is higher than determined in schools, ranging from 87.3% to 92.3%. The average indoor settled dust-bound BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183, and BDE-209 congeners in rural homes were determined to be 0.41, 2.91, 0.67, 2.70, 0.97, 22.4, 11.1, and 2196 ng/g, respectively. For sub-urban homes, those were 1.76, ND, 0.10, 2.49, 0.80, 10.0, 1.85, and 1489 ng/g, respectively, while for urban homes, were 0.82, 34.5, 1.53, 4.49, 0.95, 22.4, 1.22, and 2235 ng/g, respectively. In urban, sub-urban, and rural areas, the I/O ratios of settled dust-bound PBDE concentrations were ranged from 2.71 to 21.2, from 1.78 to 19.9, and from 1.95 to 30.2, respectively.

Among the residential sampling points in rural areas, the highest Σ BDE concentration associated with indoor settled dust was determined to be 5585 ng/g in Helvacı Village, located north of İzmir and south of AIOS, while the second-highest settled dust-bound Σ BDE concentration of 3748 ng/g was in Küner Village, affiliated with Menderes district, south of Izmir. The lowest indoor settled dust-bound Σ BDE concentration in rural areas was detected at the residential sampling point in Kuşçular Village with 323 ng/g. The fact that the lowest dust-bound Σ BDE concentrations were found in Kuşçular in both the house and school sampling in rural areas might indicate that this area is one of the least affected by outdoor sources like industrial and urban emissions. The highest concentration being determined in Helvacı Village, located south of AOSB, might be an indication of the effects of AIOS on indoor SVOC levels. The second-highest concentration in rural areas was determined to be 3748 ng/g at the residential sampling point in Küner Village, affiliated with Menderes district, south of Izmir, being located far from industrial zones in Izmir suggests the presence of a strong indoor PBDE sources.

Among the residential sampling points in sub-urban areas, the highest concentration was determined to be 3568 ng/g in Çiğli. Being located south of AOIS and potentially affected by emissions from both AOIS and Çiğli Industrial Zone within the city boundaries. The lowest concentrations were determined to be in Urla with a level of 456 ng/g in sub-urban area of İzmir. This phenomenon might be related to the use of

aluminum window system that provides relatively higher infiltration (decreases the indoor SVOCs) than that in PVC window systems and distance to the industrial sites.

Among the residential sampling in urban areas, the highest concentration was determined to be 6043 ng/g in Bornova, while the lowest concentration was found to be 368 ng/g at the residential sampling point in Güzelyalı. Güzelyalı, where the lowest PBDE concentrations were determined among residential sampling points in three different levels of urbanization across the Izmir, was the only home sampling location without carpets. The absence of carpets might be a significant factor affecting SVOC levels due to the carpets acts as a source and contribute to dust accumulation (increases the residence of SVOCs and particle aging) in indoor environments. The use of synthetic carpets increased in recent years. The results of studies in literature support this notion. A study conducted in New Zealand determined PBDE levels in indoor settled dust by analyzing carpets, reporting a strong correlation between PBDE concentrations in carpet and levels in the blood (Coakley et al., 2013). In the sampling conducted in rural and sub-urban areas, the ratio of BDE-47/BDE-99 congeners concentrations was determined to be 1.07 and 1.01, respectively. Since this ratio in commercial penta-BDE mixtures is typically in the range of 0.8-1.0, it can be inferred that the main source of penta-BDEs in homes in these areas might be a commercial penta-BDE mixture (Genisoglu et al., 2019).

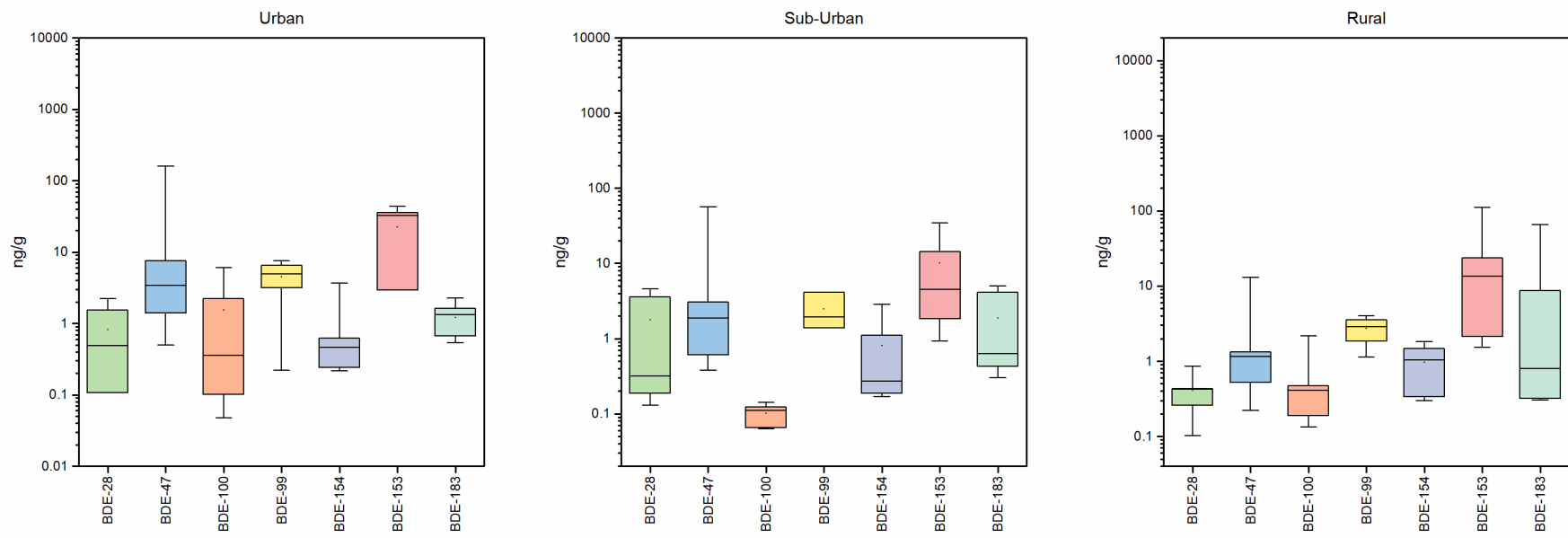


Figure 4.12. Settled dust-bound PBDE (wo BDE-209) concentrations in indoor environments of homes according to the urbanization level

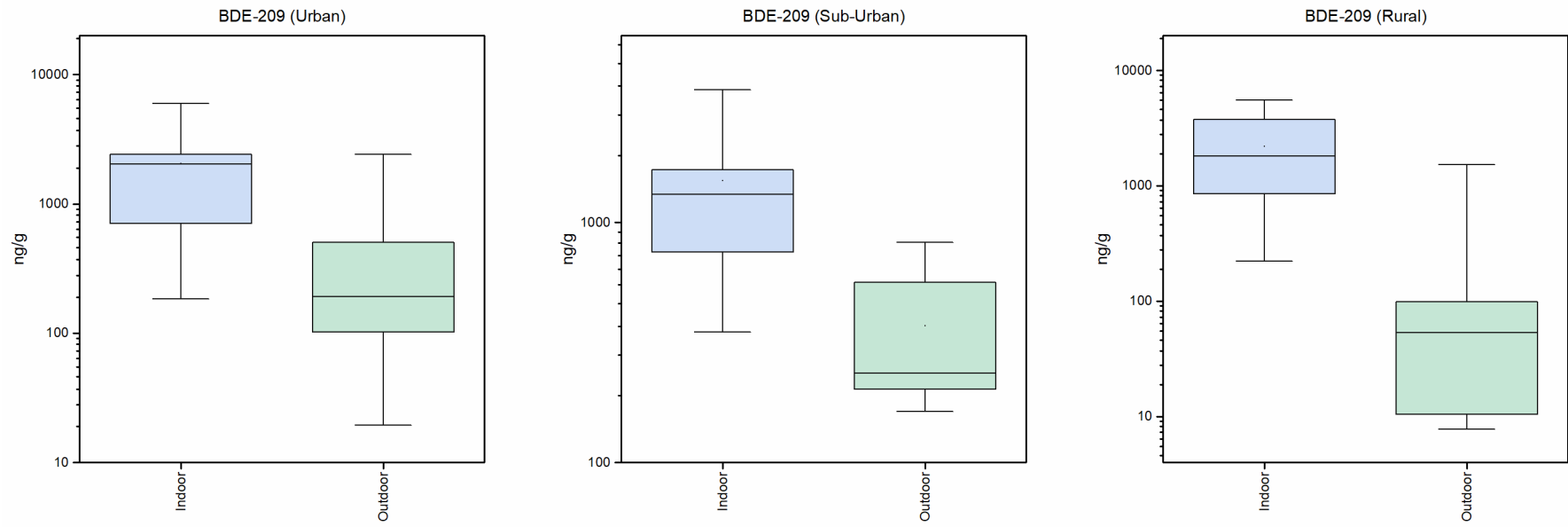


Figure 4.13. Settled dust-bound BDE-209 concentrations in indoor environments of homes according to the urbanization level

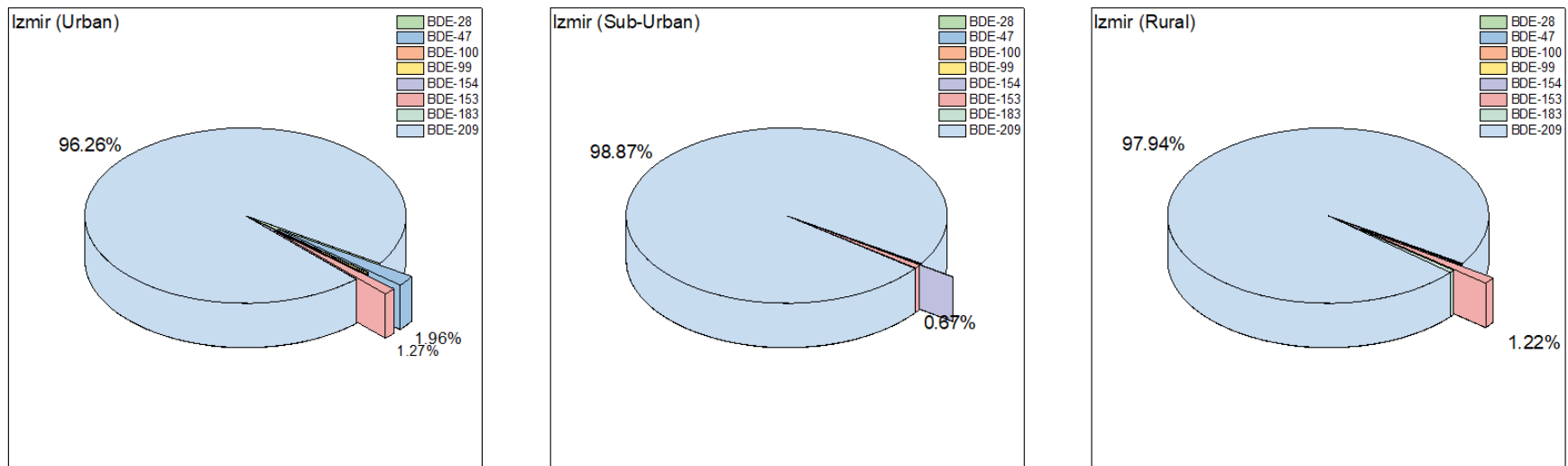


Figure 4.14. Settled dust-bound PBDE concentration compositions in homes

4.1.3. Settled Dust-Bound PBDEs in Café/Bar/Restaurants

The settled dust-bound PBDE levels in indoor environments of cafes/bars/restaurants (C/B/R) are shown in Figure 4.15 and Figure 4.16. While the average Σ BDE concentration in C/B/R samples was determined to be 1032 ng/g, those in rural, sub-urban, and urban areas were 579, 595, and 1656 ng/g, respectively. The contribution of the BDE-209 to the settled dust-bound Σ BDE concentration in C/B/Rs varies between 85.9% and 99.7%. While concentrations were observed to be higher in C/B/Rs in urban areas compared to other regions, they decreased towards the rural areas. The relatively high PBDE levels in urban C/B/Rs might be related to the use of textiles and polyurethane foam in the production of seating. As one moves towards rural areas, the simplification of decoration and the use of furniture mostly made of wood and metal may be reasons for the lower PBDE concentrations in sub-urban and rural areas. Overall, lower concentrations in C/B/Rs compared to homes and schools might be also attributed to factors such as more frequent cleaning in workplaces, younger particles on the floor due to regular cleaning, and high ventilation rate, which may not have reached equilibrium in the indoor environment yet. The results of Principal Component Analysis (PCA) of PBDE levels in dust samples from C/B/Rs are shown in Figure 4.17. The PCA analysis results do not indicate a significant PBDE source in C/B/Rs, suggesting the presence of various sources.

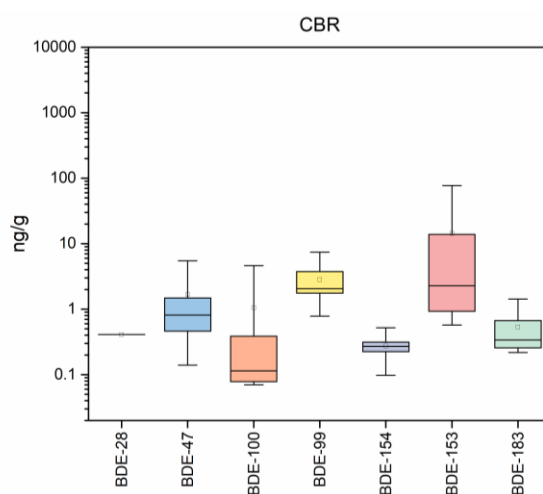


Figure 4.15. Settled dust-bound PBDE (wo BDE-209) concentrations in indoor environments of C/B/Rs

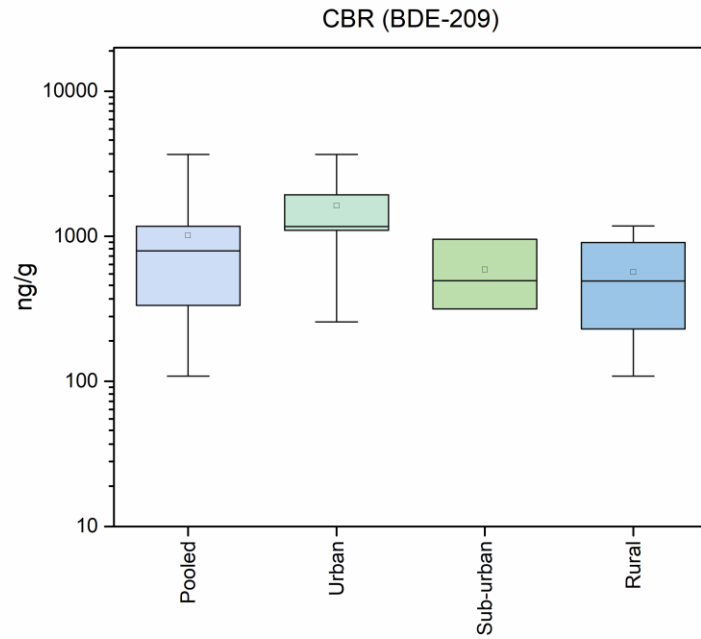


Figure 4.16. Settled dust-bound BDE-209 concentrations in indoor environments of C/B/Rs

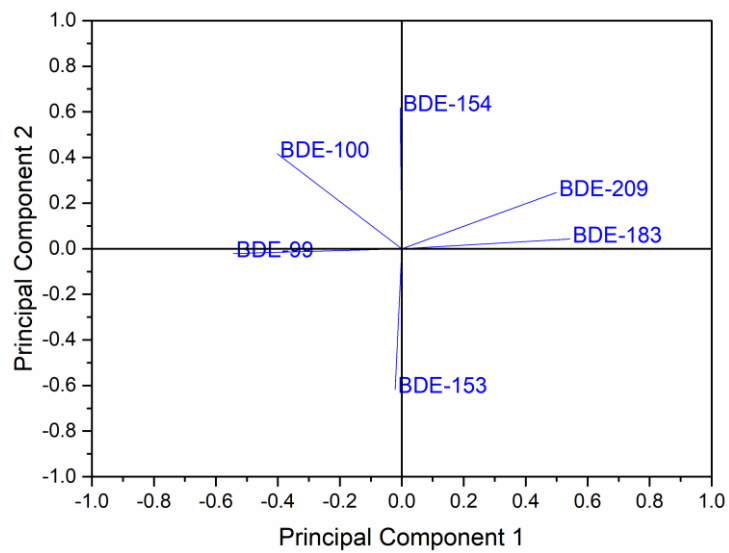


Figure 4.17. Loading plot of indoor settled dust-bound PBDEs in C/B/Rs

Table 4.1. shows the indoor dust-bound PBDE levels in the literature. The median dust-bound Σ BDE concentrations in homes in this study, 1526 ng/g, was similar to the 1567 ng/g in the study by Pasecnaja et al. (2021). In fact, the concentration of BDE-209 in dust in homes was determined to be 1510 ng/g in both studies. Although the median settled dust-bound Σ BDE concentration (1704 ng/g) in schools was higher than the 248 ng/g determined by Young et al. (2021), and the 31.1 ng/g determined by Adeyi et al. (2020), that was lower than the 4355 ng/g, determined in nursing schools, and the 8110 ng/g, in schools in Ireland (Wemken et al., 2019). Due to the source density, age, and type of building, as well as emissions from the outdoor environment due to proximity to industrial areas, the concentration and congener profile of indoor SVOCs (especially flame retardants) vary compared to atmospheric levels and congener profiles. In this study, the concentrations of other PBDE congeners except BDE-209 in homes and schools were determined to be 16 and 25 ng/g, respectively. In a study conducted in male and female dormitories, the concentrations of other PBDE congeners except BDE-209 were determined to be 28.2 and 9.41 ng/g, which were similar to the levels we obtained. According to the literature, generally higher PBDE levels were determined in schools than that in residents and offices. Due to high PBDE levels in schools, students might be under the risk of serious health problems related to the PBDEs. In addition to exposure through respiration, the amount of dust accidentally ingested by children is much higher than that of adults, resulting in PBDE doses absorbed through the digestive system that are much higher than those of adults. Therefore, developing strategies to reduce indoor PBDE concentrations in schools is extremely important to reduce health risks associated to the indoor exposure in schools.

Due to their high octanol-air partition coefficients, PBDEs tend to bound on organic surfaces, so as the accumulation of PBDEs on organic surfaces such as dust particles, directly affects both dust and air concentrations in indoor environments. As the particle age increases, the adsorption of organic compounds also increases. Therefore, the presence of dust-retaining floor coverings such as carpets and extending the cleaning period in indoor environments may lead to high PBDE concentrations. Hence, if carpets are used as flooring, care should be taken to perform periodic cleaning especially floor vacuuming and wiping indoor surfaces.

Table 4.1. Settled dust-bound PBDEs (ng/g) in indoor environments

Sampling Site	BDE-28	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	BDE-209	ΣBDE	Ref
School*	0.55	91.2	0.63	11.4	1.03	126	13.3	2149	2393	This Study
School**	0.38	131	0.48	11.4	1.02	53.0	6.82	1679	1704	
Home*	1.01	15.7	0.81	3.39	0.91	20.1	4.85	1998	2039	
Home**	0.37	1.36	0.16	3.15	0.44	11.0	0.78	1510	1526	
C/B/R*	0.41	1.68	1.05	2.83	0.27	14.4	0.54	1013	1032	
C/B/R**	0.41	0.81	0.11	2.05	0.27	2.25	0.34	794	806	
Home**	2.13	13.8	4.48	16.6	3.92	4.6	11.0	1510	1567	(Pasecnaja et al., 2021)
Smf**	3.98	60.9	27.2	12.7	9.18	18.3	19.5	95.8	248	(Young et al., 2021)
Office**	8.10	48.8	21	129	5.31	19.5	51.6	381	628	
Male dormitory**	1.94	3.90	4.92	4.99	-	11.1	1.39	-	28.2	(Wu et al., 2021)
Female dormitory**	0.32	1.30	0.54	-	-	3.70	3.55	-	9.41	
Copy Center**	1.17	10	8.87	7.95	1.55	305	2.79	-	337	
Nursery School**	180	340	370	270	240	220	230	<0.04	4355	(Ibeto et al., 2021)
Office**	140	140	240	350	40	90	130	110	2095	
School**	2.1	-	7.60	2.82	9.98	2.17	19.4	4.14	31.1	(Adeyi et al., 2020)
Home**	0.67	34.1	66.8	40.4	17	3.71	40.2	8.68	227	
Home**	0.24	2.55	0.92	3.07	0.46	0.57	5.91	128	141	(Civan and Kara, 2016)
Home**	-	7.6	-	13	-	-	1	13000	13021	(Wemken et al., 2019)
School**	-	5	-	5.10	-	-	<0.83	8100	8110	

*Average concentration

**Median concentration

4.2. Indoor and Outdoor Air PBDE Levels in Living Environments in İzmir- TÜRKİYE

4.2.1. Indoor and Outdoor Air PBDEs in Schools

The indoor and outdoor air PBDE concentrations in schools are shown in Figure 4.18 and Figure 4.19. The average Σ BDE levels in indoor and outdoor air of schools were determined to be 360 and 265 pg/m^3 , respectively, and those medians were 417 and 108 pg/m^3 , respectively. While the average indoor air BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183, and BDE-209 concentrations in schools were determined to be 5.84, 20.6, 4.25, 28.2, 4.26, 11.6, 5.87, and 486 pg/m^3 , respectively, those median concentrations were 1.71, 10.0, 4.34, 13.3, 2.06, 6.35, 2.53, and 492 pg/m^3 , respectively. The I/O ratio of indoor and outdoor air ranged between 1.46 and 13.7. The median BDE-47/99 concentration ratio in indoor and outdoor air of schools were 0.58 and 0.52, respectively, while those were >1 in dust samples. This situation could be explained by the effects of two different mechanisms: (i) accumulation of PBDEs in dust due to their tendency to adhere to organic surfaces because of their high octanol-air partition coefficient, and (ii) dilution of gas-phase components with outdoor air through ventilation mechanisms. The CV value for BDE-209 in indoor air concentrations is determined as 0.40, while this value is 0.65 in outdoor concentrations. It was determined that the concentration variation of BDE-209 was relatively low compared to other targeted PBDEs. The CV values of other PBDE congeners in indoor and outdoor air ranged from 0.92 to 1.44 and from 0.89 to 1.49, respectively.

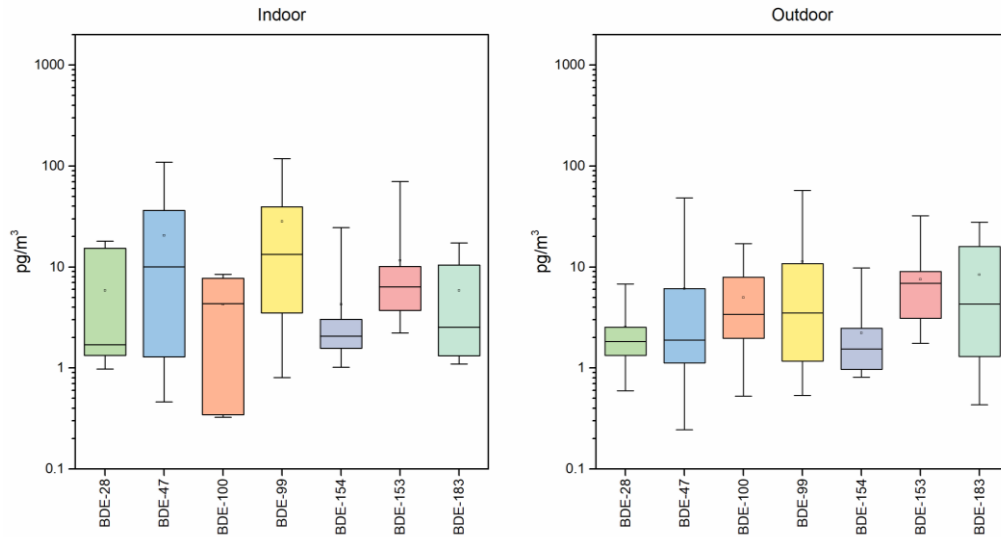


Figure 4.18. Indoor and outdoor air PBDE concentrations (wo BDE-209) in schools

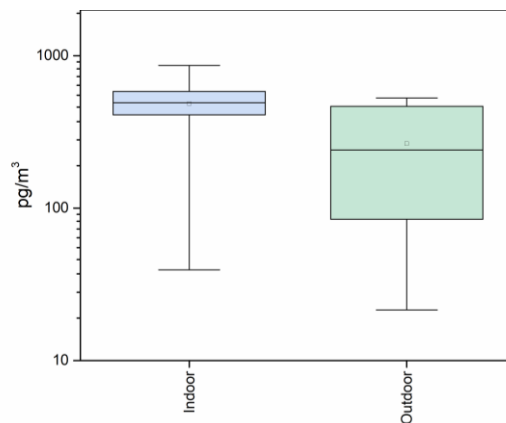


Figure 4.19. Indoor and outdoor BDE-209 concentrations in schools

Indoor and outdoor air PBDE concentrations in urban, sub-urban, and rural schools are shown in Figure 4.20 and Figure 4.21. The contribution of the BDE-209 to the Σ BDE concentration in indoor air in urban, sub-urban, and rural schools were determined to be 83.5%, 90.3%, and 85.9%, respectively (Figure 4.22). Due to being historically the most commercially produced formula was deca-BDE, the most abundant congener in environmental media is BDE-209 (Genisoglu et al., 2019). In urban areas, the contribution of BDE-47 and BDE-99 to the Σ BDE concentration were 4.82% and

7.99%, respectively, while those were 2.17% and 1.81% for schools in sub-urban areas, and 2.46% and 2.08% for schools in rural areas, respectively.

The average indoor air concentrations of BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183, and BDE-209 congeners urban schools were determined to be 1.77, 32.1, 3.79, 53.3, 3.38, 12.0, 3.57, and 557 pg/m^3 , respectively. In sub-urban area, the average concentrations of those congeners in indoor air in schools were determined to be 5.52, 10.2, 4.02, 8.47, 3.47, 3.40, 10.7, and 423 pg/m^3 , while those were 15.2, 13.7, 4.96, 11.6, 2.65, 18.0, 9.19, and 478 pg/m^3 , respectively in rural area. The average outdoor ΣBDE concentrations in schools were determined to be 455, 268, and 65.4 pg/m^3 in urban, sub-urban, and rural areas, respectively, while those in indoor were 556, 469, and 666 pg/m^3 , respectively. In a study conducted in schools in Ireland, the median ΣBDE concentrations in indoor air was determined to be 245 pg/m^3 (Wemken et al., 2019), whereas in our study, this value was 431 pg/m^3 . In the same study, concentrations in homes were determined to be 418 pg/m^3 . In a study conducted in homes in Canada, the median total concentration of BDE-28, BDE-47, and BDE-99 congeners was determined to be 72.8 pg/m^3 , while in our study, the median concentration sum of those in indoor air in schools was 25.1 pg/m^3 .

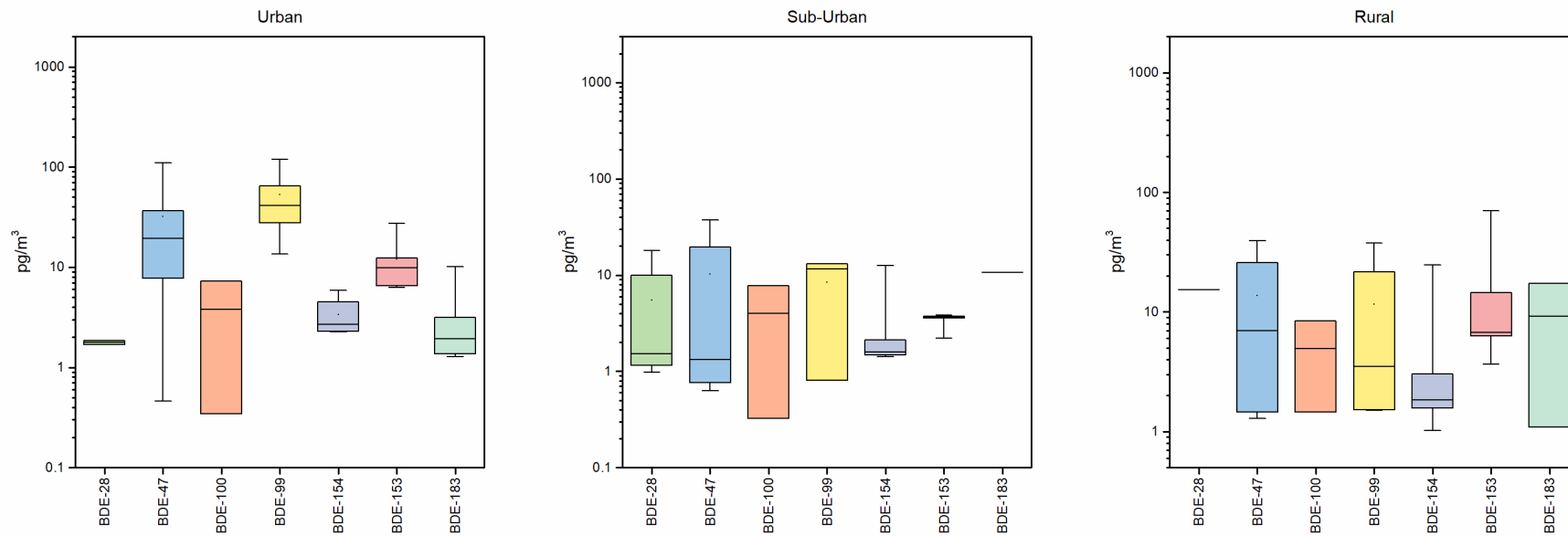


Figure 4.20. Indoor air PBDE (wo BDE-209) concentrations in schools according to the urbanization level

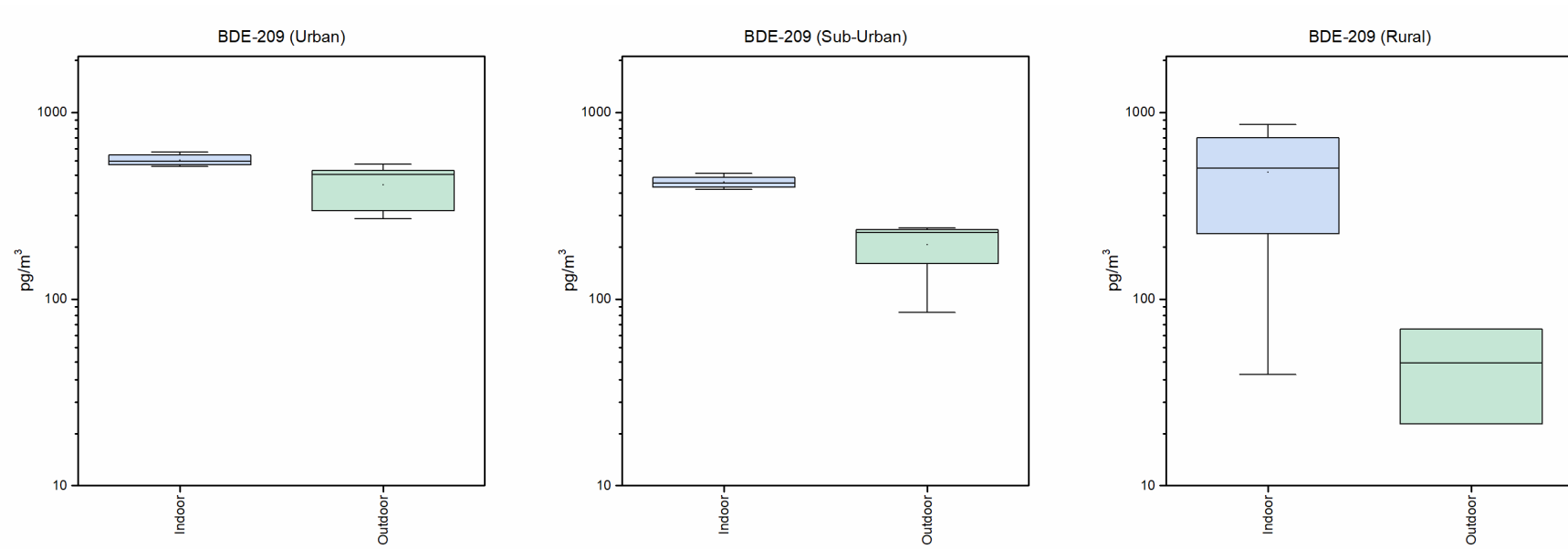


Figure 4.21. Indoor and outdoor air BDE-209 concentrations in schools according to the urbanization level

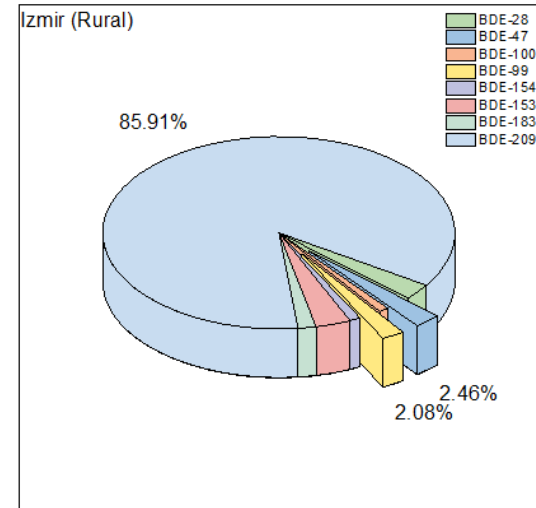
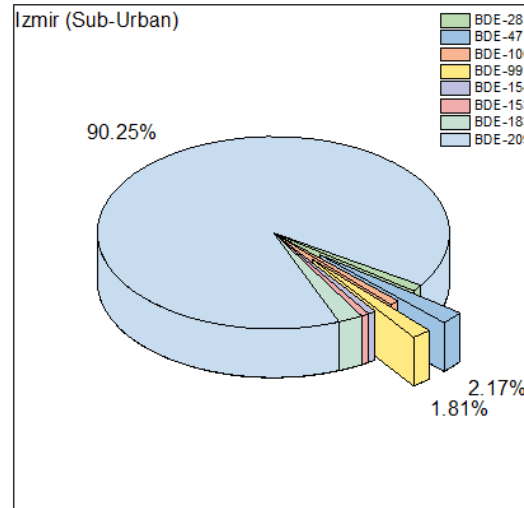
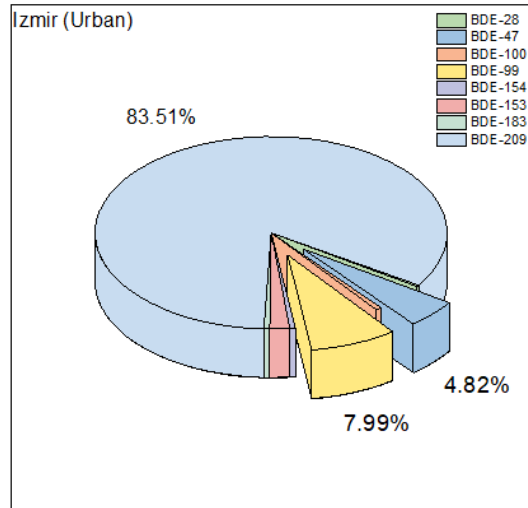


Figure 4.22. Indoor air PBDE concentration compositions in schools

The loading plot of PCA analysis of indoor air PBDEs is shown in Figure 4.23. While BDE-47 and BDE-99 congeners were not significantly correlated by PC1, BDE-209 significantly affected by PC2. PC2 might be an indicator of the direct emissions from commercial deca-BDE product. The effects of PC1 on indoor air PBDE levels were similar without BDE-47 and -99. While the commercial octa- and penta-BDE mixtures were abundantly used in the production of electronic equipments, plastics, and textiles, commercial penta-BDE mixtures were used in the polyurethane foam furnitures. PC1 might be an indicator of direct emissions from electronic equipments, cable, and plastics in indoor environments of schools.

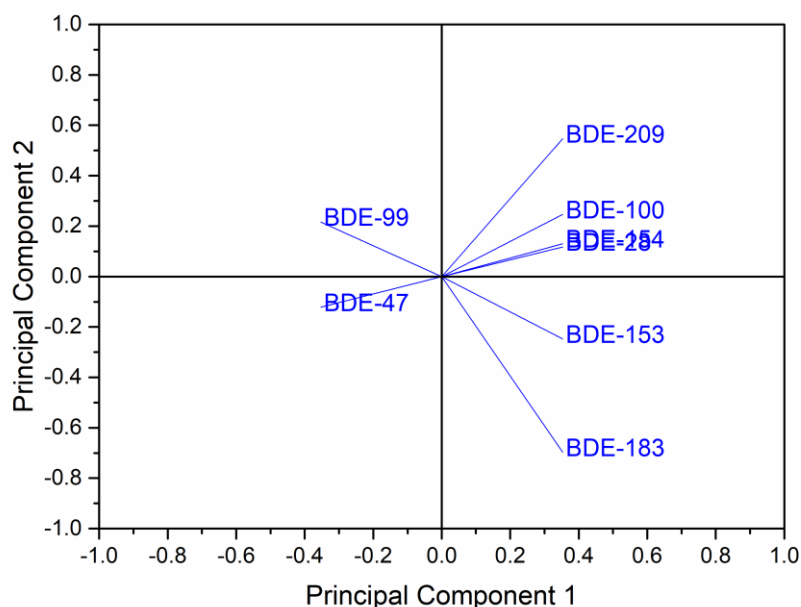


Figure 4.23. Loading plot of indoor air PBDEs in schools

The dust-air partitioning coefficients (K_D) were calculated using the dust and air concentrations determined in schools (Table 4.2), following the formula $K_D (m^3/\mu g) = X_D (\mu g/\mu g)/C_D (\mu g/m^3)$ (Li et al., 2014). The calculated $\log_{10}K_D$ values were similar to those determined in our previous study (Genisoglu et al., 2019) and the values determined by Watkins et al. (2013) in their study conducted in Boston. While the K_D values determined by Wei et al. (2016) in France generally show similarities with the findings of this study,

the value published for the BDE-209 in the study conducted in France is relatively higher. This discrepancy is believed to occur from differences in indoor sources.

Table 4.2. Dust-Air partitioning coefficient of PBDEs ($\log_{10}K_D$)

Congener	This Study	Genisoglu et al., 2019	Watkins et al., 2013	Wei et al., 2016
BDE-28	-4.02	-3,71	-3,88	-3,62
BDE-47	-2.35	-3,15	-2,58	-2,70
BDE-100	-3.83	-2,88	-1,95	-1,74
BDE-99	-3.39	-2,77	-1,99	-1,89
BDE-154	-3.62	-2,36	-1,62	-0,90
BDE-153	-1.96	-3,01	-1,60	-1,09
BDE-183	-2.65	-1,79	-3,39	
BDE-209	-2.35	-2,83	-2,62	5,34

4.2.2. Indoor and outdoor air PBDE concentrations in homes

The PBDE concentrations in indoor and outdoor air in homes are shown in Figure 4.24 and Figure 4.25. The average indoor air BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183, and BDE-209 concentrations were 2.74, 0.87, 0.82, 10.6, 1.36, 2.28, <MDL, and 56.7 pg/m^3 , respectively, while those medians were 2.43, 0.82, <MDL, 1.53, 1.17, 2.19, 0.25, and 52.5 pg/m^3 , respectively. The average Σ BDE levels in indoor and outdoor air of homes were determined to be 53.7 and 77.6 pg/m^3 , while those medians were 63.8 and 53.0 pg/m^3 , respectively. The I/O ratio varies between 1.05 and 4.97 in air samples taken from indoor and outdoor environments of homes. The I/O ratio indicated the PBDEs were primarily sourced from indoor sources. In air samples taken from homes, the median ratio of BDE-47/BDE-99 concentrations in indoor and outdoor air is determined as 0.58 and 0.52, respectively, while these values are determined as 0.44 and 0.38 in schools.

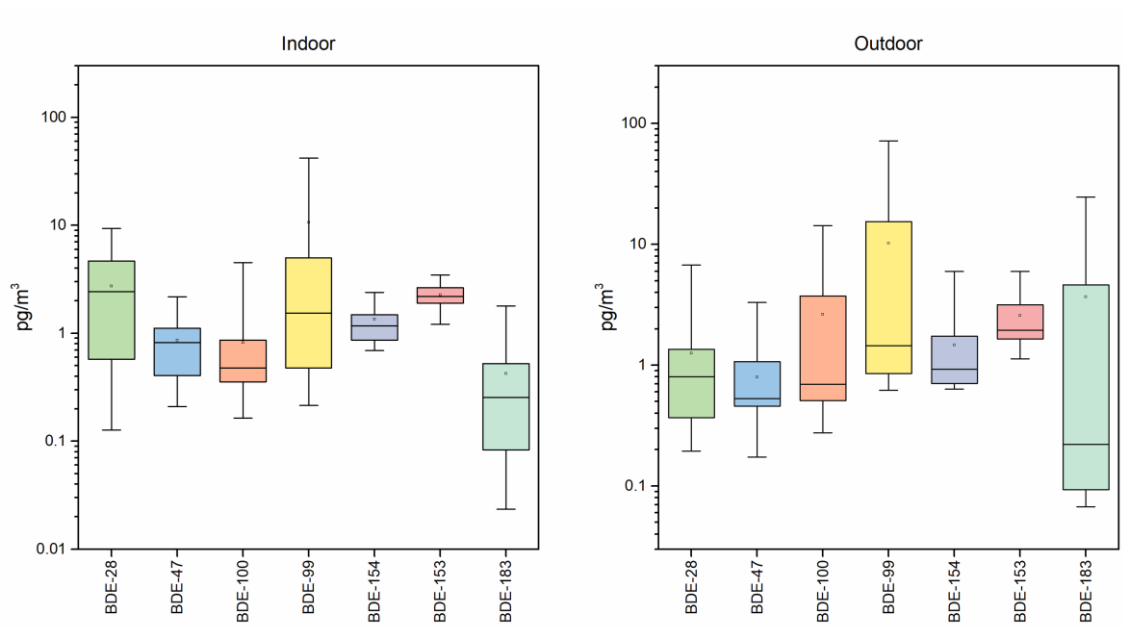


Figure 4.24. Indoor and outdoor air PBDE concentrations (wo BDE-209) in homes

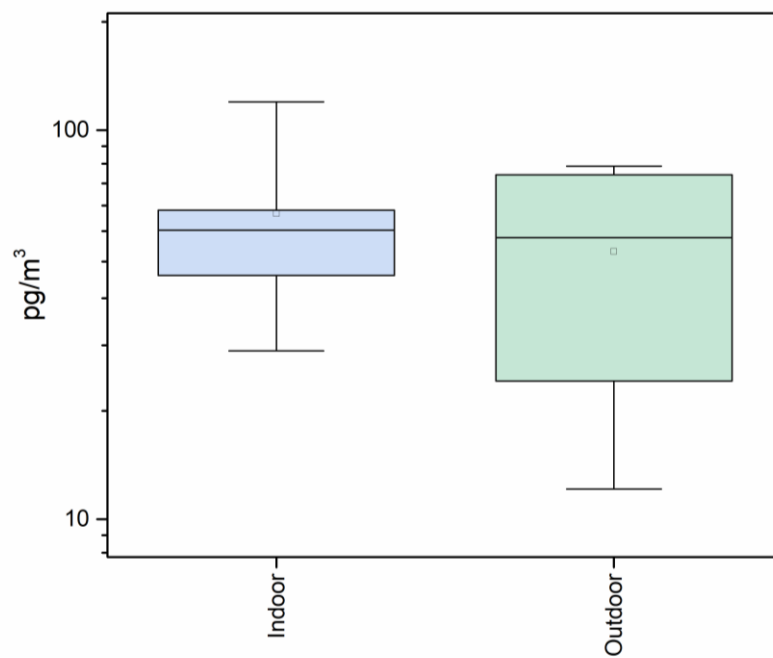


Figure 4.25. Indoor and outdoor air BDE-209 concentrations in homes

PBDE levels classified according to urbanization levels are shown in Figure 4.26 and Figure 4.27. As seen in Figure 4.28, the contribution of the BDE-209 component to the Σ BDE concentration in indoor air of urban, sub-urban, and rural houses is determined to be 71%, 85.6%, and 89.6%, respectively. As it has been historically one of the most produced PBDE congeners commercially, it can be observed at high concentrations in both dust and gas phases (Genisoglu et al., 2019). The contribution of the BDE-153 congener to the Σ BDE concentration in urban houses is an average of 11.3%, while in sub-urban and rural areas, this ratio is determined to be 19.4% and 9.26%, respectively.

The average concentrations of BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183, and BDE-209 congeners in the indoor air of urban houses were determined to be 2.62, 1.34, 0.59, 13.9, 1.59, 2.93, 0.65, and 57.3 pg/m³, respectively. The average concentrations of these congeners in the indoor air of houses in sub-urban areas were found to be 3.18, 0.64, 0.65, 6.58, 1.13, 2.13, <MDL, and 48.3 pg/m³, while in rural areas, these values were 2.44, 0.54, 1.22, 11.4, 1.36, 1.78, <MDL, and 61.1 pg/m³, respectively. The TBA results of PBDE levels detected in indoor and outdoor air in houses are shown in Figure 4.29 and Figure 4.30, respectively. While PBDE levels in indoor air are distributed into four groups, they are divided into three different groups in outdoor air. The groups in which PBDE concentrations are distributed in indoor air are: i) BDE-28, ii) BDE-209, iii) BDE-47 and BDE 153, iv) BDE-99, BDE-100, BDE-154, and BDE-183. According to the TBA analysis, the groups formed by PBDE congeners in outdoor air are: i) BDE-47 and BDE-209, ii) BDE-28 and BDE-154, and iii) BDE-153, BDE-100, BDE-99, and BDE-183.

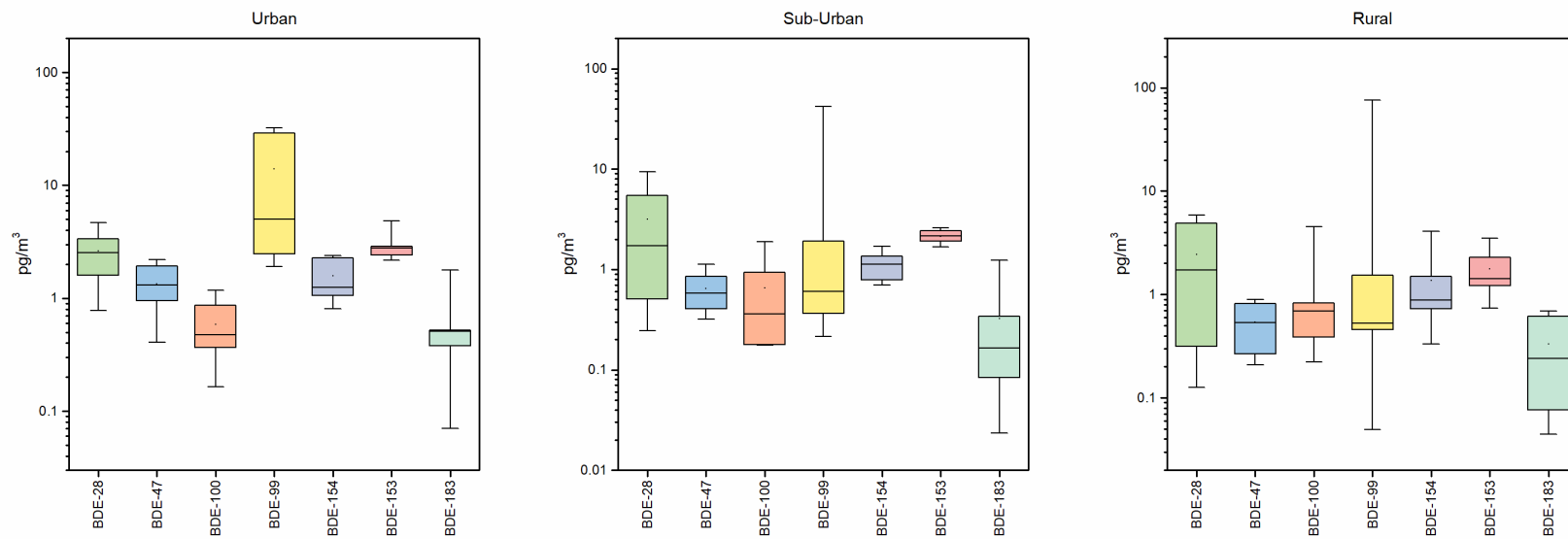


Figure 4.26. Indoor air PBDE (wo BDE-209) concentrations in homes according to the urbanization level

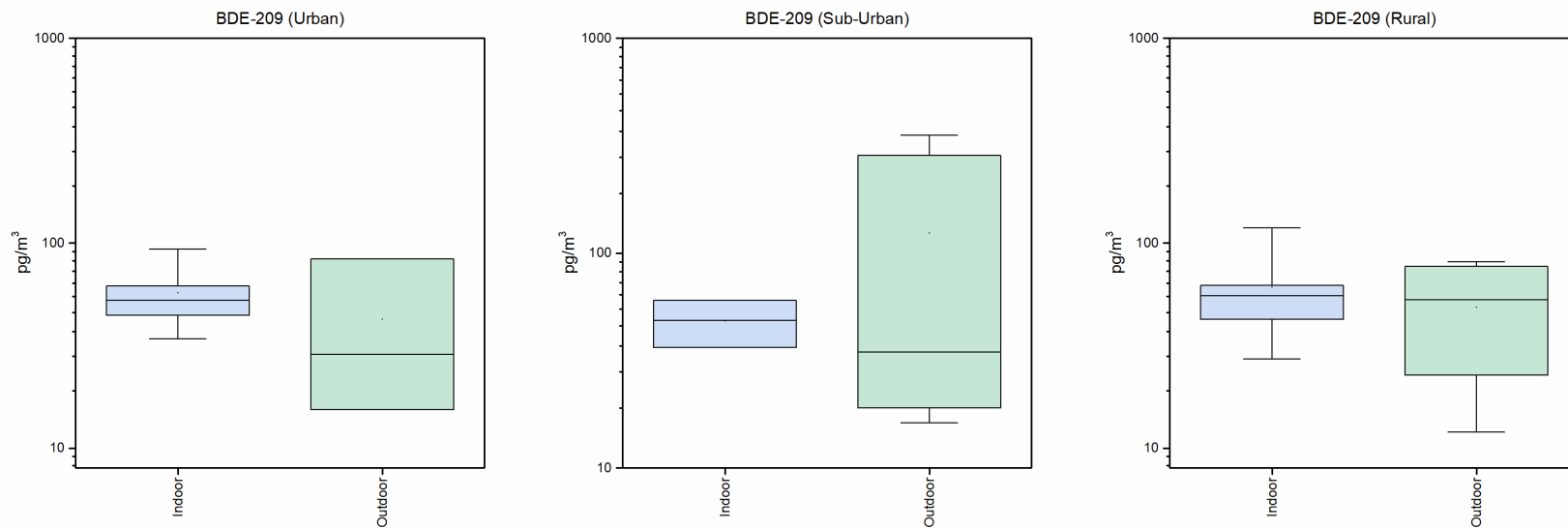


Figure 4.27. Indoor and outdoor air BDE-209 concentrations in homes according to the urbanization level

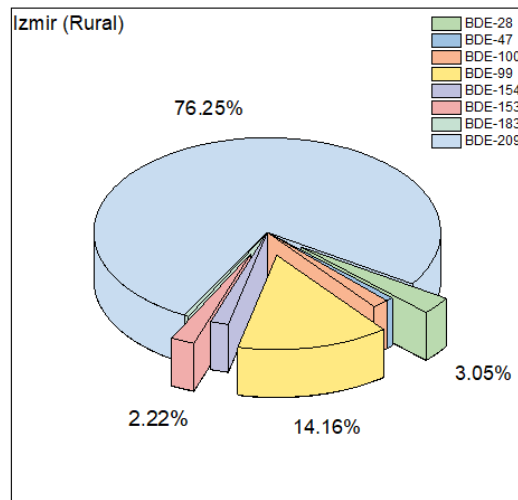
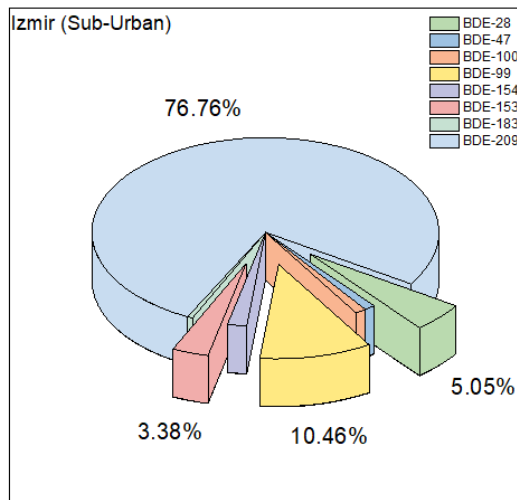
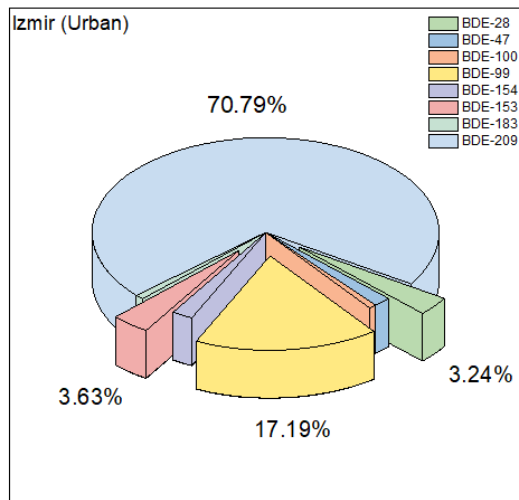


Figure 4.28. Indoor air PBDE concentration compositions in homes

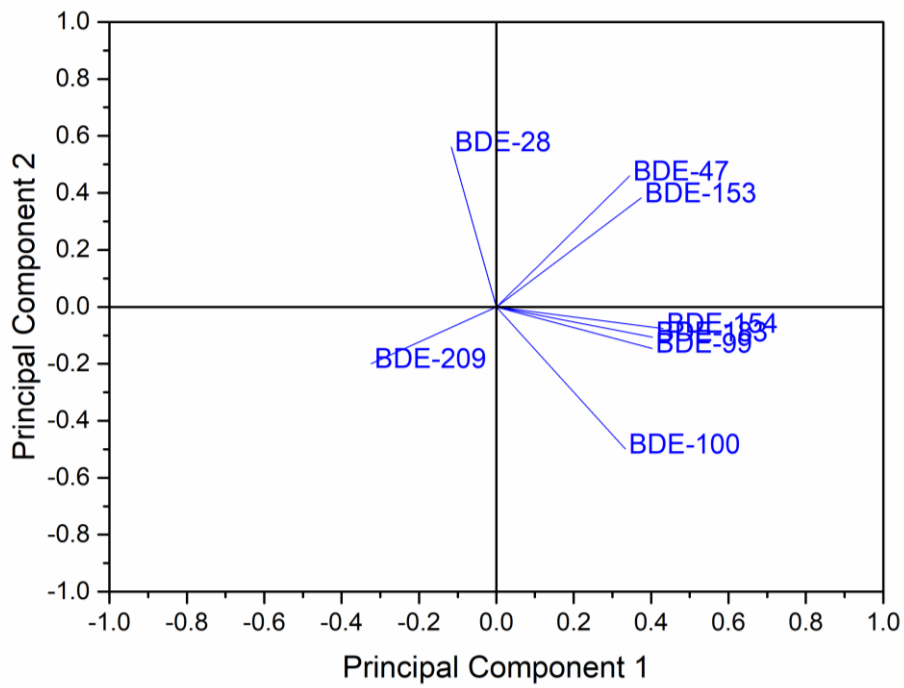


Figure 4.29. Loading plot of indoor air PBDEs in homes

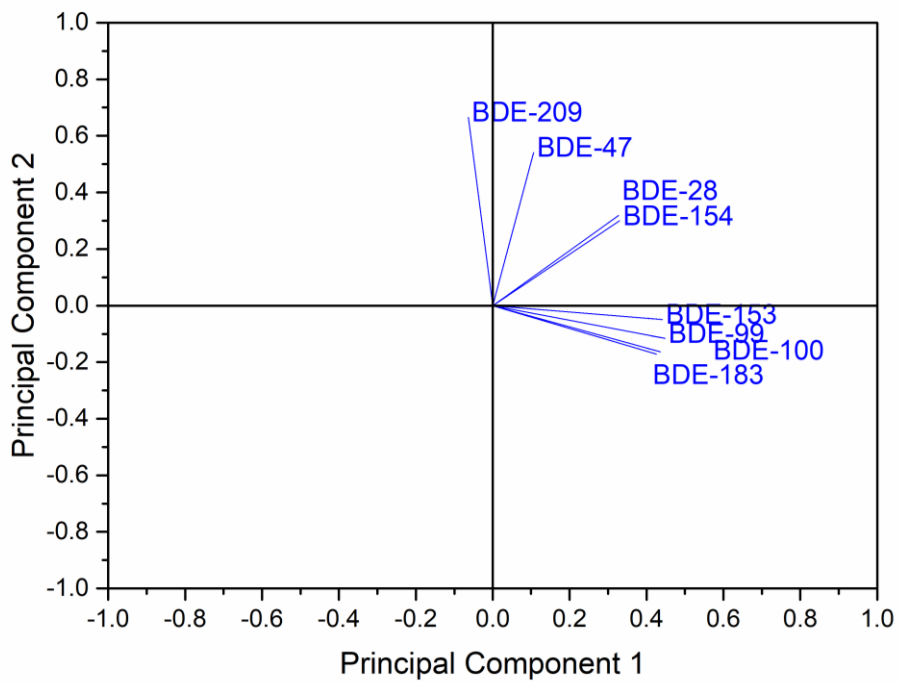


Figure 4.30. Loading plot of outdoor air PBDEs in homes

The calculated $\log_{10}K_D$ values are consistent with those obtained in our previous study (Genisoglu et al., 2019) and with the values obtained in the schools mentioned in the previous section and those determined in the literature (Watkins et al., 2013). Although the K_D values determined in a study conducted in France generally show similarities with the findings of this study, the value published for the BDE-209 component in the study from France is relatively higher (Wei et al., 2016). This difference is thought to arise from the diversity of indoor sources. However, despite the lower concentrations of dust in houses compared to schools, which leads to lower PBDE concentrations in indoor air in houses, the effect on the dust-air partition coefficient is minimal. Since the obtained coefficients are at similar levels, dust and gas phase concentrations from both houses and schools were combined to derive the distributions of site-specific dust-gas phase partition coefficients (Table 4.3 and Table 4.4).

Table 4.3. Dust-Air Partitioning ($\log_{10}K_D$) of PBDEs in indoor environments

PBDEs	School	Home	Genisoglu et al., 2019	Watkins et al., 2013	Wei et al., 2016
BDE-28	-4,02	-3,75	-3,71	-3,88	-3,62
BDE-47	-2,35	-2,02	-3,15	-2,58	-2,70
BDE-100	-3,83	-3,29	-2,88	-1,95	-1,74
BDE-99	-3,39	-3,78	-2,77	-1,99	-1,89
BDE-154	-3,62	-3,47	-2,36	-1,62	-0,90
BDE-153	-1,96	-2,36	-3,01	-1,60	-1,09
BDE-183	-2,65	-2,22	-1,79	-3,39	
BDE-209	-2,35	-1,81	-2,83	-2,62	5,34

Table 4.4. Distribution parameters of Dust-Air Partitioning ($\log_{10}K_D$) of PBDEs

PBDEs	Distribution	Parameter
BDE-28	Lognormal	Location: $6,35 \times 10^{-4}$ Mean: $2,83 \times 10^{-2}$ SD: $6,70 \times 10^{-2}$
BDE-47	Gamma	Location $1,39 \times 10^{-5}$ Scale: $2,16 \times 10^{-3}$ Shape: $3,08 \times 10^{-1}$
BDE-100	Lognormal	Location: $3,68 \times 10^{-5}$ Mean: $8,73 \times 10^{-3}$ SD: $3,86 \times 10^{-2}$
BDE-99	Weibull	Location $7,01 \times 10^{-5}$ Scale: $1,05 \times 10^{-3}$ Shape: $5,30 \times 10^{-1}$
BDE-154	Lognormal	Location: 0,00 Mean: $3,15 \times 10^{-3}$ SD: $1,33 \times 10^{-2}$
BDE-153	Lognormal	Location: 0,00 Mean: $7,82 \times 10^{-4}$ SD: $1,21 \times 10^{-3}$
BDE-183	Lognormal	Location: 0,00 Mean: $1,79 \times 10^{-2}$ SD: $5,19 \times 10^{-2}$
BDE-209	Lognormal	Location: $5,84 \times 10^{-5}$ Mean: $1,66 \times 10^{-2}$ SD: $7,34 \times 10^{-2}$

SD: Standard Deviation

4.3. Indoor and Outdoor Settled Dust-Bound AFR Levels in Living Environments in İzmir- TÜRKİYE

4.3.1. Settled Dust-Bound AFRs in Schools

The AFR levels in dust samples collected from schools are shown in Figure 4.31. The average concentrations of Σ DBE-DBCH, BEH-TEBP, TBCO, HBB, TBP-DBPE, EH-TBB, HBCDD, BTBPE, syn-DP, and anti-DP in indoor dust samples from schools were determined to be 269, 1.39, 2.03, 5.12, 0.13, 9.24, 449, 585, 1.79, and 4.31 ng/g, respectively. The average indoor settled dust-bound Σ AFR concentration was 1328 ng/g, whereas this value was 170 ng/g for outdoor dust samples. The concentration range of these compounds detected in indoor dust of schools is determined to be 5.23-1934, 0.56-2.42, 0.21-7.62, 0.10-18.9, 0.10-0.31, 0.15-36.1, 32.2-1015, 51.1-1298, 0.1-8.46, and 0.1-22.8 ng/g, respectively, with detection frequencies of 95%, 38%, 62%, 95%, 20%, 100%, 95%, 100%, 100%, and %100. The maximum concentration was 1934 ng/g for DBE-DBCH isomers, while the order of average concentrations as were BTBPE > HBCDD > Σ DBE-DBCH > EH-TBB > HBB > anti-DP > TBCO > syn-DP > BEH-TEBP > TBP-DBPE. The average ratio of anti/syn-DP concentrations was 2.41, close to commercial DP products. In outdoor dust from schools, the average concentrations of Σ DBE-DBCH,

TBCO, HBB, EH-TBB, HBCDD, BTBPE, syn-DP, and anti-DP were determined to be 21.3, 0.37, 0.11, 0.05, 0.92, 14.0, 30.1, and 0.25 ng/g, respectively. The average I/O concentration ratios for Σ DBE-DBCH, TBCO, HBB, TBP-DBPE, EH-TBB, HBCDD, BTBPE, syn-DP, and anti-DP compounds in school dusts were calculated to be 3.41, 7.00, 1.20, 1.11, 7.10, 14.9, 10.9, 9.89, and 12.2, respectively (Figure 4.32). It was generally determined that indoor sources affected the AFR levels in the collected dust samples. The AFR compound with the highest concentration in outdoor dust was found to be Σ DBE-DBCH. The reasons for this may be explained by the direct emissions from materials containing DBE-DBCH isomers and the more volatile nature of DBE-DBCH isomers compared to other AFR compounds, leading to their emission to the indoor environment from sources and subsequent adsorption onto particle surfaces through dry deposition (Drage et al., 2016).

In indoor dust samples collected from schools, the contribution of BTBPE to Σ AFR concentration was determined to be 44.1%, while its contribution to Σ AFR concentration in outdoor dust samples was 31.8% (Figure 4.33 and Figure 4.34). The compound contributing the most to Σ AFR concentration in outdoor dust was DBE-DBCH isomers, with a contribution of 46.6%. The contribution of Σ DBE-DBCH to the indoor dust-bound AFRs was determined to be 20.3%. The contribution of HBCDD compound to Σ AFR concentration in indoor and outdoor dust was determined to be 33.8% and 17.8%, respectively. The contribution of HBB to Σ AFR concentration in indoor dust was 2.53%, while the contribution of other compounds to Σ AFR concentration in indoor and outdoor dust is less than 1%.

Dust-bound AFR concentrations in rural, sub-urban, and urban schools are shown in Figure 4.35. While the average concentrations of Σ DBE-DBCH, BEH-TEBP, TBCO, HBB, TBP-DBPE, EH-TBB, HBCDD, BTBPE, syn-DP, and anti-DP in indoor dust of rural schools were 210, 0.56, 1.65, 1.55, 0.10, 6.29, 285, 421, 1.89, and 4.68 ng/g, respectively, those in sub-urban schools were 293, 1.40, 1.08, 3.83, 0.31, 9.90, 369, 676, 2.20, and 5.48 ng/g, and were 311, 1.55, 3.59, 10.9, 0.10, 11.5, 670, 658, 1.27, and 2.99 ng/g in urban schools, respectively. While the average outdoor dust-bound levels of TBCO, HBB, TBP-DBPE, EH-TBB, HBCDD, BTBPE, syn-DP, and anti-DP in rural schools were 0.29, 12.4, 0.10, 1.87, 10.8, 17.6, 0.13, and 0.22 ng/g, respectively, those average were 0.15, 0.41, 0.21, 1.27, 62.7, 108, 0.15, and 0.29 ng/g, respectively, in sub-urban schools and 0.36, 0.11, 0.10, 0.92, 13.9, 30.1, 0.25, and 0.52 ng/g, respectively, in urban schools. The reason for the significantly low I/O concentration ratio of the HBB

compound (Figure 4.32) in rural areas is due to the high concentration detected in the outdoor sample taken from the RU5 (Yaka Village) sampling point.

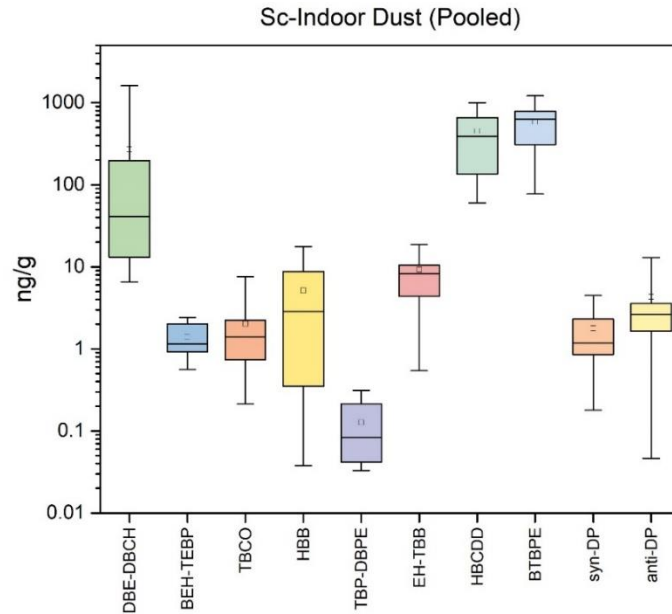


Figure 4.31. Indoor settled dust-bound AFRs in schools

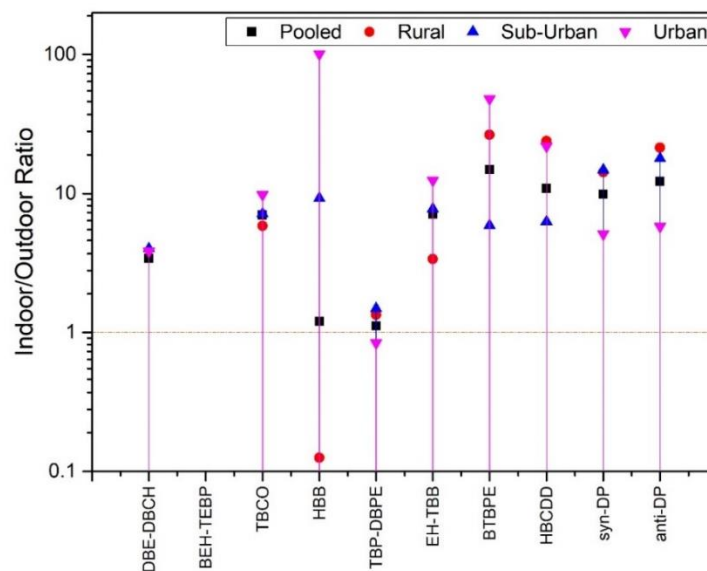


Figure 4.32. I/O concentration ratio of dust-bound AFRs in schools

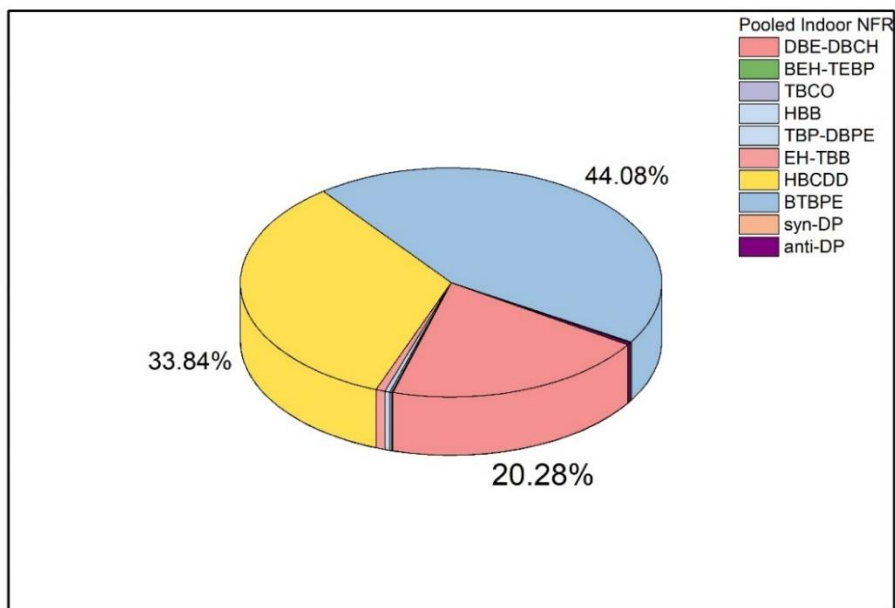


Figure 4.33. Concentration profiles of indoor dust-bound AFRs in schools

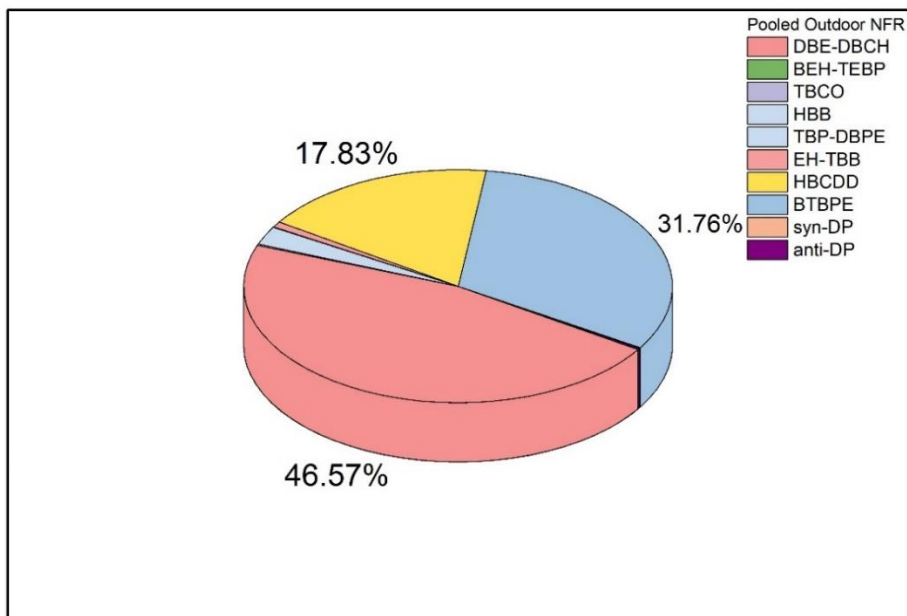


Figure 4.34. Concentration profiles of outdoor dust-bound AFRs in schools

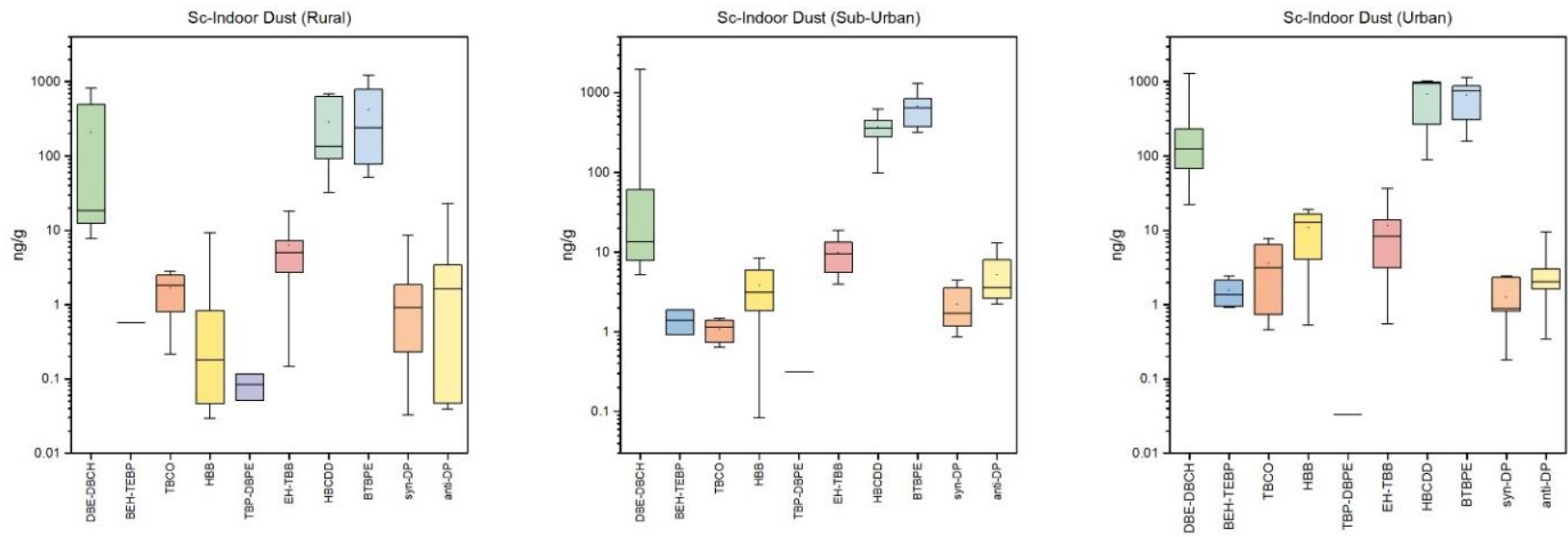


Figure 4.35. Settled dust-bound AFR concentrations in indoor environments of rural, sub-urban, and urban schools

4.3.2. Settled Dust-Bound AFRs in Homes

In the dust samples collected from homes, AFR levels are shown in Figure 4.36. The average concentrations of Σ DBE-DBCH, BEH-TEBP, TBCO, HBB, TBP-DBPE, EH-TBB, HBCDD, BTBPE, syn-DP, and anti-DP in indoor dust samples were determined to be 678, 3.83, 2.15, 0.39, 0.11, 4.79, 87.24, 105, 1.27, and 2.83 ng/g, respectively, with detection frequencies of 90%, 5%, 48%, 100%, 33%, 100%, 95%, 100%, 100%, and 100%. The indoor dust-bound Σ DBE-DBCH, BEH-TEBP, TBCO, HBB, TBP-DBPE, EH-TBB, HBCDD, BTBPE, syn-DP, and anti-DP concentrations were determined to be in the range of 2.86-5938, 3.83-3.83, 0.14-3.53, 0.07-1.35, 0.04-0.26, 0.31-16.9, 9.57-563, 15.4-344, 0.08-3.97, and 0.16-12.6 ng/g, respectively, while those averages in outdoors were <MDL, 0.37, 4.29, 0.10, 1.02, 25.9, 49.2, 0.34, and 0.57 ng/g, respectively. The Σ DBE-DBCH levels were within a similar range as in the study conducted in Italian homes (Simonetti et al., 2020) and the BEH-TEBP concentrations were similar to those in the study conducted in homes in Istanbul. I/O ratios shows the dust-bound AFRs in homes were primarily affected by indoor sources (Figure 4.37). The AFR compound with the highest I/O concentration ratio was Σ DBE-DBCH with an average of 30.3. The average I/O dust-bound concentration ratios of TBCO, HBB, TBP-DBPE, EH-TBB, HBCDD, BTBPE, syn-DP, and anti-DP in homes were 12.1, 2.65, 1.15, 13.8, 10.8, 7.05, 8.08, and 11.9, respectively. that was determined that the outdoor dust concentrations of TBP-DBPE in sub-urban areas are higher compared to indoor concentrations. The HBCDD compound, which was not detected in indoor air samples, was determined to be present in dust samples at an average level of 105 ng/g. In a study conducted in Istanbul, median HBCDD levels in homes at all urbanization levels were determined to be in the range of 160-510 ng/g (Kurt-Karakus et al., 2017).

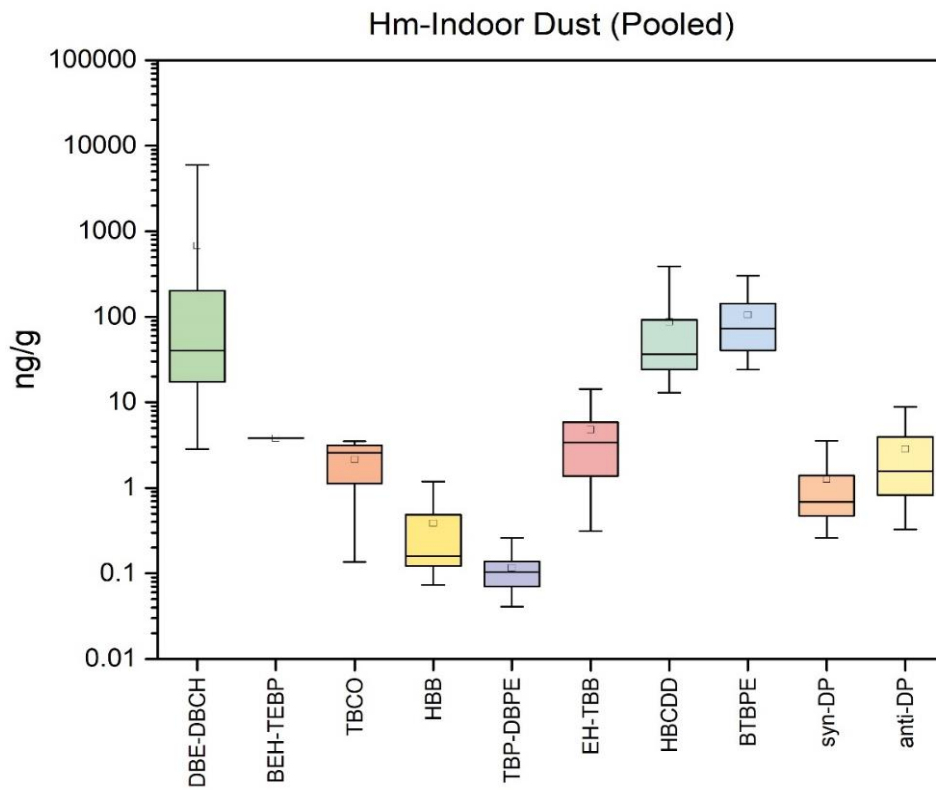


Figure 4.36. Indoor settled dust-bound AFRs in schools

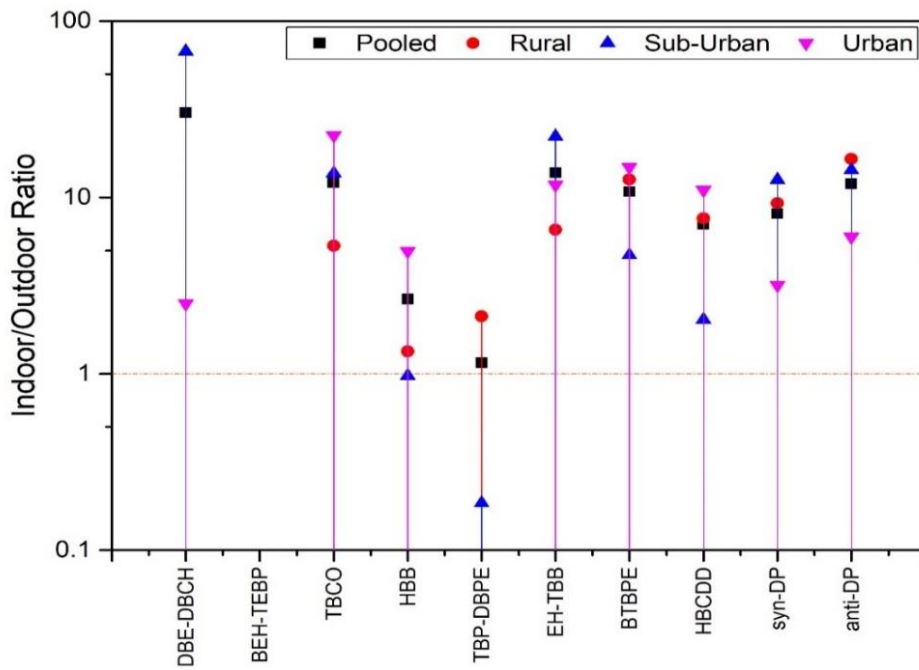


Figure 4.37. I/O concentration ratio of dust-bound AFRs in homes

The concentration profiles of indoor and outdoor settled dust-bound AFRs are shown in Figure 4.38 and Figure 4.39. DBE-DBCH was dominated (75.5%) the indoor settled dust-bound AFR concentrations. While the average concentration fraction of HBCDD in indoor dust in homes was determined to be 12.4%, concentration fraction of BTBPE was 15.1%. The concentration fractions of other AFR compounds in indoor dust were determined to be lower than the level of 1%. Σ DBE-DBCH, HBCDD, and BTBPE compounds were also dominated the AFR concentration profile in outdoor settled dust in homes. While DBE-DBCH isomers were half of the concentration of targeted AFR compounds in outdoor dust in homes, the contribution of HBCDD and BTBPE concentration to the total AFR concentration has increased to 28.7% and 15.1%, respectively, despite the decrease in their concentrations compared to indoor dust.

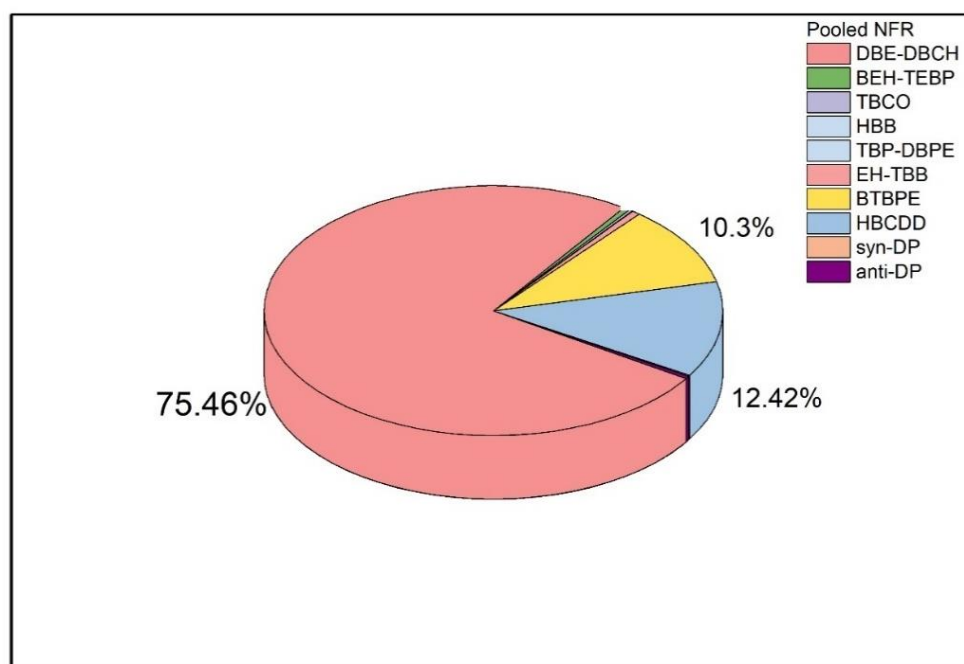


Figure 4.38. Concentration profiles of indoor dust-bound AFRs in homes

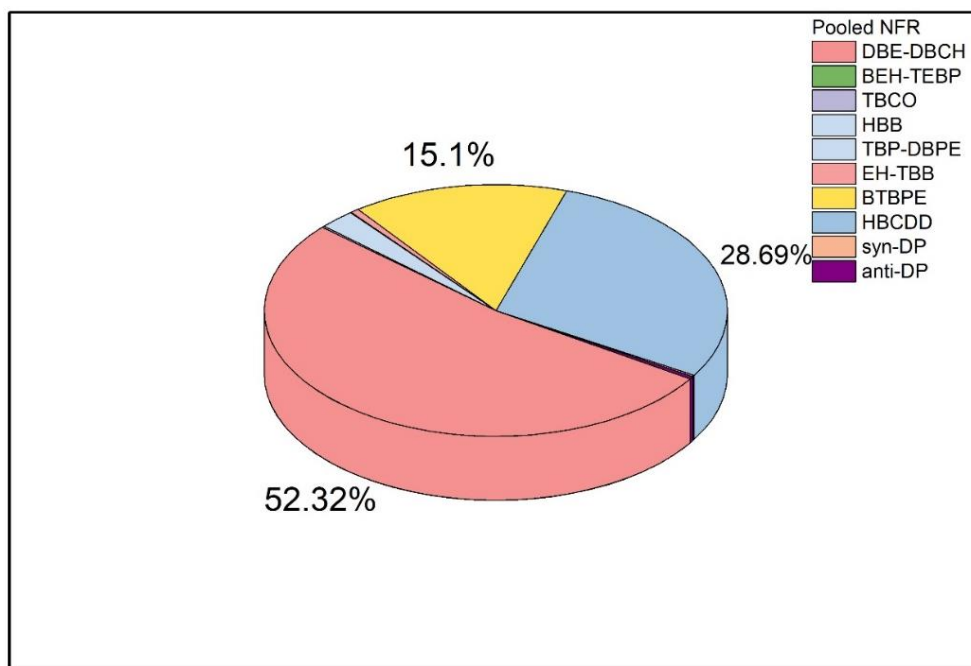


Figure 4.39. Concentration profiles of outdoor dust-bound AFRs in homes

The settled dust-bound AFR concentrations in indoor environments of urban, sub-urban and rural homes are shown in Figure 4.40. While the indoor dust-bound average concentrations of Σ DBE-DBCH, BEH-TEBP, TBCO, HBB, TBP-DBPE, EH-TBB, HBCDD, BTBPE, syn-DP, and anti-DP in rural homes were determined to be 1208, <MDL, 2.46, 0.30, 0.13, 5.19, 78.2, 81.88, 0.86, and 1.90 ng/g, respectively, those average in sub-urban homes were 948, <MDL, 2.98, 0.27, 0.11, 5.20, 40.1, 98.3, 1.41, and 3.29 ng/g, and in urban homes were 29.9, 3.83, 1.30, 0.59, <MDL, 3.99, 142, 136, 1.54, and 3.34 ng/g, respectively. In a study conducted in İstanbul-Türkiye, the total BDE-DBCH isomer concentration in urban area was determined to be an average of 62 ng/g, while in sub-urban was 3.60 ng/g and rural was 29 ng/g (Kurt-Karakus et al., 2017). While the concentrations of other targeted AFR compounds in this study are within the range of concentrations determined in İstanbul, the averages and medians in İzmir are lower than those determined in İstanbul. This discrepancy could be explained by the small sample size of the İstanbul study (urban n=3, sub-urban n=4, rural n=3) affecting the concentration values on the average. The concentrations we obtained are seen to be higher than the concentrations determined in a study conducted in Egypt. When studies on brominated flame retardants in the literature are examined, it is seen that despite the

widespread use of PBDEs for many years, similar ranges of concentrations can be expected to be detected in every region, albeit depending on source intensity with electronic and electrical devices, construction materials, and furniture completing their global dispersion (Genisoglu et al., 2019; Kurt-Karakus et al., 2017; Law et al., 2008; Li and Jia, 2014; Meeker et al., 2009; Venier et al., 2016; Watkins et al., 2013). However, it is observed that the levels of AFRs, called replacement flame retardants, vary a broad concentration range between studies (Al-Omran and Harrad, 2017; de la Torre et al., 2020; Drage et al., 2016; Genisoglu et al., 2019; Kurt-Karakus et al., 2017). This variation can be explained by the variability in source type and intensity due to the possibility that products containing legacy flame retardants have not yet been replaced with new ones.

BEH-TEBP compound could not be detected in outdoor samples taken from the three urbanization levels where the study was conducted. In outdoor dust samples collected from rural areas, the average concentrations of TBCO, HBB, TBP-DBPE, EH-TBB, HBCDD, BTBPE, syn-DP, and anti-DP were determined to be 0.28, 12.4, 0.07, 1.16, 9.59, 18.6, 0.14, and 0.18 ng/g, respectively. In sub-urban areas, the concentrations of those compounds in outdoor dust were 0.50, 0.40, 0.14, 0.98, 52.5, 91.2, 0.27, and 0.39 ng/g, while in urban areas, they were 0.37, 2.30, 0.09, 1.02, 25.9, 29.2, 0.35, and 0.56 ng/g, respectively. DBE-DBCH isomers were not detected in samples taken from homes' outdoor environments in rural areas, while they were found at levels of 7.02 ng/g in sub-urban areas and 152 ng/g in urban areas.

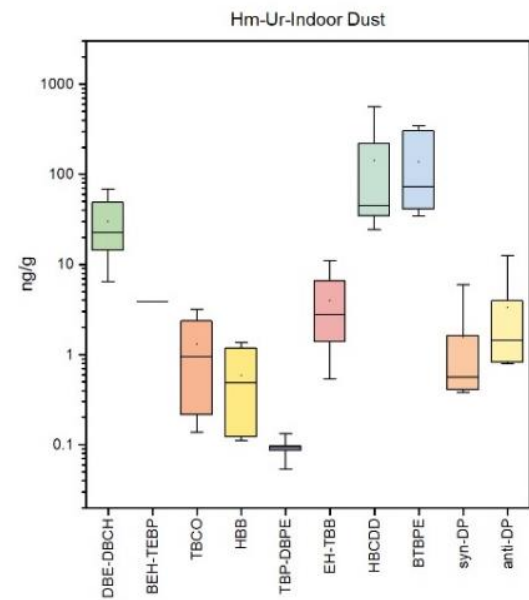
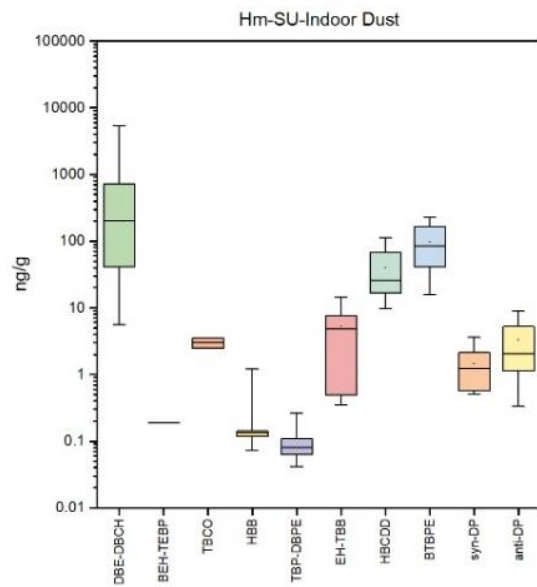
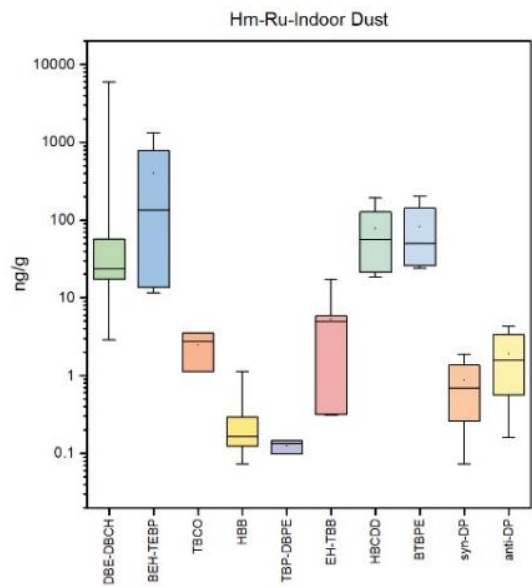


Figure 4.40. Settled dust-bound AFR concentrations in indoor environments of rural, sub-urban, and urban homes

4.3.3. Settled Dust-Bound AFRs in C/B/Rs

The settled dust-bound AFR concentrations in indoor environments of C/B/Rs are shown in Figure 4.41. Σ DBE-DBCH was determined to be the dominant AFR compound with an average concentration of 812 ng/g. The BEH-TEBP was detected at only one sampling point in the sub-urban C/B/Rs, with a concentration of 0.20 ng/g, while it was not detected at any other C/B/Rs. The average settled dust-bound concentrations of TBCO, HBB, TBP-DBPE, EH-TBB, HBCDD, BTBPE, syn-DP, and anti-DP were determined to be 0.42, 0.83, 0.13, 1.83, 109, 86.6, 0.72, and 1.84 ng/g, respectively. While the detection frequencies of settled dust-bound TBCO and TBP-DBPE were 64%, and 50%, remaining targeted AFRs were detected in all C/B/R samples. It was determined that the concentration of the anti-DP isomer in the indoor settled dust of C/B/R is on average 1.87 times higher than that of the syn-DP. Although this value was relatively lower than the ratio in commercial DP products ('3'), it was similar to other sampling points. The contributions of AFR compounds to Σ AFR concentration in C/B/Rs are shown in Figure 4.42. The contribution of Σ DBE-DBCH to Σ AFR concentration is 80.1%, while the contributions of HBCDD and BTBPE compounds are 10.8% and 8.54%, respectively. The concentration of Σ DBE-DBCH isomers ($C_{\Sigma\text{DBE-DBCH-rural}} = 1874$ ng/g) was the highest in rural areas, while the concentrations of HBCDD and BTBPE ($C_{\Sigma\text{HBCDD-urban}} = 194$ ng/g and $C_{\Sigma\text{BTBPE-urban}} = 108$ ng/g) were determined to be higher in urban C/B/Rs compared to rural and sub-urban areas. According to the urbanization location of C/B/Rs, the average concentrations of Σ DBE-DBCH, TBCO, HBB, TBP-DBPE, EH-TBB, HBCDD, BTBPE, syn-DP, and anti-DP compounds were determined to be 1874, 0.65, 0.91, 0.18, 1.15, 47.7, 66.9, 0.62, and 1.03 ng/g, respectively, in rural area; 461, 0.24, 0.66, <MDL, 2.44, 44.4, 74.9, 0.54, and 1.10 ng/g, respectively, in sub-urban area; and 339, 0.22, 0.89, 0.10, 1.80, 194, 108, 0.91, and 2.86 ng/g, respectively, in urban area (Figure 4.43). The average settled dust-bound AFR concentrations in this study similar to the reported concentration levels in literature (de la Torre et al., 2020; Genisoglu et al., 2019; Hassan and Shoeib, 2015; Kurt-Karakus et al., 2017).

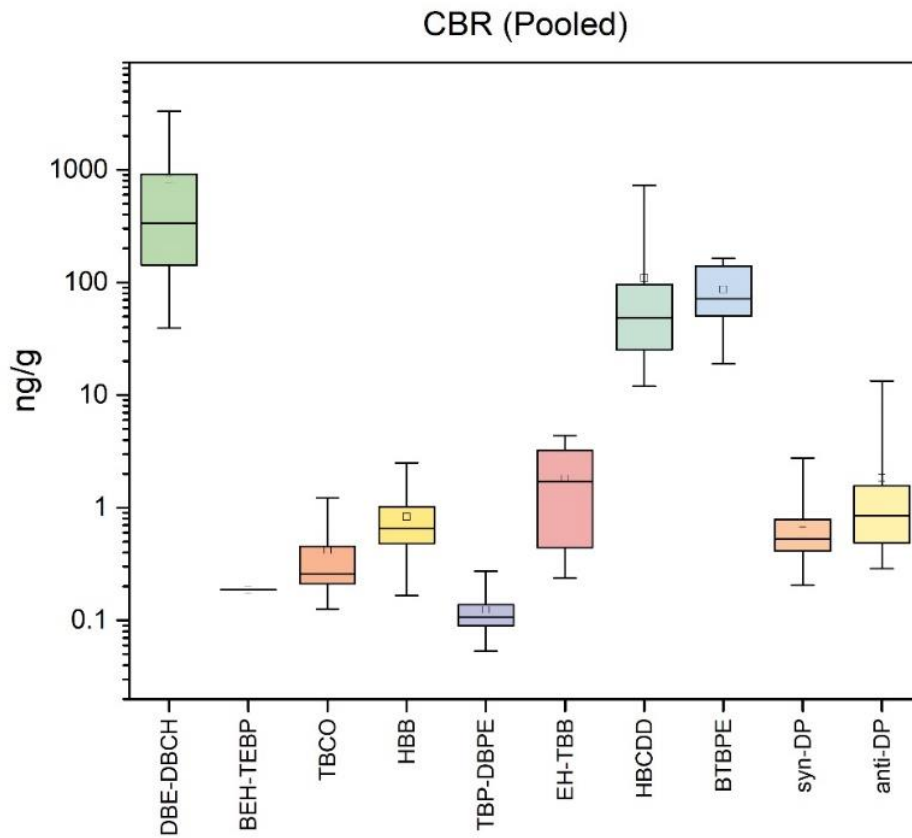


Figure 4.41. Indoor settled dust-bound AFRs in C/B/Rs

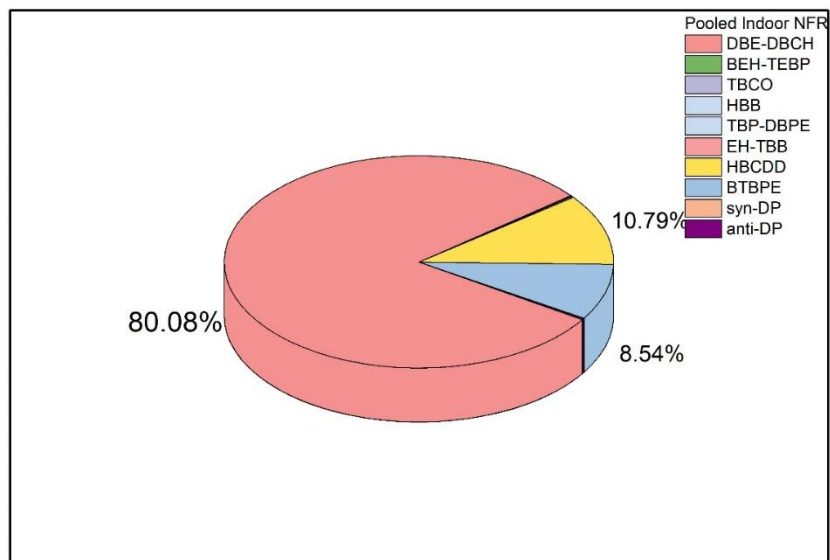


Figure 4.42. Concentration profiles of indoor dust-bound AFRs in C/B/Rs

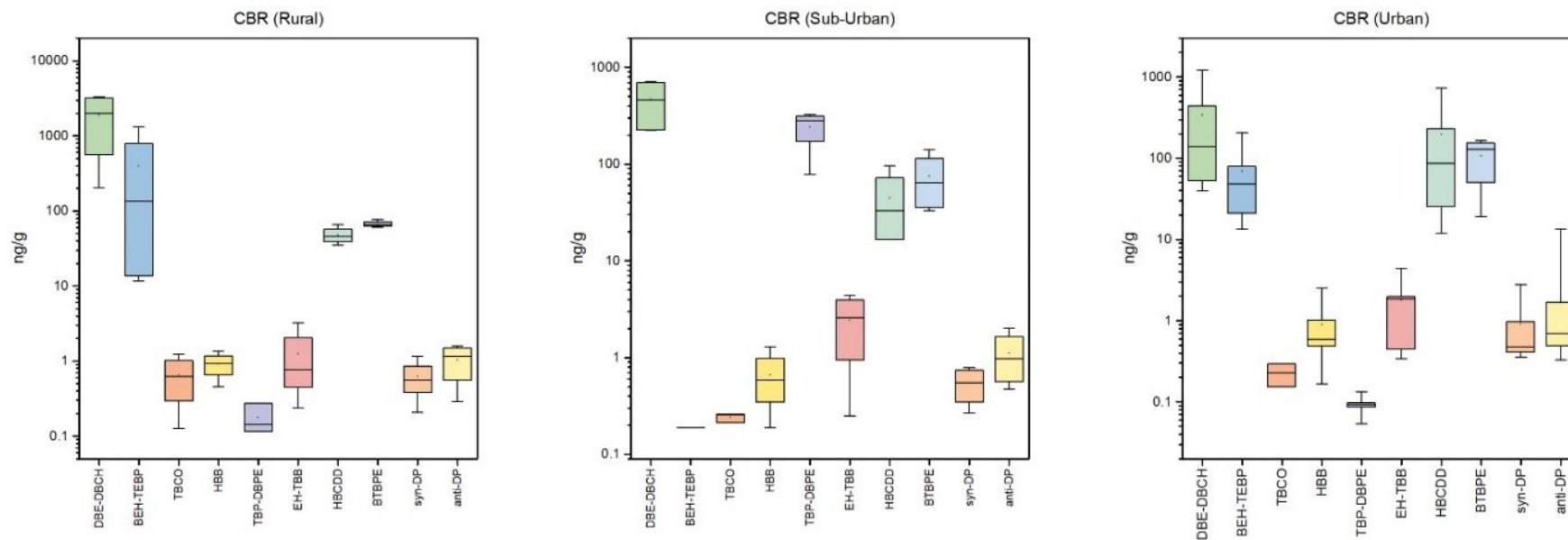


Figure 4.43. Settled dust-bound AFR concentrations in indoor environments of rural, sub-urban, and urban C/B/Rs

4.4. Indoor and Outdoor Air AFR Levels in Living Environments in İzmir- TÜRKİYE

4.4.1. Indoor and Outdoor Air AFRs in Schools

The indoor and outdoor air AFR concentrations in schools are shown in Figure 4.44 and Figure 4.45, while those concentration profiles are shown in Figure 4.46 and Figure 4.47. The indoor air concentrations of EH-TBB were higher than the other targeted AFR compounds. The average indoor air concentrations of Σ DBE-DBCH, BEH-TEBP, TBCO, HBB, TBP-DBPE, EH-TBB, HBCDD, BTBPE, syn-DP, and anti-DP in schools were determined to be 22.5, 6.46, 2.90, 0.24, 6.43, 630, 174, 12.3, and 18.7 pg/m^3 , respectively, while those in outdoor air were 9.76, 0.57, 0.61, 2.81, 3.11, 83.8, 34.3, 7.29, and 18.8 pg/m^3 , respectively. Detection frequencies of Σ DBE-DBCH, BEH-TEBP, TBCO, HBB, TBP-DBPE, EH-TBB, HBCDD, BTBPE, syn-DP, and anti-DP in indoor air were 85%, 52%, 81%, 19%, 57%, 71%, 86%, 57%, and 48%, respectively. The indoor air Σ DBE-DBCH concentration in schools were approximately half of those reported in a study conducted in Norway. Although the Σ DBE-DBCH levels determined in homes and schools are lower than those in Norway, they are within a similar range as studies conducted in Sweden and the United Kingdom.

The $f_{\text{EH-TBB}} (C_{\text{EH-TBB}} / (C_{\text{EH-TBB}} + C_{\text{BEH-TEBP}}))$ ratio was determined to be 0.99 in both indoor and outdoor air of schools. While the $f_{\text{EH-TBB}}$ ratios obtained in indoor and outdoor air samples from schools are in line with the levels determined in the study conducted in Istanbul, they were higher than the range determined in the Great Lakes Region of the United States, which were 0.26-0.54, and the average value determined in Canada's Subarctic region, which was 0.48 (Kurt-Karakus et al., 2017; Ma et al., 2012). The average anti/syn DP ratio was 1.18 in indoor air of schools while 2.35 in outdoor air samples.

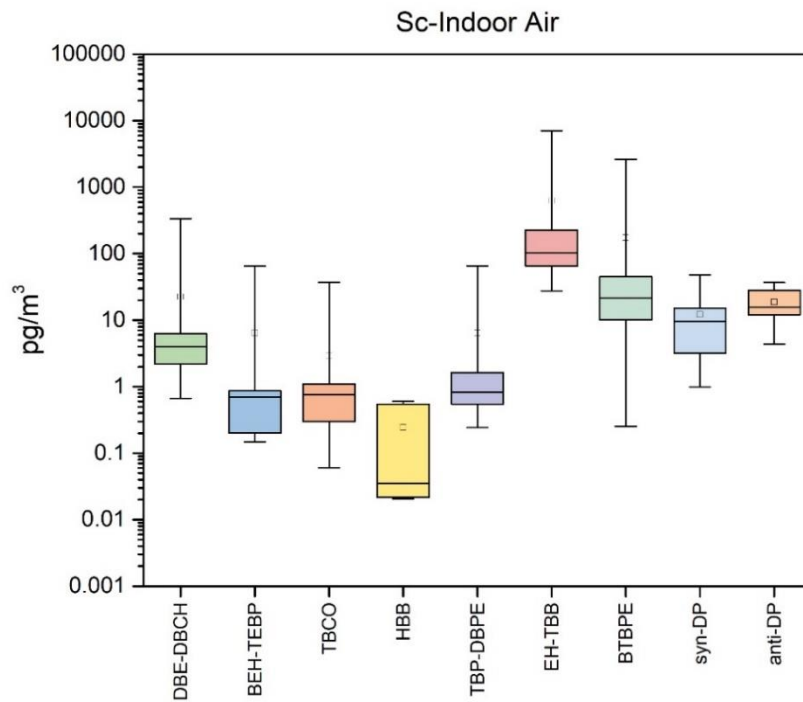


Figure 4.44. Indoor air AFR concentrations in schools

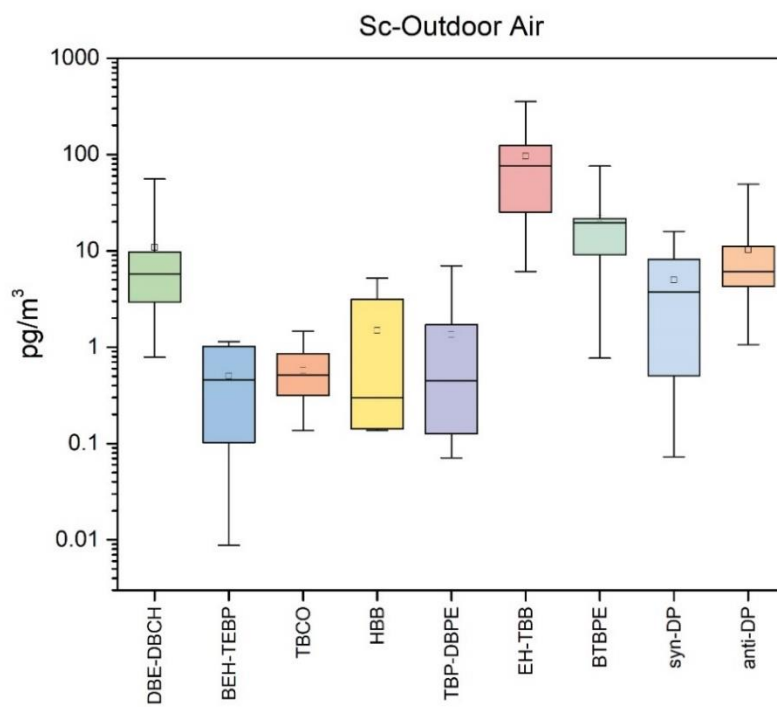


Figure 4.45. Outdoor air AFR concentrations in schools

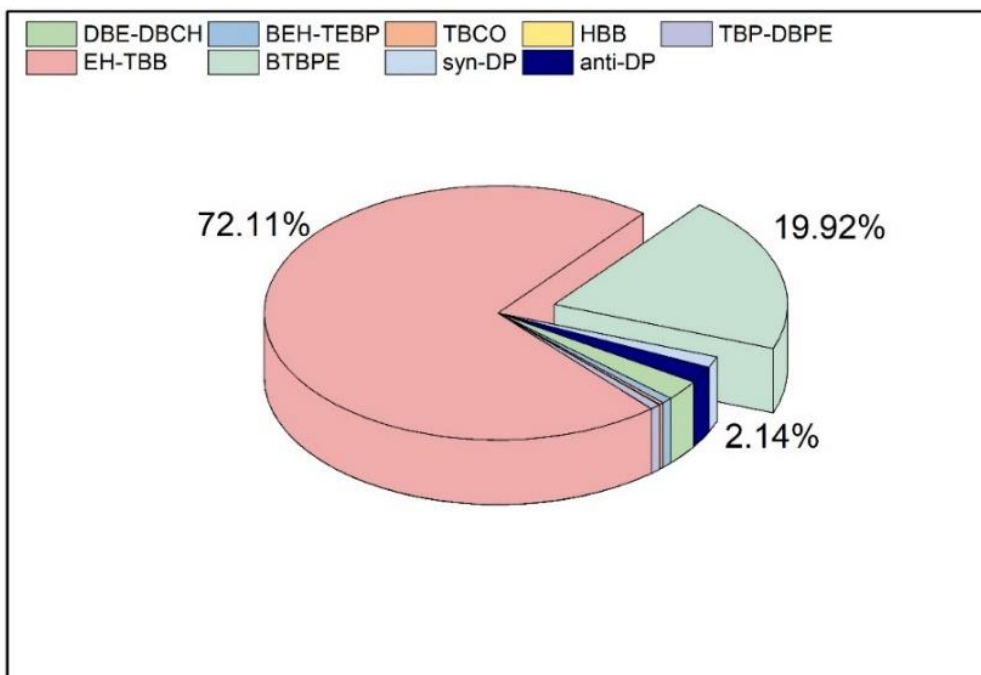


Figure 4.46. Concentration profiles of indoor air AFRs in schools

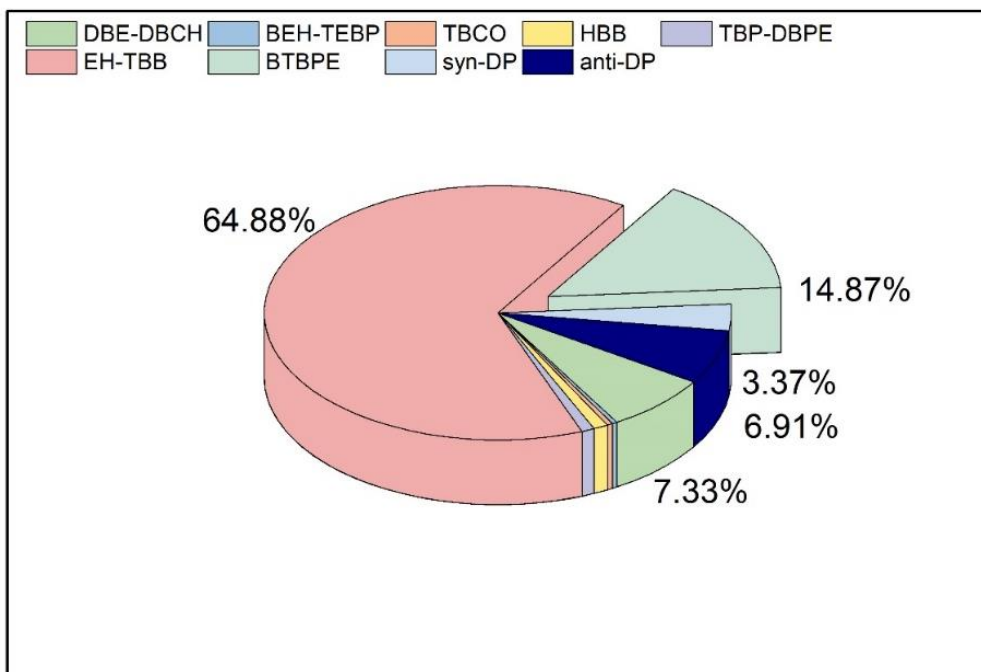


Figure 4.47. Concentration profiles of outdoor air AFRs in schools

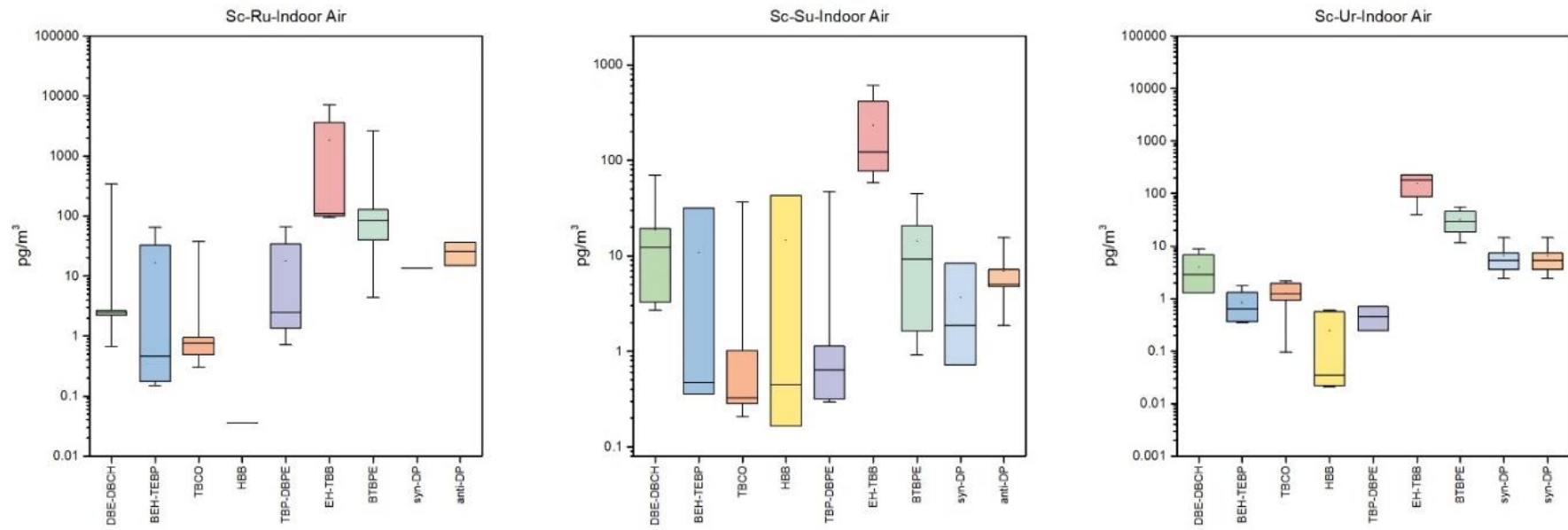


Figure 4.48. Indoor air AFR concentrations of rural, sub-urban, and urban schools

The indoor air AFR concentrations schools are shown in Figure 4.49. While the average indoor air Σ DBE-DBCH, BEH-TEBP, TBCO, HBB, TBP-DBPE, EH-TBB, HBCDD, BTBPE, syn-DP, and anti-DP concentrations in rural schools were determined to be 68.9, 16.5, 7.93, 0.03, 17.8, 1850, 573, 13.5, and 25.8 pg/m^3 , respectively, those were 5.40, 0.56, 0.37, 0.29, 0.88, 203, 11.1, 16.8, and 21.5 pg/m^3 in sub-urban schools, and 22.6, 6.46, 2.90, 0.24, 6.43, 629, 173, 12.3, and 18.7 pg/m^3 in urban schools. The highest AFR levels were determined in a sample taken from a primary school located in Küner Village, Menderes-İzmir. Since Küner Village is the furthest sampling point from industrial zones among the sampling points and similar study conducted in Istanbul was not report the effects of urbanization levels on AFR concentrations, it could be concluded that the level of urbanization and industrialization does not affect the indoor AFR concentrations on sampling site may due to the lack of local industrial AFR sources and indoor source characteristics that affected by urbanization.

4.4.2. Indoor and Outdoor Air AFRs in homes

The indoor and outdoor air Σ DBE-DBCH, BEH-TEBP, TBCO, HBB, TBP-DBPE, EH-TBB, HBCDD, BTBPE, syn-DP, and anti-DP levels in homes are shown in Figure 4.49 and Figure 4.50, while those concentration profiles are shown in Figure 4.51 and Figure 4.52. EH-TBB was determined to be the dominant AFR compound in indoor air of homes, with an average of 251 pg/m^3 . The average indoor air concentrations of Σ DBE-DBCH, BEH-TEBP, TBCO, HBB, TBP-DBPE, HBCDD, BTBPE, syn-DP, and anti-DP in homes were determined to be 26.3, 3.50, 2.74, 4.89, 4.20, 21.8, 6.46, and 12.2 pg/m^3 , respectively, with a detection frequencies of 95%, 57%, 95%, 48%, 81%, 86%, 86%, 52%, and 81%, respectively. The average concentration ratio of anti-DP and syn-DP isomers in indoor air in homes was determined to be 1.89, while the median was 3.42, close to the value of '3' in technical DP mixtures. EH-TBB and BEH-TEBP compounds, replacement flame retardants of Penta-BDEs, were the main components of Firemaster 550 and Firemaster BZ-54 technical mixtures (Kurt-Karakus et al., 2017). The $f_{\text{EH-TBB}}$ ratio was 0.77 in the Firemaster 550 mixture and 0.70 in the Firemaster BZ-54 mixture. The calculated $f_{\text{EH-TBB}}$ ratio in the indoor air of homes varies in the range of 0.56-0.99,

which were consistent with the literature. In a study conducted in Istanbul (Kurt-Karakus et al., 2017), the f_{EH-TBB} ratio was determined to be in the range of 0.17-0.99, while in a study conducted in the UK those were determined to be in the range of 0.03-0.99 (Tao et al., 2016), in Canada were in the range of 0.30-0.99, in the United States were in the range of 0.16-0.95, and in the Czech Republic were in the range of 0.27-0.89 (Venier et al., 2016).

The outdoor air concentrations of EH-TBB in homes were determined to be close to half of those indoors, with an average level of 129 pg/m^3 , making it the dominant AFR compound in the outdoor air. The average concentrations of Σ DBE-DBCH, BEH-TEBP, TBCO, HBB, TBP-DBPE, HBCDD, BTBPE, syn-DP, and anti-DP in outdoor air of homes were determined to be 22.2, 0.59, 0.64, 1.10, 0.99, 6.64, 4.23, and 12.2 pg/m^3 , respectively. In outdoor air, the average ratio of concentrations of anti-DP and syn-DP isomers was determined to be 2.89, close to the technical DP mixtures. In this study, the f_{EH-TBB} ratio in outdoor air samples from homes was calculated to be in the range of 0.94-0.99, consistent with a study conducted in Istanbul, were higher than the range determined in the Great Lakes Region of the United States, which were ranged of 0.26-0.54, and the average value determined in Canada's Subarctic region, which was 0.48 (Kurt-Karakus et al., 2017; Ma et al., 2012).

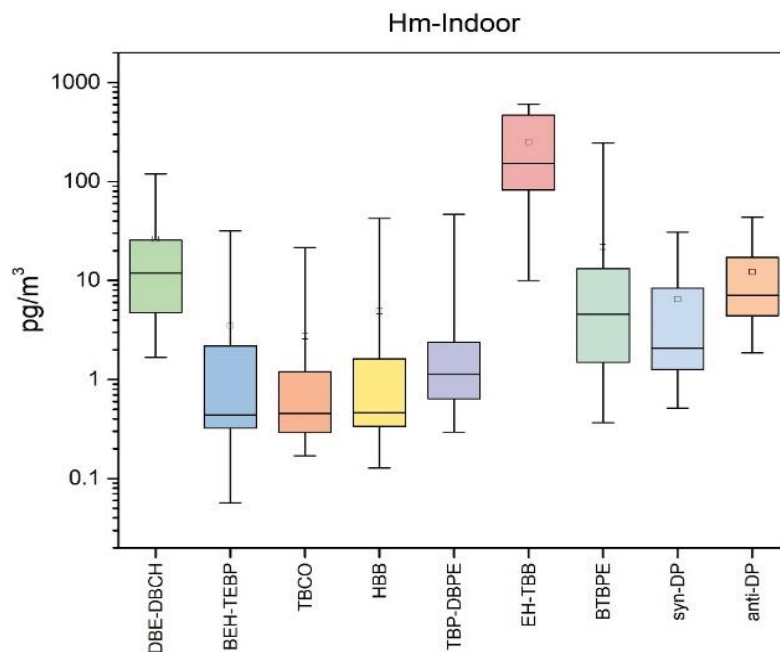


Figure 4.49. Indoor air AFR concentrations in homes

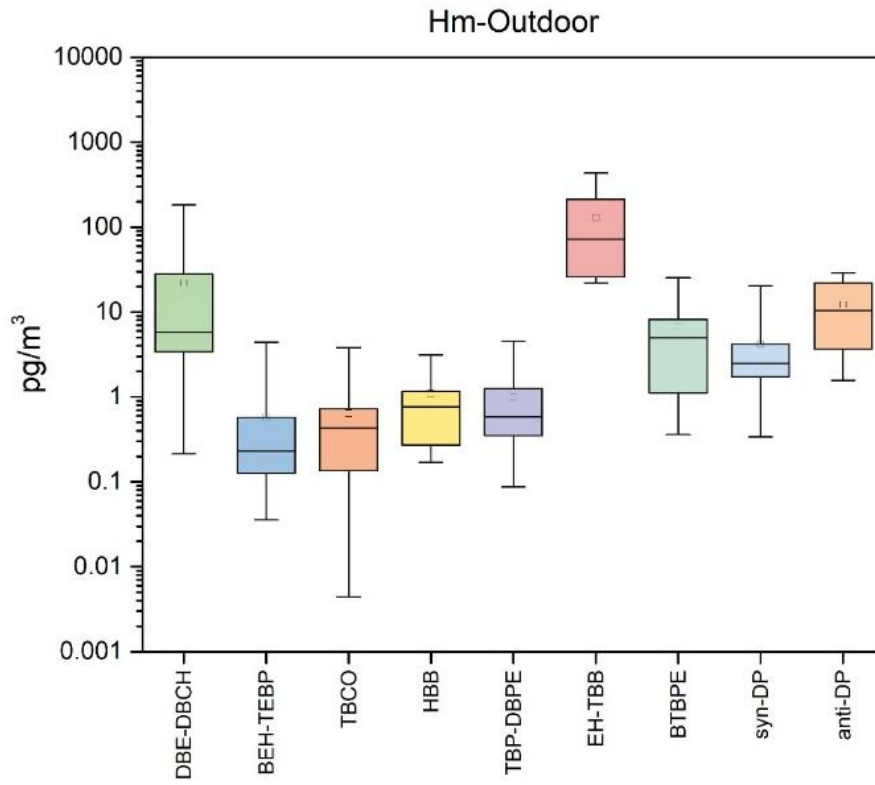


Figure 4.50. Outdoor air AFR concentrations in homes

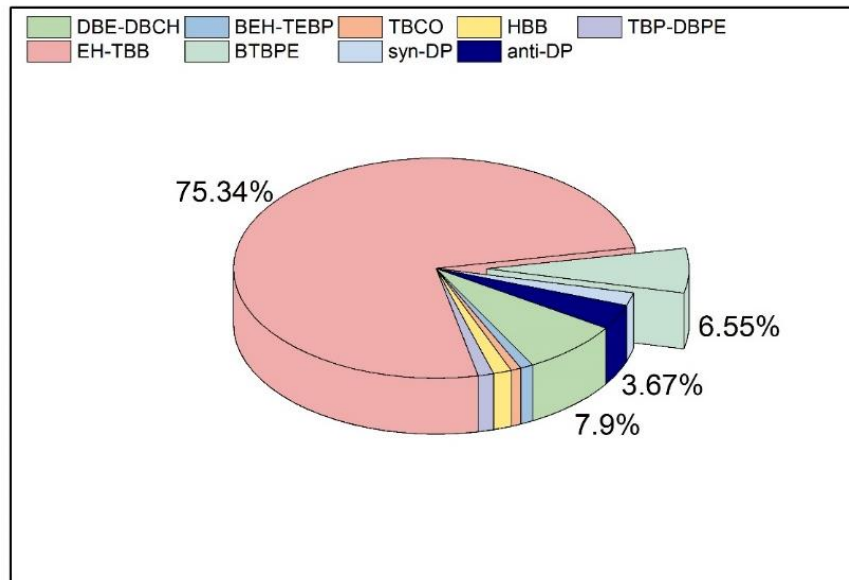


Figure 4.51. Concentration profiles of indoor air AFRs in homes

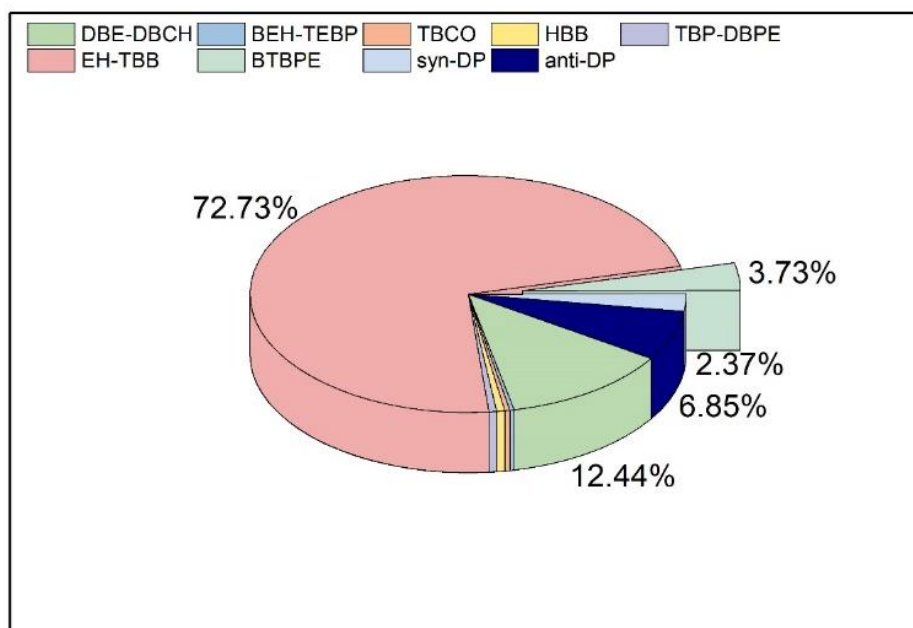


Figure 4.52. Concentration profiles of outdoor air AFRs in homes

The indoor air AFR concentrations in homes are shown in Figure 4.53. The Σ AFR levels in indoor air samples collected from homes in rural, sub-urban, and urban areas were 319, 309, and 379 pg/m^3 , respectively. In those urbanization areas, the EH-TBB was the dominant AFR compound with levels of 258, 231, and 266 pg/m^3 , respectively. When compared to median values obtained in a similar study conducted in Istanbul (Kurt-Karakus et al., 2017), indoor EH-TBB levels in homes in urban and rural areas are higher in Izmir, while the opposite was observed in sub-urban. The average Σ DBE-DBCH levels in indoor air of homes were determined to be 22.9, 18.4, and 39.5 pg/m^3 in rural, sub-urban, and urban areas, respectively, which were lower than the median values in sub-urban and urban area and higher than the median value in rural area in İstanbul (Kurt-Karakus et al., 2017). The average indoor air concentrations of BEH-TEBP, TBCO, HBB, TBP-DBPE, BTBPE, syn-DP, and anti-DP were 0.74, 0.75, 1.06, 0.86, 7.65, 10.3, and 16.9 pg/m^3 in rural homes, 10.86, 5.60, 12.23, 8.27, 12.49, 3.65, and 6.83 pg/m^3 in sub-urban homes, and 1.35, 1.72, 0.75, 3.26, 50.54, 4.74, and 11.0 pg/m^3 in urban homes. No relation has been found between the level of urbanization and indoor air AFR levels.

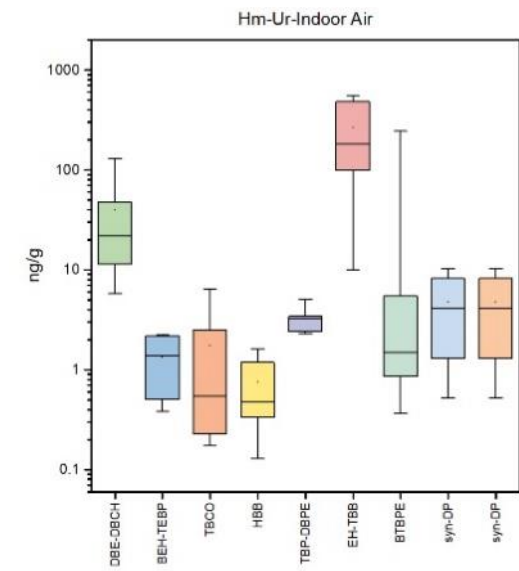
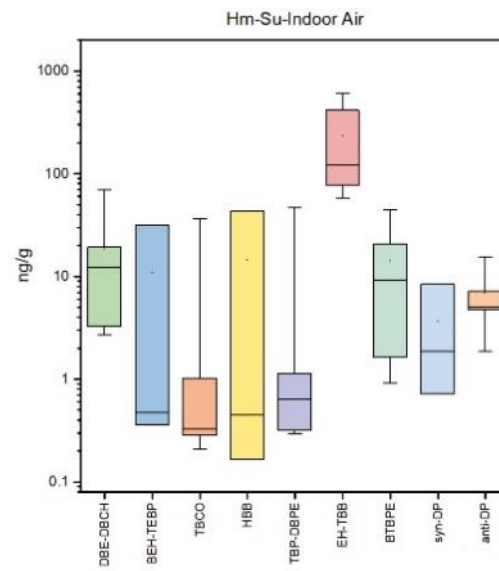
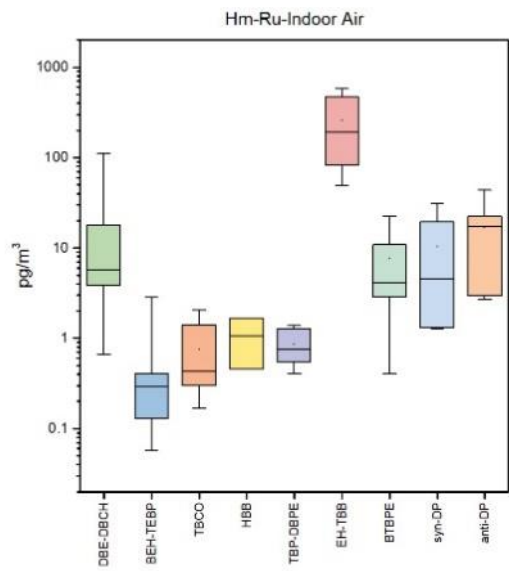


Figure 4.53. Indoor air AFR concentrations of rural, sub-urban, and urban homes

4.5. Indoor and Outdoor Settled Dust-Bound OPFR Levels in Living Environments in İzmir- TÜRKİYE

4.5.1. Settled Dust-Bound OPFRs in Schools

Indoor settled dust-bound OPFR concentrations are shown in Figure 4.54. The average indoor settled dust-bound Σ OPFR concentration in schools was determined to be 22275 ng/g, while this level was 2274 ng/g in outdoors. That was the indicator that environmental OPFRs were primarily sourced by interiors. Considering the all indoor settled dust samples from schools, the TBOEP was the most abundant OPFR compound with an average concentration of 8040 ng/g, followed by the p-TCP with 2874 ng/g, TDCPP with 2015 ng/g, and TCEP with 1940 ng/g, respectively. It is determined that the concentrations of other targeted compounds were in order of m-TCP > T2IPPP > o-TCP > TPhP > TEHP > TCPP & TCIPP > TBP > TPeP > TBP. While the detection frequencies of settled dust-bound TBP, TPhP, o-TCP, m-TCP, and p-TCP in indoor environment of schools were 86%, 62%, 71%, 95%, and 52%, respectively, other targeted OPFRs were detected in all samples. TPhP In a study conducted in China, the Σ OPFR concentration in dust samples taken from a university's computer laboratory was determined to be 16400 ng/g (Peng et al., 2017), while in Germany schools settled dust-bound Σ OPFR concentration was ranged from 10590 ng/g to 95290 ng/g, with an average of 42460 ng/g (Zhou et al., 2017). The I/O settled dust-bound concentration ratios of OPFRs in schools are shown in Figure 4.55. Although the obtained I/O ratios generally indicate the effect of indoor sources on OPFR concentrations, it is determined that the I/O ratio of p-TCP and TBOEP compounds in sub-urban areas is below 1. Studies on OPFR levels in schools are relatively limited compared to those conducted in homes and workplaces (especially in dust). Therefore, the obtained results will contribute valuable information to the literature and public health mitigation efforts.

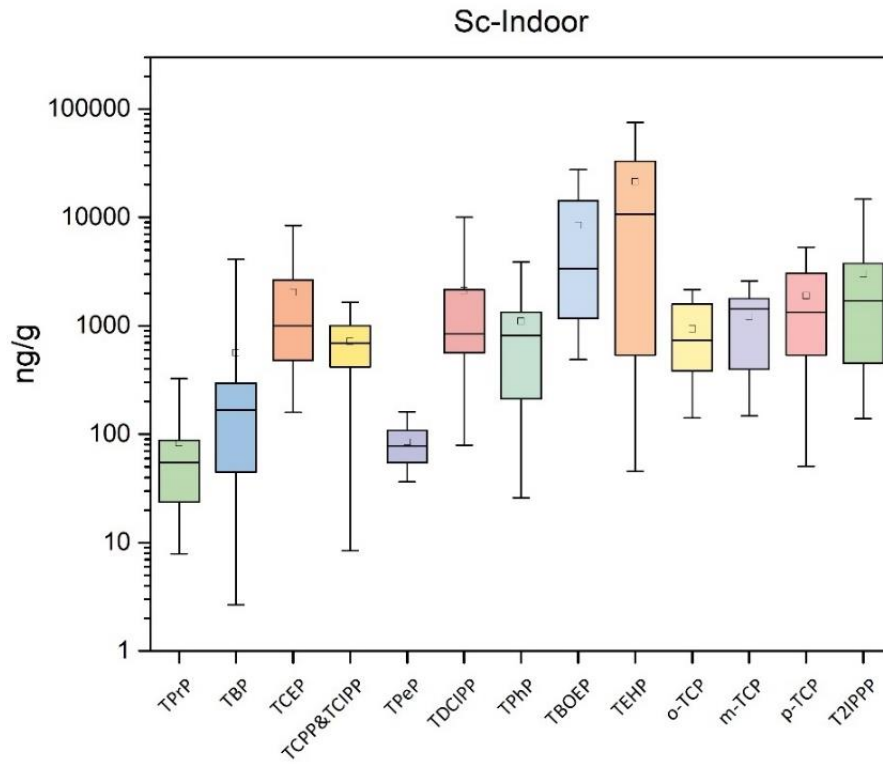


Figure 4.54. Settled dust-bound OPFR concentrations in indoor environments schools

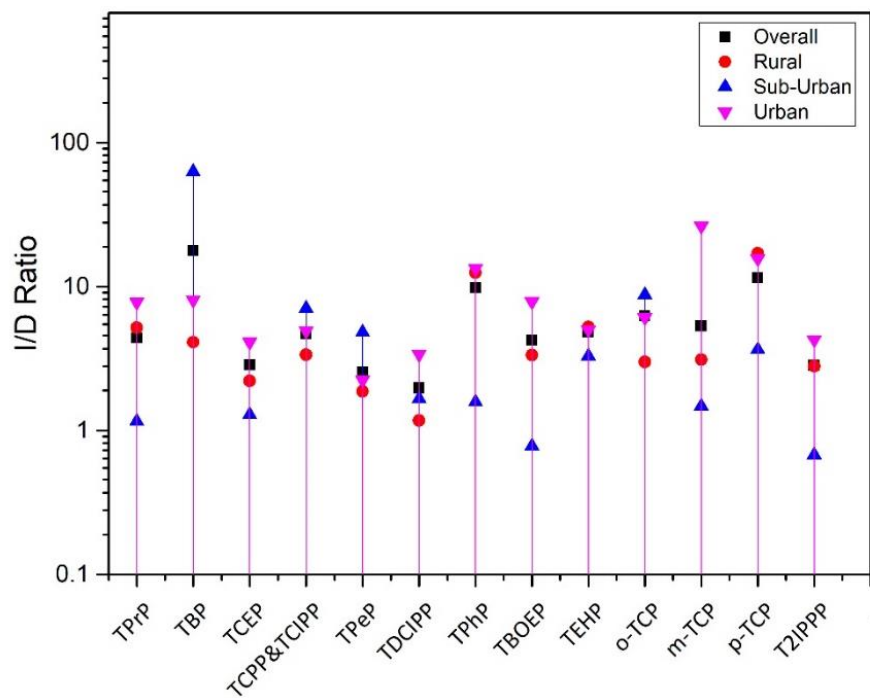


Figure 4.55. I/O concentration ratio of settled dust-bound OPFRs in schools

The indoor settled dust-bound OPFRs were segregated according to their alkyl, aryl, and chlorinated structure (Table 2.2 and Figure 4.56). While alkyl OPFR compounds contribute to 44% of the indoor settled dust-bound Σ OPFR concentration in schools, chlorinated compounds contribute 21%, and aryl compounds contribute 35%. Also, the similar segregation profile was determined in outdoor samples (Figure 4.56). When settled dust samples were grouped according to the level of urbanization, the contribution of alkyl compounds to Σ OPFR concentration in interiors of schools in rural, sub-urban, and urban areas were determined to be 47%, 34%, and 44%, respectively, while those in outdoors were in the range between 40-42%. The contribution of chlorinated compounds to Σ OPFR concentration in indoors of schools were at levels of 20-21% in rural and urban areas, while slightly higher (24%) in sub-urban schools. The contribution of aryl compounds to indoor settled dust-bound Σ OPFR concentration in sub-urban schools increases from 33-35% to 43% compared to be in rural and urban areas. This trend also shown in outdoor samples. The contribution of the TBOEP compound to both indoor and outdoor dust samples is higher than that of other OPFR compounds (Figure 4.57 and Figure 4.58). In a study conducted in Bursa, it was determined that TBOEP was the OPFR compound with the highest concentration in soil and indoor air samples (Kurt-Karakus et al., 2018). When the concentration profile obtained in dust samples compared with indoor and outdoor air samples, it is observed that the contribution of alkyl OPFR compounds increases in dust. The low volatility ($\log K_{OA} = 9.59$) and tendency to adhere to organic surfaces ($K_{OC} = 44000$) of TCP isomers lead to their accumulation in the particulate phase, thereby increasing their concentrations in dust.

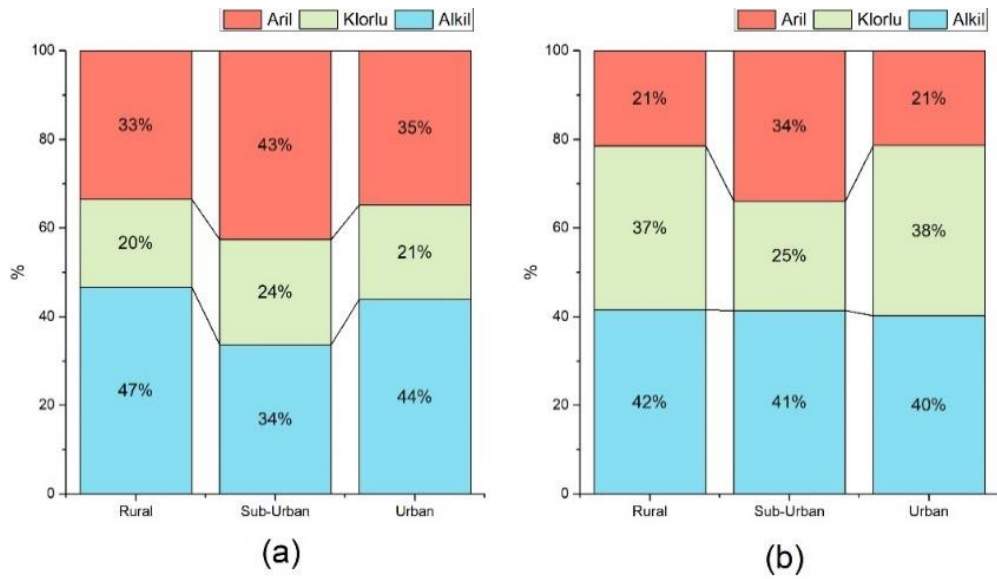


Figure 4.56. Chemical structure segregation of (a) indoor and (b) outdoor settled dust-bound OPFRs in schools

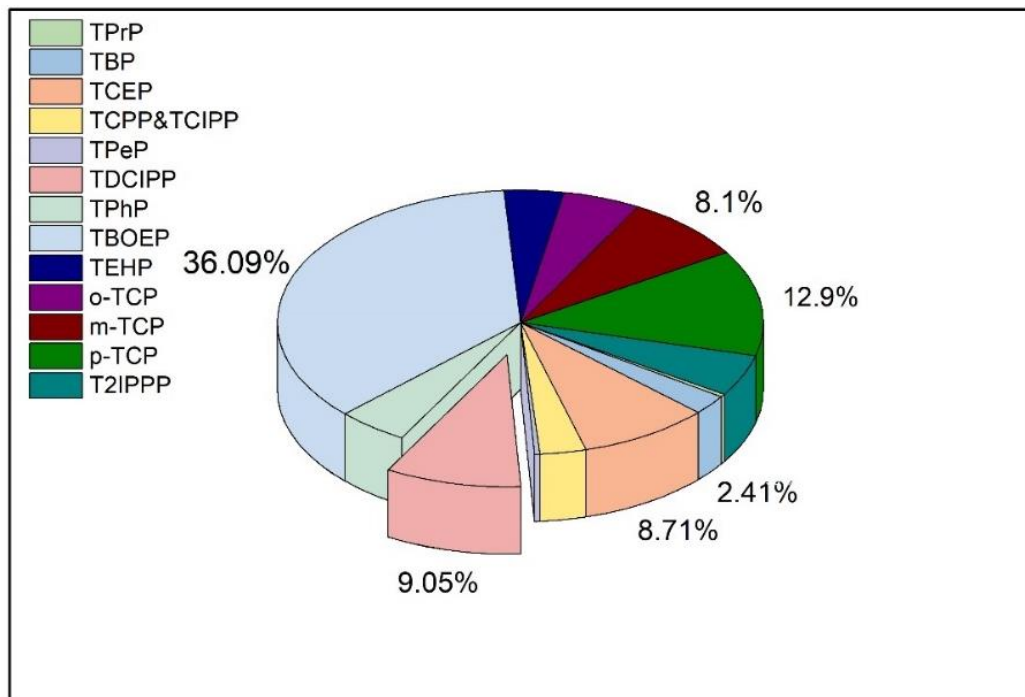


Figure 4.57. Concentration profiles of indoor settled dust-bound OPFRs in schools

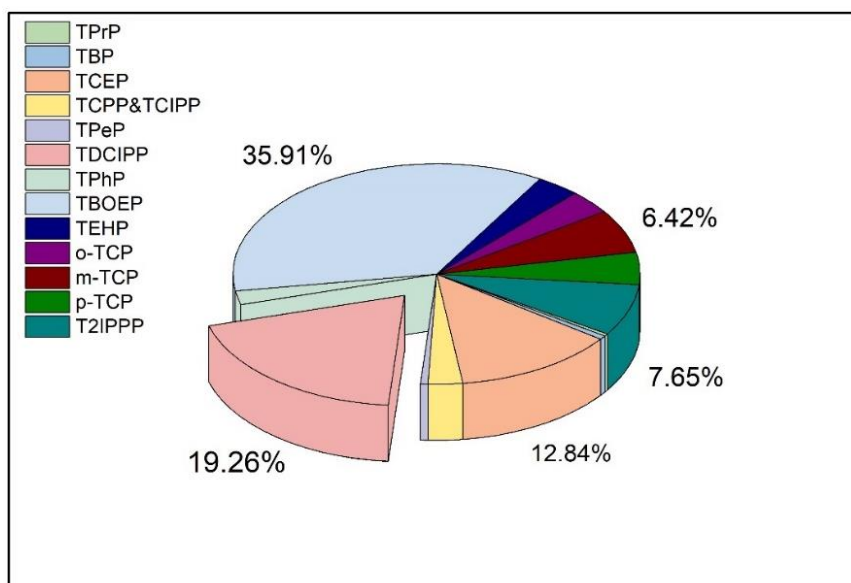


Figure 4.58. Concentration profiles of outdoor settled dust-bound OPFRs in schools

Rural, sub-urban, and urban segregated indoor settled dust-bound OPFR concentrations in schools are shown in Figure 4.59. While the average indoor settled dust-bound Σ OPFR concentration in rural schools was determined to be 19860 ng/g, those in sub-urban and urban were 8529 ng/g and 37991 ng/g, respectively. TBOEP was the most abundant OPFR in indoor settled dust samples taken from rural and urban schools with average of 7944 ng/g and 15155 ng/g, respectively, while in sub-urban schools was the second abundant OPFR compound. The concentrations of TCP isomers, those are OPFR compounds in tendency to accumulate in particle phase, were determined to be the second-abundant OPFRs in both rural and urban schools (Σ TCP_{rural}=3496 ng/g and Σ TCP_{urban}=10082 ng/g), while in sub-urban areas, with an average concentration of 3572 ng/g (Σ TCP), they were dominant in the concentration profile of OPFRs. The increase in urbanization level from rural to urban was found to increase the concentrations of TCPP&TCIPP. However, for other compounds, this phenomenon does not affect a significant trend of increase or decrease in the concentrations. Also, the distance to Aliğa OSB does not affect the levels of OPFR compounds. In fact, the school located in Yağcılar village, where the lowest PCB and PBDE levels were determined, not only has the highest indoor dust OPFR levels for rural schools but also has the fourth-highest concentration within the sampling dataset. This could be explained using alternative flame retardant-containing products instead of building materials and equipment containing legacy flame retardants, such as PBDEs.

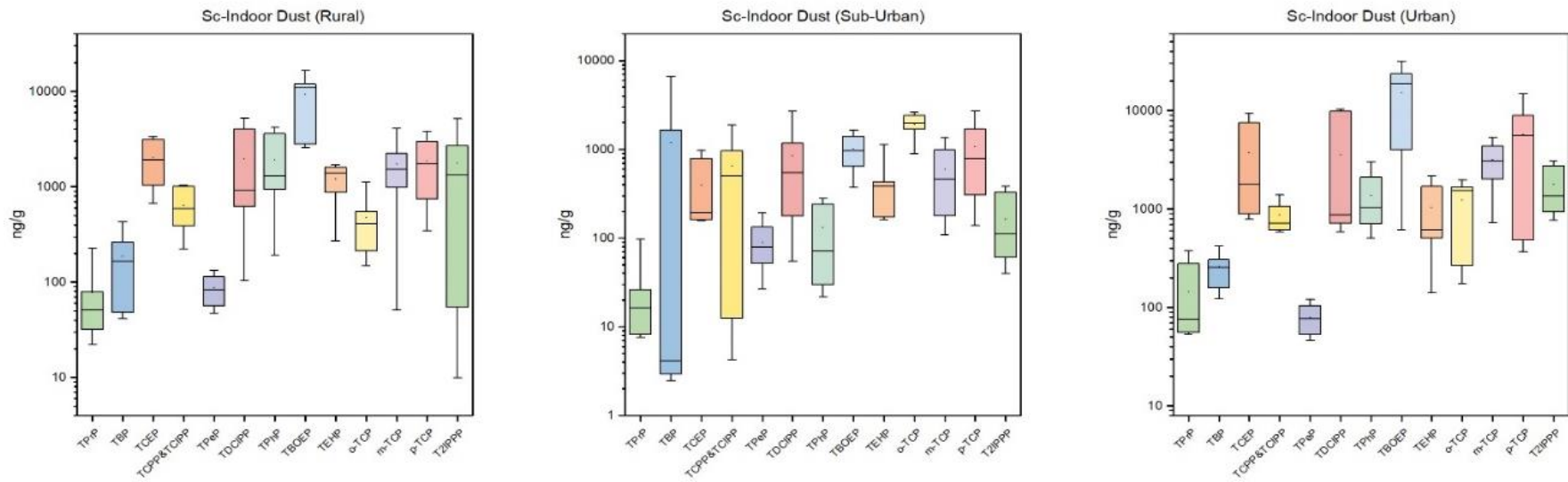


Figure 4.59. Indoor settled dust-bound OPFR concentrations of rural, sub-urban, and urban schools

4.5.2. Settled Dust-Bound OPFRs in Homes

The concentrations of OPFR compounds in indoor dust samples taken from homes are shown in Figure 4.60. The average Σ OPFR concentration in indoor dust in homes was determined to be 10516 ng/g. The OPFR compound with the highest concentration in indoor settled dust samples taken from homes was determined to be TBOEP with an average of 6084 ng/g, followed by TDCIPP with an average of 2152 ng/g. Among the aryl OPFRs, the average o-TCP concentration was determined to be 1193 ng/g, while the other isomers, p-TCP and m-TCP, were 1039 ng/g and 630 ng/g, respectively. The other two aryl OPFR compounds, TPhP and T2IPPP, which were determined at lower levels in settled dust samples taken from homes compared to TCP isomers, with an average of 48.1 ng/g and 11.0 ng/g, respectively. While the detection frequencies of settled dust-bound TEHP and o-TCP in homes were 81% and 86%, respectively, other targeted OPFR detection frequencies were >90%. In a study conducted in China (Peng et al., 2017), the median Σ OPFR concentration in indoor settled dust was determined to be 11500 ng/g, while in a study conducted in Germany (Zhou et al., 2017), the determined median concentration was 14000 ng/g. In a study conducted in Japan, the median Σ OPFR level determined in dust samples was at levels of 576730 ng/g (Araki et al., 2014). However, a study conducted in Egypt in 2014 determined Σ OPFR levels in dust much lower at 160 ng/g (Abdallah and Covaci, 2014). In a sampling study conducted in Greece between 2010 and 2014, the median Σ OPFR level was determined to be 7140 ng/g (Li et al., 2019). In addition to Greece, this study examined Σ OPFR levels in dust in 11 other countries. According to their results, the median Σ OPFR concentration in settled dust was 374 ng/g in Colombia, 1120 ng/g in China, 276 ng/g in India, 29800 ng/g in Japan, 4420 ng/g in Kuwait, 138 ng/g in Pakistan, 4110 ng/g in Romania, 5310 ng/g in Saudi Arabia, 31300 ng/g in South Korea, and 26500 ng/g in the United States. The OPFR levels determined in dust samples taken from homes in this project fall within the range determined in the literature, and it is believed that OPFR levels may be associated with income levels directly affecting the frequency of electronic appliances, furniture, and renovation activities.

The I/O concentration ratios of OPFRs in homes are shown in Figure 4.61. It was observed that the effect of indoor sources on OPFR levels in dust samples is more

dominant compared to outdoor sources. The compound with the highest average concentration level in outdoor dust was TBOEP ($C_{out} = 1940 \text{ ng/g}$), as observed in indoor environments. In outdoor dust, the concentrations of OPFR compounds were ranked as follows: TBOEP > TDCIPP > T2IPPP > TCEP > m-TCP > TEHP > p-TCP > TCPP & TCIPP > o-TCP > TPhP > TPeP > TBP > TPrP.

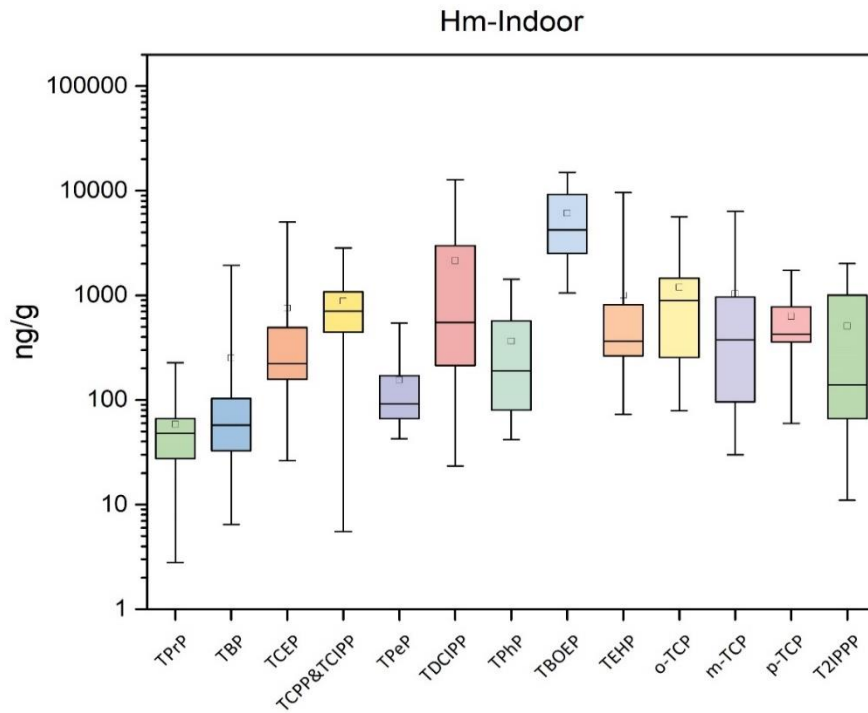


Figure 4.60. Settled dust-bound OPFR concentrations in indoor environments of homes

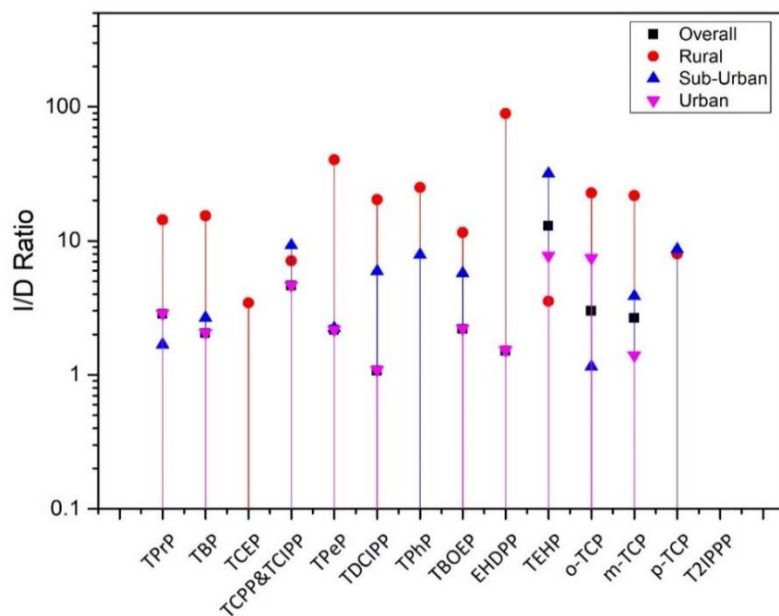


Figure 4.61. I/O concentration ratio of settled dust-bound OPFRs in homes

The segregated concentrations of alkyl, chlorinated, and aryl OPFR compounds in indoor settled dust samples from homes is shown in Figure 4.62. The contributions of alkyl, chlorinated, and aryl OPFR compounds to the indoor settled dust-bound Σ OPFR concentration in homes were determined to be 51%, 25%, and 24%, respectively, while those in outdoor were 40%, 32%, and 28%, respectively. The contribution of alkyl compounds to the Σ OPFR concentration in indoor dust were similar across three different urbanization levels (between 47% and 53%), whereas in rural areas, the contribution of aryl compounds was relatively low, and that of chlorinated compounds was higher than that in sub-urban and urban. In outdoor dust, the contribution profile of alkyl, chlorinated, and aryl OPFR compounds to the Σ OPFR concentration were similar, while in sub-urban areas, the contribution of aryl OPFR compounds is relatively higher, and that of chlorinated and alkyl compounds is lower. This situation, as shown in Figure 4.63, Figure 4.64, and Figure 4.65, has been caused by the high concentration of the T2IPPP at the Seferihisar (sub-urban) sampling point, leading to a change in the OPFR profile.

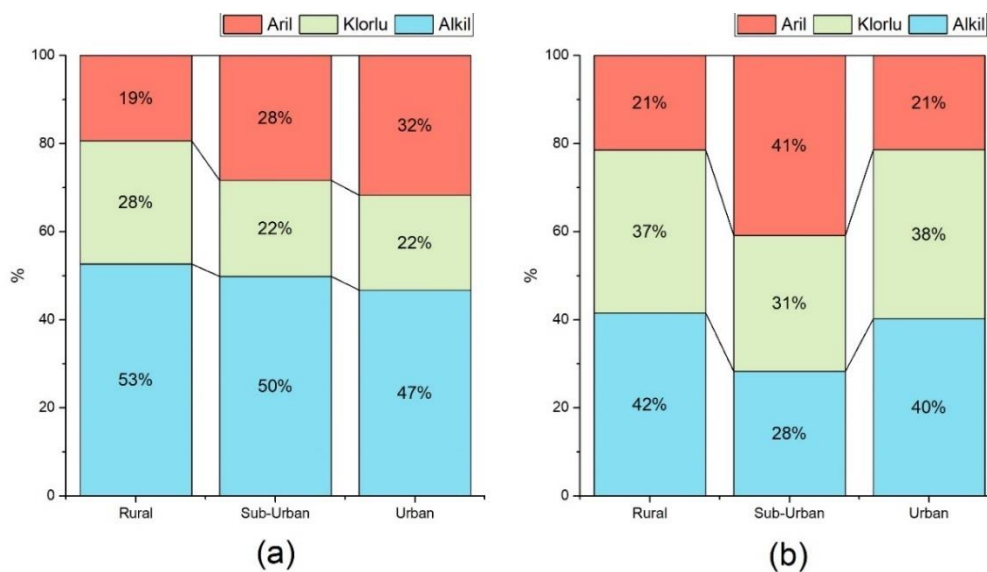


Figure 4.62. Chemical structure segregation of (a) indoor and (b) outdoor settled dust-bound OPFRs in homes

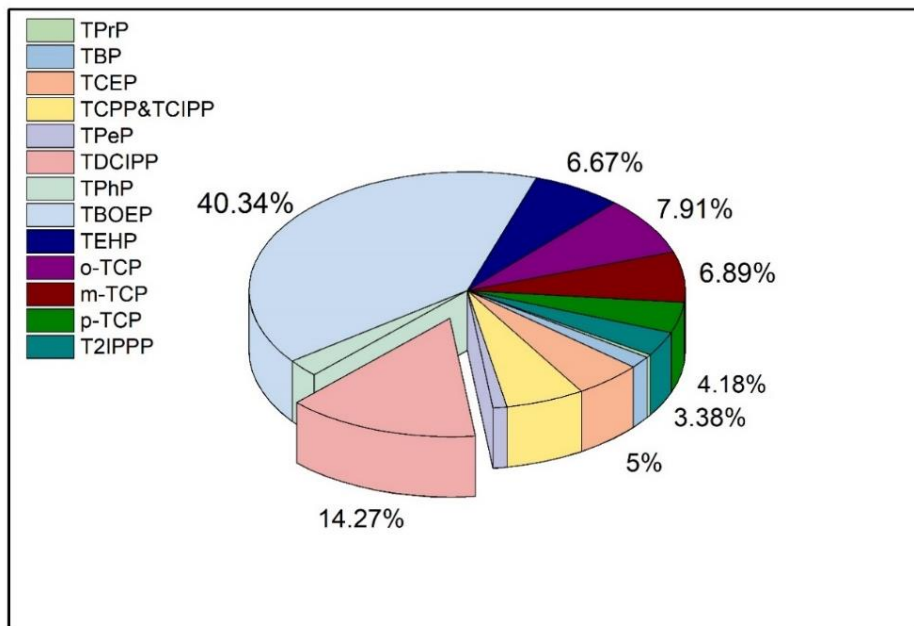


Figure 4.63. Concentration profiles of indoor settled dust-bound OPFRs in homes

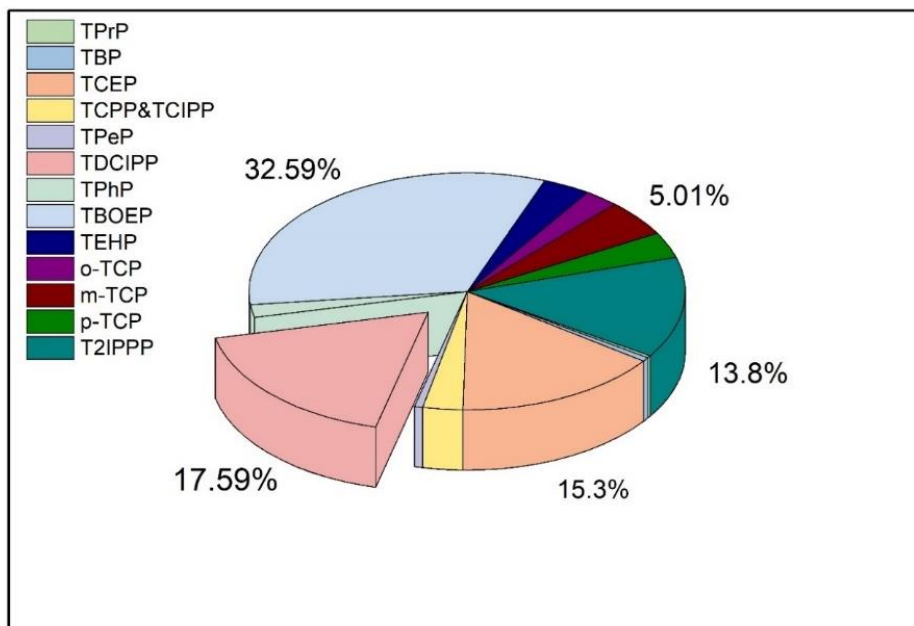


Figure 4.64. Concentration profiles of outdoor settled dust-bound OPFRs in homes

The effect of urbanization on indoor settled dust-bound OPFR concentration in homes is shown in Figure 4.65. The average Σ OPFR concentration in indoor dust was determined to be 23724 ng/g in rural area, 9187 ng/g in sub-urban area, and 8735 ng/g in urban area. The compound with the most abundant, TBOEP, has average concentrations in indoor settled dust from homes in rural, sub-urban, and urban areas of 9425, 4327, and 4247 ng/g, respectively. The average concentration of TDCIPP in these areas were 4170, 827, and 1124 ng/g, respectively, while the $C_{\Sigma TCP}$ was determined to be 3403, 2046, and 3401 ng/g, respectively. In sub-urban and urban areas, o-TCP concentrations dominate the isomer concentration profile of TCP, while m-TCP suppress in rural areas. The concentration of T2IPPP decreases from 1202 ng/g in rural area to 283 ng/g in sub-urban area, and it is determined to be 81 ng/g in urban area. For other OPFR compounds, there is no clear trend in dust-bound OPFR concentrations in homes between rural and urban. In this context, the dust levels obtained in dust samples generally do not seem to be influenced by the level of urbanization, indicating that the TBOP compound may be found in high concentrations in both dust and air samples.

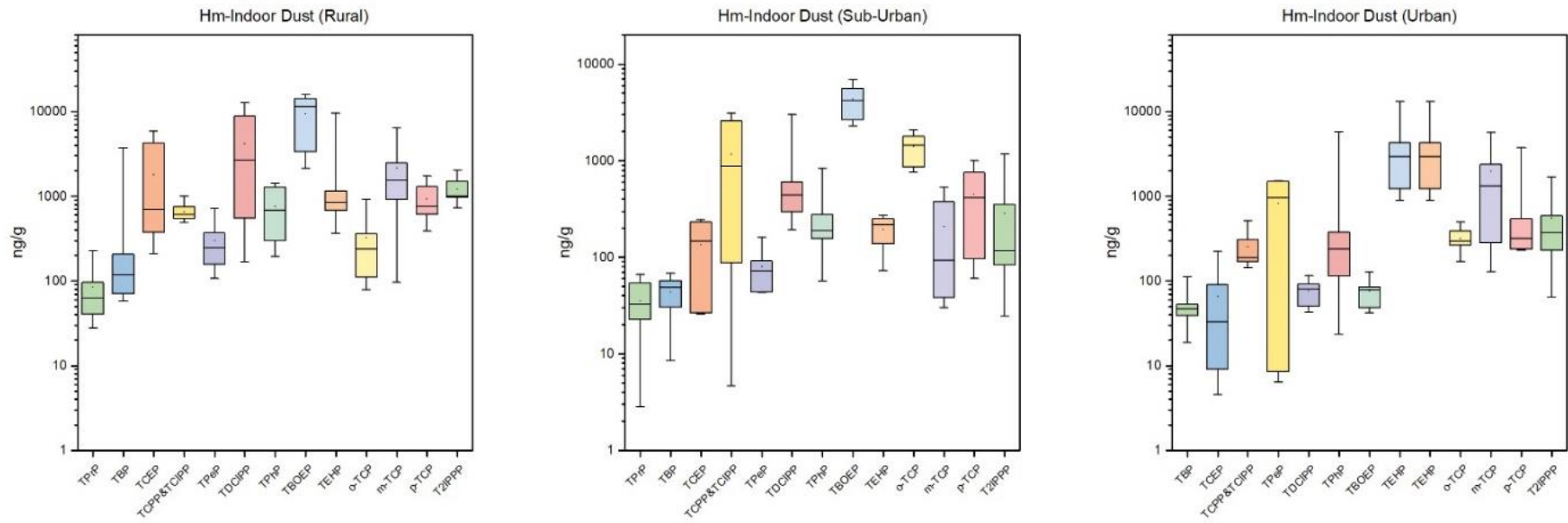


Figure 4.65. Indoor settled dust-bound OPFR concentrations of rural, sub-urban, and urban homes

4.5.3. Settled Dust-Bound OPFRs in C/B/Rs

The settled dust-bound OPFR concentrations in C/B/Rs are shown in Figure 4.66. All targeted OPFRs were detected in all settled dust samples taken from C/B/Rs. The average indoor settled dust-bound Σ OPFR concentration in C/B/Rs was determined to be 14943 ng/g. TBOEP was the most abundant OPFR in indoor dust of C/B/Rs, with an average concentration of 3860 ng/g. Following TBOEP, the concentrations were as follows: 2208 ng/g for TDCPP, 2067 ng/g for TCEP, 1701 ng/g for m-TCP, 1159 ng/g for TEHP, 1010 ng/g for TPhP, 932 ng/g for T2IPPP, 828 ng/g for TCP & TCIPP, 582 ng/g for p-TCP, 215 ng/g for TBP, 187 ng/g for o-TCP, 124 ng/g for TPrP, and 66.8 ng/g for TPeP. Among all C/B/Rs sampling points, alkyl, chlorinated, and aryl OPFR compounds account for 36.3%, 34.2%, and 29.5% of the settled dust-bound Σ OPFR concentrations, respectively. While TBOEP was the dominant alkyl compounds, TDCPP was dominant among chlorinated OPFRs, and m-TCP compound was dominant among aryl OPFRs (Figure 4.67 and Figure 4.68). It is determined that the contribution of aryl, chlorinated, and alkyl were segregated similar (37%, 31%, and 32%, respectively), while in sub-urban areas, the contribution of aryl compounds to Σ OPFR concentration has decreased relatively. In sub-urban and urban areas, the contribution of chlorinated and alkyl compounds to Σ OPFR concentration was at similar (34%-37% in sub-urban area and 36%-38% in urban area).

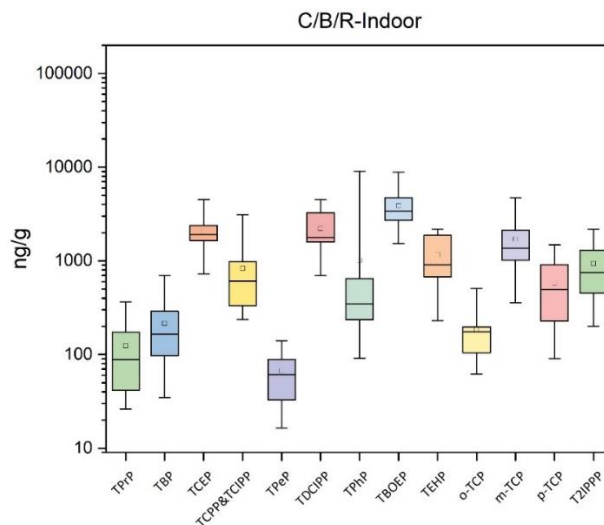


Figure 4.66. Settled dust-bound OPFR concentrations in indoor environments of C/B/Rs

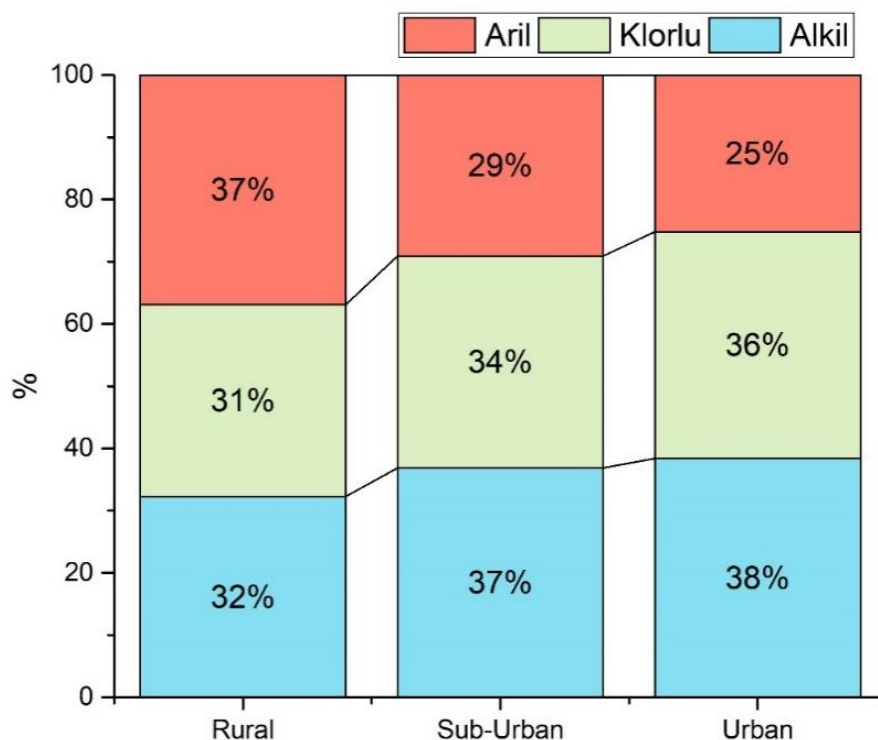


Figure 4.67. Chemical structure segregation of (a) indoor and (b) outdoor settled dust-bound OPFRs in C/B/Rs

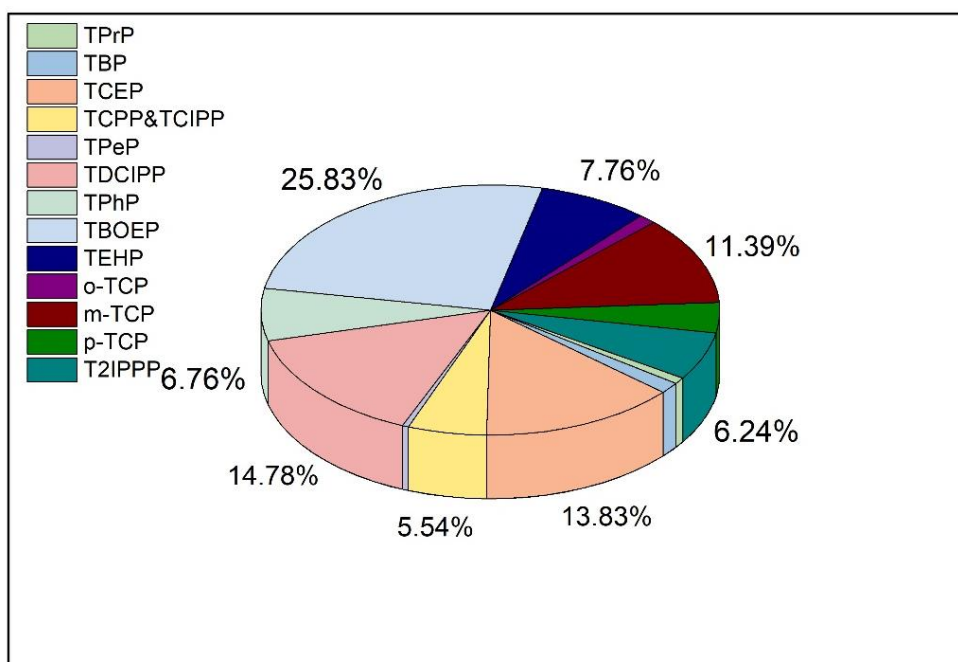


Figure 4.68. Concentration profiles of indoor settled dust-bound OPFRs in C/B/Rs

The effect of urbanization on the concentration of settled dust-bound OPFRs is shown in Figure 4.69. In rural C/B/Rs, the average settled dust-bound Σ OPFR concentration was 12982 ng/g, with the average concentration of TBOEP, an alkyl compound, determined to be 2996 ng/g. The average settled dust-bound TPhP concentration, an aryl compound, in C/B/Rs sampling points in rural areas was determined to be 2423 ng/g, while the average settled dust-bound concentration of m-TCP, aryl OPFR compound, was 1082 ng/g. The average concentrations of chlorinated OPFR compounds TCEP and TDCPP in rural area were 1939 ng/g and 1567 ng/g, respectively. In sub-urban area, the average settled dust-bound Σ OPFR concentration in C/B/Rs is determined to be 19297 ng/g, while in urban areas, the average Σ OPFR concentration is 13348 ng/g. Similarly to rural area, TBOEP was determined to be both the dominant compound in the alkyl OPFR profile and the compound with the highest concentration among the targeted compounds in sub-urban ($C_{\text{TBOEP-sub urban}}=4819$ ng/g) and urban ($C_{\text{TBOEP-urban}}=3797$ ng/g) areas.

The concentration ranking of compounds in the alkyl OPFR profile in all three levels of urbanization was as follows: TBOEP>TEHP>TBP>TPeP>TPrP, while the ranking of chlorinated OPFR compounds was determined as TDCPP>TCPP & TCIPP>TCEP. In rural areas, the concentration of TPhP compound ($C_{\text{TPhP-rural}}=2423$ ng/g) was dominant in the aryl OPFR profile, with the concentrations of aryl OPFRs being ranked as TPhP>m-TCP>T2IPPP>p-TCP>o-TCP. In sub-urban and urban areas, the compound with the highest concentration in the aryl OPFR profile was m-TCP ($C_{\text{m-TCP-sub urban}}=2550$ ng/g and $C_{\text{m-TCP urban}}=1549$ ng/g). The concentrations of aryl OPFR compounds in sub-urban area were ranked as m-TCP>T2IPPP>p-TCP>TPhP>o-TCP, while in urban areas, they were ranked as m-TCP>T2IPP>p-TCP>TPhP>o-TCP.

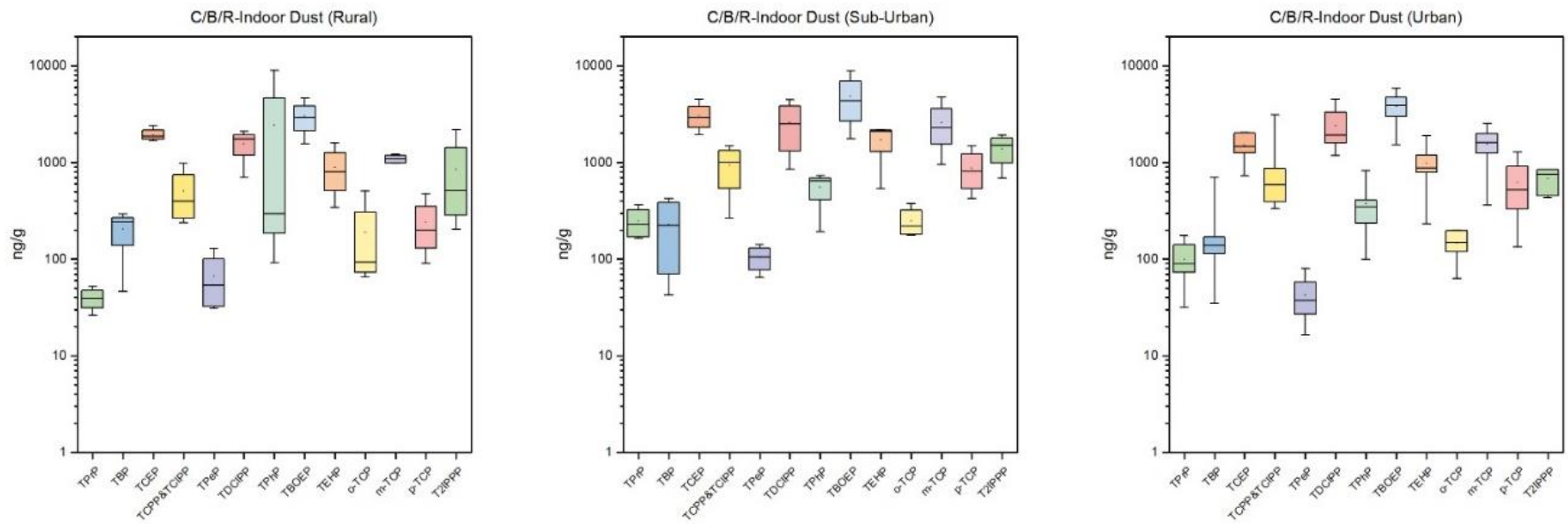


Figure 4.69. Indoor settled dust-bound OPFR concentrations of rural, sub-urban, and urban C/B/R

4.6. Indoor and Outdoor Air OPFR Levels in Living Environments in İzmir- TÜRKİYE

4.6.1. Indoor and Outdoor Air OPFRs in Schools

The indoor air OPFR concentrations in schools are shown in Figure 4.70. The average indoor air Σ OPFR concentration in schools was determined to be those similar in homes, at 32.3 ng/m³. While the detection frequencies of TBP, TPhP, o-TCP, m-TCP, and p-TCP in indoor air samples taken from schools were 86%, 62%, 71%, 95%, and 52%, respectively, others were detected in all samples. The most abundant OPFR compound in indoor air of schools was determined to be TBOEP, with an average of 12.9 ng/m³, followed by TCEP at 10.2 ng/m³. The average concentration of TDCIPP in indoor air was determined to be 3.91 ng/m³, while TCPP & TCIPP was 1.93 ng/m³, TPrP was 1.06 ng/m³ and TBP 1.02 ng/m³. The concentrations of other OPFR compounds were found to be less than 1 ng/m³ on average. The I/O concentration ratios of OPFR compounds in schools are shown in Figure 4.71. An I/O concentration ratio above 1 for all compounds indicates that the OPFRs in indoor air of schools were sourced by indoor sources, mass transport from outdoor to indoor environment was minimal. In a study conducted in Germany in different locations, it was stated that the Σ OPFR concentrations in indoor air ranged from 3.30 to 751 ng/m³ (median Σ OPFR = 40.2 ng/m³) (Lingli Zhou et al., 2017). Additionally, it was mentioned that OPFR levels in indoor air were 7 times higher, with a median Σ OPFR level in indoor air of schools determined to be close to our average concentration level at 36.2 ng/m³. In their study, Zhou et al. (2017) reported that while the concentration profile of OPFR compounds varied in indoor air samples collected from automobiles, homes, schools, flooring/carpet stores, nursing homes, and building supply stores, chlorinated OPFRs were dominant in other indoor environments, while non-chlorinated OPFRs were dominant in nursing homes, flooring/carpet stores, and schools.

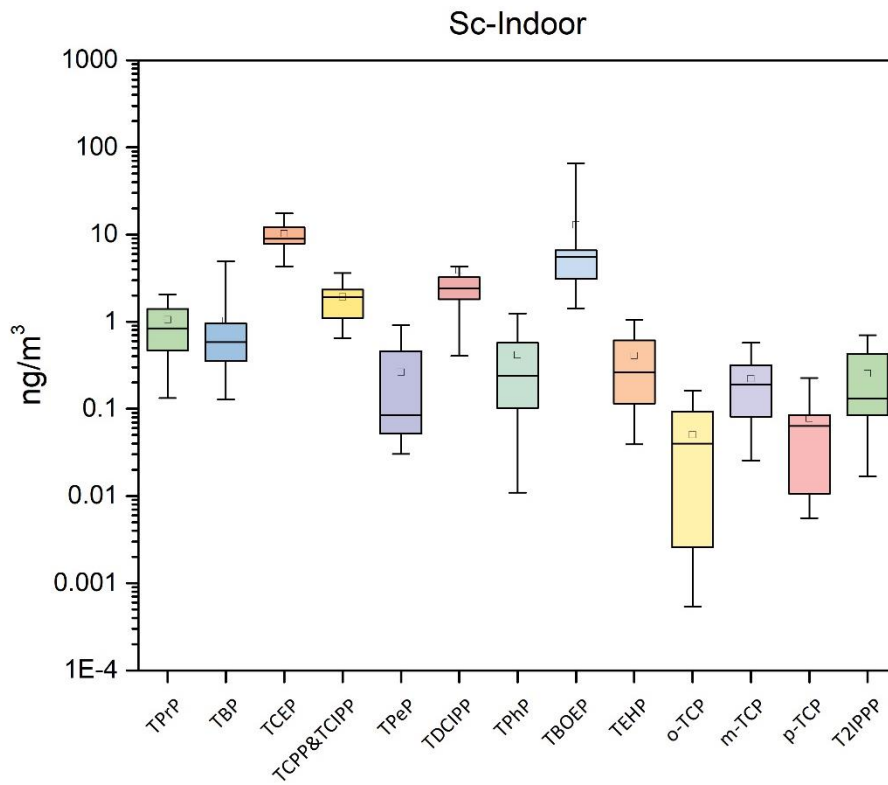


Figure 4.70. Indoor air OPFR concentrations in schools

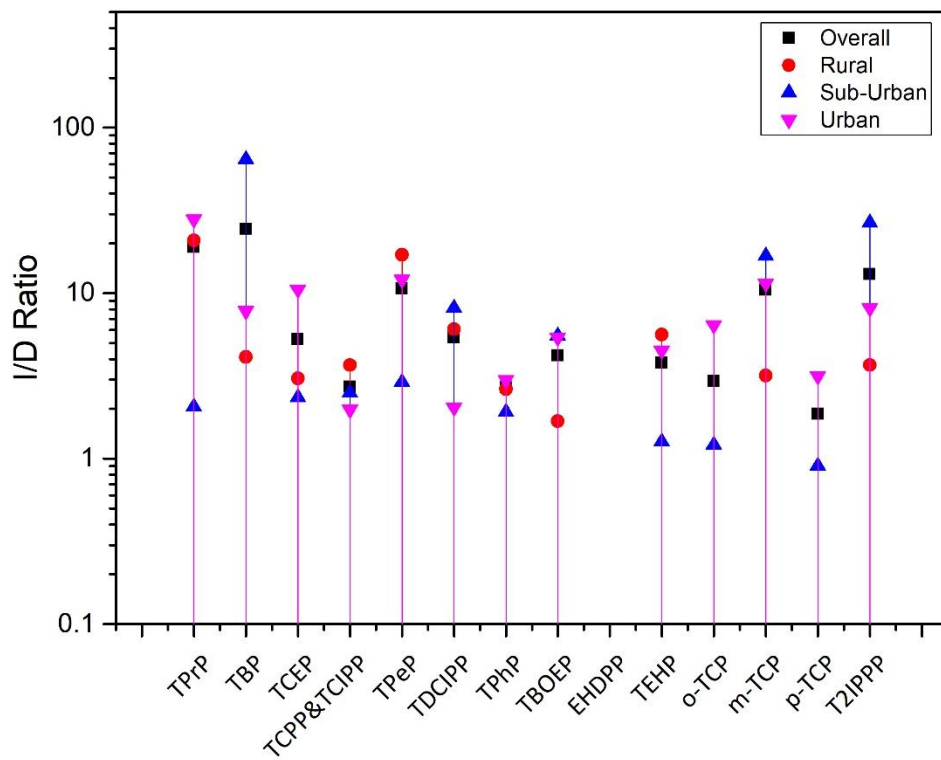


Figure 4.71. I/O concentration ratio of OPFRs in air at schools

The contribution of alkyl, chlorinated, and aryl OPFR compounds to the Σ OPFR concentration is shown in Figure 4.72, while indoor and outdoor air OPFR concentration profile is shown in Figure 4.73 and Figure 4.74, respectively. In indoor air samples collected from schools, the contributions of alkyl, chlorinated, and aryl OPFR compounds to the Σ OPFR concentration were determined to be 47.9%, 49.7%, and 2.40%, respectively, while in outdoor air, those were 39.5%, 57.6%, and 2.90%, respectively. Since the outdoor air samples are from nearby areas, they are expected to be similar to the outdoor air in homes due to the infiltration of outdoor air. However, when comparing indoor samples, it is observed that the contribution of alkyl OPFR compounds to the total concentration of targeted OPFRs increases. The most abundant alkyl OPFR was TBOEP, while TCEP was the most abundant chlorinated OPFR. In indoor air samples, as the urbanization level increases from rural to urban areas, it is observed that the contribution of alkyl OPFR compounds to Σ OPFR levels increases while the contribution of chlorinated compounds decreases. In outdoor air samples, the contribution of aryl OPFRs to Σ OPFR levels was relatively high in sub-urban and urban areas. The relatively high octanol-air partition coefficients of aryl OPFRs lead to their tendency to remain and accumulate in the particle phase. The low contribution of aryl OPFR compounds to the Σ OPFR concentrations in both indoor and outdoor air samples can be explained by their low tendency to be in the gas phase.

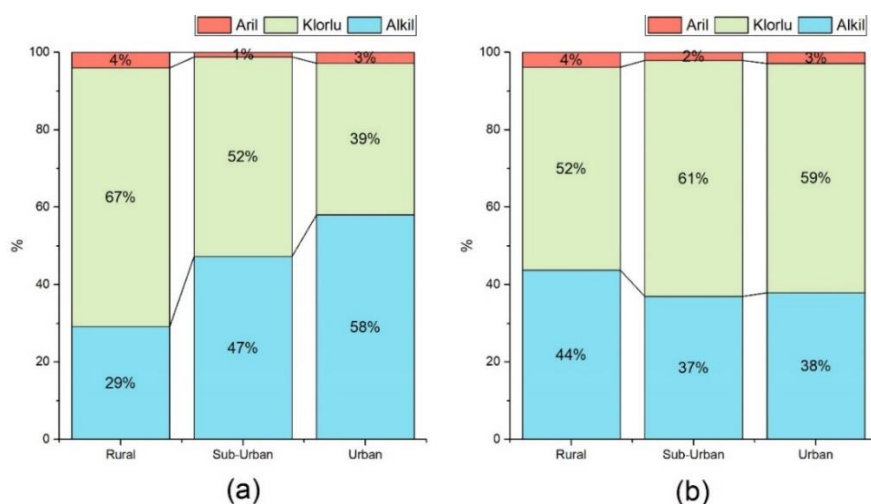


Figure 4.72. Chemical structure segregation of (a) indoor and (b) outdoor air OPFRs in schools

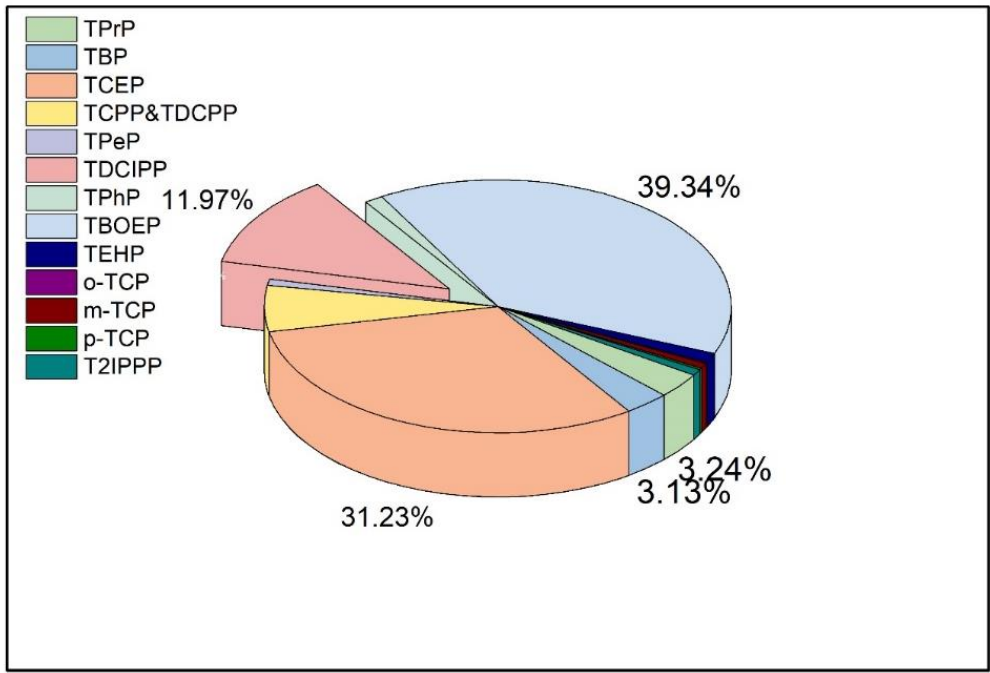


Figure 4.73. Concentration profiles of indoor air OPFRs in schools

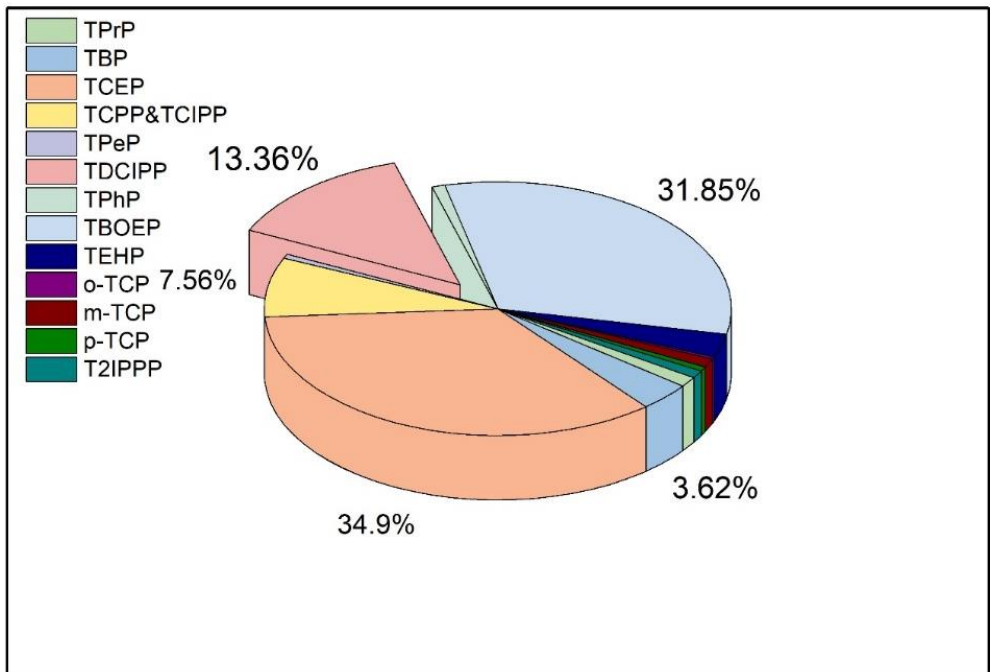


Figure 4.74. Concentration profiles of outdoor air OPFRs in schools

When indoor air samples from schools are categorized into three classes based on urbanization level (Figure 4.75), the average Σ OPFR concentration is determined to be 27.0 ng/m³ in rural areas, 34.0 ng/m³ in sub-urban areas, and 42.0 ng/m³ in urban areas, similar to the urbanization levels in homes. The average indoor air concentration of TCEP compound in rural, sub-urban, and urban areas is determined to be 10.3, 8.13, and 12.2 ng/m³, respectively, while these values for TCPP&TCIPP are 2.23, 1.70, and 1.87 ng/m³, for TDCIPP are 1.93, 7.52, and 2.28 ng/m³, and for TBOEP are 4.43, 14.0, and 20.25 ng/m³, respectively. The compounds TPrP, TBP, TPeP, TPhP, o-TCP, m-TCP, p-TCP, and T2IPPP are found to be at average levels of 0.78, 0.40, 2.23, 0.45, 0.65, 0.40, 0.02, 0.14, 0.02, and 0.35 ng/m³, respectively, in rural areas, 0.50, 0.99, 0.18, 0.27, 0.40, 0.03, 0.14, 0.05, and 0.10 ng/m³, respectively, in sub-urban areas, and 1.89, 1.68, 0.16, 0.33, 0.43, 0.08, 0.37, 0.10, and 0.32 ng/m³, respectively, in urban areas. As one moves from rural to urban areas, it is determined that the concentration of TBOEP compound in indoor air of schools increases, while no trend of increase or decrease is observed for other compounds.

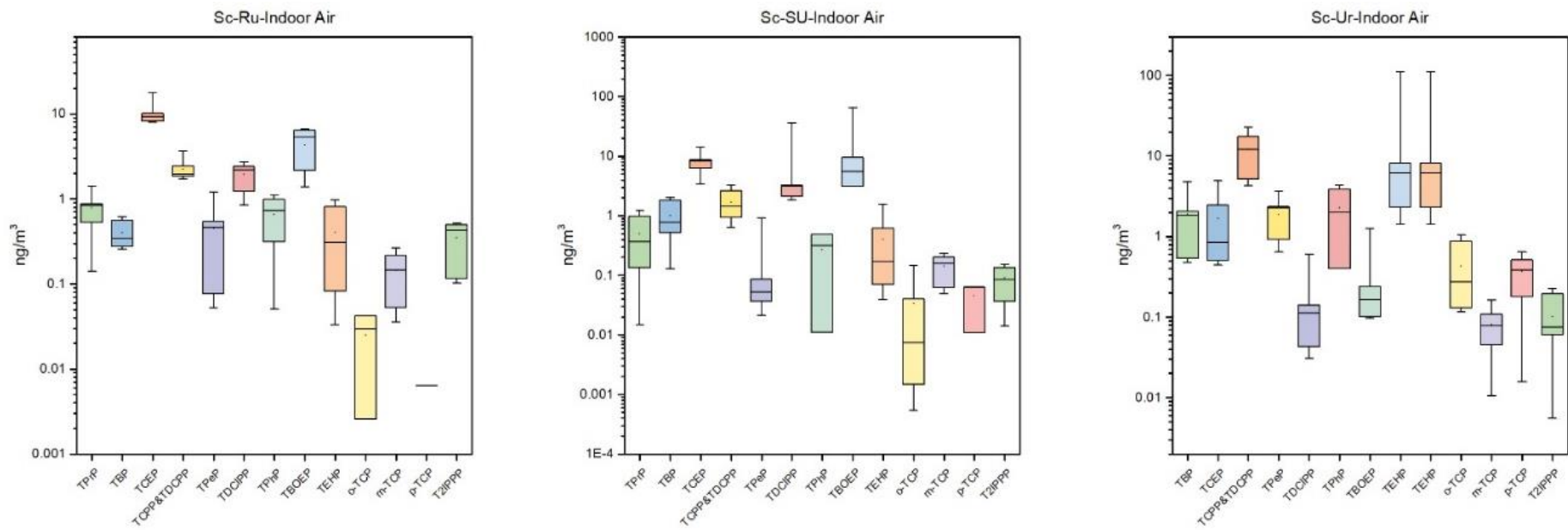


Figure 4.75. Indoor air OPFR concentrations of rural, sub-urban, and urban schools

4.6.2. Indoor and Outdoor Air OPFRs in Homes

The indoor air OPFR concentrations in homes are shown in Figure 4.76. The average Σ OPFR concentration in homes was determined to be 32.6 ng/m^3 . All targeted OPFRs were detected in all indoor air samples taken from homes. The most abundant OPFR in indoor air was determined to be TCEP, with an average of 14.8 ng/m^3 , followed by TBOEP with an average of 8.07 ng/m^3 . The average concentrations of TDCIPP and TCPP&TCIPP compounds in indoor air of homes are determined to be 3.30 and 3.27 ng/m^3 , respectively, while other targeted OPFR compounds including TPrP, TBP, TPeP, TPhP, TEHP, o-TCP, m-TCP, p-TCP, and T2IPPP were $0.95, 0.55, 0.25, 0.21, 0.84, 0.06, 0.19, 0.05, 0.06 \text{ ng/m}^3$, respectively. Since the indoor air concentrations of OPFR compounds are significantly influenced by various factors such as source density and ventilation conditions, levels ranging from pg/m^3 to $\mu\text{g/m}^3$ have been determined in the literature. In a sampling study conducted in childcare homes for newborns in China between 2013-2014 (Li et al., 2019), the average Σ OPFR concentration was determined to be 7.43 ng/m^3 , while in a sampling study conducted in homes in Norway (Xu et al., 2016), the median value of Σ OPFR concentrations in indoor air was determined to be 163 ng/m^3 . In a sampling study conducted in Australia, indoor air samples taken from homes, offices, and hotels reports the Σ OPFR levels of $23, 56, \text{ and } 58 \text{ ng/m}^3$, respectively (He et al., 2018), while in Japan, indoor air in homes determined a Σ OPFR concentration of 217 ng/m^3 (Saito et al., 2007). A study conducted in Sweden, where one of the highest levels of OPFRs in indoor environments, reported the median concentration of Σ OPFR concentration in offices could reach up to 340 ng/m^3 , and that the levels of OPFRs in both indoor and outdoor air were much higher than those of halogenated flame retardants and PBDEs (Wong et al., 2018). The I/D concentration ratios of TprP, TBP, TCPP&TCIPP, TPeP, TDCIPP, TPhP, TBOEP, TEHP, o-TCP, m-TCP, p-TCP, and T2IPPP compounds in the air are determined to be $13.3, 6.21, 2.72, 2.60, 1.75, 55.4, 15.8, 1.49, 2.09, 2.22, 1.27, 3.96, \text{ and } 2.25$, respectively (Figure 4.77). A study conducted in China in 2016 determined that the total concentration of 7 OPFR compounds (TBP, TCEP, TCPP, TCIPP, TBEP, and TPhP) in suspended particulate matter in outdoor air ranged from 1.5 to 54.6 ng/m^3 (average Σ OPFR = 19.4 ng/m^3 in sub-urban areas, average Σ OPFR = 6.6 ng/m^3 in urban areas) (Ren et al., 2016).

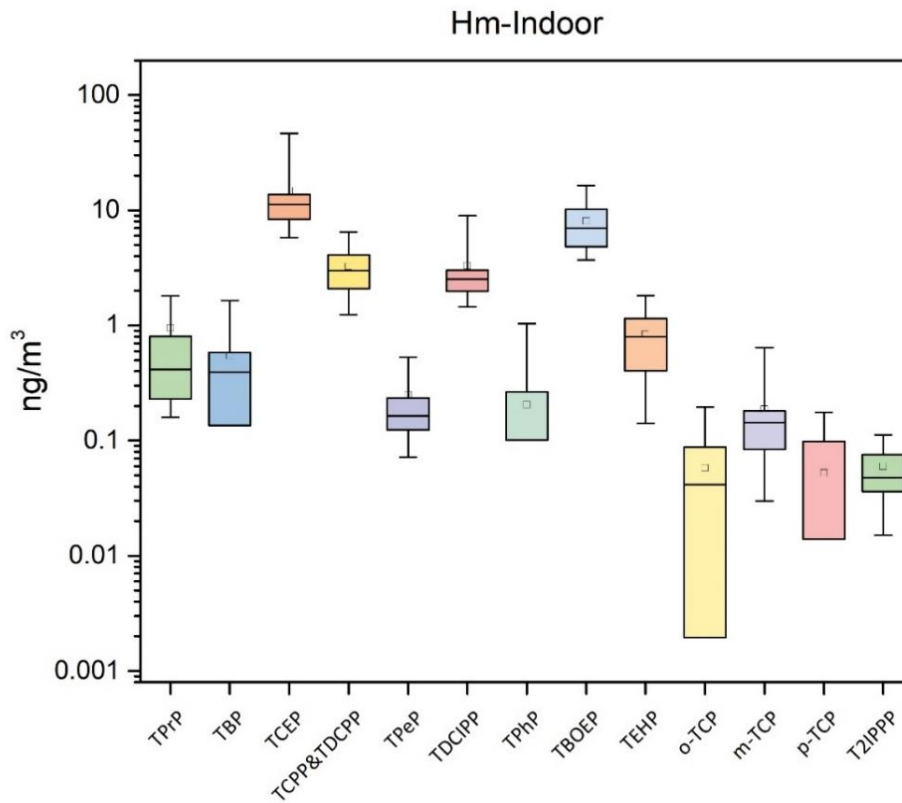


Figure 4.76. Indoor air OPFR concentrations in homes

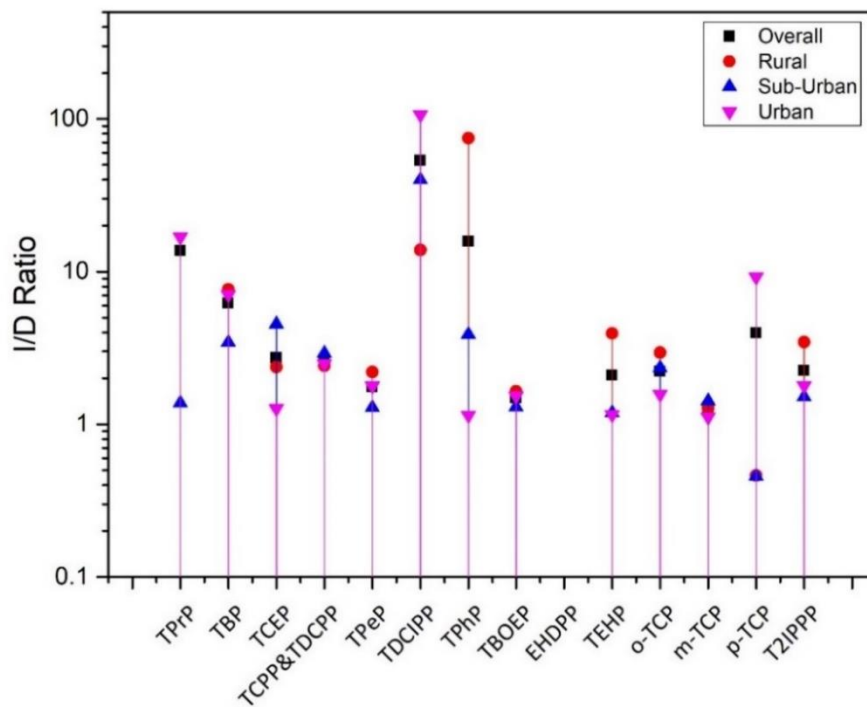


Figure 4.77. I/O concentration ratio of OPFRs in air at homes

The contribution of alkyl, chlorinated, and aryl OPFR compounds to the Σ OPFR concentrations in rural, sub-urban, and urban areas is shown in Figure 4.78. The contribution of alkyl, chlorinated, and aryl OPFR compounds to the Σ OPFR concentration in indoor of homes were determined to be %32.7, %65.6, and %1.70, respectively, while those in outdoor air were %40.6, %57.0, and %2.40, respectively. In studies targeting OPFRs, alkyl and chlorinated OPFR compounds generally tend to be relatively higher levels (Cao et al., 2019). In China, chlorinated compounds such as TCEP and TCPP were commonly used in surface coatings, PVC coatings, textiles, and polyurethane foam production, while in other countries, chlorinated compounds like TCIPPP, alkyl compounds like TBEP, and aryl compounds like TPhP are commonly used (van der Veen and de Boer, 2012). TPhP, an aryl OPFR compound, forms pyro phosphoric acid after generating phosphoric acid during thermal degradation, which acts as a heat barrier (Lee et al., 2002). Despite being an effective flame retardant, its melting point of 49 °C and vapor pressure of 1.2×10^{-6} mm Hg make it highly volatile, resulting in its replacement by flame retardants with lower environmental release (van der Veen and de Boer, 2012). Therefore, although TPhP levels are generally found to be low levels, its determined to be the most abundant OPFR in furniture foams in a study conducted in the United States in 2009, as well as in dust samples taken from childcare facilities in 2018, demonstrates the influence of source differences and intensity.

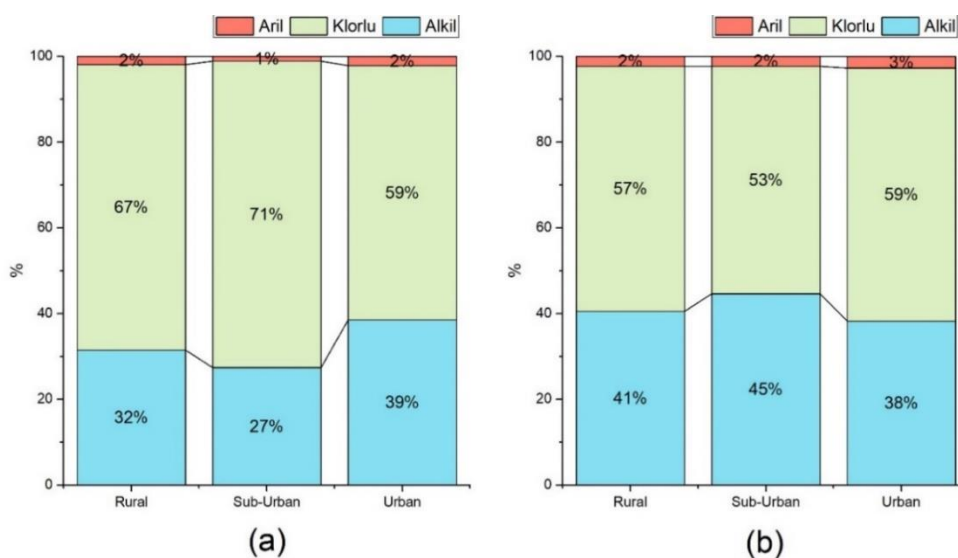


Figure 4.78. Chemical structure segregation of (a) indoor and (b) outdoor air OPFRs in homes

The concentration profiles of OPFRs in indoor and outdoor air at homes are shown in Figure 4.79 and Figure 4.80. In both indoor and outdoor samples, TCEP was the dominant OPFR, followed by the TBOEP. In a study conducted in Bursa, it was determined that TBOEP compound was the dominant component in the concentration profile of outdoor air (Kurt-Karakus et al., 2018). The concentrations of TDCIPP constitute approximately 10.1% and 8.84% of the Σ OPFRs in indoor and outdoor air of homes, respectively, while the concentrations of TCPP&TCIPP in indoor and outdoor air fractions were 10.0% and 8.43%, respectively. The fraction of TEHP in outdoor air was 4.57%, while this value has decreased to approximately half in indoor air. TBOEP and TCIPP compounds were determined to be the most abundant OPFR compounds in tissues taken from dolphins in studies conducted in Spain and South Africa (Aznar-Aleman et al., 2019; Sala et al., 2019). In another monitoring study conducted on tissues of mullet, trout, and carp, TBOEP and TEHP were determined to be the most abundant OPFR compounds (Santín et al., 2016). Based on these studies, exposure to high levels of OPFR compounds in indoor air is considered important due to their bioaccumulation, especially because of spending a long time in indoor environments. Increasing the use of flame retardants with low vapor pressure and high octanol-air partition coefficient could be an alternative method to reduce exposure through inhalation. Aryl OPFR compounds like TCP have a low tendency to remain in the gas phase. These substances adhere to organic surfaces or remain in the particulate phase, contributing to the decrease in concentrations in the ambient air.

Indoor air OPFR concentrations in rural, sub-urban, and urban homes are shown in Figure 4.81. The average indoor air Σ OPFR concentrations in rural, sub-urban, and urban homes were determined to be 27.6 ng/m³, 34.4 ng/m³, 35.9 ng/m³, respectively. The average indoor air concentration of the TCEP in rural, sub-urban, and urban homes were 13.8, 18.8, and 11.9 ng/m³, respectively, while TCPP&TCIPP were 2.57, 3.40, and 3.82 ng/m³, respectively, TDCIPP were 1.96, 2.36, and 5.57 ng/m³, respectively, and TBOEP were 6.67, 6.20, and 11.33 ng/m³, respectively. The concentrations of the TPrP in sub-urban areas and the TEHP in rural areas were determined to be above 1 ng/m³, while the indoor air concentrations of other compounds are below 1 ng/m³ in all regions.

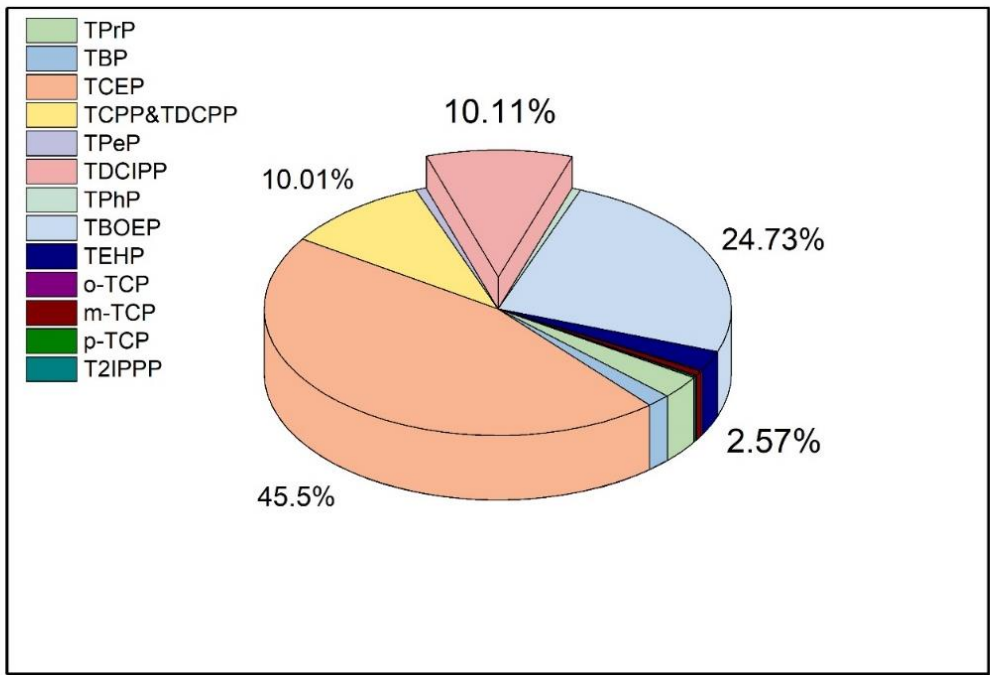


Figure 4.79. Concentration profiles of indoor air OPFRs in homes

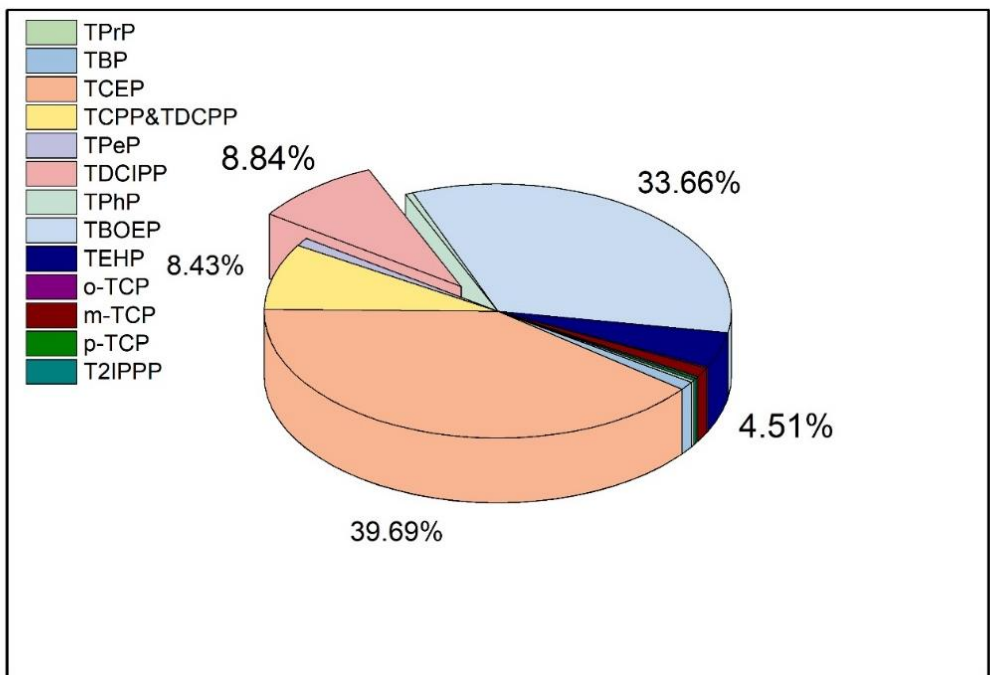


Figure 4.80. Concentration profiles of outdoor air OPFRs in homes

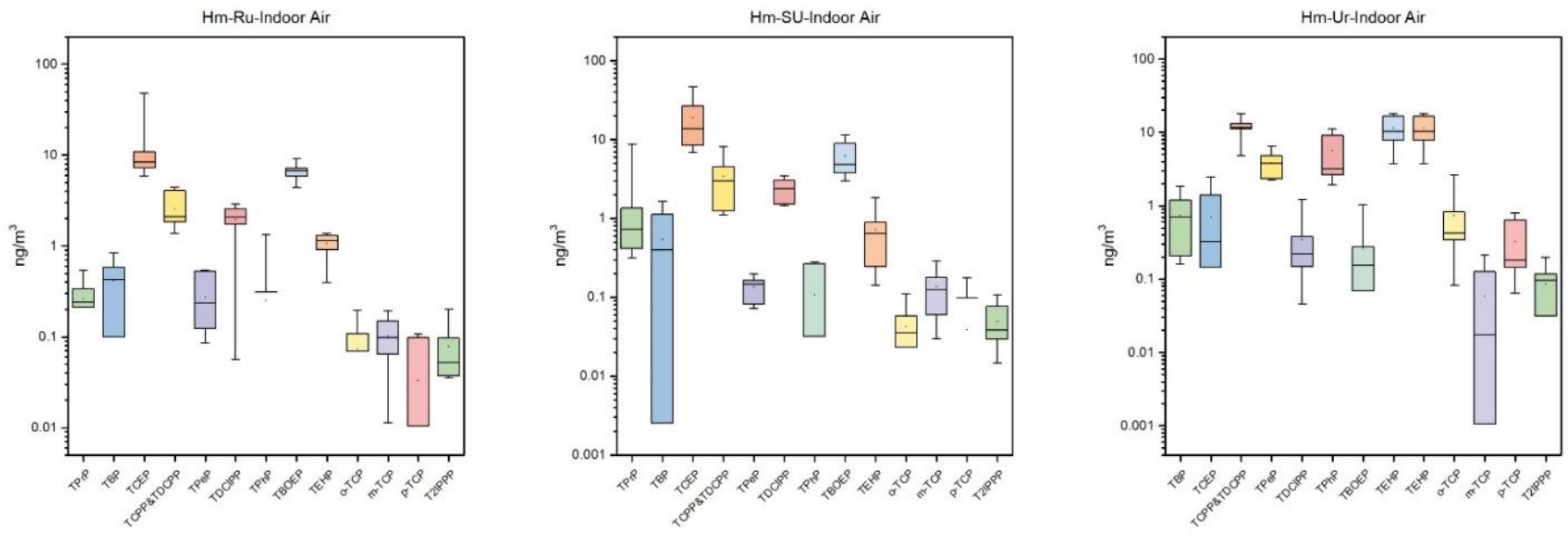


Figure 4.81. Indoor air OPFR concentrations of rural, sub-urban, and urban homes

4.7. Indoor and Outdoor PAH Levels in Living Environments in İzmir-TÜRKİYE

4.7.1. Indoor and Outdoor Settled Dust-Bound PAHs

Indoor and outdoor dust-bound Σ PAH concentrations were determined to be 8265 and 5204 ng/g, respectively (Figure 4.82). While the detection frequencies of indoor settled dust-bound Nap, Acy, Ace, Flu, Phe, Ant, Fla, Pyr, Chr, B(a)A, B(bk)F, B(a)P, Ind, DB(ah)A, and B(ghi)P were as 93%, 57%, 21%, 100%, 100%, 57%, 100%, 100%, 100%, 100%, 93%, 100%, and 71, respectively, those levels for Nap, Chr, B(bk)F, Ind, DB(ah)A, and B(ghi)P in homes were 90%, 95%, 55%, 60%, 70%, and 65%, respectively. Remaining targeted PAHs in settled dust samples from homes and all targeted PAHs in settled dust samples from schools were detected in all samples. It was determined that the high settled-dust-bound PAH concentrations in C/B/Rs increased the overall average. When the C/B/Rs were subtracted from the data, the average settled-dust-bound Σ PAH concentration in indoor environment was to be 5018 ng/g. The average indoor settled dust-bound low molecular weight (LM) PAHs concentration was determined to be 1158 ng/g, while the average settled dust-bound high molecular weight (HM) PAH concentration was 7175 ng/g. The average settled dust-bound LM PAH and HM PAH concentrations in outdoor environments were determined to be 684 ng/g and 4530 ng/g, respectively. LM PAHs sourced from petroleum emissions and combustion reactions, while HM PAHs have mostly occurred in combustion reactions (Singh et al., 2023). PAH levels in C/B/Rs were generally determined to be higher compared to other indoor environments due to smoking and cooking with open fires (Arfaenia et al., 2022; Kamal et al., 2016; Rostami et al., 2019). The relatively high PAH concentrations in indoor dust samples collected from C/B/Rs might be associated with emissions from the kitchen along with smoking in both open and enclosed spaces. In indoor dust samples, the average concentrations of Nap, Acy, Ace, Flu, Phe, Ant, Fla, Pyr, Chr, B(a)A, B(bk)F, B(a)P, Ind, DB(ah)A, and B(ghi)P were determined to be 418, 148, 253, 82, 123, 359, 88, 253, 592, 141, 1323, 4892, 156, 302, and 330 ng/g, respectively, those average in outdoors were

50.7, 47.1, 38.2, 40.3, 212, 517, 168, 106, 107, 82.7, 763, 4177, 308, 47.2, and 91.4 ng/g, respectively (Figure 4.83).

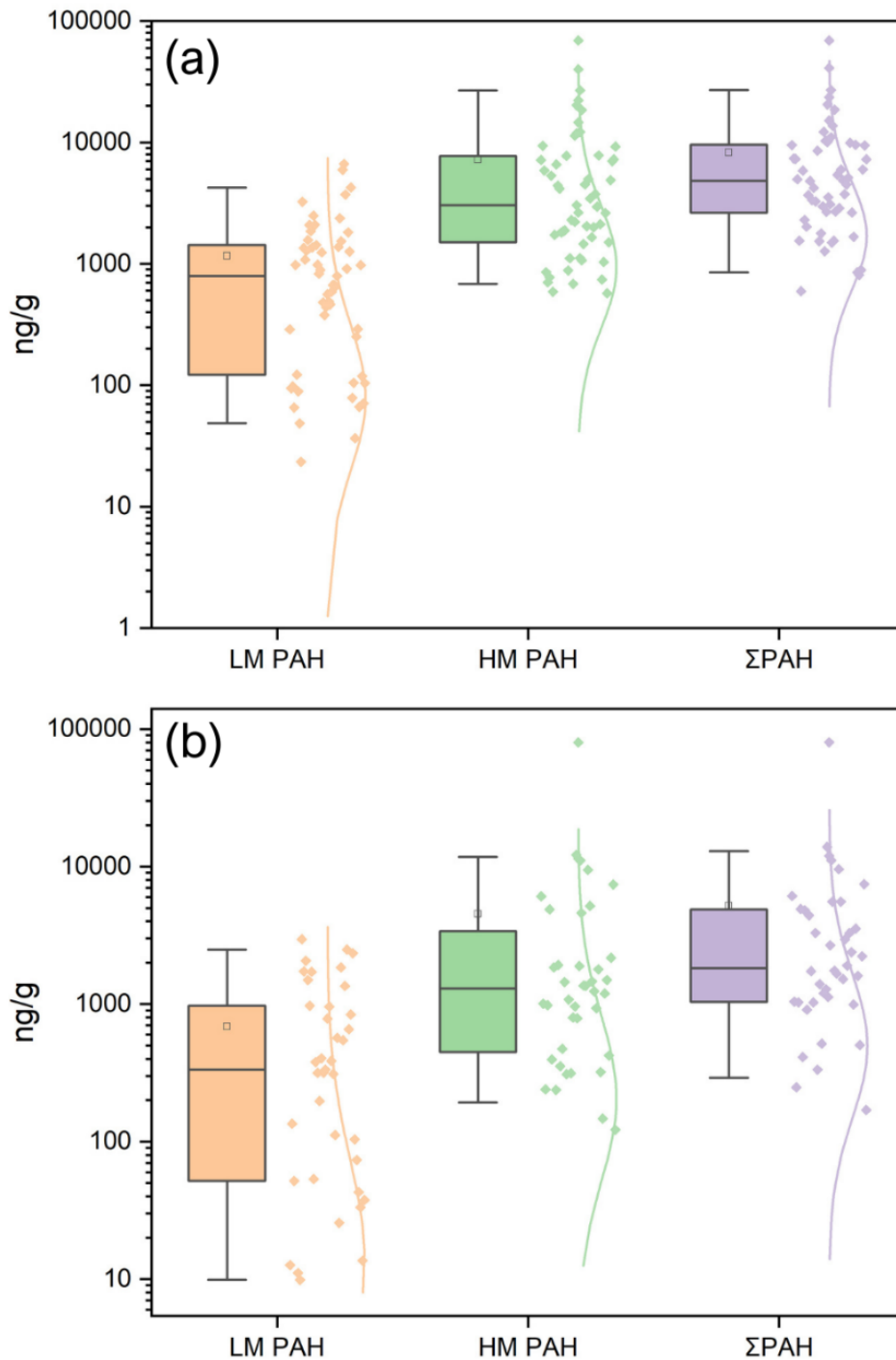


Figure 4.82. Settled dust-bound LM PAH, HM PAH, and ΣPAH concentrations in (a) indoor and (b) outdoor environments

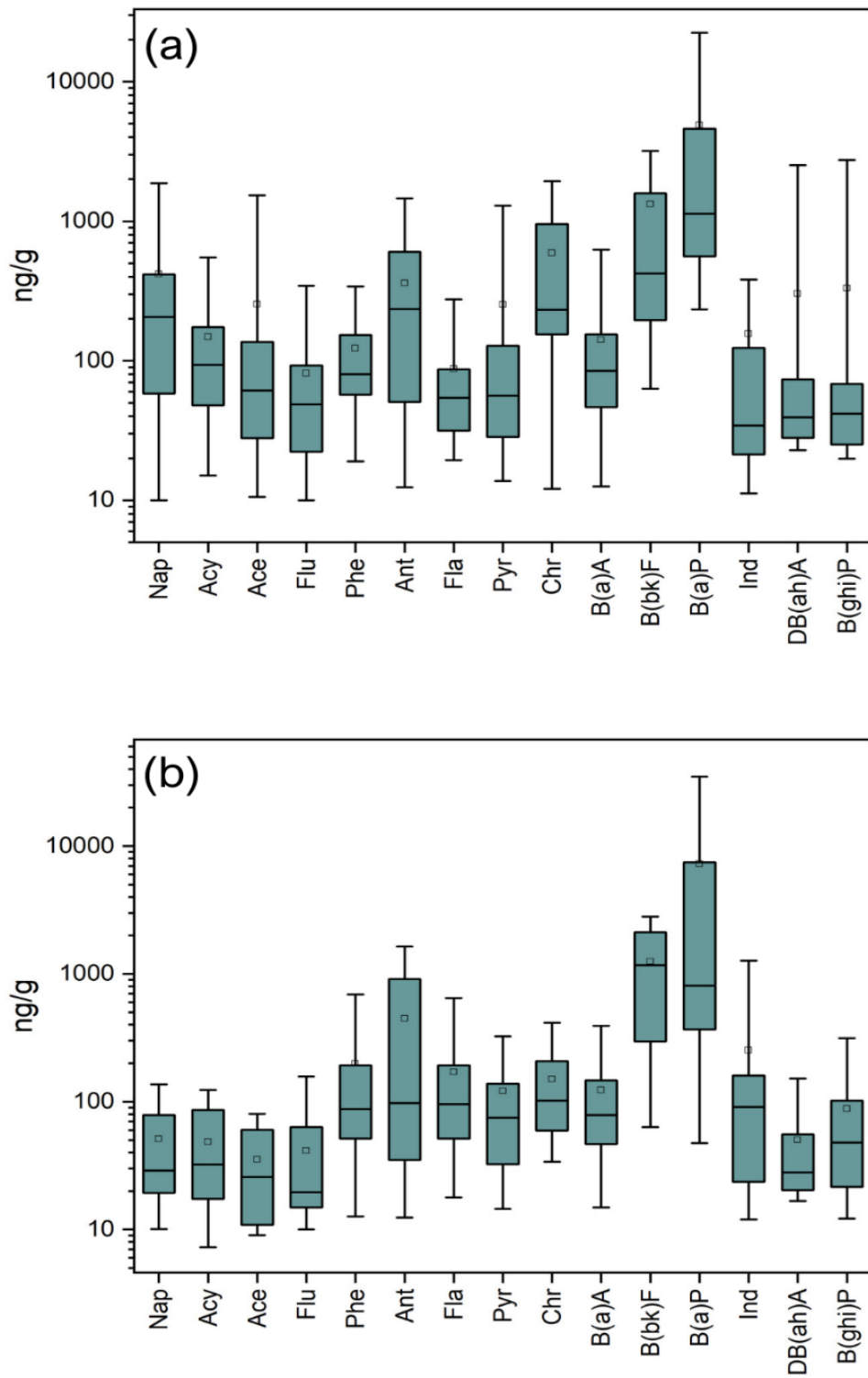


Figure 4.83. Settled dust-bound PAH concentrations in (a) indoor and (b) outdoor environments

The settled dust-bound Σ PAH concentrations in interiors of homes in urban, sub-urban, and rural areas were determined to be 4094, 3211, and 4860 ng/g, respectively. The contribution of PAH compounds to the settled dust-bound Σ PAH concentrations in interiors of homes is shown in Figure 4.84. The contribution of B(a)P concentrations to the indoor settled dust-bound Σ PAH concentrations in homes was determined to be relatively higher, while both of B(a)P and Pyr were the predominant compounds in the concentration profile in sub-urban homes. In rural areas, the concentration profile of Σ PAH in indoor dust samples from homes indicates that B(bk)F > Ant > B(a)P were the dominant compounds.

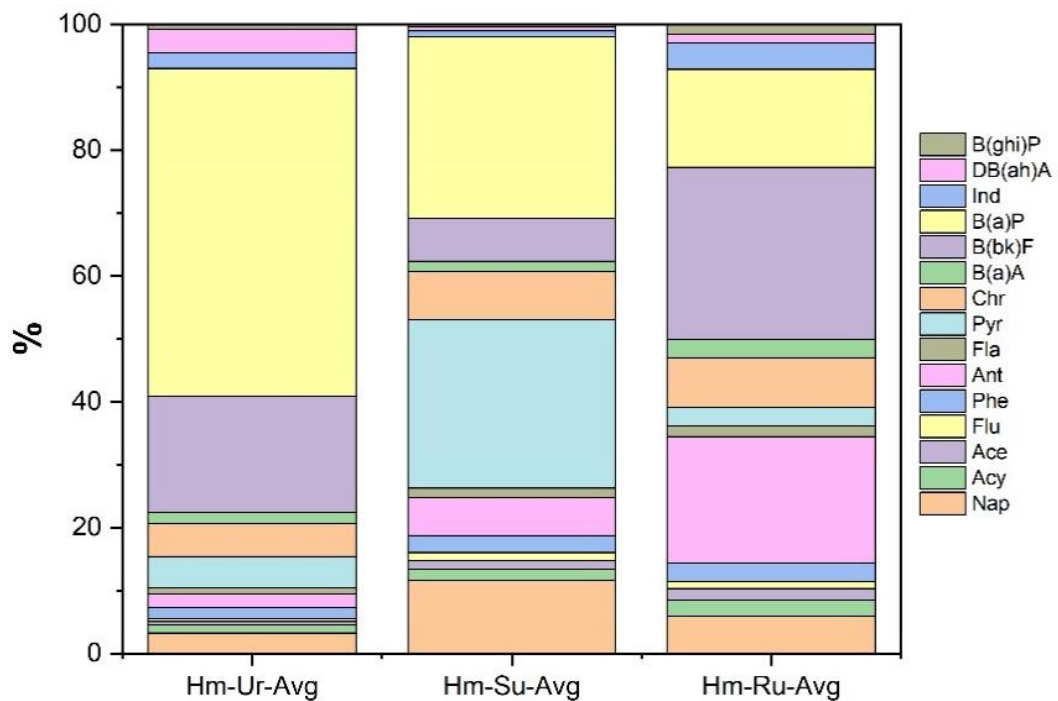


Figure 4.84. Concentration profiles of settled dust-bound PAHs in homes

Nowadays, some diagnostic ratios have been published for the estimation of PAH sources (Tobiszewski and Namieśnik, 2012). A ratio of LM PAH/HM PAH concentration below 1 indicates dominance of petroleum emissions, while a ratio above 1 suggests dominance of formation during combustion reactions (Zhang et al., 2008). Additionally, the Ant/(Ant+Phe) concentration ratio also indicates the effects of petroleum (<0.1) and combustion emissions (>0.1) (Pies et al., 2008). The Fla/(Fla+Pyr) concentration ratio indicates potential sources including petroleum emissions (<0.4), fossil fuel combustion (0.4-0.5), and grass, wood, and coal combustion (>0.5) (de La Torre-Roche et al., 2009). In samples taken from indoor environments of urban, sub-urban, and rural areas, it is determined that Ant/(Ant+Phe) ratio were higher than 0.1, while LM PAH/HM PAH ratio are also above 1 (Figure 4.85). With Ant/(Ant+Phe) values exceeding 0.1 and LM PAH/HM PAH values above 1, it indicates that the influence of combustion emissions is dominant. Fla/(Fla+Pyr) ratios indicate that petroleum emissions were dominant at five sampling points, while at other points, emissions from wood and coal combustion were dominant.

According to the PCA conducted on settled dust-bound PAH concentrations in homes, it was determined that 94% of the concentration variation was affected by two main components (Figure 4.86). PC2 was identified to influence the concentrations of LM PAH compounds, whereas PC1 affects the concentrations of HM PAH compounds. LM PAH compounds are known to be found in liquefied petroleum gases and petroleum-derived fuels (Goto et al., 2021). Therefore, it was presumed that PC2 represents the effects of natural gas and LPG-derived fuels used in homes. High molecular weight PAHs are mostly formed as a result of combustion of fossil fuels, biomass, and heavy petroleum-derived fuels like diesel (Tobiszewski and Namieśnik, 2012). Additionally, those are formed during cooking over open flames or at high temperatures (Lin et al., 2022; Luo et al., 2024; Sharma and Sarkar, 2023). While PC2 might represent the effect of fuels used, PC1 might be the represent of PAH emissions of combustion reactions.

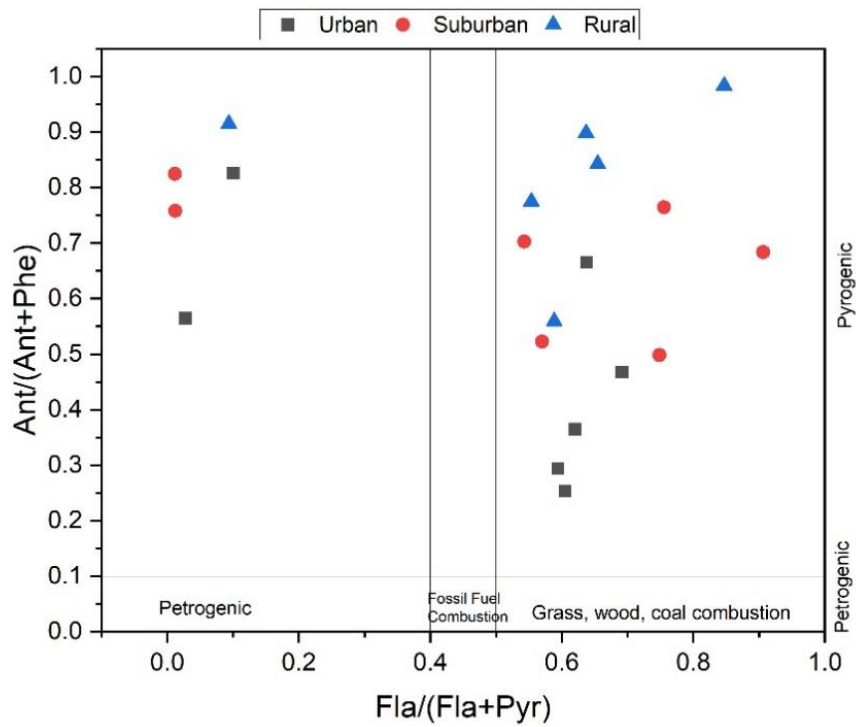


Figure 4.85. Diagnostic ratios and associated potential sources of indoor settled dust-bound PAHs in homes

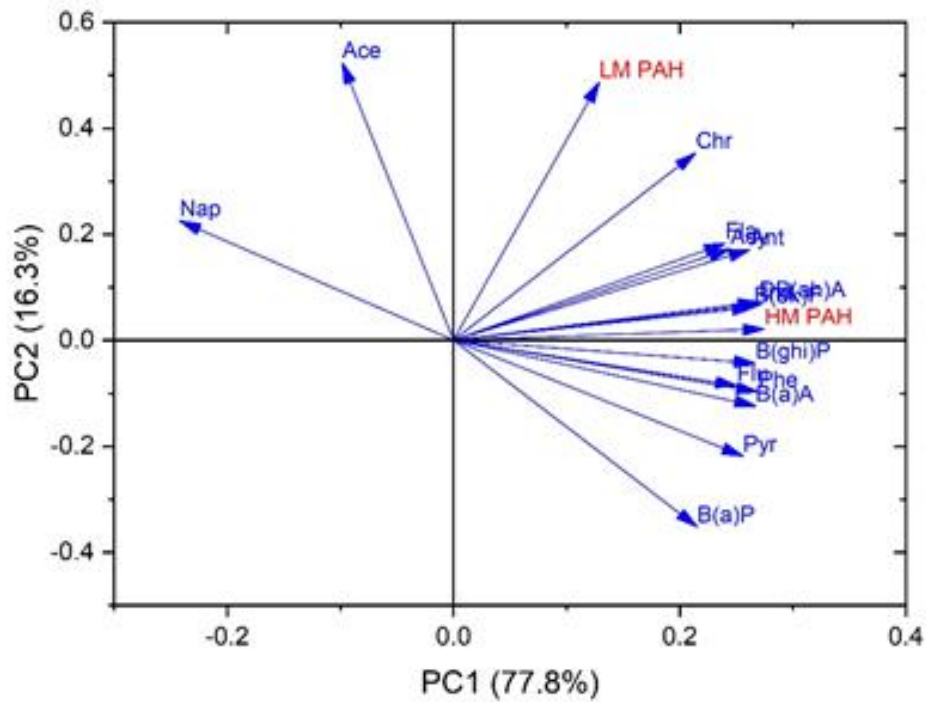


Figure 4.86. PCA loading plots of indoor settled dust-bound PAHs in homes

The settled dust-bound Σ PAH concentrations in interiors of schools in urban, sub-urban, and rural areas were determined to be 7814, 7097, and 2879 ng/g, respectively. The contribution of PAH compounds to the settled dust-bound Σ PAH concentrations in schools is shown in Figure 4.87. The concentrations of DB(ah)A > B(ghi)P > Nap compounds were determined to be higher compared to other settled dust-bound PAH compounds in urban schools. In sub-urban schools, the settled dust-bound concentrations of B(bk)F > B(a)P were higher than other targeted PAHs, while in urban schools, Pyr > DB(ah)A > B(a)P were higher.

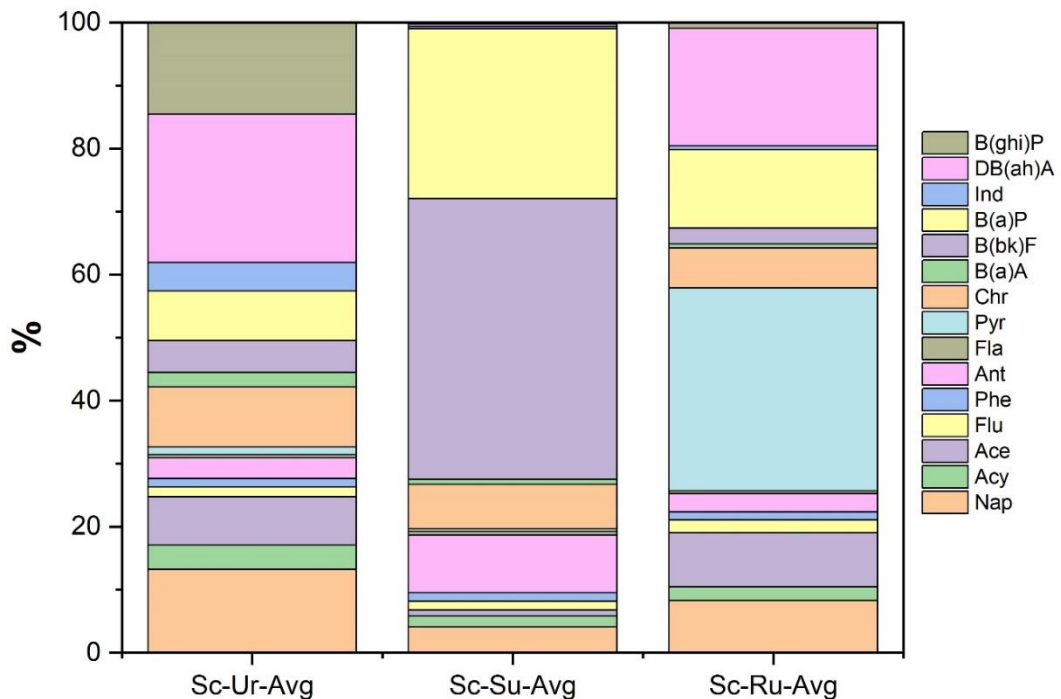


Figure 4.87. Concentration profiles of settled dust-bound PAHs in schools

The LM PAH/HM PAH concentration ratios were generally determined to be lower than 1 in urban, sub-urban, and rural schools. Although diagnostic ratio represents that PAHs are predominantly formed in combustion reactions, in some areas, the LM PAH/LM PAH ratio exceeds to 1. While the Ant/(Ant+Phe) ratio was determined to be higher than 0.1 in all samples, the Fla/(Fla+Pyr) diagnostic ratio indicates that some

schools in rural and urban areas were affected by petroleum emissions. The Fla/(Fla+Pyr) ratio suggests that the dust-bound PAHs in schools in sub-urban areas were affected by the combustion of wood and coal fuels, but the obtained diagnostic ratios were on the border of emissions from the combustion of fossil fuels (Figure 4.88). Therefore, emissions from fossil fuel combustion may have also affected these samples.

PCA of settled dust-bound PAH concentrations in indoor environments of schools revealed that four principal components (PC1-4) affect the concentration variations of PAH compounds. The loadings of the three components identified as having the highest impact in the PCA are provided in Figure 4.89. PC1 was found to affect both LM PAH and HM PAH concentrations, while PC2 affects HM PAH, and PC4 affects LM PAH concentrations. PC3 significantly affects the concentrations of B(a)A, DB(ah)A, and Ind compounds. The strong correlation between B(a)A concentration and traffic emissions suggests that PC3 may represent traffic emissions (Tobiszewski and Namieśnik, 2012). PC1 exhibits a strong correlation with Fla concentrations, while the no-effect on Pyr concentrations may indicate the concentration variations might be affected by wood and coal burning ($Fla/Fla+Pyr > 0.5$). PC2 might be the indicator of diesel and fossil fuel combustion, open-fire cooking, and high-temperature cooking sources, due to the strong correlation with the concentration variation of LM PAH compounds.

The Σ PAH concentrations in dust samples collected from C/B/R areas in urban, sub-urban, and rural regions were determined to be 23179, 20911, and 9696 ng/g, respectively. B(a)P concentrations were predominant in the settled dust-bound Σ PAH concentration in C/B/Rs (Figure 4.90). The settled dust-bound B(a)P concentration in urban, sub-urban, and rural areas were determined to be 20039, 15444, and 8367 ng/g, respectively, while the B(b)F ranked second with concentrations of 2289, 1470, and 558 ng/g, respectively. The dominance of HM PAH concentrations was considered an indicator of smoking, cooking over open flames or at high temperature sources were predominant in C/B/s.

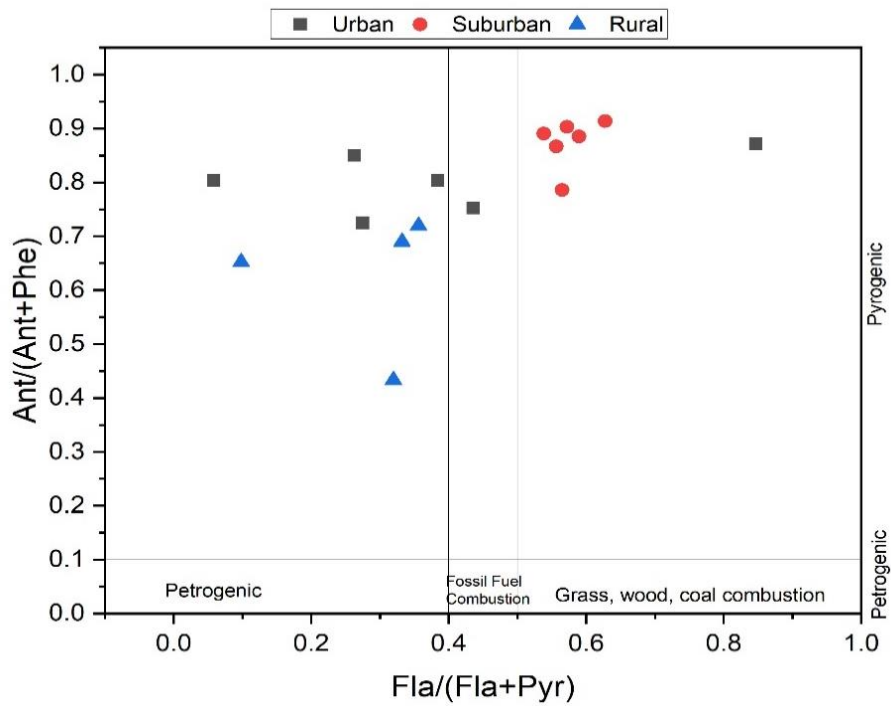


Figure 4.88. Diagnostic ratios and associated potential sources of indoor settled dust-bound PAHs in schools

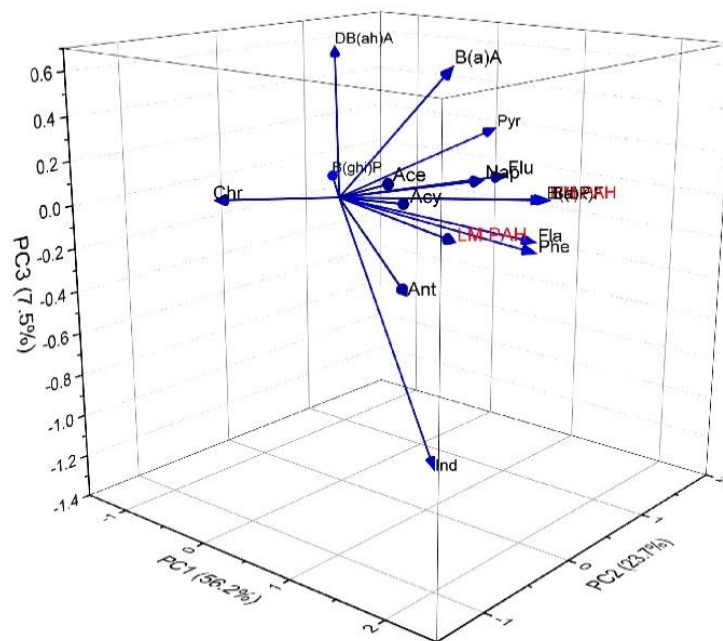


Figure 4.89. PCA loading plots of indoor settled dust-bound PAHs in schools

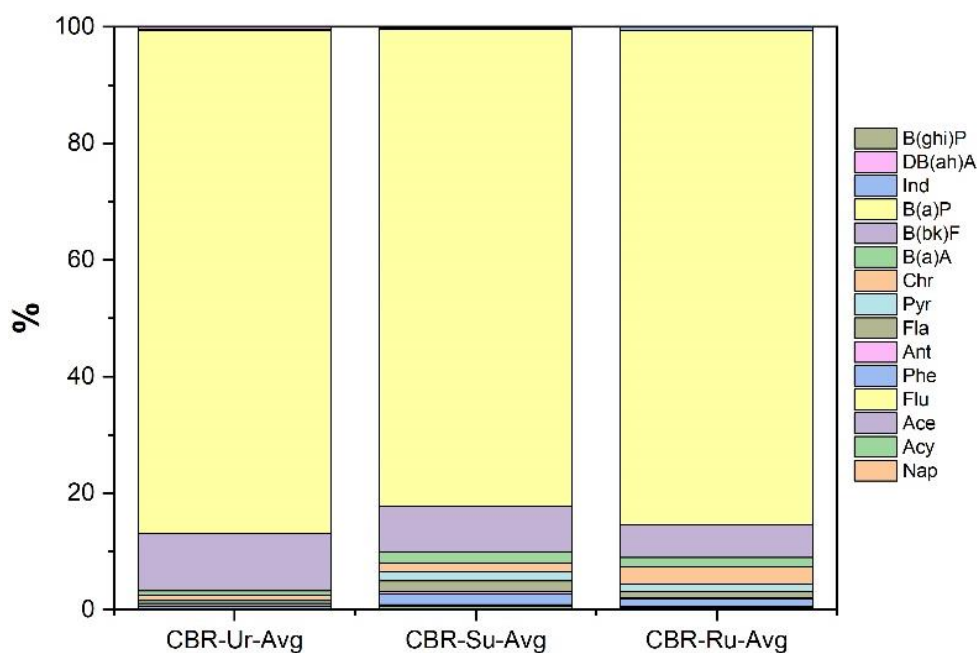


Figure 4.90. Concentration profiles of settled dust-bound PAHs in C/B/Rs

4.7.2. Indoor and Outdoor Air PAHs

The Σ PAH concentrations in indoor and outdoor air in Izmir were determined to be 45.6 and 158 ng/m³, respectively (Figure 4.91). The Σ PAH concentrations in outdoor air samples collected from homes and schools were determined to be 79.3 and 235 ng/m³, respectively. In indoor air samples, the average Σ PAH concentration in schools was determined to be 33.0 ng/m³, while it was 58.9 ng/m³ in homes. Although the high concentration values determined in outdoor air in schools increased the difference between the average Σ PAH concentrations of indoor and outdoor air, it was found that the median indoor and outdoor air concentrations were closer to each other ($C_{in-median} = 22.6$ ng/m³; $C_{out-median} = 43.6$ ng/m³). The median LM PAH and HM PAH concentration in indoor air were determined to be 9.80 ng/m³ and 15.5 ng/m³, respectively, while their concentrations in outdoor air were determined to be 28.1 ng/m³ and 19.7 ng/m³, respectively (Figure 4.92). The concentration levels obtained in indoor and outdoor air samples indicate that PAH compounds were higher in the gas phase in outdoor air (Median I/O_{LM PAH}=0.32; Median I/O_{HM PAH}=0.84). In indoor air samples, the median concentrations of Nap, Acy, Ace, Flu, Phe, Ant, Fla, Pyr, Chr, B(a)A, B(bk)F, B(a)P, Ind, DB(ah)A, and B(ghi)P compounds were determined to be 3.74, 0.87, 0.50, 0.95, 2.91,

0.15, 3.34, 0.27, 0.04, 0.47, 3.57, 5.43, 0.11, 0.21, and 0.07 ng/m³, respectively, while in outdoor air, they were determined to be 3.48, 0.95, 1.23, 2.58, 17.32, 1.15, 0.52, 3.73, 0.49, 1.80, 4.68, 5.16, 0.19, 0.22, and 0.08 ng/m³, respectively.

The diagnostics ratio diagram showing the potential sources of PAHs (Figure 4.93). It is observed that the outdoor air in urban and sub-urban areas is mainly affected by emissions from fossil fuels, wood, and coal combustion, while petroleum emissions also affect the PAH levels in outdoor air. In rural areas, the PAH concentrations in outdoor air samples were estimated to be attributed to diesel fuel used in vehicles commonly used in rural areas such as tractors, off-road vehicles, and agricultural machinery, as well as emissions resulting from wood and coal combustion. The average B(a)A/(B(a)A+CHR) diagnostic ratio in outdoor air samples was determined to be 0.79. A B(a)A/(B(a)A+CHR) diagnostic ratio above 0.35 is associated with emissions from vehicles (Akyüz and Çabuk, 2008).

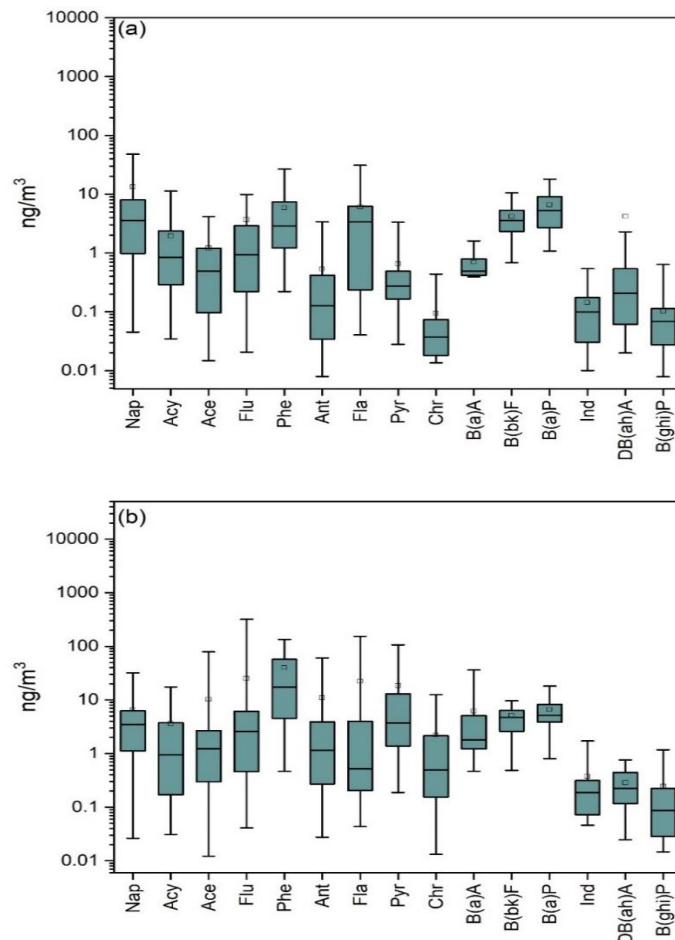


Figure 4.91. Indoor (a) and outdoor (b) air PAH concentrations

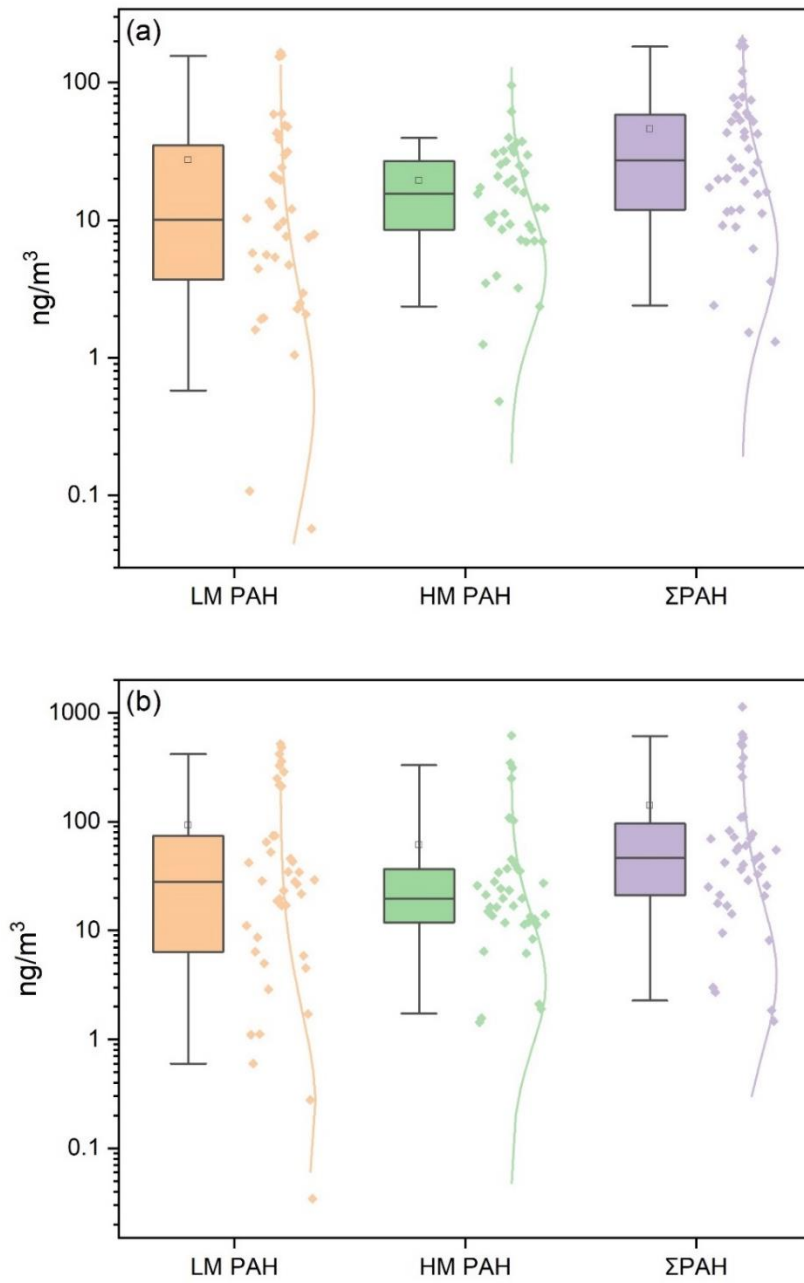


Figure 4.92. Indoor (a) and outdoor (b) air LM PAH, HM PAH, and ΣPAH concentrations

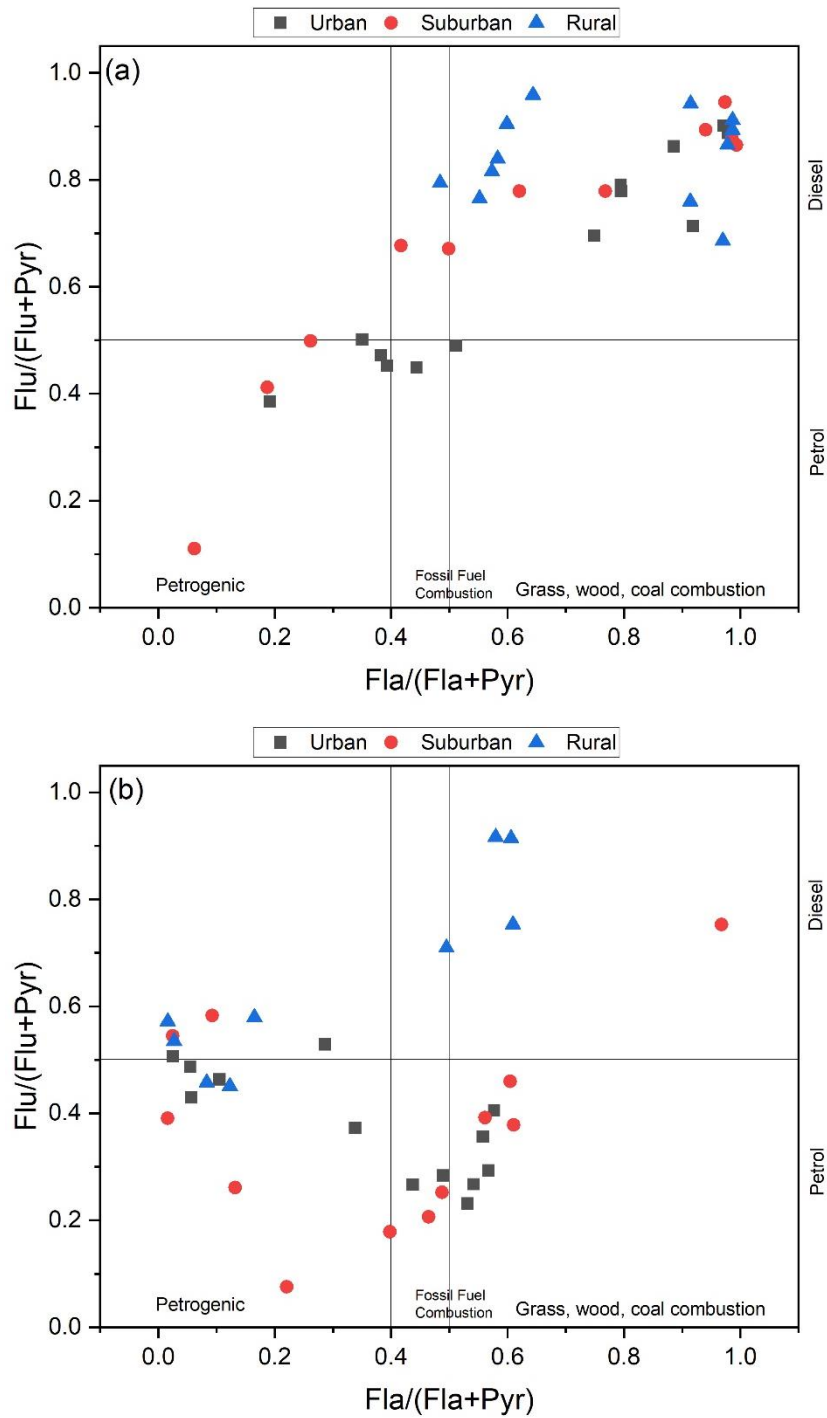


Figure 4.93. Diagnostic ratios and associated potential sources of (a) indoor and (b) outdoor air PAHs

The indoor air PAH concentrations in homes and schools are shown in Figure 4.94. The average concentration of Nap, Acy, Ace, Flu, Phe, Ant, Fla, Pyr, Chr, B(a)A, B(bk)F, B(a)P, Ind, DB(ah)A, and B(ghi)P compounds in indoor air in homes were determined to be 22.8, 2.09, 1.11, 2.42, 6.40, 0.49, 10.1, 0.66, 0.10, 0.60, 4.68, 7.67, 0.14, 0.34, 0.06 ng/m³, respectively, while those in schools were 4.62, 1.92, 1.32, 5.17, 5.46, 0.62, 0.99, 0.66, 0.10, 0.88, 3.81, 5.27, 0.16, 7.21, 0.13, and 0.12 ng/m³, respectively. The detection frequencies of those PAHs in homes were 100%, 95%, 81%, 100%, 100%, 100%, 100%, 90%, 86%, 86%, 100%, 100%, 38%, 43%, 10%, 10%, respectively, while those in schools were 100%, 95%, 96%, 100%, 86%, 86%, 86%, 100%, 38%, 29%, 100%, 71%, 62%, 76%, and 81%, respectively. The higher levels of indoor air PAH concentrations in homes compared to schools might be due to thermal process-related emissions such as emissions from the kitchen to the home and potential smoking, as well as the use of naphthalene tablets for moth protection, cosmetics, medicines, and insecticides (Figure 4.95).

The PCA loading plot of indoor air PAH concentrations are shown in Figure 4.96. It was determined that four principal components accounted for 90% of the concentration variations of indoor air PAH concentrations. PC1 was found to have a 55% effect on the variation of PAH concentrations in indoor air, while the effect of PC2-4 was determined to be in the range of 10-11%. PC1 was found to significantly affect the concentration variations of Acy, Ace, Flu, Phe, Ant, Pyr, and B(bk)F compounds, while PC2 influenced the concentrations of Nap and B(a)P compounds. Considering that PC1 affects almost all PAH compounds, it can be said to represent kitchen emissions (associated to petrogenic PAH emissions from natural gas or liquidized petroleum gas and cooking emissions). Studies have shown that cigarette consumption significantly affects the formation of Nap and B(a)P (Hecht, 1999; Schmeltz et al., 1976; Vu et al., 2015). Therefore, PC2 was considered to be associated with cigarette consumption. PC3 only affects the concentrations of Fla. High Fla concentrations are associated with the burning of plants, wood, and coal (Tobiszewski and Namieśnik, 2012; Zhang et al., 2008). Therefore, PC3 is thought to represent the combustion of organic materials for heating and the transport of combustion by-products from the outdoor environment. Since PC4 only affects the concentrations of HM PAH compounds, it can be said to be associated with fuels such as diesel fuels and coal.

The PCA loading plot of outdoor air PAH concentrations is shown in Figure 4.97. Three principal components (PC1-3) that represent 91% of the concentration variations

of outdoor air PAH concentrations were determined. PC1 was found to significantly affect the outdoor air PAH concentrations. The effect on LM PAH and HM PAH levels by PC1 suggests a relationship with emissions from petroleum fuels and their combustion. PC2 significantly affects the concentrations of B(kf)P. Since B(bk)F compounds are associated with industrial emissions, particularly from aluminum smelters (Callén et al., 2011), PC2 may be related to industrial emissions. The concentrations of Phe and B(a)P compounds were estimated to be affected by PC3. Since Phe and B(a)P compounds are associated with the combustion of organic fuels, PC3 might be represent the combustion of organic fuels, primarily wood.

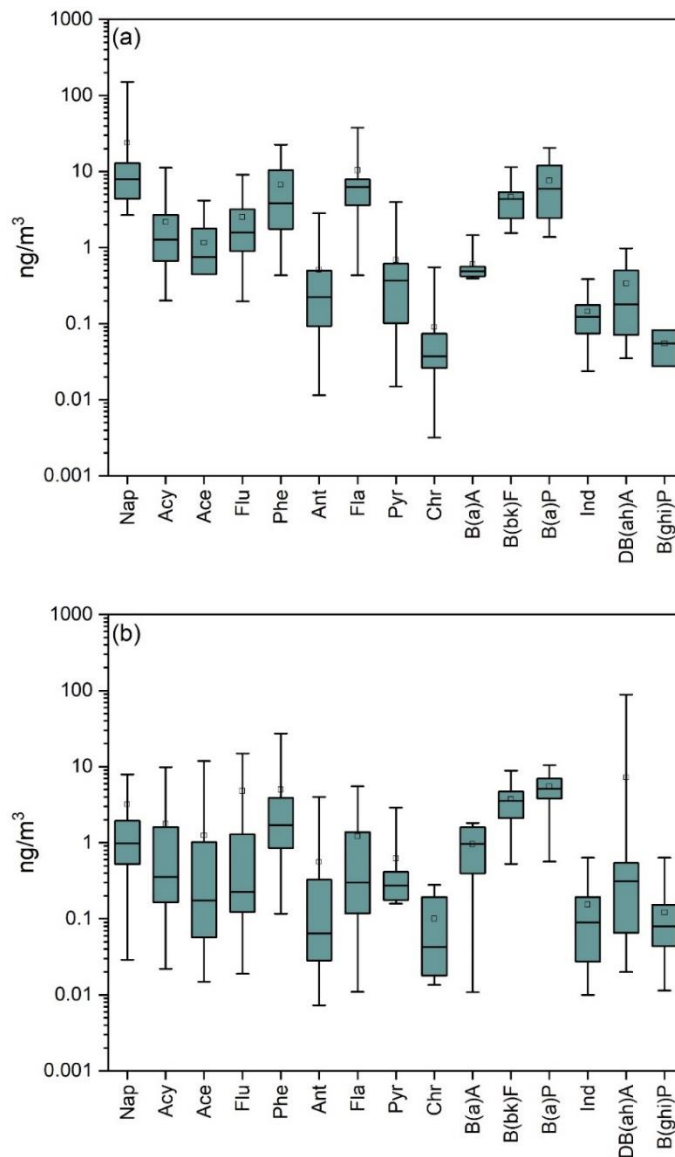


Figure 4.94. Indoor air PAH concentrations in (a) homes and (b) schools



Figure 4.95. Ingredient of commercial naphthalene (100%) tablet

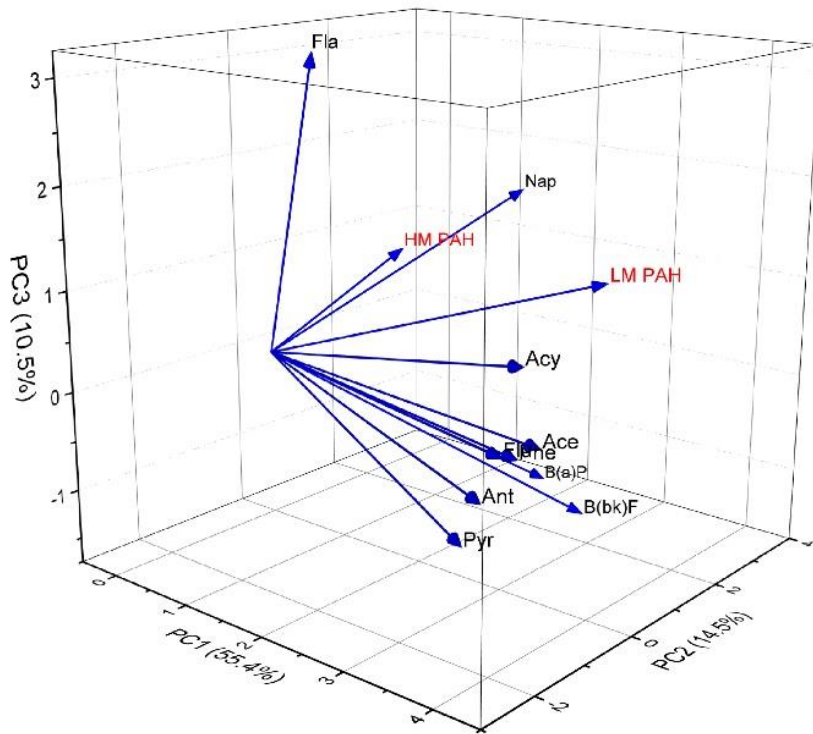


Figure 4.96. PCA loading plots of indoor air PAHs

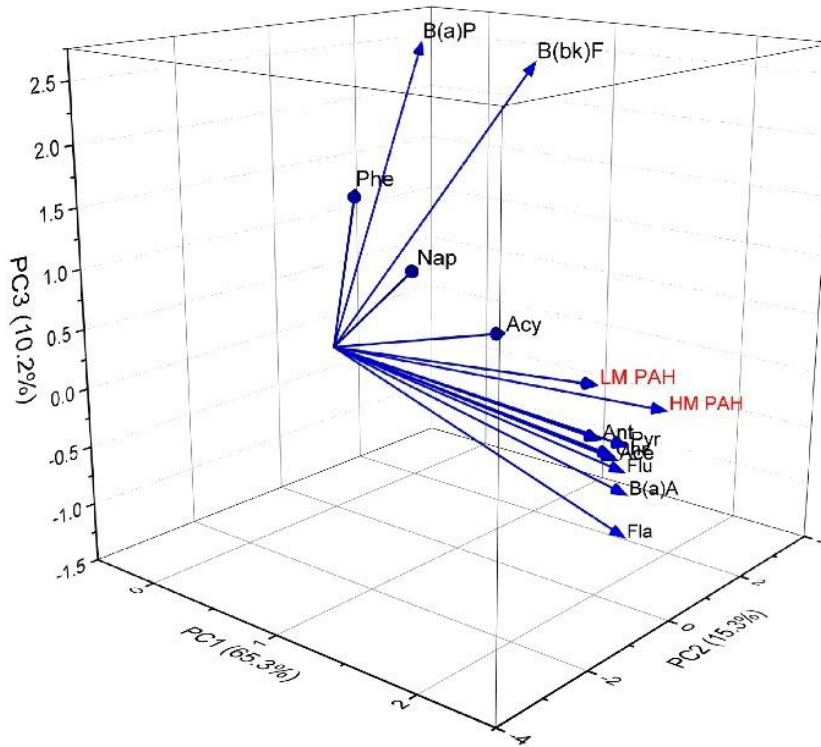


Figure 4.97. PCA loading plots of indoor air PAHs

4.8. Indoor and Outdoor PCB Levels in Living Environments in İzmir-TÜRKİYE

4.8.1. Settled Dust-Bound PCBs

The PCB levels in indoor dust samples collected from schools are shown in Figure 4.98. Mono-CBs were not detected and Octa- and Deca-CBs were detected with a frequency of less than half of the samples, so they are not shown in the graph and are not included in the comparison. Similar to PBDEs, it was found that PCB levels in dust samples from schools were higher than those in samples taken from homes. Hexa-CBs were the dominant homolog group in the indoor dust of schools, with a median of 1956

ng/g. Hexa-CBs were followed by the Penta-CB homolog group with 599 ng/g. Di-CB homolog group was determined to be the lowest PCBs in the indoor environment of schools.

The PCB levels in outdoor dust samples collected from schools are shown in Figure 4.99. Hexa-CBs have the highest outdoor settled dust-bound concentration with a median concentration of 99.9 ng/g, followed by Penta-CBs at 62.5 ng/g. When considering the I/O concentration ratios of settled dust-bound PCBs in schools, that was observed that all homolog groups except for Di-CBs have I/O ratios greater than 1. Especially in schools at sampling points SU3 and SU6, the I/O concentration ratios were found to be higher than 890. When these extreme values are removed from the dataset, the average I/O concentration ratios for homolog groups range between 0.3 and 18.9. When comparing the air (Edebali 2022) and settled dust-bound PCBs, I/O ratios of settled dust-bound PCBs were determined to be higher than that in air samples in same sampling locations. This was thought to be due to the indoor air being affected by the outside (natural ventilation) and the presence of PCB sources indoors causing PCB emissions in the particulate phase/accumulation gaseous compounds on the particle surface, and differences in cleaning schedules, which significantly impact dust accumulation indoors.

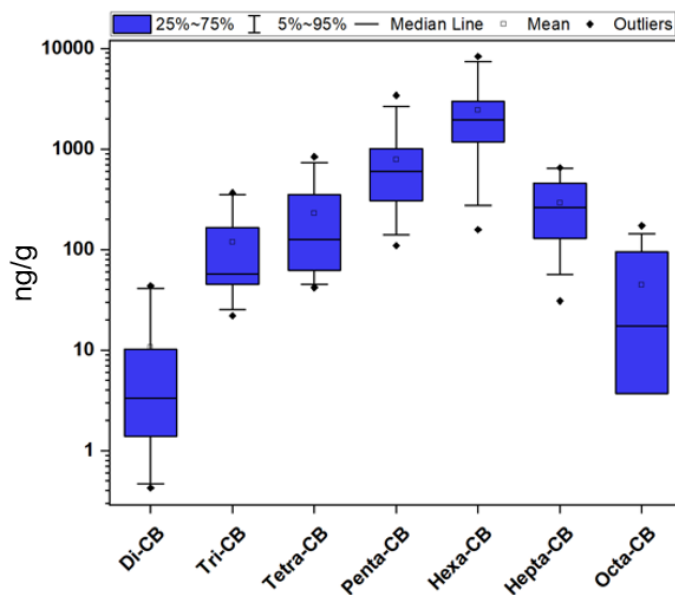


Figure 4.98. Settled dust-bound PCB concentrations in indoor environments of schools

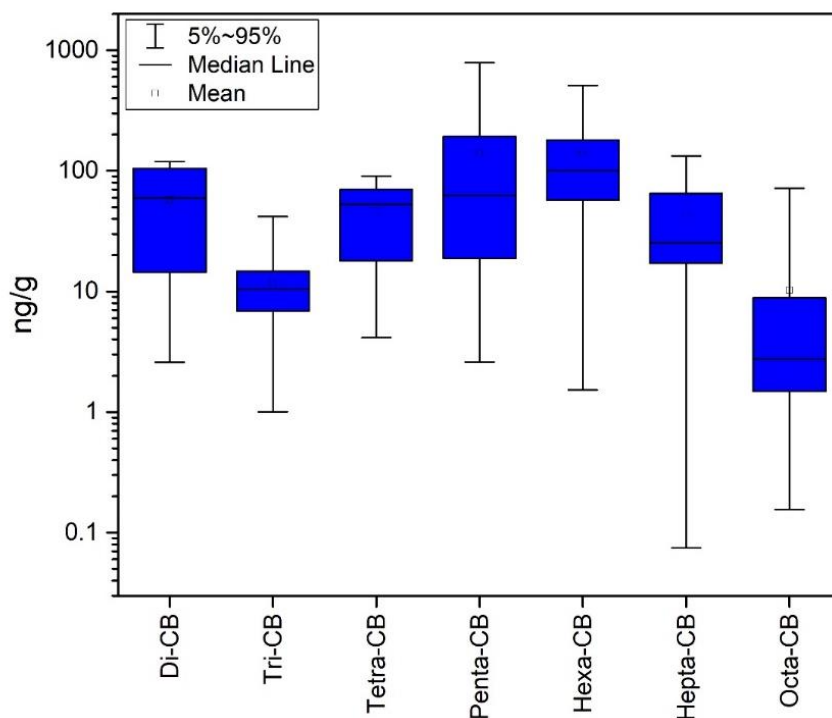


Figure 4.99. Settled Dust-Bound PCB concentrations in outdoor environments of schools

The settled dust-bound PCB concentrations in the indoor environment of homes are shown in Figure 4.100. Since Mono-CBs were not detected and Deca-CBs were detected with a frequency of less than half of the samples, those were ignored. Unlike the indoor air samples taken from the same points (Edeballi 2022), Hexa-CBs, with a median concentration of 120 ng/g, were the PCB homolog group most abundant detected. Hexa-CBs were followed by Penta-CBs with 75.0 ng/g; Tetra-CBs with 44.4 ng/g; Hepta-CBs with 33.1 ng/g and Tetra-CBs with 44.4 ng/g. The median concentration level of the Tri-CB homolog group, which was detected at the highest concentration in the air samples, was 21.0 ng/g in the dust, while its average was determined as 60.6 ng/g.

The settled dust-bound PCB concentrations in the outdoor environment of homes are shown in Figure 4.101. The highest concentration of the outdoor settled dust-bound PCBs was identified as Hexa-CBs with a median level of 41.4 ng/g. It was followed by Hepta-CBs with 24.37 ng/g and Tetra-CBs with 22.5 ng/g. Although the median concentrations of the Hexa-CBs and Hepta-CBs homolog were found to be different, the mean concentrations were close with 31.9 ng/g for Hexa-CB and 31.4 ng/g for Hepta-CBs. When the I/O ratios of PCB concentrations in the home soil samples were examined,

that was determined that Tri-CBs were the homolog group with the highest indoor environment concentrations compared to those in outdoor environment with a 67 I/O ratio, followed by Hexa-CBs, which had outdoor environment soil concentrations 48.9 times higher than the outdoor environment, with 22.7 I/O ratio, followed by Tetra-CBs. The I/O ratios of other homolog groups range from 1.54 to 14.3.

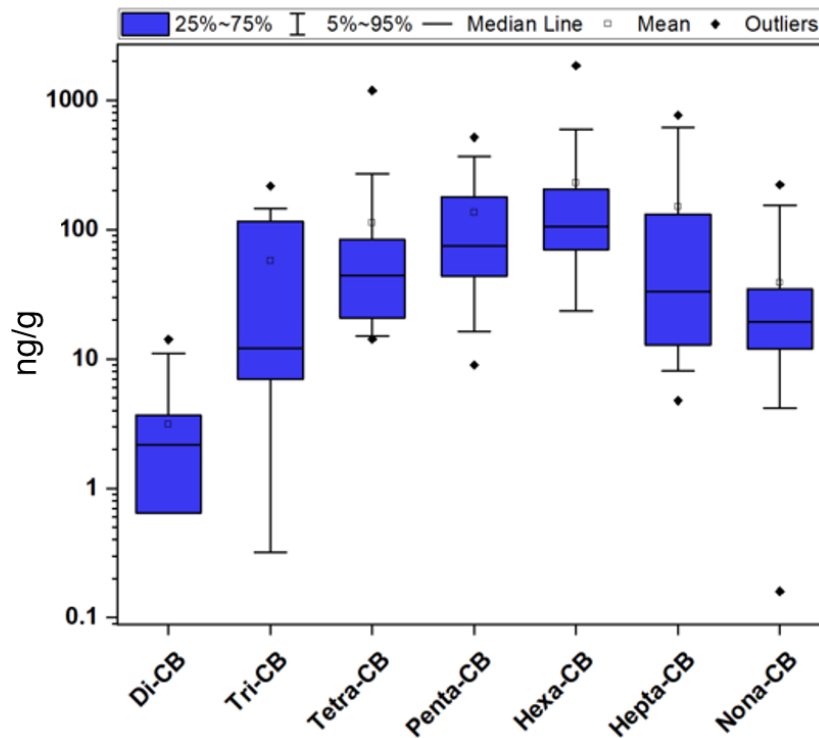


Figure 4.100. Settled Dust-Bound PCB concentrations in indoor environments of homes

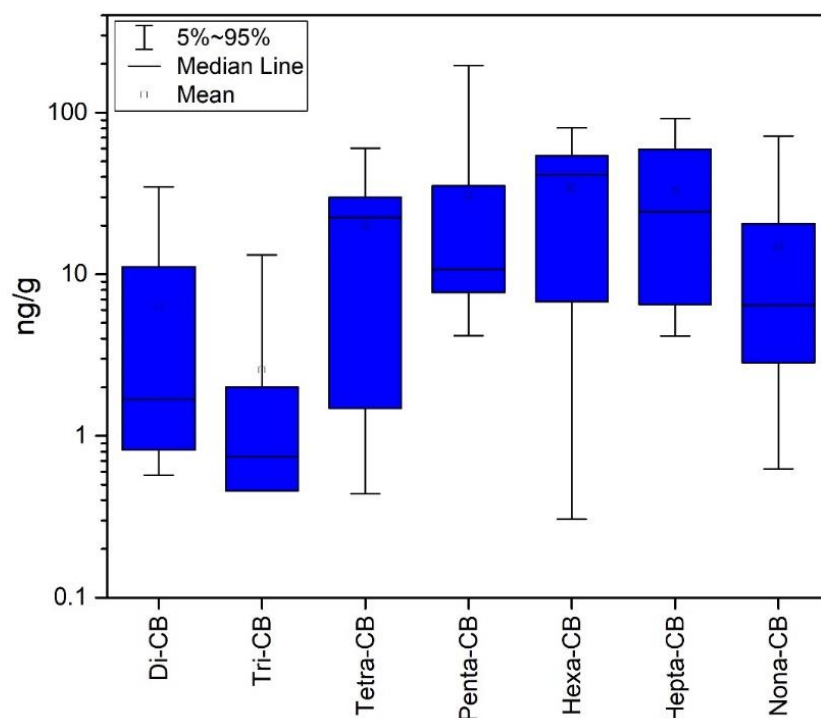


Figure 4.101. Settled Dust-Bound PCB concentrations in outdoor environments of homes

The loading plot of PCA analysis of pooled indoor settled dust-bound PCBs is shown in Figure 4.102, indoor dust-bound PCBs in homes in Figure 4.103, indoor dust-bound PCBs in schools in Figure 4.104, and pooled outdoor dust-bound PCBs in Figure 4.105. Components with eigenvalue greater than 1 were considered meaningful. In the pooled indoor dust samples, that was determined the effect of three PC (PC1-PC3) accounted for 78% of the concentration changes. PC1 had an effect on almost all homolog groups, that was relatively low for Di-CB and Hepta-CB (EV values of 0.21 and 0.24, respectively). The EV coefficient of PC1 on Tri-CB, Tetra-CB, Penta-CB, Hexa-CB and Octa-CB homolog groups was determined as 0.42, 0.43, 0.49, 0.30 and 0.46, respectively. PC2 was determined to have an effect on the Hexa-CB (EV = 0.47) and Hepta-CB (EV = 0.50) in the indoor settled dust, while has no effect on other homolog groups. While the effect of PC3 was highest on Octa-CB (EV = 0.53), the Di-CB (EV = 0.36) and Hexa-CB (EV = 0.34) homolog groups are also affected by PC3.

The three PC were determined in PCA analysis of the indoor settled dust-bound PCB concentrations homes. Three PC (PC1-PC3) affects the %85.4 of the total

concentration variation. PC1 had an important effect on the concentration variation of Tetra-CB, Penta-CB and Hexa-CB homolog groups (eigenvalue values between 0.50-0.56), while Hepta-CB (EV = 0.32) and Octa-CB (EV = 0.23) levels had relatively less effect.

Three PC were determined in PCA analysis of the settled dust-bound PCB concentrations in schools. PC1-PC3 affects the 79% of the total settled dust-bound concentration variation in schools. While the PC1 influenced the concentration variations of Di-CB, Tri-CB and Penta-CB (with EV values ranging from 0.35 to 0.53), there was no effect on the other homolog group concentrations. PC2 affects the concentrations of all homolog groups except Di-CB. While PC2 had the most effect on the concentration variation of Tetra-CB (EV=0.62), lowest effect was determined on the concentration variation of Hexa-CB (EV=0.24). EV values of the other homolog groups in PC2 ranged from 0.33 to 0.41. PC3 had a significant effect on the Octa-CB levels in the indoors of the schools (EV=0.72) and also affected the concentration variation of Di-CB (EV=0.30) and Hexa-CB (EV=0.40). No effect of PC3 on the other homolog groups was determined.

It has been determined that three PC influence the PCB concentrations in outdoor settled dusts. Those PCs can explain 85.6% of the concentration variation. While PC1 influences the concentration variation of all PCBs in outdoor settled dust samples, PC2 only has an effect on the concentration variation of Di-CB (EV=0.54) and Tetra-CB (EV=0.48) homolog groups. While it has been determined that PC3 does not influence the concentrations of Tri-CB, Penta-CB and Hexa-CB homolog groups, it has the most effect on the concentration variation of Tetra-CB (EV=0.41) and Hepta-CB (EV=0.33). PC3 also influences the concentration variation of Di-CB (EV=0.29) and Octa-CB (EV=0.20) homolog groups.

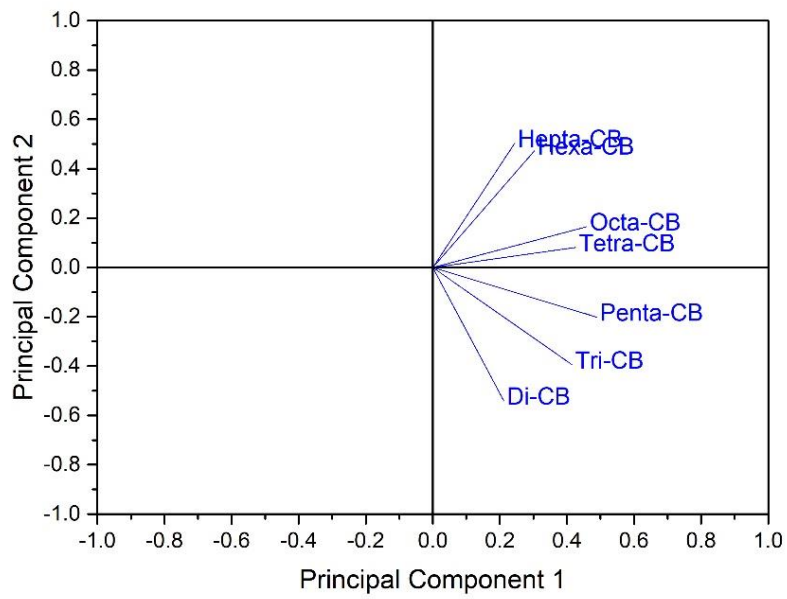


Figure 4.102. PCA loading plots of settled dust-bound PCBs in indoor environments

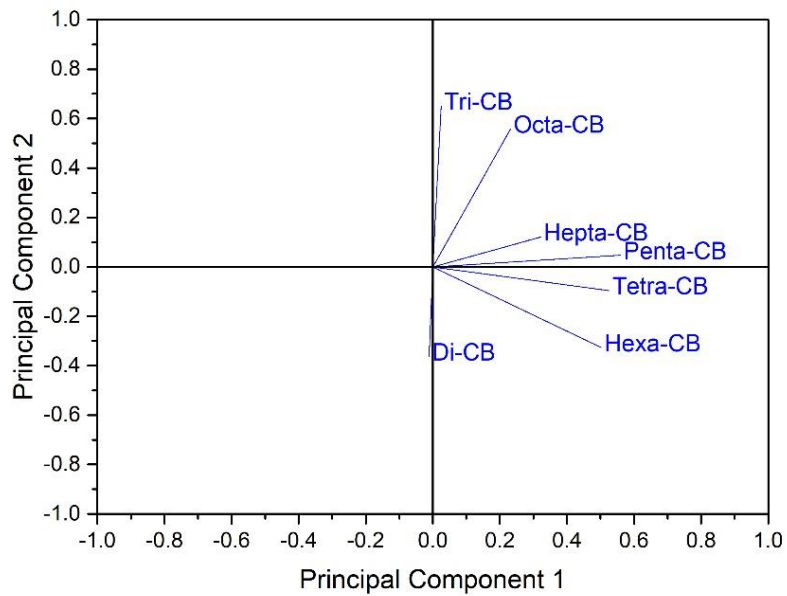


Figure 4.103. PCA loading plots of settled dust-bound PCBs in indoor environments of homes

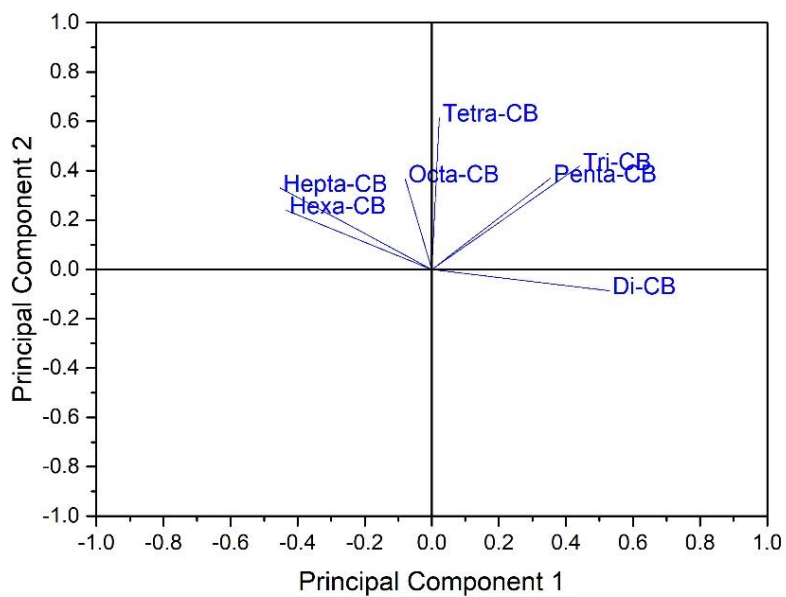


Figure 4.104. PCA loading plots of settled dust-bound PCBs in indoor environments of schools

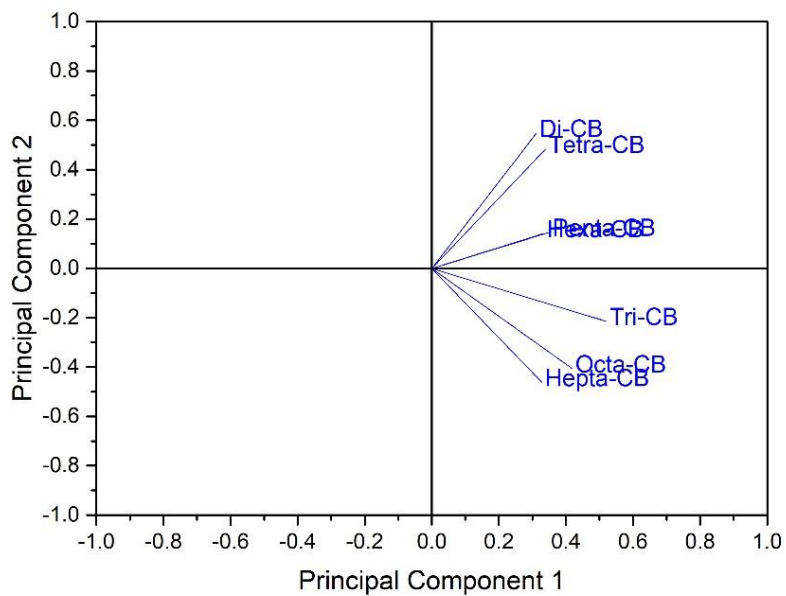


Figure 4.105. PCA loading plots of settled dust-bound PCBs in outdoor environments

4.8.2. Dust-Gas Partitioning of PCBs

The association between molecular weight and dust-gas partitioning of PCBs is an important factor in determining their atmospheric fate. The dust-gas partitioning coefficient, K_D , is a measure of the relative affinity of a compound for dust and gas phases in the atmosphere. Generally, compounds with higher molecular weights have higher K_D values, meaning that they are more likely to remain in the dust phase in the atmosphere. For PCBs, the K_D values generally increase with increasing molecular weight, indicating that higher molecular weight PCBs have a greater affinity for the dust phase. As a result, higher molecular weight PCBs are more likely to remain in the dust compartment of the environment, and thus are more likely to deposit onto terrestrial surfaces. Thus, the molecular weight of PCBs plays an important role in determining their atmospheric fate, as heavier compounds are more likely to remain in the dust phase and deposit onto terrestrial surfaces. The dust-air partition coefficients of indoor PCBs were calculated using the indoor air concentrations determined by Edeballi (2022) and settled dust-bound concentrations of this thesis project. Upon inspection of the calculated partition coefficients, it was observed that PCBs tend to accumulate in dust as the molecular weight increases (Figure 4.106). The average $\log_{10}K_D$ values for Di-CB, Tri-CB, Tetra-CB, Penta-CB, Hexa-CB and Hepta-CB homolog groups were determined to be -4.24, -3.82, -3.21, -2.49, -2.35 and -2.04, respectively. As molecular weight increases, there is a tendency for organic substances to accumulate and/or remain in the particle phase. The results obtained support the particle phase accumulation characteristics of semi-volatile organic compounds at high molecular weights.

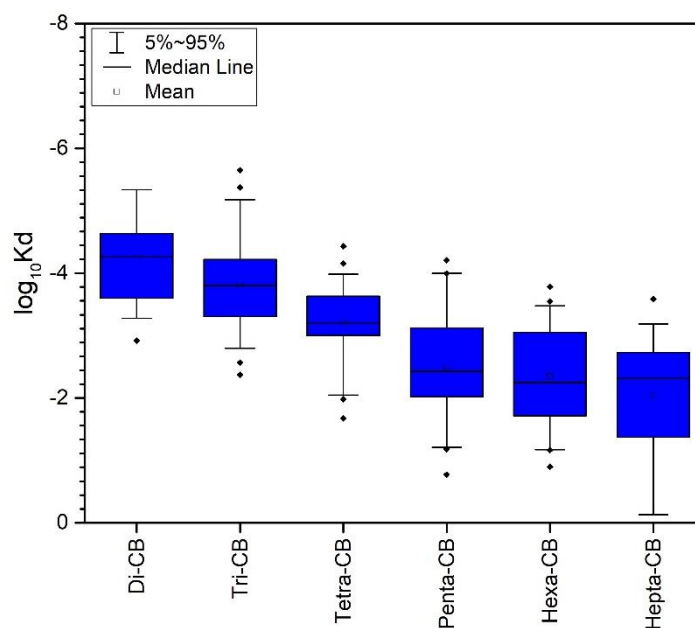


Figure 4.106. Dust-gas partitioning coefficients of PCBs ($\log_{10}K_D$)

4.9. PBDE Concentrations in Foods

The median Σ PBDE concentration in food samples taken from homes was determined to be 10.0 ng/g, with an average of 16.3 ng/g. The median concentration of BDE-28, -47, -100, -99, -154, -153, -183, and -209 congeners in food samples taken from homes were 0.27, 0.83, 2.26, 0.47, 1.93, 2.15, 1.28, and 0.23 ng/g, respectively (Figure 4.107). A study conducted in the United States reported Σ PBDE levels in fish species ranging from 8 ng/g to 88 ng/g (Johnson-Restrepo et al., 2005). Another study in Nigeria reported the average Σ_8 PBDE concentrations in aquatic organisms at 0.75 ng/g, in oils at 0.08 ng/g, and in meat products at 0.06 ng/g (Babalola and Adeyi, 2018). A 2011 report from the EFSA Panel on Contaminants in the Food Chain (CONTAM Panel) summarized studies on food in European countries, noting that BDE-183 and BDE-209 congeners were common in eggs, and BDE-209 was prevalent in milk and dairy products. Additionally, congener profiles and concentrations in seafood were determined to be variable (CONTAM, 2011). Another study published in 2010 focused PBDEs in U.S. food reported Σ_{24} PBDE concentrations of 0.01 ng/g in cow's milk, 1.55 ng/g in sardines, and 6.21 ng/g in butter.

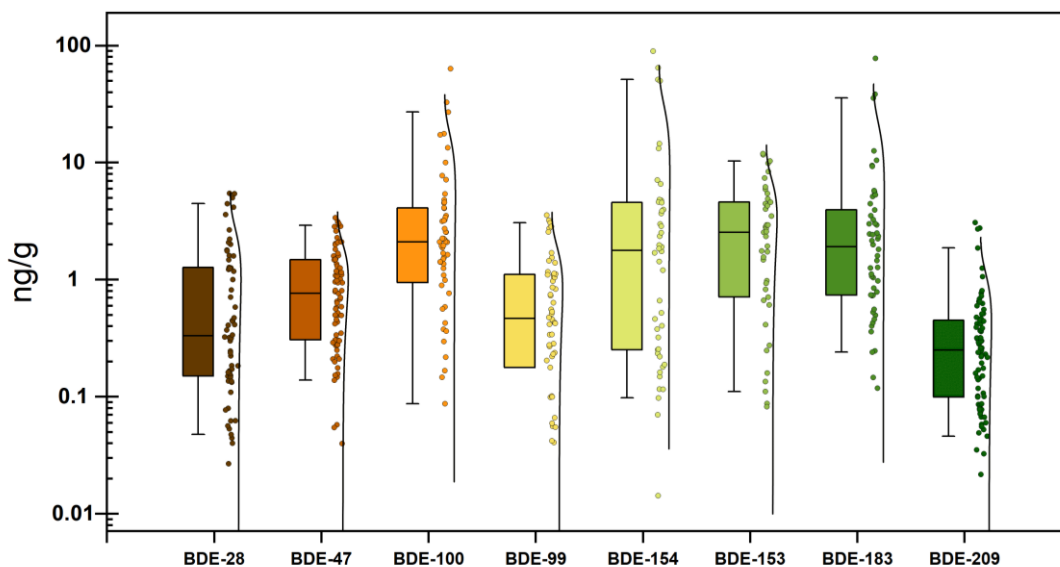


Figure 4.107. PBDE concentrations in foods taken from homes

The PBDE profile in food samples taken from homes is shown in Figure 4.108. Although BDE-209 was identified as the congener contributing the most to the Σ_8 PBDE concentration in the dust and air samples collected for the project, it was the congener contributing the least to the Σ_8 PBDE concentration in food samples. In the food samples from homes, BDE-100 and BDE-153 congeners contributed approximately half of the Σ_8 PBDE concentration (24.3% and 23.1%, respectively). BDE-154 contributed 19.7%, and BDE-183 contributed 13.7% to the Σ_8 PBDE concentration. The contributions of other congeners to the Σ_8 PBDE concentration were below 10%.

Despite BDE-209's dominance in environmental systems, that was determined to be lower concentrations in foods. A study on soil contaminated with PBDEs found that BDE-209 concentrations decreased by about 59.7% at 250°C (Liu et al., 2023). Additionally, studies on carp digestive systems show that PBDEs can undergo debromination, converting into lower-brominated congeners (Benedict et al., 2007). These findings suggest that thermal and biodegradation mechanisms significantly impact the PBDE profile in foods. The different congener profiles observed in dust and air samples compared to food samples support this idea.

The results indicate that high-temperature cooking processes might convert PBDEs in foods into more toxic forms, such as dioxins and furans (PBDD/F).

Determining whether PBDD/Fs form in cooked foods, despite not being target compounds of this project, is crucial for public health. There are few studies on the effect of cooking on PBDEs, with varying results, indicating the need for more research. A 2013 study (Bendig et al., 2013) suggested that microwave cooking partially degrades BDE-209, while a 2020 study (Zhang et al., 2020) found that boiling and frying do not degrade PBDEs. This 2020 study proposed that while PBDEs do not degrade during cooking, their bioavailability decreases due to protein structure changes in foods.

In vegetable oils, the presence of *o,p'*-DDT or iron(III) chloride at high temperatures can cause about 10% degradation of BDE-209, forming mono-chlorinated or polybrominated diphenyl ethers (Bendig et al., 2012a). Another study involving salmon fillets cooked with vegetable oil found that 25% of BDE-209 degraded into lower-brominated congeners and, to a lesser extent, furans (Bendig et al., 2012b). Considering these scientific publications (Bendig et al., 2012a, 2012b, 2013) were from the same research group, consistent analytical procedures eliminate inter-laboratory variability, highlighting the impact of cooking methods on PBDE degradation. The average Σ 8PBDE concentrations in food samples taken from rural, sub-urban, and urban homes were determined to be 15.5, 18.2, and 14.3 ng/g, respectively (Figure 4.109). The concentrations of BDE-100 and BDE-154 congeners were predominant in food samples from rural and semi-urban homes, while in urban areas, the congener concentrations were relatively segregated equal (Figure 4.110). In food samples from homes in rural and semi-urban areas, BDE-154 contributed 47.9% and 45.4% to the Σ 8PBDE concentrations, respectively, while in urban areas, its contribution was about 7%. In urban samples, BDE-153 and BDE-183 were more prominent in the concentration profile, contributing 23.4% and 37.1%, respectively.

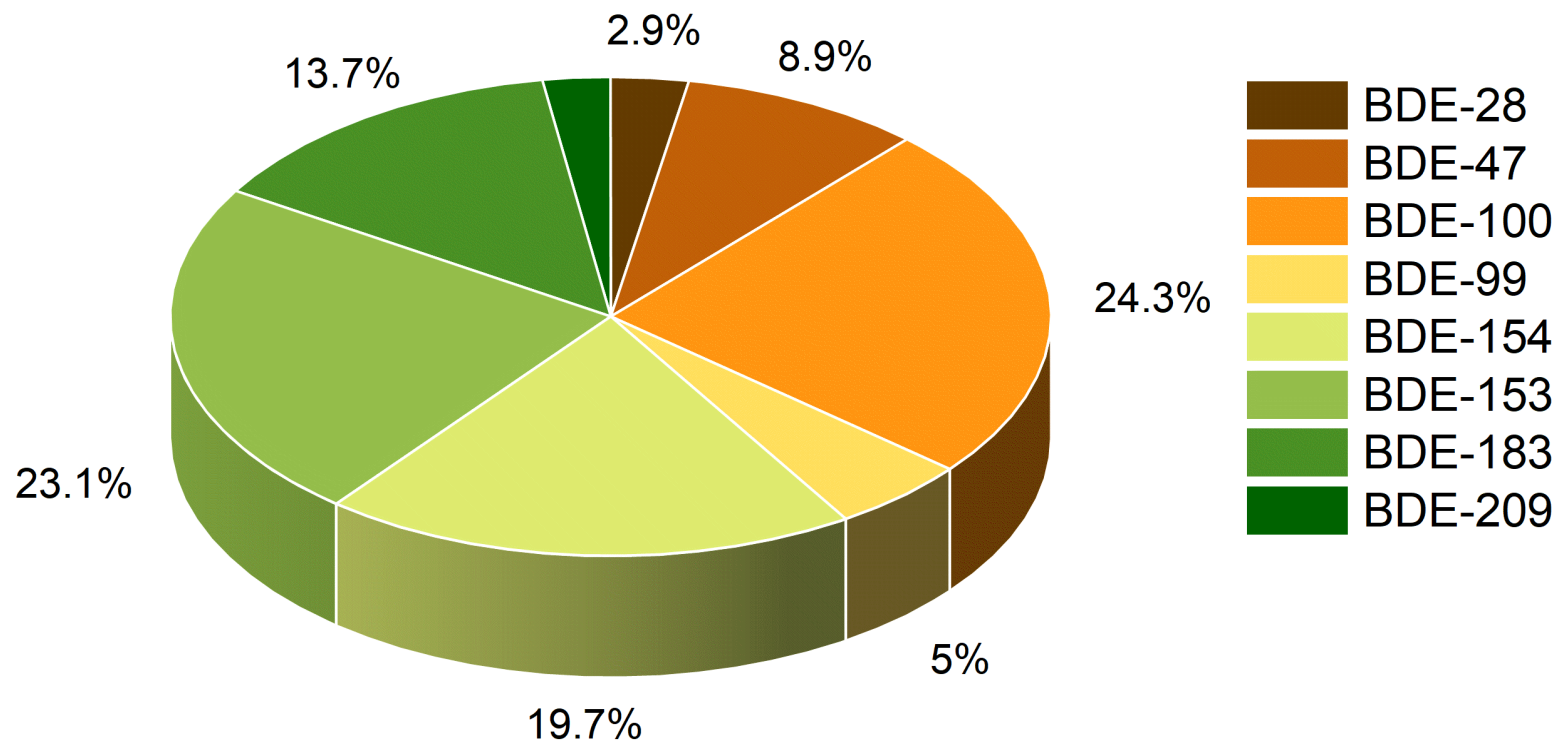


Figure 4.108. PBDE congener profile in food samples taken from homes

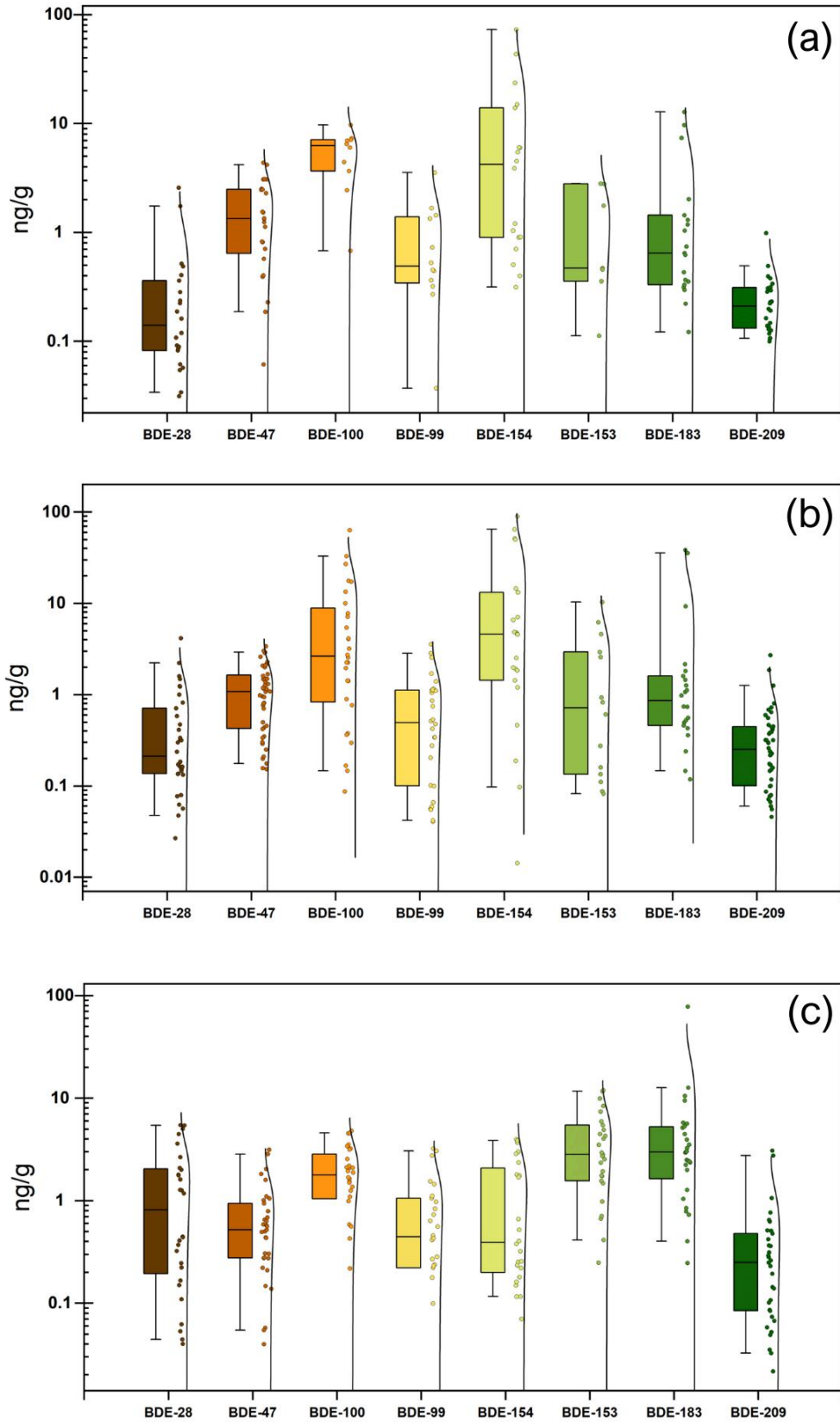


Figure 4.109. PBDE concentrations in food samples taken from (a) rural, (b) sub-urban, and (c) urban homes

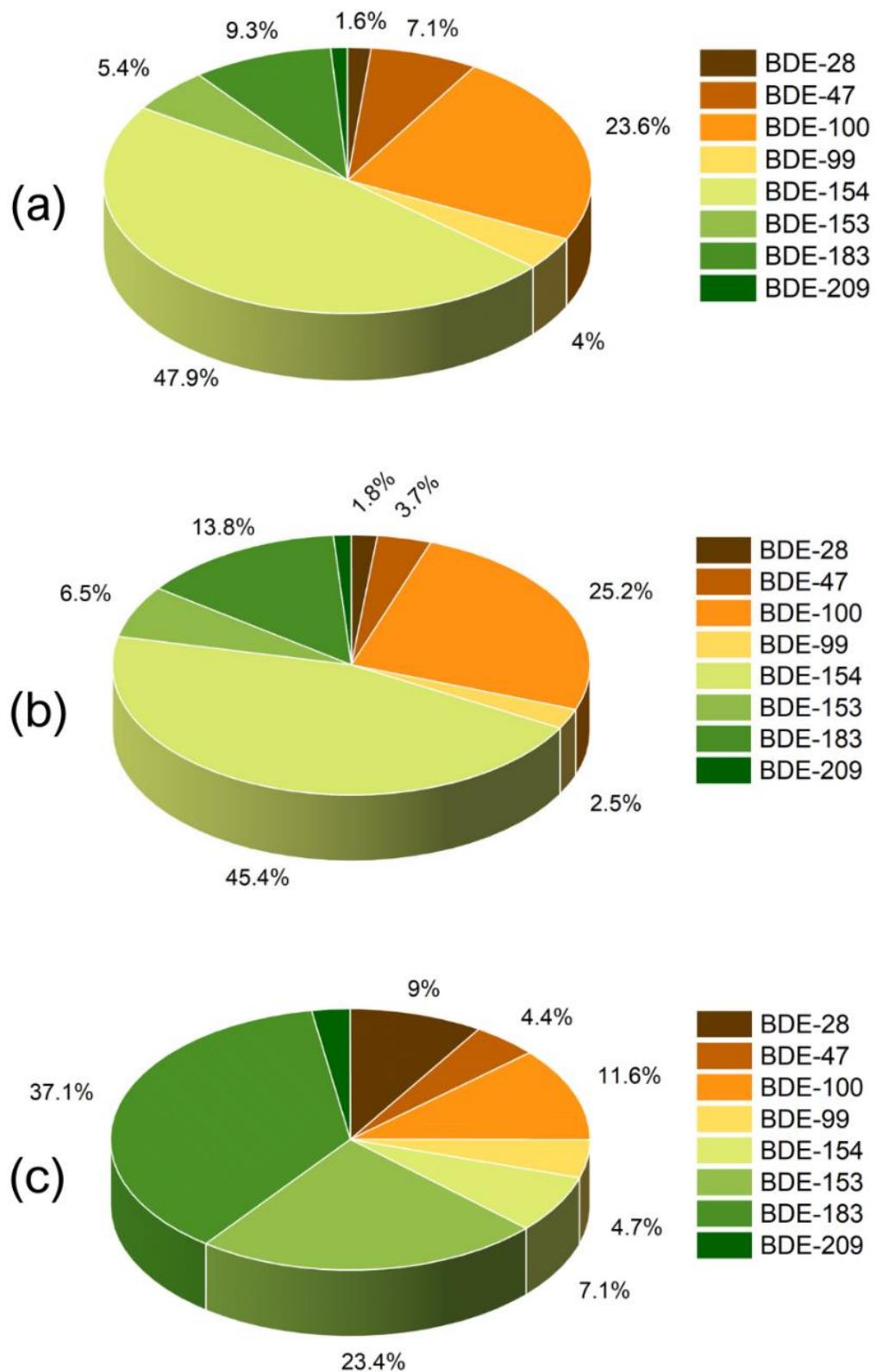


Figure 4.110. PBDE congener profiles in food samples taken from (a) rural, (b) sub-urban, and (c) urban homes

The median Σ 8PBDE concentration in food samples taken from schools was determined to be 4.82 ng/g, with an average concentration of 11.3 ng/g (Figure 4.111). The median concentrations of BDE-28, -47, -100, -99, -154, -153, -183, and -209 congeners in those samples were determined to be 0.20, 0.81, 1.48, 0.15, 0.31, 0.63, 0.98, and 0.26 ng/g, respectively. PBDE concentrations in food samples from schools were noticeably lower compared to those from homes. This discrepancy could be attributed to the lower use or absence of animal products and fats, which are relatively more expensive than vegetable products and oils, in school canteens compared to homes. PBDEs in environmental systems tend to accumulate in soil, with very low levels transferring to plants through roots (0.3-0.5%). In plants, these compounds can undergo transformation mechanisms, converting into lower-brominated PBDEs and hydroxy and methoxy derivatives, resulting in low concentrations of legacy PBDEs in plant tissues (Dobslaw et al., 2021).

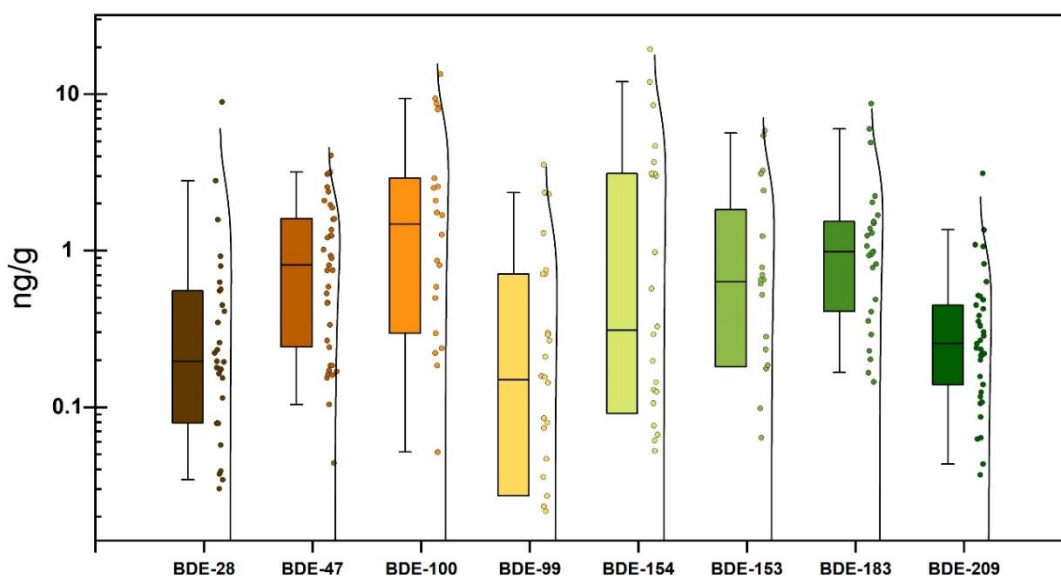


Figure 4.111. PBDE concentrations in foods taken from schools

The PBDE congener profile in food samples taken from schools is shown in Figure 4.112. Similar to the food samples taken from homes, the contributions of BDE-100, BDE-183, and BDE-154 to the Σ 8PBDE concentration in school samples were 26.6%, 14%, and 23.4%, respectively. BDE-47 and BDE-183 each contributed around

10% to the Σ_8 PBDE concentration, while BDE-28, BDE-99, and BDE-209 contributed 6%, 4.6%, and 3.7%, respectively.

BDE-209 was the lowest concentration congener in food samples, despite being the dominant congener in air and dust samples from these environments. Previous studies (Genisoglu et al., 2019; Ayri et al., 2023) reported BDE-209 to be prevalent in both indoor and outdoor environments, but it was detected in relatively low concentrations in food in this project. This discrepancy is thought to be due to metabolic and thermal degradation, although concrete evidence is needed to confirm this theory. The lack of sufficient studies in the literature limits definitive conclusions, but the results of this project contribute to public health insights and the scientific understanding of PBDE transformation during cooking. This project lays the groundwork for further research on PBDE transformations during cooking.

The PBDEs concentrations in food samples collected from rural, semi-urban, and urban schools are shown in Figure 4.113. The Σ_8 PBDE concentrations in food samples from schools in rural, semi-urban, and urban areas were determined to be 21.3, 11.8, and 6.57 ng/g, respectively. It was found that the Σ_8 PBDE concentration in the foods from school canteens in rural areas was approximately twice as high as that in semi-urban areas and about three times higher than that in urban areas. The higher PBDE concentrations in food samples from schools in rural areas, specifically those effects of the AOIS in Helvacı and Kozak Köy, are thought to be due to the use of animal products and fats, which are reported to contain higher PBDE levels compared to plant products, and/or easier access to agricultural and livestock products from areas affected by AOIS.

The average concentrations of BDE-28, -47, -100, -99, -154, -153, -183, and -209 congeners in the food from rural schools were determined to be 0.35, 1.54, 10.5, 0.62, 2.52, 3.06, 2.02, and 0.63 ng/g, respectively. While those in sub-urban schools were 0.26, 1.56, 2.33, 0.77, 5.02, 0.70, 0.83, and 0.36 ng/g, respectively, and in urban schools were 1.19, 0.44, 1.54, 0.18, 0.11, 0.75, 1.98, and 0.37 ng/g, respectively.

The contributions of PBDE congeners to the Σ_8 PBDE concentration in food samples from schools in rural, semi-urban, and urban areas are shown in Figure 4.125. In rural areas, BDE-100 contributed to half of the Σ_8 PBDE concentration, while in semi-urban areas, nearly half of the Σ_8 PBDE concentration came from BDE-154. In urban areas, the contributions of BDE-183 and BDE-100 to the Σ_8 PBDE concentration were 30.2% and 23.5%, respectively. The contribution of BDE-209 to the Σ_8 PBDE concentration was 3.0% in rural and semi-urban areas and 5.6% in urban areas.

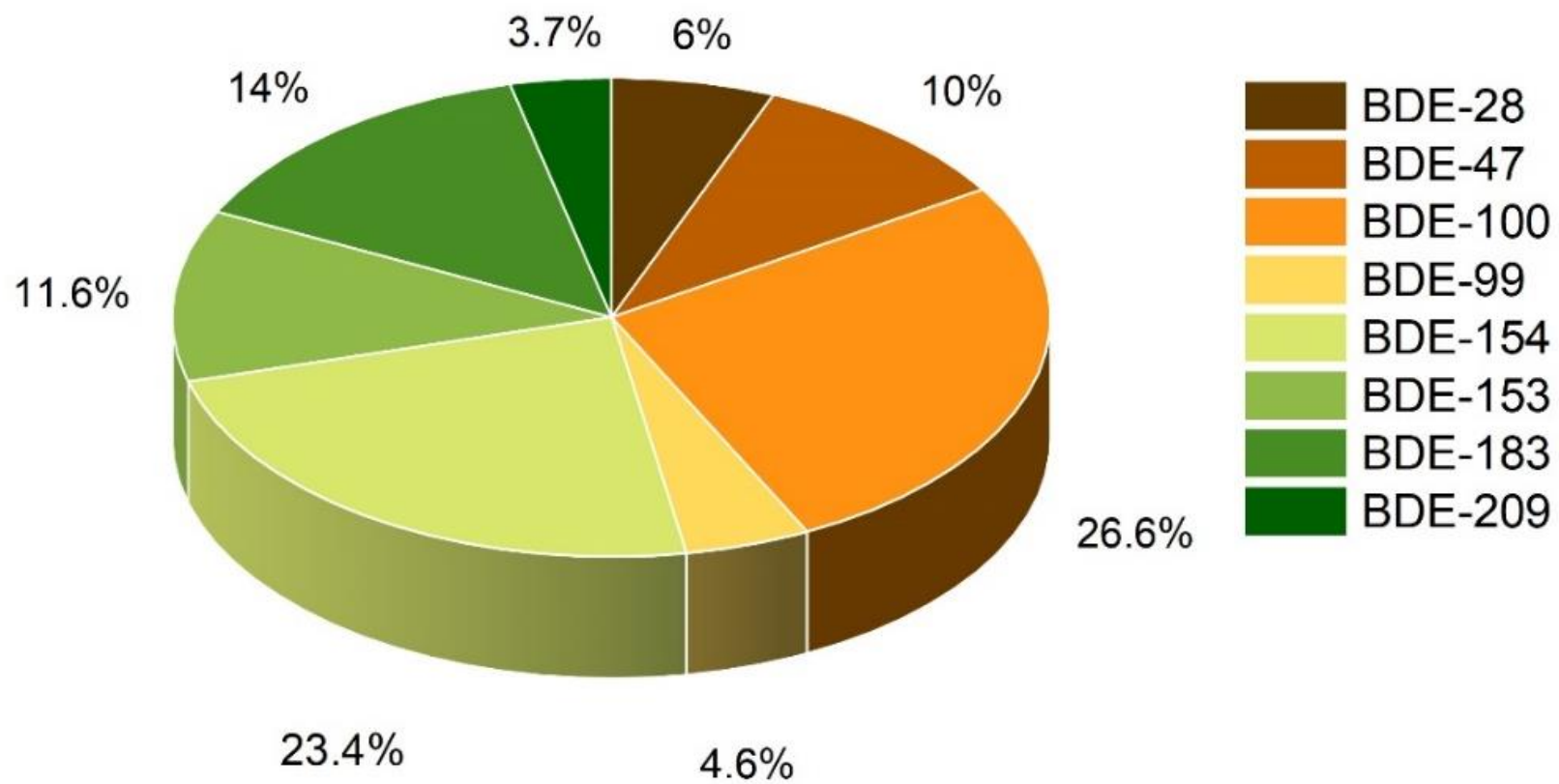


Figure 4.112. PBDE congener profile in food samples taken from schools

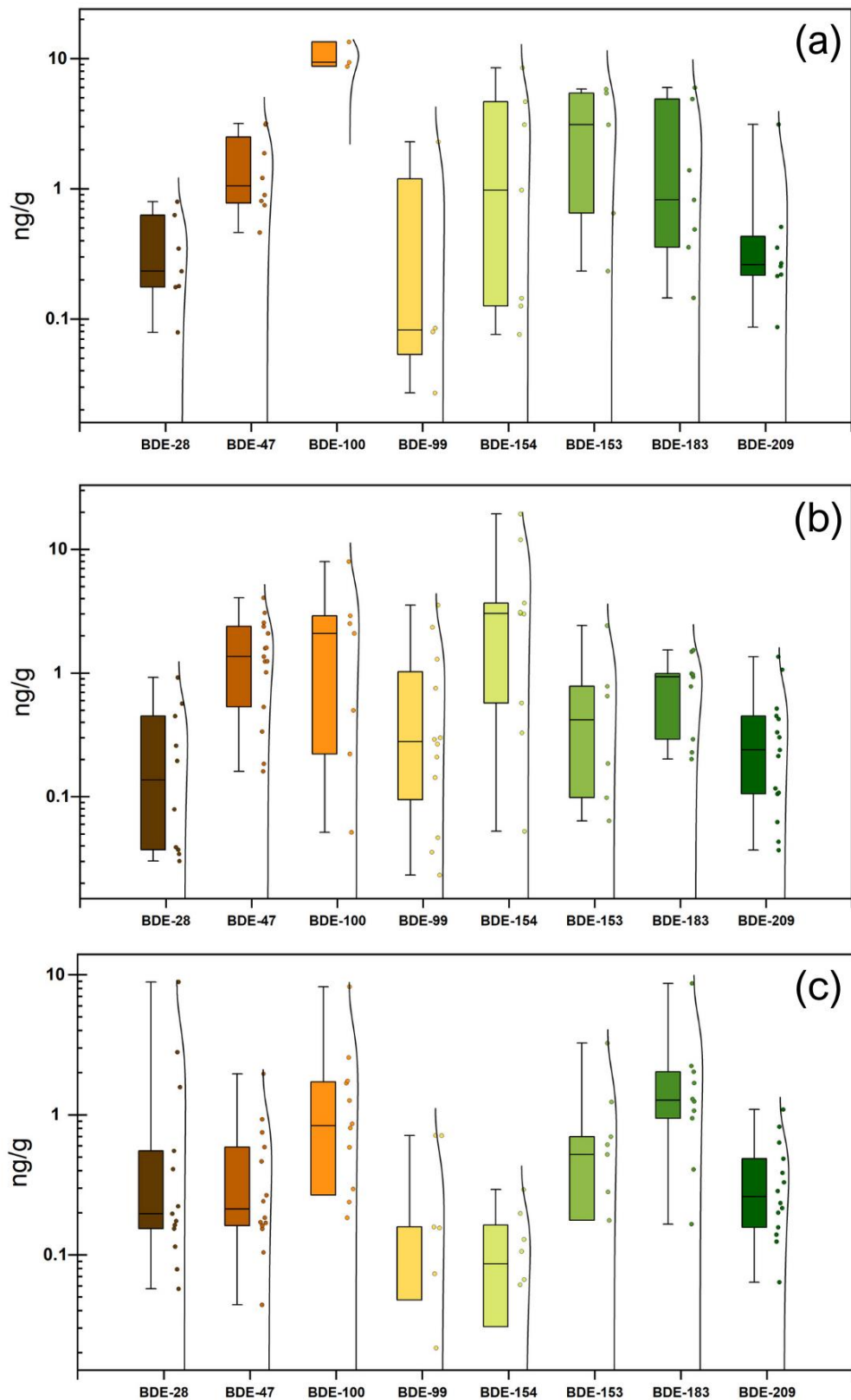


Figure 4.113. PBDE concentrations in food samples taken from (a) rural, (b) sub-urban, and (c) urban schools

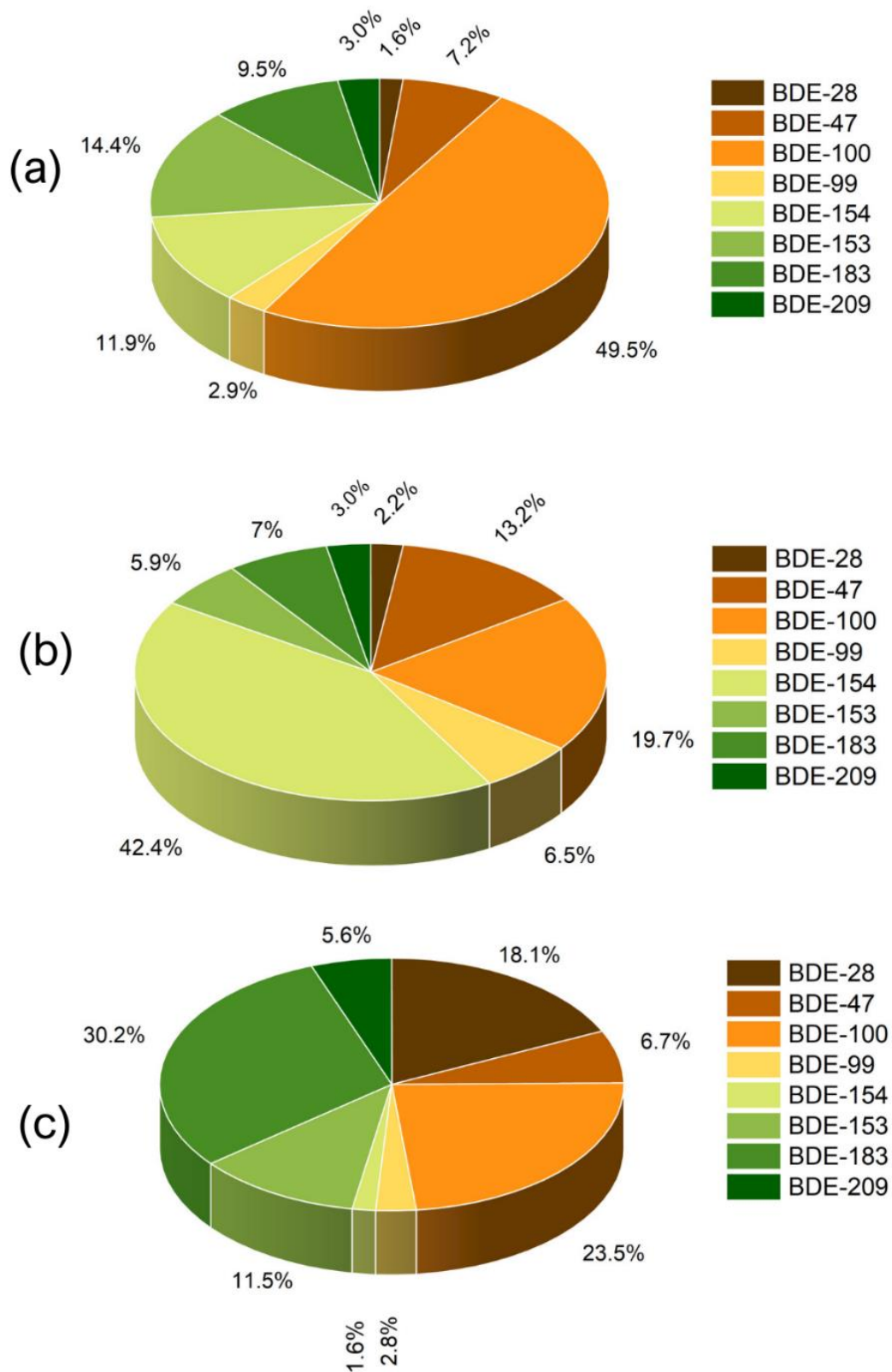


Figure 4.114. PBDE congener profiles in food samples taken from (a) rural, (b) sub-urban, and (c) urban schools

According to the PCA analysis of pooled PBDE concentrations in foods, four PC were estimated to affects the variation of PBDE concentrations in food samples from homes and schools (Figure 4.115). PC1 accounts for 28.2% of the variation in PBDE concentrations in the food samples, while PC2, PC3, and PC4 account for 17.4%, 15.5%, and 12.6% of the variation, respectively.

A lot of factors affecting PBDE concentrations in food samples, compared to air and dust samples, could be attributed to several reasons. These include the use of animal and agricultural products that may be contaminated, the proximity of food production sites to industrial sources, organic pollutant contamination in soil, the method and degree of cooking, and the inclusion of animal products such as meat and fats, which are known to have relatively higher concentrations of organic pollutants.

Due to the consistency in source density and type in indoor environments such as homes, schools, nurseries, and gyms, the variability in air and dust samples is relatively low. In contrast, food samples may exhibit varying levels of organic matter and especially lipid/fat content, even within the same type of food, due to differences in their ingredients and preparation methods (Babalola and Adeyi, 2018; Chang et al., 2017; Dobslaw et al., 2021; Fernandes et al., 2004; Martellini et al., 2016; Schechter et al., 2006).

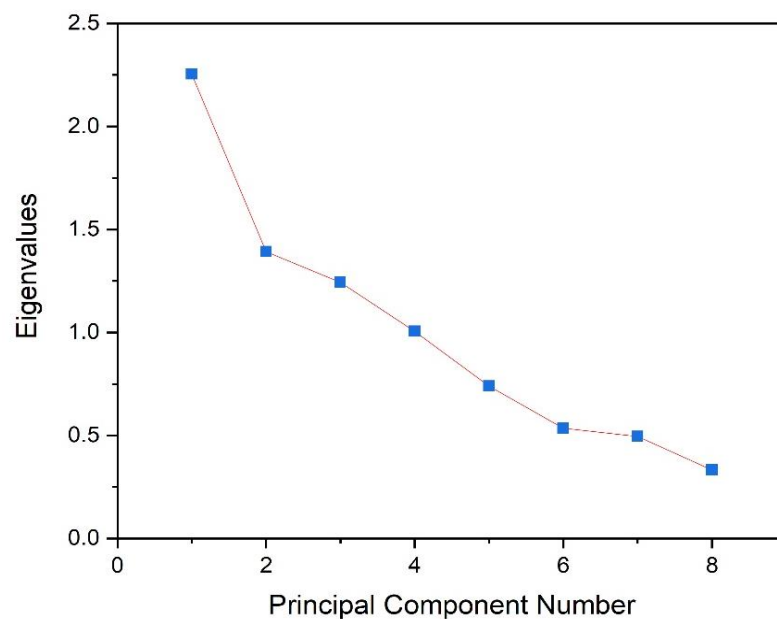


Figure 4.115. PCA of PBDE concentrations of foods in İzmir

The PCA loading plots of the first three PCs of PBDE concentration variation in food meal samples collected from homes and schools is shown in Figure 4.116. PC1 has an effect on the concentration changes of target congeners except BDE-209 (eigenvector=0.28-0.48). Since PC1 does not have an effect on the concentrations of BDE-209 in meal samples, which is the dominant congener in environmental systems, it is thought to represent the congener concentrations in animal and plant products before processing rather than bromination or degradation mechanisms that may occur during processing. PC2 only has an effect on the concentrations of BDE-209, suggesting its representation of the presence of animal products in meals due to the very low levels of BDE-209 uptake by plants and the transformation of BDE-209 into lower brominated congeners in tissues.

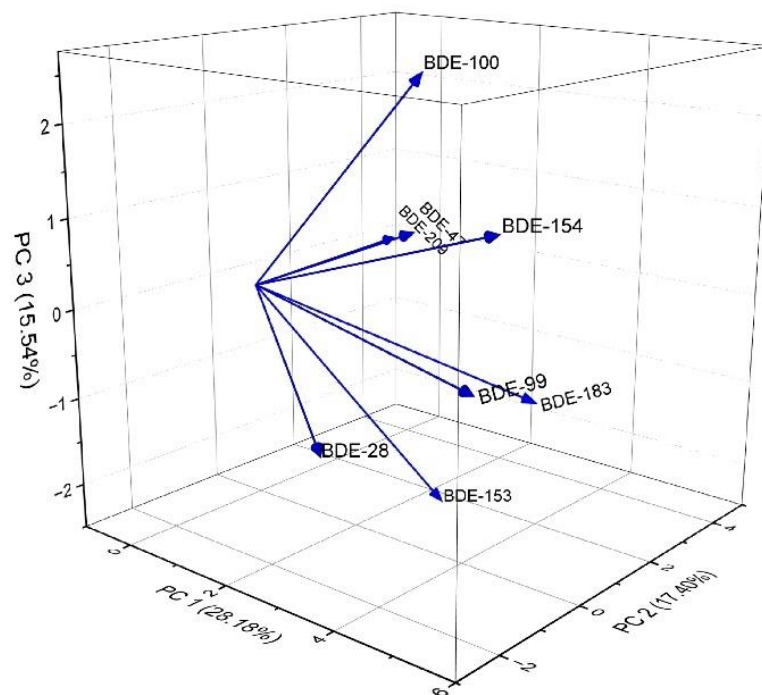


Figure 4.116. PCA loading plots of PBDEs in foods in İzmir

The loading plots of PCA conducted on PBDE concentrations of foods from homes is shown in Figure 4.117. Three PC (EV>1) were determined to be contribution of the 63.3% of PBDE concentration variation in food samples from homes. It was found

that PC1 (eigenvector > 0.40) has the greatest influence on the concentration variation of BDE-99, -100, and -154 congeners, while PC1 and PC2 (eigenvector ≈ 0.37) equally affect the concentration of BDE-28. PC2 also significantly affects the concentration of the BDE-153 (eigenvector = 0.62) in foods from homes. Also, PC3 significant effect the concentrations of BDE-47, -183, and -209 congeners (eigenvector = 0.41-0.61) in foods from homes.

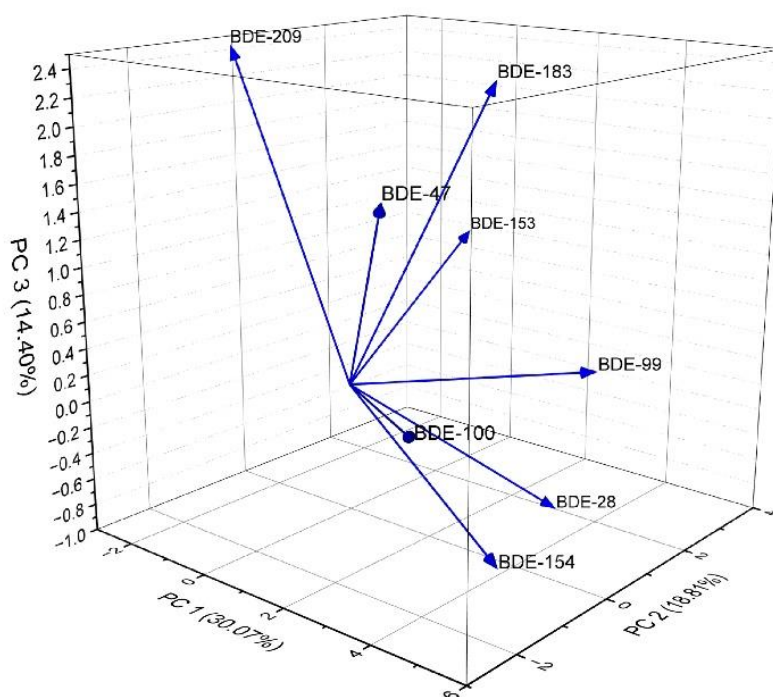


Figure 4.117. PCA loading plots of PBDEs in food samples from homes

The loading plots of PCA conducted on PBDE concentrations of foods from schools is shown in Figure 4.118. It was determined that three PC in PCA influenced 80.6% of the PBDE concentration variation. Since the eigenvalue of TB3 is very close to 1 (0.98), the third principal component was also considered. The BDE-28 was significantly separated from the other targeted PBDE congeners in PCA analysis of food samples from schools. The concentration variation of the BDE-28 was significantly influenced by PC3 (EV = 0.88), while it was also affected by PC2 (EV = 0.28). The

concentrations of BDE-100, -154, -153, -183, and -209 were affected by PC1 (eigenvector = 0.37-0.47), while the concentration of BDE-99 was affected by PC2.

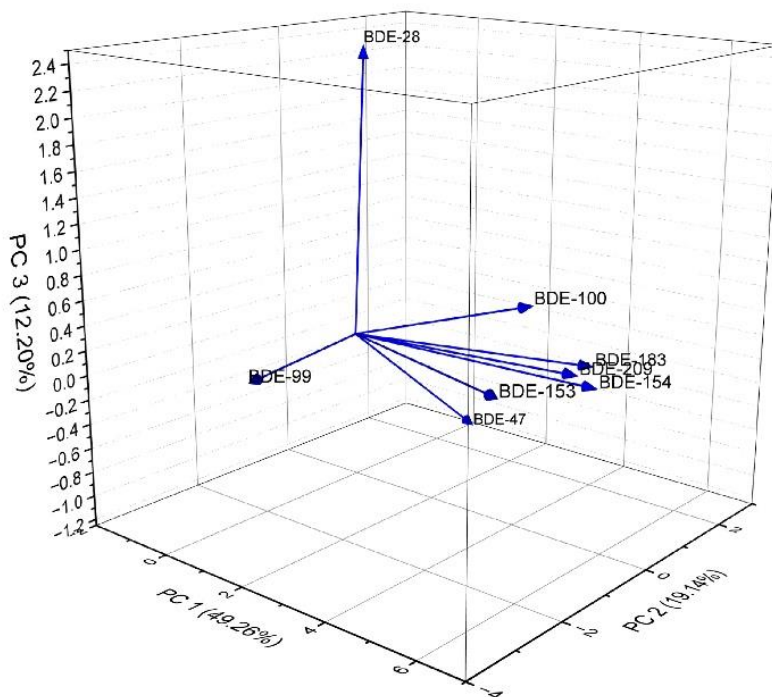


Figure 4.118. PCA loading plots of PBDEs in food samples from schools

4.10. AFR Concentrations in Foods

The AFR concentrations in foods were also determined. The α DBE-DBCH, β DBE-DBCH, BEH-TEBP, HBB, TBP-DBPE, TBCO, EH-TBB, and HBCDD compounds were detected in 61%, 56%, 2%, 8%, 9%, 8%, 6%, and 16% of the samples, respectively. The average concentrations of those in the detectable samples were determined to be 6.60, 2.46, 0.31, 0.98, 2.36, 1.00, 5.08, and 12.1 ng/g, respectively. In 37 meal samples collected from schools, the average concentrations of α DBE-DBCH, β DBE-DBCH, BEH-TEBP, HBB, TBP-DBPE, TBCO, EH-TBB, and HBCDD were determined to be 5.29, 1.57, 2.62, 1.02, 1.39, 0.39, 1.71, and 1.28 ng/g, respectively. α DBE-DBCH and β DBE-DBCH compounds were detected in 46% and 49% of the

samples collected from schools, while the other compounds were detected in less than 14% of the samples (Figure 4.131). In previous studies, the concentrations of AFR compounds in food were found to be in the range of pg/g to ng/g (Fernandes et al., 2016; Zuiderveen et al., 2020). Due to the use of AFRs after PBDEs, and their less widespread presence in environmental systems compared to PBDEs, foods might be less contaminated with AFR compounds.

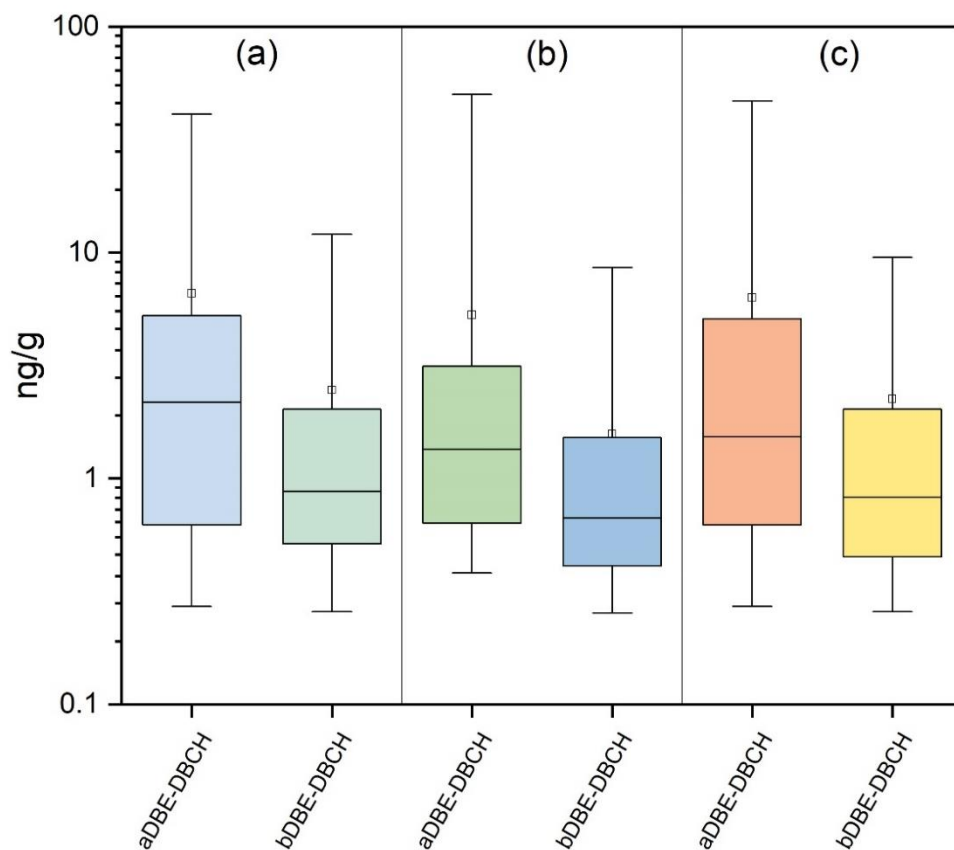


Figure 4.119. DBE-DBCH concentration in foods: (a) homes, (b) schools, and (c) pooled

4.11. PAH Concentrations in Foods

The average Σ PAH concentration in food samples collected from homes and schools in İzmir was determined to be 337 ng/g. The average concentration of low

molecular weight (LM) PAH compounds was 82.7 ng/g, while high molecular weight (HM) PAH compounds was 258.8 ng/g (Figure 4.120). The higher concentrations of HM PAH compounds in foods might be due to the evaporation tendencies of LM PAH compounds and the potential formation of HM PAH compounds from organic matter and fats during high-temperature cooking processes.

A recent study on unprocessed foods reported Σ PAH concentrations in vegetables, fruits, and meat products ranging from 16.4 to 137 ng/g, 86.0 to 225 ng/g, and 0.1 to 23.4 ng/g, respectively (Guo et al., 2023). This study reported that the concentrations of Flu and B(a)P compounds were higher than other targeted PAH compounds, suggesting that PAHs formed from the high-temperature combustion of coal, oil, and biomass contaminated agricultural areas and subsequently fresh food products.

In another study conducted in Kuwait, Σ PAH concentrations in foods prepared using grilling and smoking methods reached up to 1292 ng/g (Alomirah et al., 2011). According to Alomirah et al. (2011), the average Σ PAH concentrations in various types of food ranged from 13.2 ng/g to 648 ng/g. Similarly, a study in China reported Σ PAH concentrations in deep-fried dough sticks (*youtiao*) to be between 9.90 and 89.97 ng/g (Li et al., 2016).

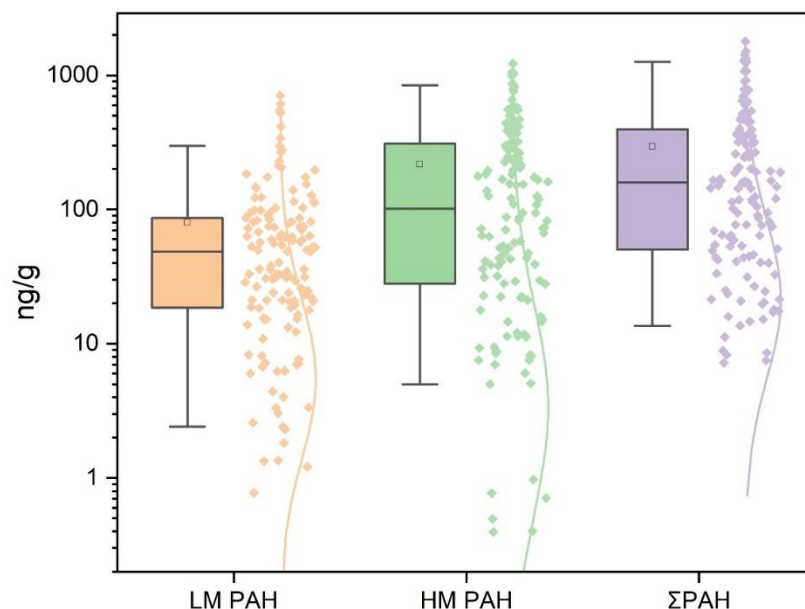


Figure 4.120. LM PAH, HM PAH, and Σ PAH concentrations in foods

The average Σ PAH concentrations in food samples taken from homes and schools were determined to be 344 and 322 ng/g, respectively. The average concentrations of Nap, Acy, Ace, Fla, Ant, Phe, Pyr, Chr, B(a)A, B(b)F, B(a)P, Ind, DB(ah)A, and B(ghi)P compounds in food samples from homes were determined to be 17.3, 10.3, 41.1, 2.67, 4.08, 4.52, 31.0, 6.85, 161, 27.5, 18.2, 6.03, and 0.70 ng/g, respectively, while those average in food samples from schools were determined to be 12.8, 14.5, 47.9, 2.41, 5.39, 4.00, 5.59, 24.4, 8.04, 6.56, 128, 27.7, 28.5, and 4.54 ng/g, respectively (Figure 4.121). In urban, sub-urban, and rural areas, the average Σ PAH concentration in meal samples taken from homes was determined to be 286, 287, and 513 ng/g, respectively, while in meal samples taken from schools in these areas, the average Σ PAH concentration was determined to be 473, 179, and 364 ng/g, respectively (Figure 4.122).

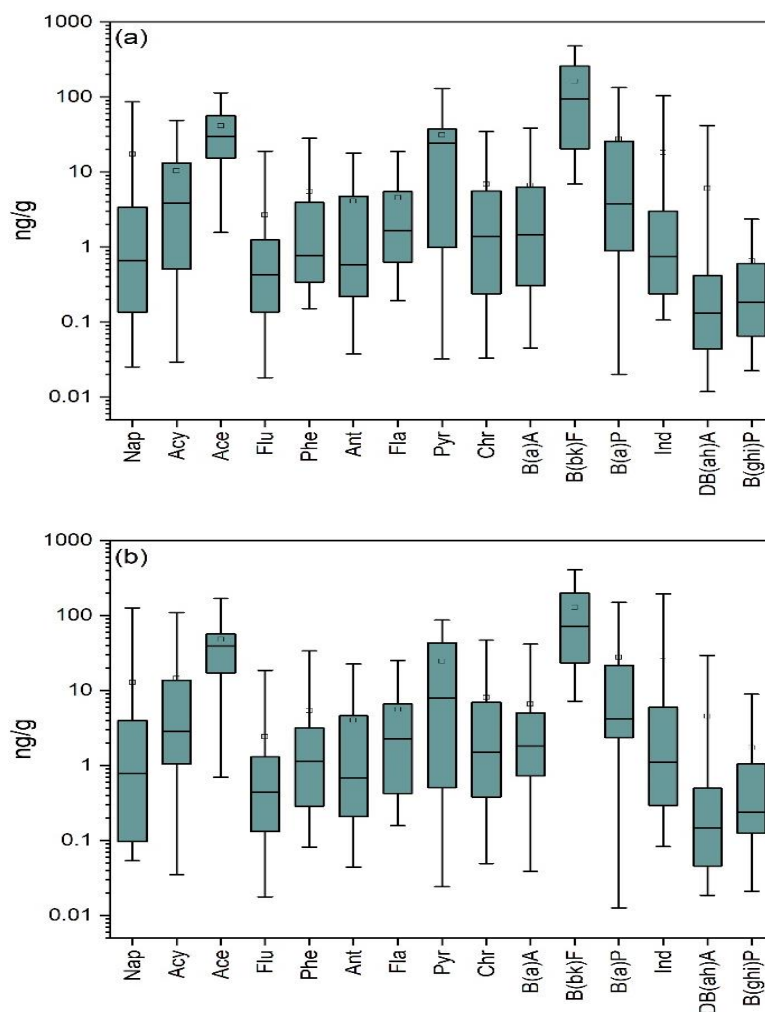


Figure 4.121. The concentrations of PAHs in food samples from (a) homes and (b) schools

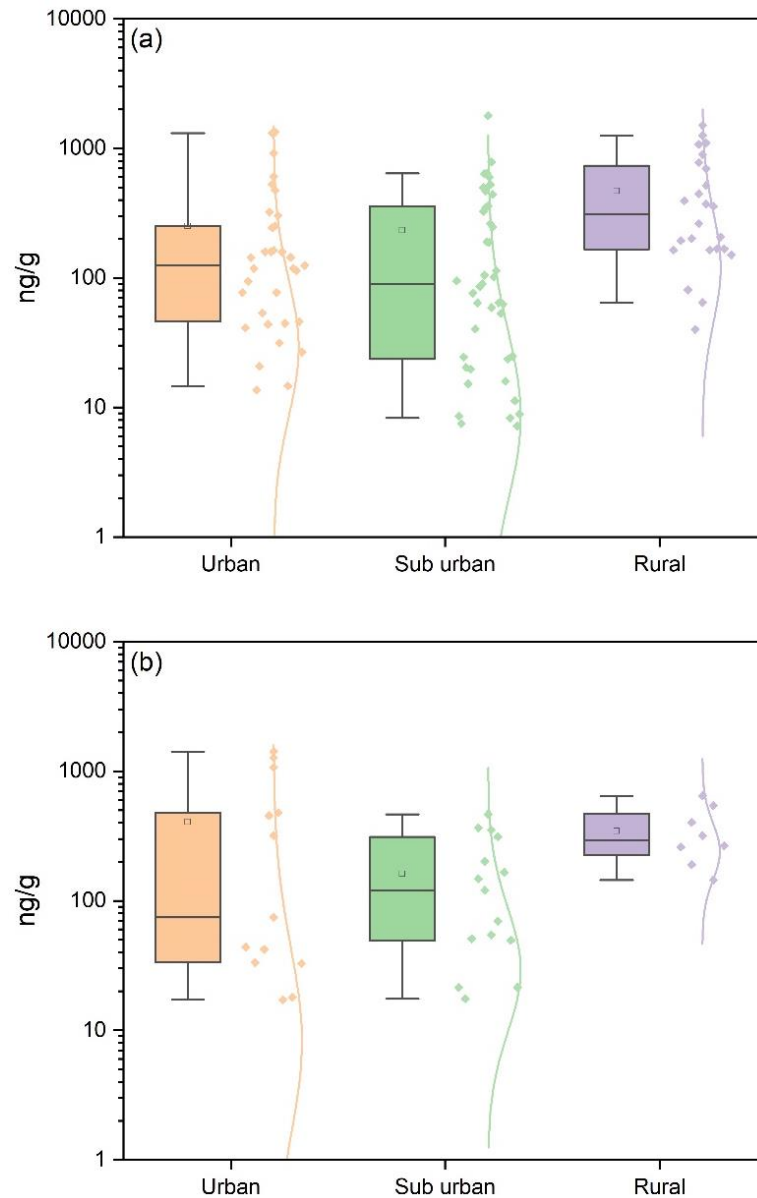


Figure 4.122. ΣPAH concentrations in foods taken from (a) homes and (b) schools

Diagnostic ratios could be used to estimate the sources of PAH compounds in foods (Guo et al., 2023). The diagnostic ratios obtained from the PAH concentrations determined in the food samples indicate that the PAH compounds in meals may have originated from various sources (Figure 4.123). The Fla+(Fla+Pyr) ratios determined in the food samples suggest that contamination from petroleum emissions may have affected the concentration of PAHs in foods, while the Ind/Ind+(BghiP) diagnostic ratio may indicate contamination from combustion emissions of fuels such as wood and coal. However, the cooking process itself can also contribute to PAH formation in meals,

factors such as cooking temperature, meal content, and cooking method can also affect the PAH composition in meals.

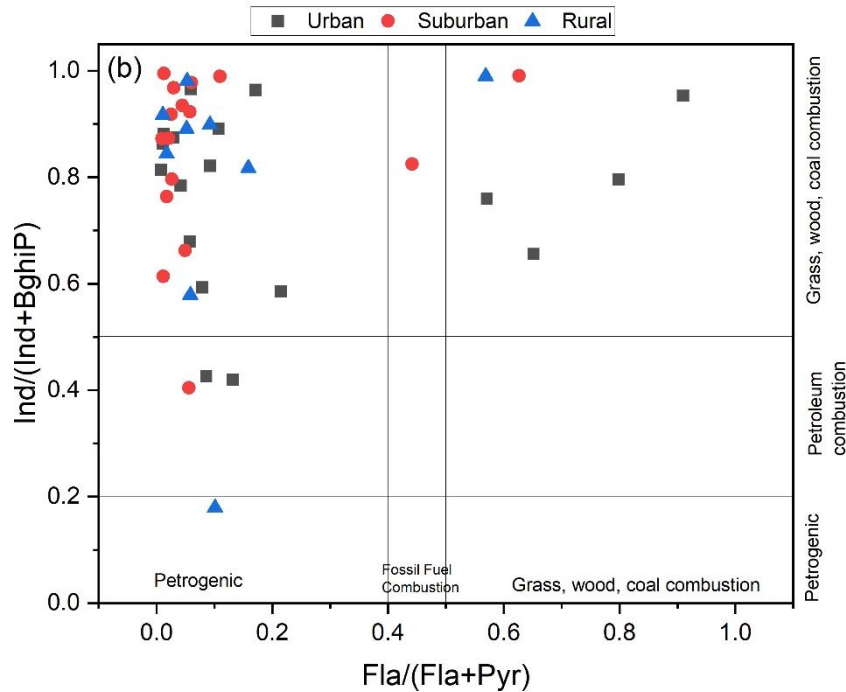


Figure 4.123. Diagnostic ratios of PAH compounds in foods

In the PCA performed on the concentrations of PAH compounds in food samples, three principal components (PC1-3) determined to account for 83% of the variation in PAH concentrations in the foods (Figure 4.124). PC1 had an effect ($\text{EV} > 0.20$) on the concentration variation of Nap, Acy, Ace, Flu, Phe, Ant, Chr, B(a)A, B(bk)F, B(a)P, Ind, LM PAH, and HM PAH compounds, while PC2 represented the concentration variation of Ant, Fla, and DB(ah)A ($\text{EV} > 0.39$). Since PC1 influenced the concentrations of almost all PAH compounds, this PC may be related to the composition of the products used in meal preparation and the chosen cooking method. The increase of Fla concentrations is associated to emissions from combustion of organic matter, wood, and coal, while an increase of Ant concentrations relative to Phe might be associated with all combustion reactions (Tobiszewski and Namieśnik, 2012). Therefore, PC2 might be associated with cooking over an open flame, such as grilling.

The third principal component influenced the concentrations of Acy, Pyr, Chr, and B(ghi)P compounds (EV >0.23). Since the increasing of the Pyr, Chr, and B(ghi)P concentrations approach the diagnostic ratios for PAH sources related to petroleum emissions, PC3 may be associated with exposure to petroleum emissions during the use of petroleum-derived fuels or during the production or processing of food products.

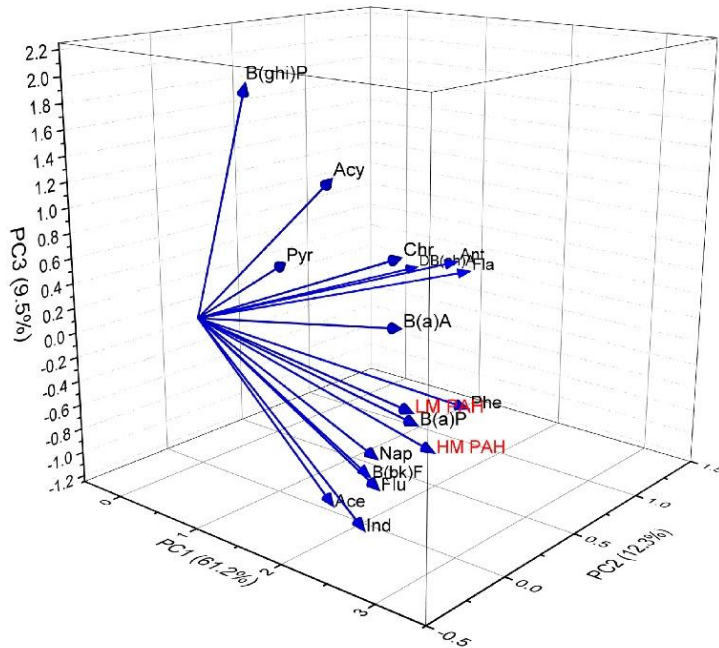


Figure 4.124. PCA loading plot of PAH concentrations in foods

4.12. Exposure and Health Risk Assessment

4.12.1. Exposure and Health Risk Assessment of Settled Dust-Bound and Airborne PBDEs

The median accidental ingestion route ADD levels estimated for BDE-28 to BDE-183 were ranged from 2.51×10^{-10} to 8.15×10^{-9} mg/kg-day, while the median ADD level for BDE-209 was significantly higher at 9.26×10^{-7} mg/kg-day due to the higher dust-bound concentrations. Also, the median LADD for BDE-209 was estimated to be

3.70×10^{-7} mg/kg-day. The probability distributions of the estimated CTR of accidental ingestion of dust-bound PBDEs are shown in Figure SM 2 -Figure SM 5. The median CTR levels for BDE-47, BDE-99, BDE-153, and BDE-209, resulting from accidental ingestion of settled dust, were estimated to be in the range between 1.85×10^{-5} and 1.32×10^{-4} , which were significantly below the threshold level of '1'. The maximum CTR levels were also estimated to be lower than the threshold. The estimated probability distribution of CR levels for BDE-209 is shown in Figure SM 6. The median and maximum CR values for BDE-209, due to accidental ingestion of settled dust, were estimated to be at least two orders of magnitude lower than the acceptable risk level of 10^{-6} . In conclusion, the CTR and CR levels associated with accidental ingestion of settled dust may not individually pose significant health risks for sample population.

Because there are no risk factors available for PBDEs only the exposures were estimated for inhalation route. Estimated exposure levels of BDE compounds through inhalation route are shown in Figure SM 7 and Figure SM 14. The highest exposure level was estimated for the BDE-209 with an average of 4.57×10^{-6} mg/kg-day, while the lowest exposure level was estimated for the BDE-100 with an average of 9.45×10^{-9} mg/kg-day. The median estimated inhalation exposure levels of BDE-28, BDE-47, BDE-99, BDE-154, BDE-153 and BDE-183 ranged from 4.68×10^{-9} to 4.65×10^{-7} . The estimated inhalation exposure levels obtained in this study were similar to the levels obtained in our previous study (Genisoglu et al., 2019).

4.12.2. Health Risk Assessment of Settled Dust-Bound and Airborne PAHs

Health risks of PAH compounds in air and soil dust samples have been modeled in terms of benzo[a]pyrene (B[a]P) unit toxicity equivalent concentrations ($TEQ_{(B[a]P)}$). $TEQ_{(B[a]P)}$ were obtained by summing the equivalent concentrations determined using the B[a]P toxicity equivalent factor (TEF, Table SM 3) for each PAH compound ($TEQ_{(B[a]P)} = \sum C_i \times TEF_i$) (Dumanoglu et al., 2017).

Cancer risks that may result from accidental ingestion of settled dust-bound PAHs are shown in Figure SM 15. While the average CR level modeled through $TEQ_{(B[a]P)}$

concentration levels was determined to be 2.04×10^{-6} , the median cancer risk level was determined to be 3.02×10^{-7} . When estimated CR for the accidental ingestion route of PAHs were classified, it was observed that the average cancer risk level falls within the acceptable risk class ($10^{-6} < CR < 10^{-5}$) (Legay et al., 2011). Although the risks in the 95th percentile of the risk distribution resulting from accidental ingestion was estimated to be within the acceptable risk class, it was important to pay attention to sensitive groups such as those with illnesses, elders and young's.

Cancer risks that may result from inhalation exposure to PAH compounds are shown in Figure SM 16. The average and median CR levels modeled using $TEQ_{(B[a]P)}$ concentration levels were estimated to be 8.83×10^{-7} and 8.83×10^{-7} , respectively. The cancer risk level in the 95th percentile of the risk distribution resulting from inhalation exposure was estimated to be 2.58×10^{-6} . Although the cancer risk levels from inhalation exposure were significantly lower and within acceptable risk levels compared to those resulting from accidental ingestion of settled dust-bound PAHs, that was considered that the aggregate dose from both inhalation and ingestion, along with the addition of other POPs, may affect the cancer risks of PAH compounds in the air.

4.12.3. Dietary Exposure and Health Risk Assessment of POPs

The exposure levels and health risks that may arise through dietary ingestion were modeled using Monte Carlo simulation. The project's sampling design involves the consumption of one portion (150 g) each of three types of food products in a single dinner. The World Health Organization recommends the daily consumption of 400 g of vegetables and fruits for healthy eating (WHO, 2021). To approximate the natural distribution of POP compounds to which the population was exposed, it was assumed in the exposure modeling that 450 g of food is consumed daily for a lifetime, with no consideration of the main components such as vegetables, meat, legumes, and oil in the samples taken from randomly consumed meals without grouping them.

The average exposure levels of BDE-28, -47, -99, -100, -153, -154, -183, and -209 congeners modeled for the Izmir population through dietary ingestion were estimated to be in the range of 10^{-5} - 10^{-6} mg/kg-day while those medians were around 10^{-6} mg/kg-day. At the 95th percentile, the exposure levels of BDE-28, -47, -100, -153, and -183 congeners were around 10^{-5} mg/kg-day, while the exposure levels of BDE-100 and -154

congeners were estimated to be around 10^{-4} mg/kg-day. The exposure level of the BDE-209 at the 95th percentile was estimated to be at 10^{-6} mg/kg-day. The average dietary CTR levels of BDE-47, -99, -153, and -209 were estimated to be at the levels of 10^{-4} , 10^{-1} , 10^{-1} , and 10^{-4} , respectively (Figure SM 17-Figure SM 20). The highest CTR level at the 95th percentile belongs to the BDE-99 congener with 5.53×10^{-1} . While the average and median values of the CR for dietary exposure to the BDE-209 congener were estimated to be at 1.88×10^{-9} and 1.08×10^{-9} , even at the 95th percentile, it was at the level of 6.10×10^{-9} (Figure SM 21). The health risks of dietary PBDE exposure were determined to be at insignificant levels.

CR that may result from dietary exposure to PAH compounds are shown in Figure SM 22. The average and median CR levels modeled using $TEQ_{(B[a]P)}$ were estimated to be at 1.86×10^{-4} and 2.53×10^{-5} levels, respectively. The modeling study estimated that approximately 25% of the population has significant CR ($<10^{-4}$) associated with dietary exposure to PAH compounds. The modeled risk levels were similar to those reported in literature studies (Guo et al., 2023; Xia et al., 2010). The estimated risk levels highlight the importance of using less high-temperature or open-flame cooking methods that lead to PAH formation, especially in the preparation of meals consumed by children and sensitive groups, to reduce cancer risks associated with PAHs.

CHAPTER 5

CONCLUSION

This study assessed the levels and distribution of various persistent organic pollutants (POPs) in indoor and outdoor environments of schools and homes, emphasizing potential exposure risks to children. Higher PBDE levels were found in the settled dust and indoor air of schools compared to homes, with BDE-209 being the predominant congener. Children's exposure is significantly influenced by these high concentrations due to their higher breathing rates and dust ingestion relative to body size.

AFRs and OPFRs were also prevalent, with DBE-DBCH isomers being the dominant AFR in homes, and TBOEP the most abundant OPFR in both schools and homes. OPFR concentrations were notably higher indoors, underscoring the significance of indoor sources. PAHs and PCBs were found in both environments, with urban homes showing higher PAH concentrations compared to sub-urban and rural areas. Schools exhibited higher indoor PAH levels than homes, possibly due to specific indoor activities and sources like kitchen emissions and smoking. High PAH concentration in foods may indicate the importance of cooking temperatures.

Comprehensive analysis results indicate that children may be exposed to significant levels of these pollutants due to the time spent in schools and homes, necessitating targeted strategies to mitigate exposure. Urbanization and proximity to industrial areas exacerbate pollutant levels, necessitating localized interventions. Recommendations include stricter regulations on harmful flame retardants, improved ventilation and filtration in schools and homes, and public education on reducing exposure risks. Further research that focused the effects of ventilation on environmental concentrations of POPs in indoor environments and effects of cooking methods on especially PAH concentrations using local foods is needed to understand the long-term health impacts and the effectiveness of intervention methodologies. Addressing the presence and impact of POPs is crucial for safeguarding children's health and creating healthier living environments.

CHAPTER 6

FUTURE WORKS

Some studies planned, based on the experience obtained from this PhD thesis project, are as follows in the following topics: *Non-Target Screening of Halogenated POPs Using Advanced Techniques (POP-Screen Project)*, which aims to employ advanced methods for detecting and characterizing non-targeted persistent organic pollutants (POPs) in this study. *Monitoring the Metabolites of Identified POPs*, focusing on tracking the degradation products and metabolites of determined POPs to understand their environmental fate and potential health impacts. *Monitoring of the Polychlorinated and Bromochloro Alkanes*, aiming to assess the levels and trends of these emerging persistent organic pollutants to inform regulatory measures and environmental protection efforts. These planned studies aim to expand our understanding of pollutant chemodynamics and contribute to more effective strategies for environmental and human health protection.

6.1. Non-Target Screening of Halogenated POPs Using Advanced Techniques (POP-Screen Project)

Non-target screening using high-resolution mass spectrometry (HRMS) is a powerful approach for detecting and identifying halogenated POPs (Leon et al., 2019). HRMS is an advanced analytical technique that measures the mass-to-charge ratio (m/z) of ions with high accuracy and precision. Time-of-Flight (TOF), orbitrap, Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometry techniques are the most popular and promising methods for molecule identification. The resolution of HRMS allows the differentiation of compounds with very similar m/z values, making it particularly suitable for identifying compounds in complex mixtures. The high sensitivity, specificity, and comprehensive detection capabilities of HRMS make it an indispensable tool in environmental monitoring and pollution assessment.

HRMS screening has some challenges such as complex data interpretation, database limitation and sample matrix effects. The vast amount of data generated in NTS requires advanced computational tools and expertise for accurate interpretation and identification of unknown compounds is often limited by the availability of reference spectra in databases. Also, complex environmental matrices can interfere with the detection and identification of compounds. Advanced data analysis tools, use isotopic pattern for identifying compounds in deconvolution process, such as HaloSeeker, enviMass, and CPSeeker provide great convenience in processing HRMS data. Despite the challenges, advancements in HRMS technology and data analysis are poised to further enhance our ability to monitor and mitigate the impacts of these persistent pollutants.

6.2. Monitoring the Metabolites of Identified POPs

POPs are organic compounds characterized by their resistance to environmental degradation and ability to bioaccumulate in organisms, posing significant risks to human health and the environment. Understanding their metabolism, particularly through Phase 1 and Phase 2 processes, is crucial for assessing their toxicological impacts and developing effective management strategies.

Phase 1 metabolism involves enzymatic reactions that introduce or unmask functional groups on molecules, often making them more polar and potentially more reactive (e.g. OH-PAHs, OH-PBDEs, and OH-PCBs). Phase 2 metabolism involves conjugation reactions where Phase 1 metabolites are further processed to increase their water solubility and facilitate excretion from the body. So, identification of Phase 2 metabolites in wastewater stream may provide the assessing exposed doses of POPs and associated health risks of all population. Phase 1 and Phase 2 metabolism of POPs are essential processes that govern their toxicity and environmental persistence. Future research and monitoring studies on metabolism balance of POPs in human body, occurrence in wastewater stream, developing health risk assessment tools using metabolomic data are necessary to mitigate their adverse effects on human health and the environment effectively.

6.3. Monitoring of the Polychlorinated and Bromochloro Alkanes

Chlorinated paraffins (CPs) mostly composed of polychlorinated alkanes (PCAs) are a group of complex mixtures of chlorinated n-alkanes classified by carbon chain length into short-chain (SCCPs, C₁₀-C₁₃), medium-chain (MCCPs, C₁₄-C₁₇), and long-chain (LCCPs, C_{>17}) varieties. These chemicals are characterized by varying degrees of chlorination, typically ranging from 30% to 70%, and are used primarily as industrial lubricants and flame retardants due to their chemical stability and fire-retardant properties (McGrath et al., 2024, Zhang et al, 2023, Ye et al., 2023). Marketing research reported that the SCCP and MCCP production and usage decreased after 2014 (McGrath et al., 2024). In spite of those replacements are still not identified in the market, McGrath et al. (2024) put forward that demand may indeed be by LCCP and bromochloro alkanes (BCA). While 1728 molecular compositions are possible for PCAs, 32280 molecular compositions are possible for BCAs.

Research needs to encompass a thorough understanding of the environmental behavior, persistence, and potential for bioaccumulation of PCAs and BCAs across various environmental compartments (such as air, water, and soil), including their transformation products under diverse conditions. It is essential to conduct detailed toxicological studies to evaluate the potential health impacts of especially for BCAs on both human health and ecosystems, assessing factors such as acute and chronic toxicity, carcinogenicity, mutagenicity, and reproductive effects. Comparative analyses with similar chemicals can offer insights into their relative hazards. Moreover, identifying emission sources and exposure pathways for BCAs, encompassing industrial processes, waste disposal methods, and potential human exposure routes (such as inhalation, ingestion, and dermal contact), is critical. Understanding the global distribution of BCAs, including production and usage hotspots, can shed light on regional disparities in exposure and environmental implications. Analyzing long-term production and usage trends may also aid in anticipating future challenges related to environmental sustainability and public health.

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APPENDIX A

SUPPLEMENTARY MATERIAL

Table SM 1. Distribution fitting parameters of settled dust-bound PBDEs (ng/g)

PBDE	Distribution	Parameters
BDE-28	Lognormal	Location:0.07; Mean:1.23; SD:5,34
BDE-47	Lognormal	Location:0,14; Mean:63,55; SD:1733
BDE-99	Lognormal	Location:0,00; Mean:6,85; SD:8,85
BDE-100	Lognormal	Location:0.04 Mean:0.99 SD:4.23
BDE-153	Lognormal	Location:0.55; Mean:136.27; SD:1683
BDE-154	Lognormal	Location:0.07; Mean:0.80; SD:1.06
BDE-183	Lognormal	Location:0.10; Mean:6.00; SD:32.78
BDE-209	Lognormal	Location:0.00; Mean:1888; SD:1981

Table SM 2. Distribution Parameters of the Indoor Air PBDEs (pg/m³)

PBDE	Distribution	Parameters
BDE-28	Lognormal	Location:0.07; Mean:3.04; SD:6.04
BDE-47	Pareto	Location:0.44; Shape:0.68
BDE-100	Lognormal	Location: 0.12; Mean:1.29; SD:1.63
BDE-99	Lognormal	Location: 0.00; Mean:1120; SD:2045
BDE-154	Lognormal	Location: 0.54; Mean:2.40; SD:3.11
BDE-153	Lognormal	Location: 0.57; Mean:5.76; SD:7.81
BDE-183	Lognormal	Location: 0.59; Mean:10.3; SD:6773
BDE-209	Lognormal	Location: 0.00; Mean:602; SD:5438

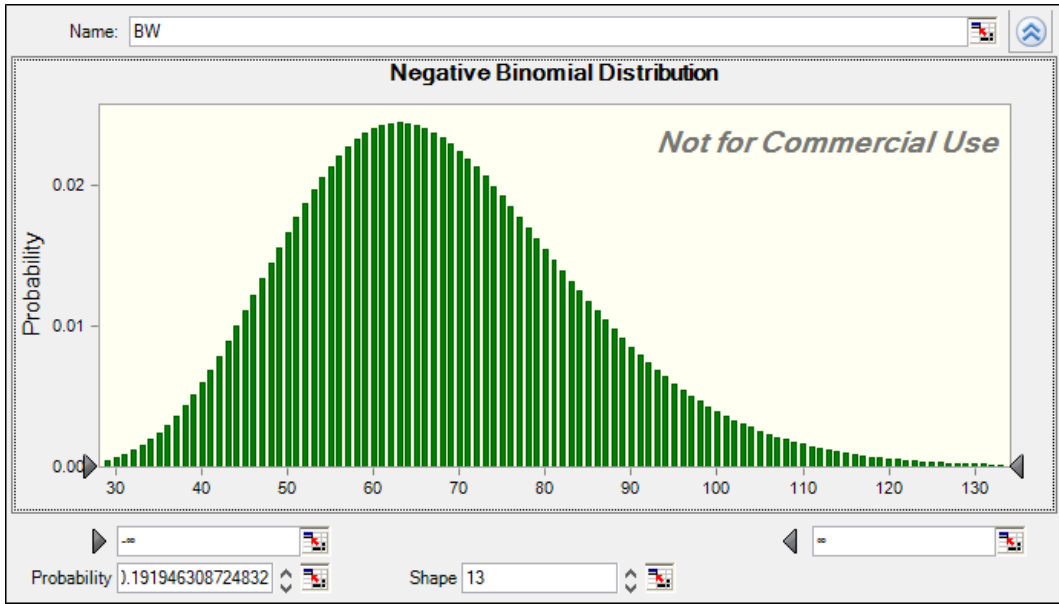


Figure SM 1. Body weight distribution (kg)

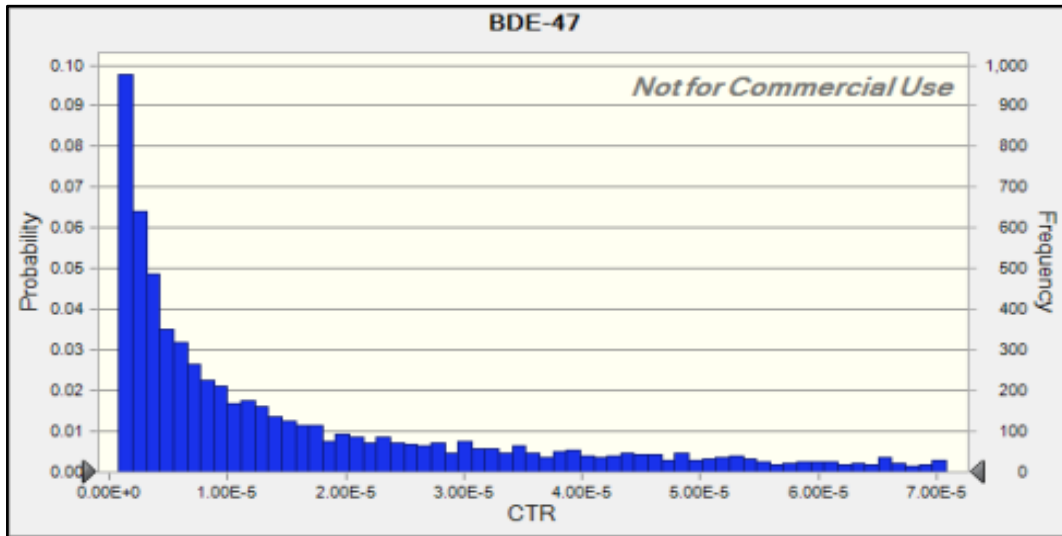


Figure SM 2. CTR levels of BDE-47 through accidental ingestion pathway

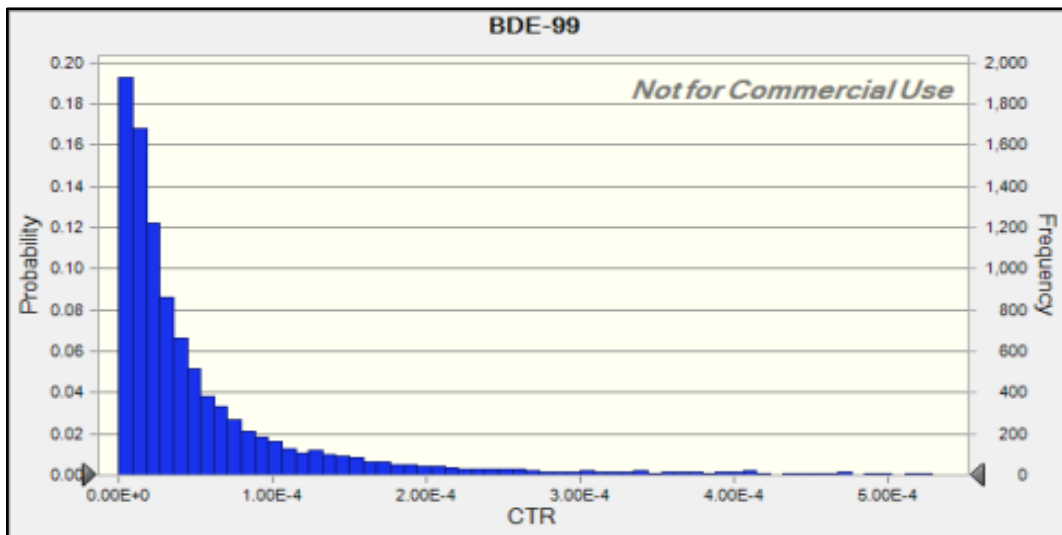


Figure SM 3. CTR levels of BDE-99 through accidental ingestion pathway

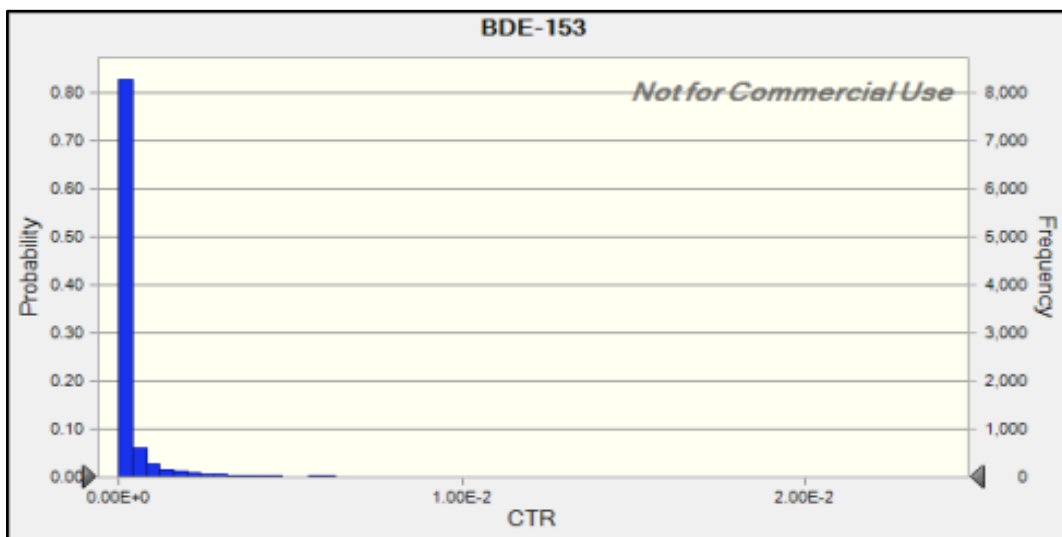


Figure SM 4. CTR levels of BDE-153 through accidental ingestion pathway

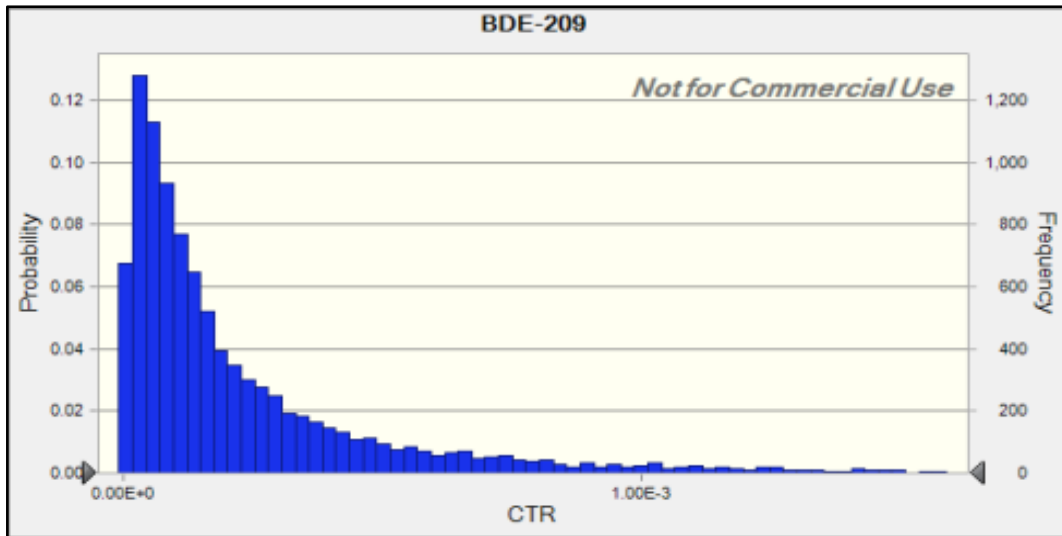


Figure SM 5. CTR levels of BDE-209 through accidental ingestion pathway

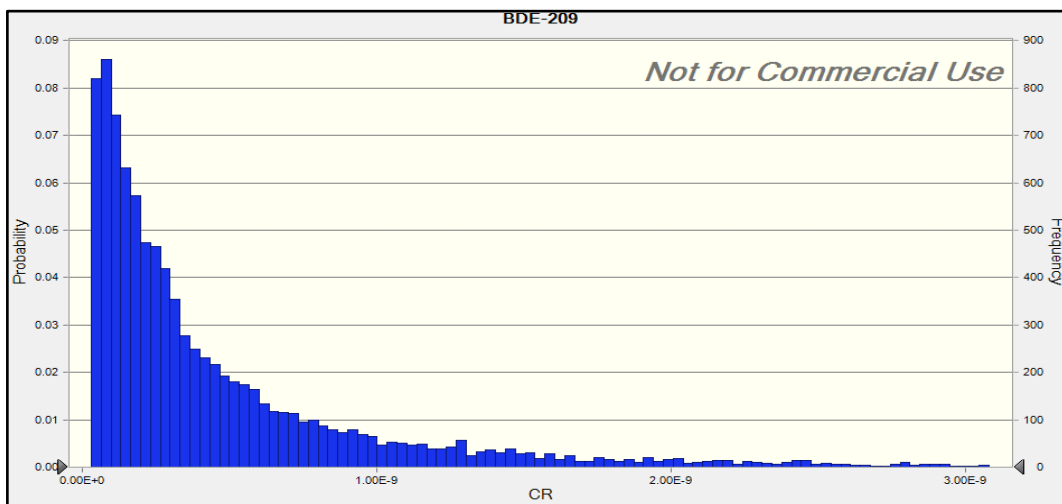


Figure SM 6. CR levels of BDE-209 through accidental ingestion pathway

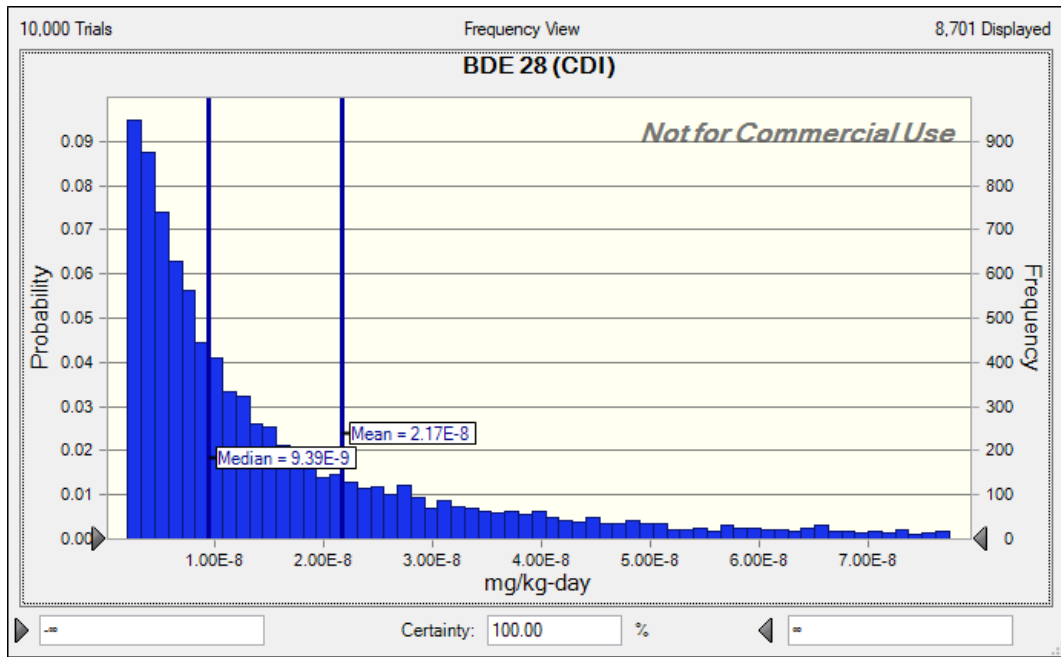


Figure SM 7. BDE-28 exposure levels through inhalation route

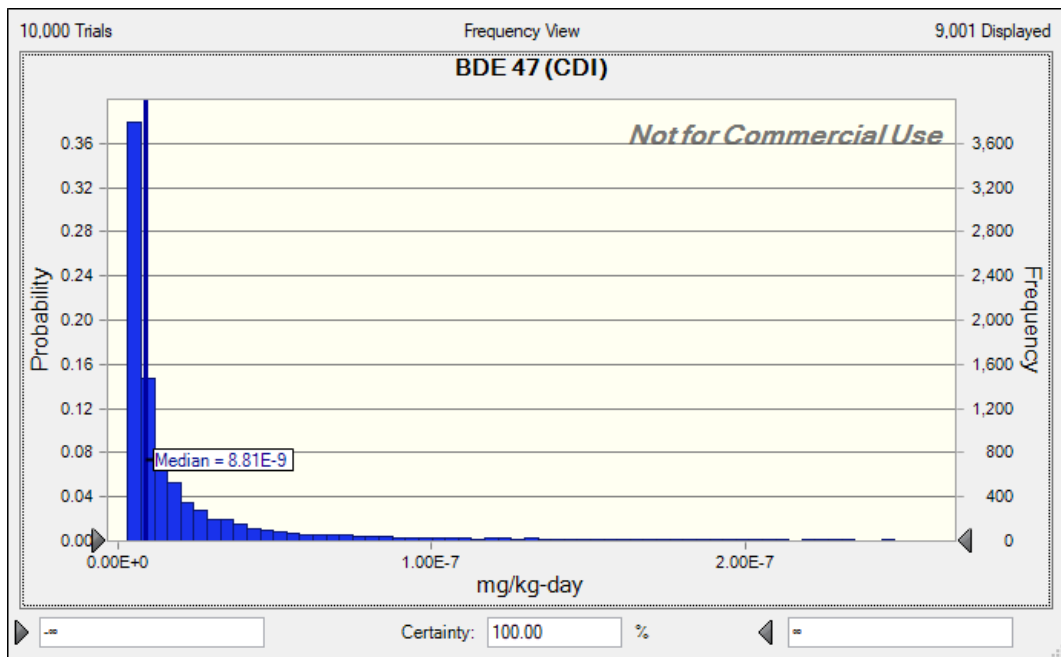


Figure SM 8. BDE-47 exposure levels through inhalation route

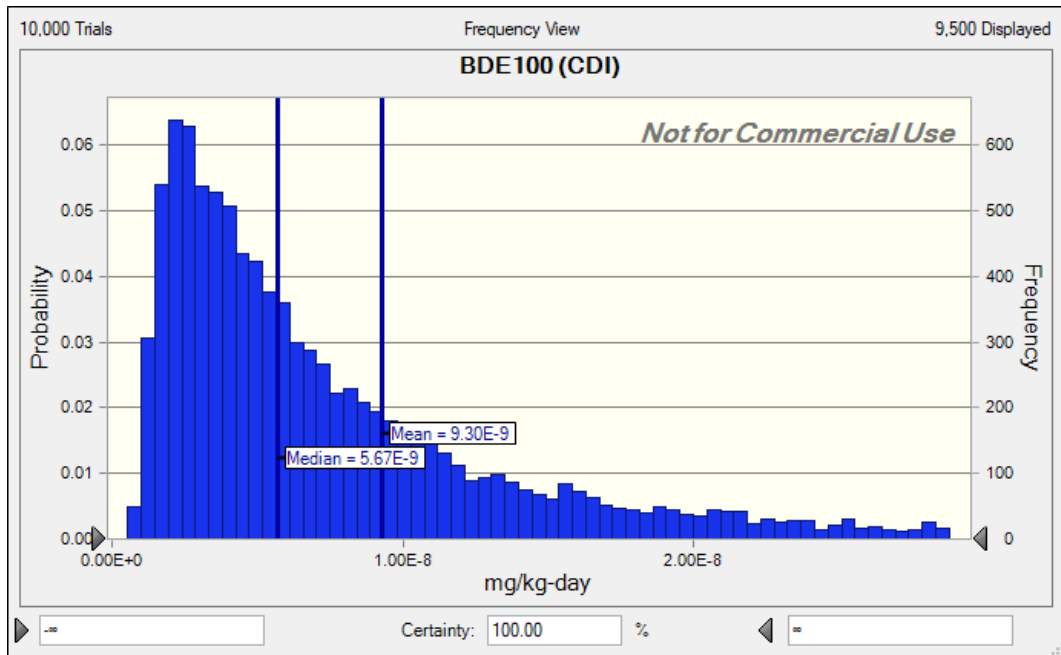


Figure SM 9. BDE-100 exposure levels through inhalation route

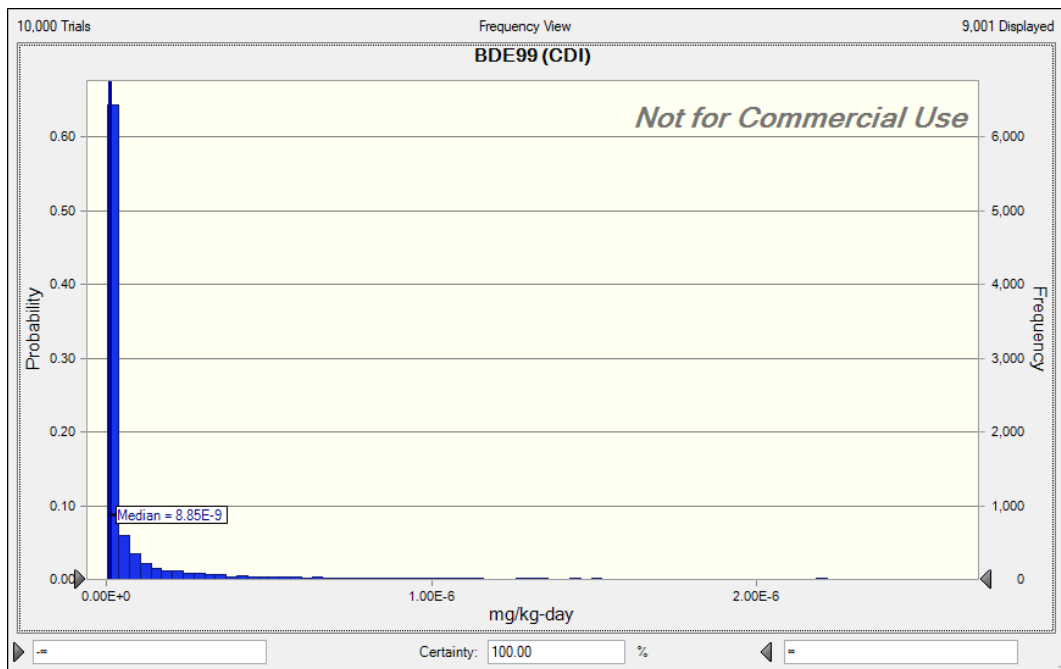


Figure SM 10. BDE-99 exposure levels through inhalation route

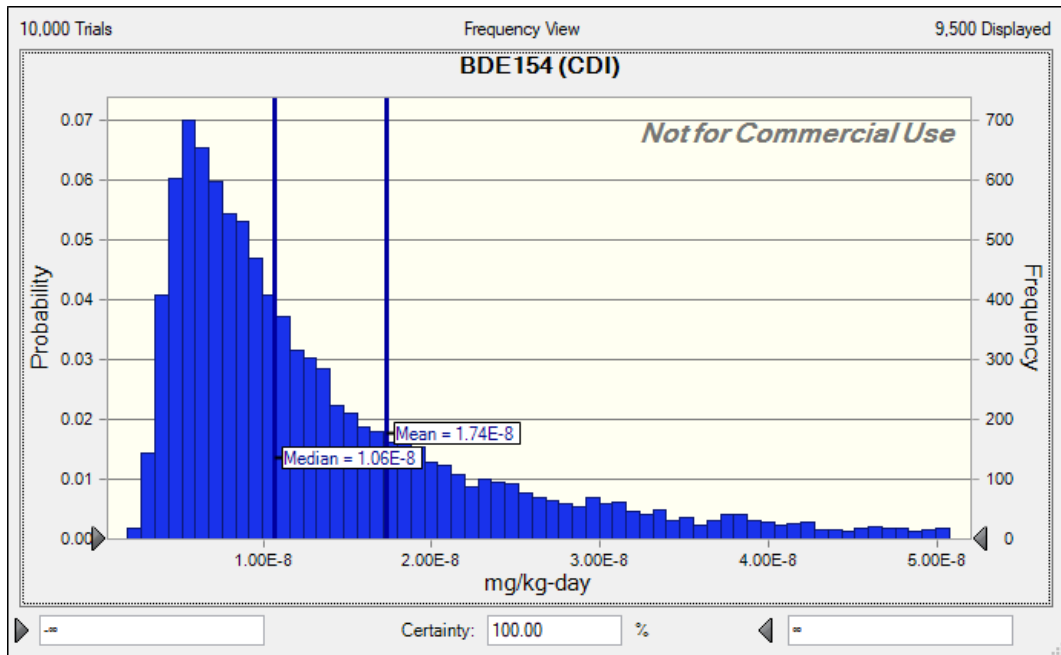


Figure SM 11. BDE-154 exposure levels through inhalation route

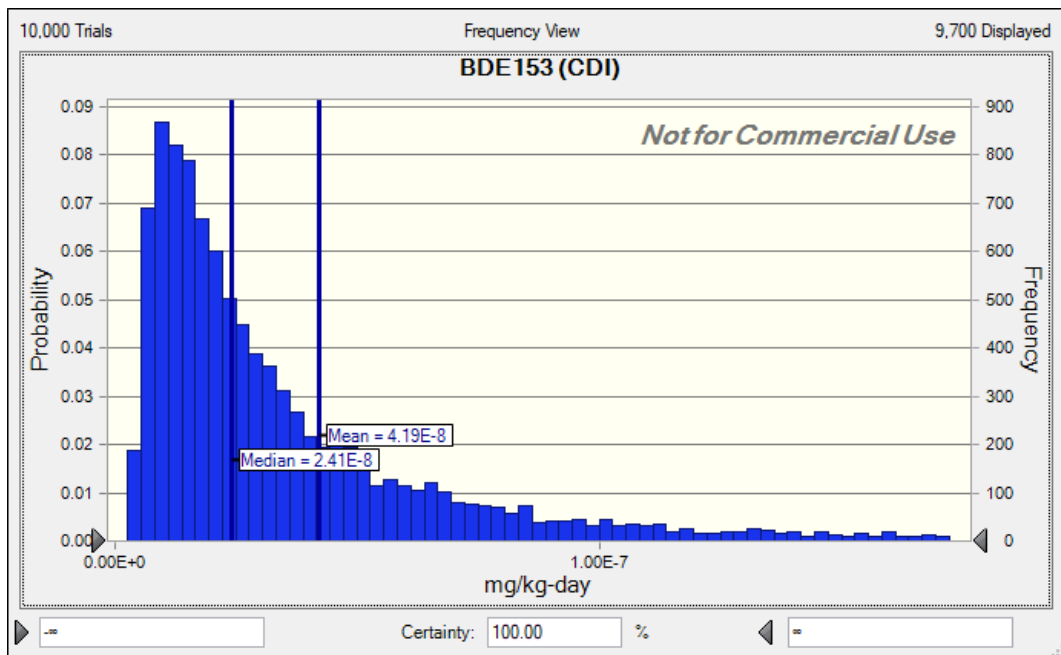


Figure SM 12. BDE-153 exposure levels through inhalation route

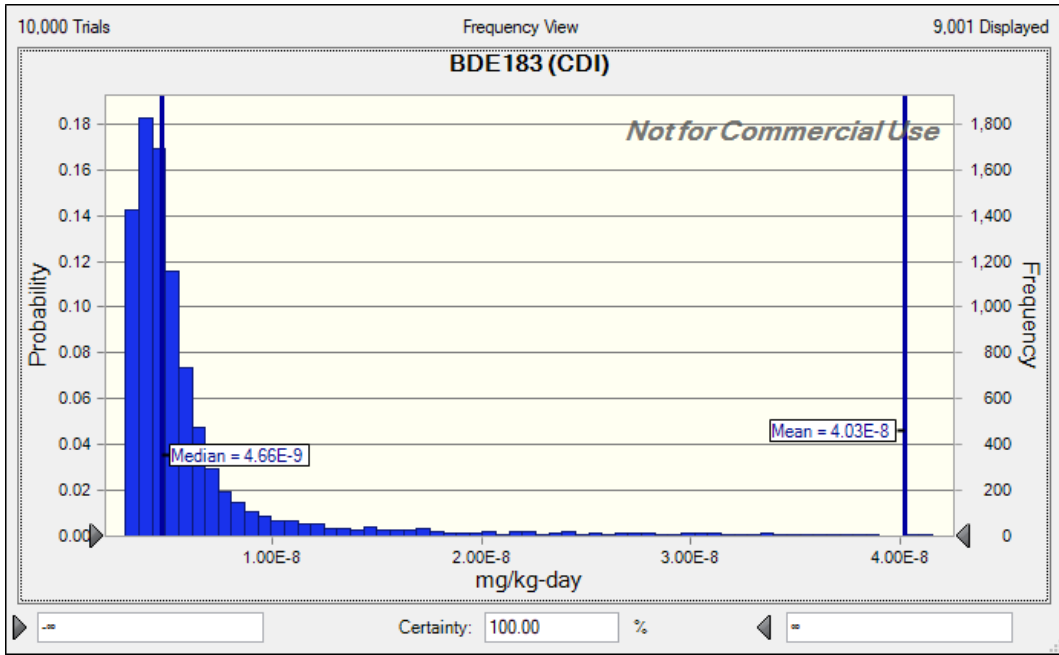


Figure SM 13. BDE-183 exposure levels through inhalation route

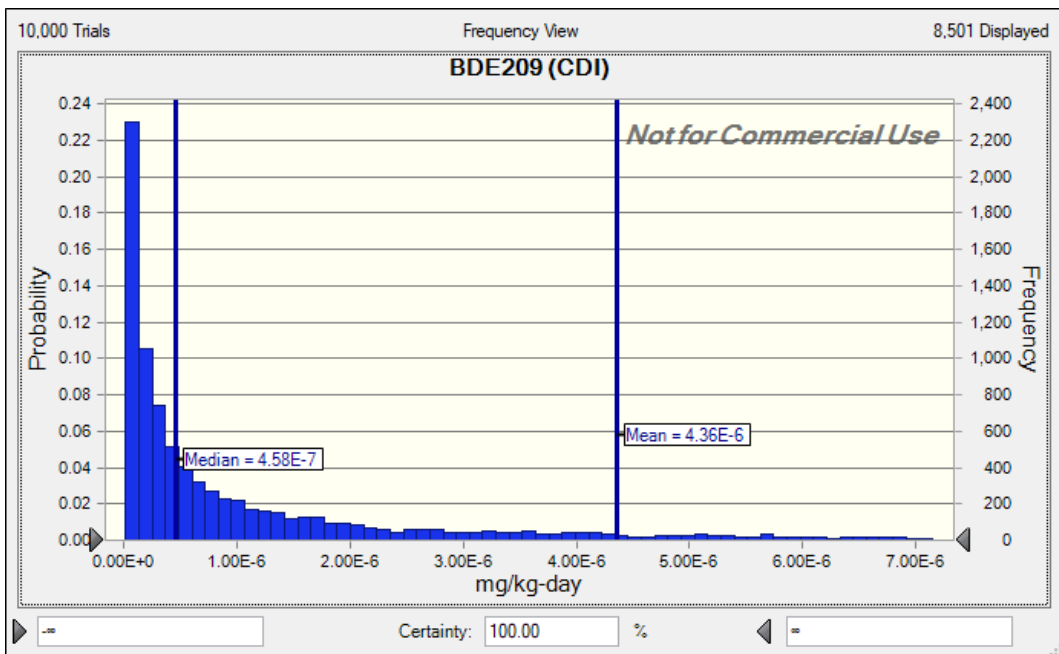


Figure SM 14. BDE-209 exposure levels through inhalation route

Table SM 3. TEF values of PAH compounds

PAH	TEF
Nap	0.001
Acy	0.001
Ace	0.001
Flu	0.001
Phe	0.001
Ant	0.01
Fla	0.001
Pyr	0.001
Chr	0.01
B(a)A	0.1
B(b+k)F	0.1
B(a)P	1
Ind	0.1
DB(ah)A	1
B(ghi)P	0.01

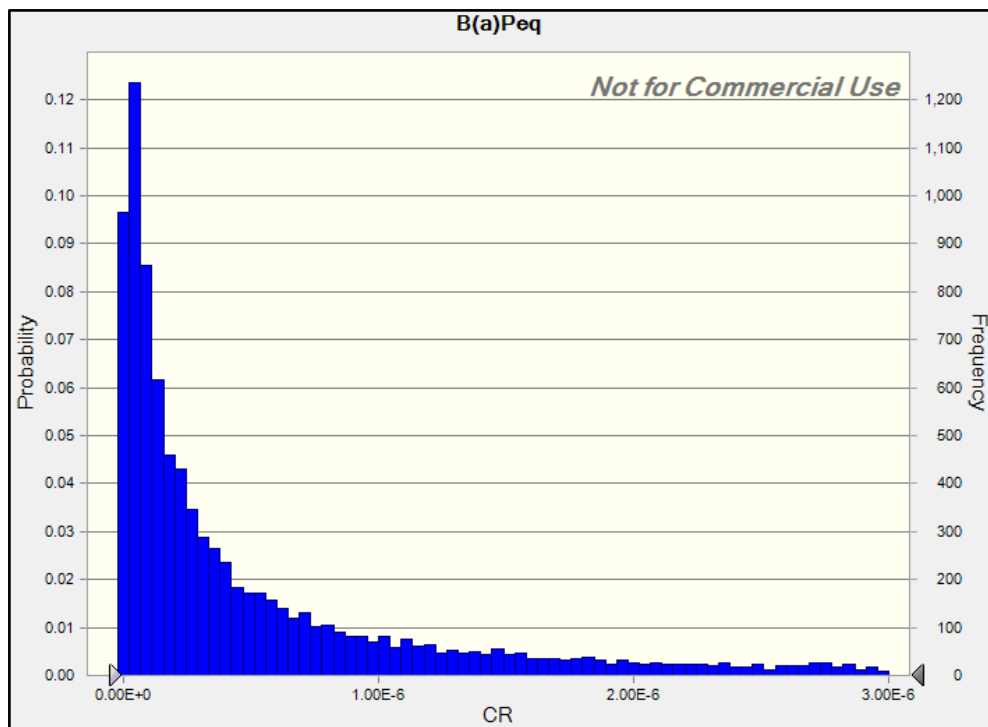


Figure SM 15. CR levels of PAHs through accidental ingestion route

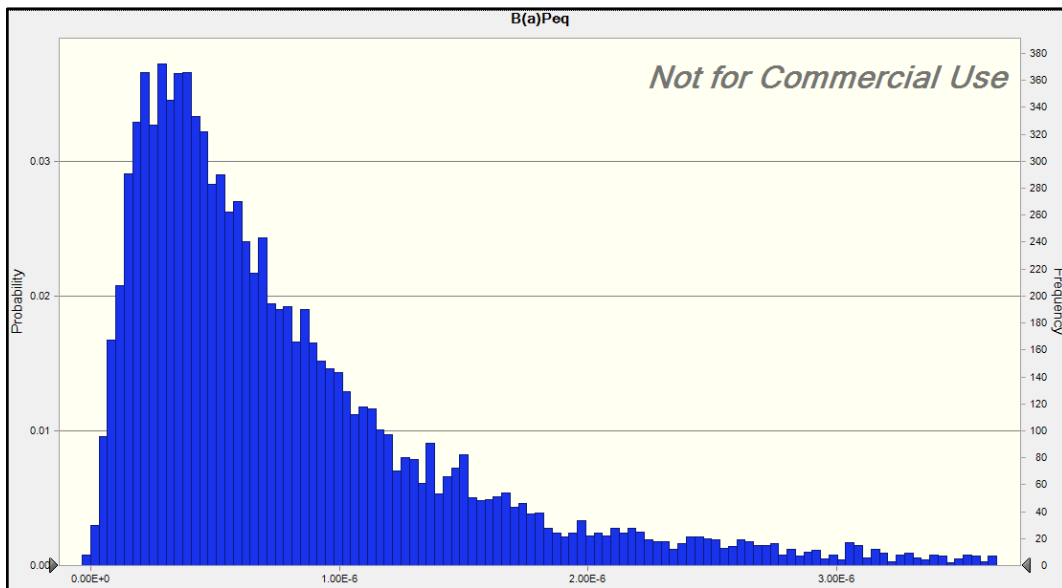


Figure SM 16. CR levels of PAHs through inhalation route

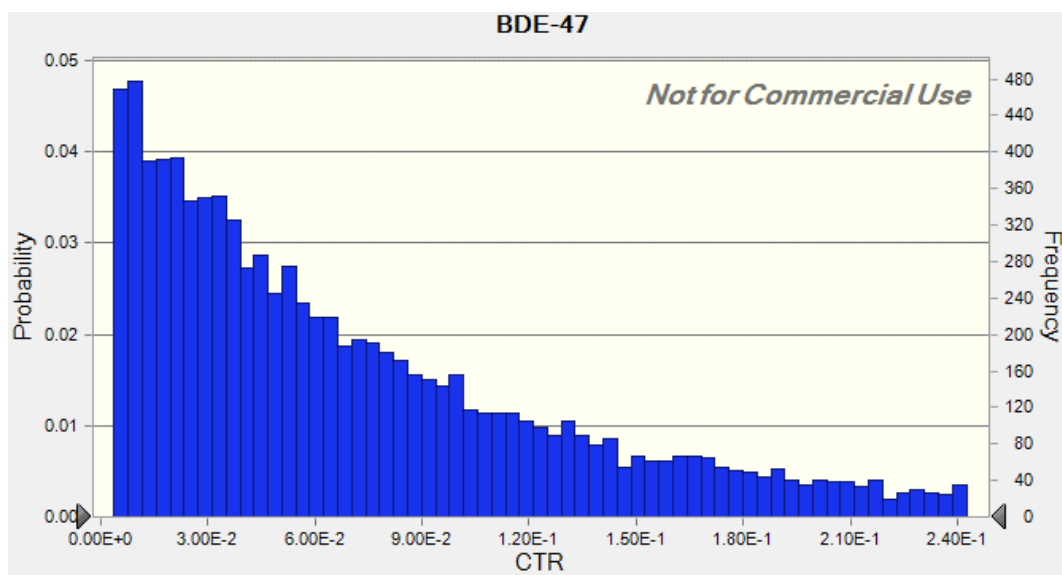


Figure SM 17. CTR levels of BDE-47 through dietary ingestion

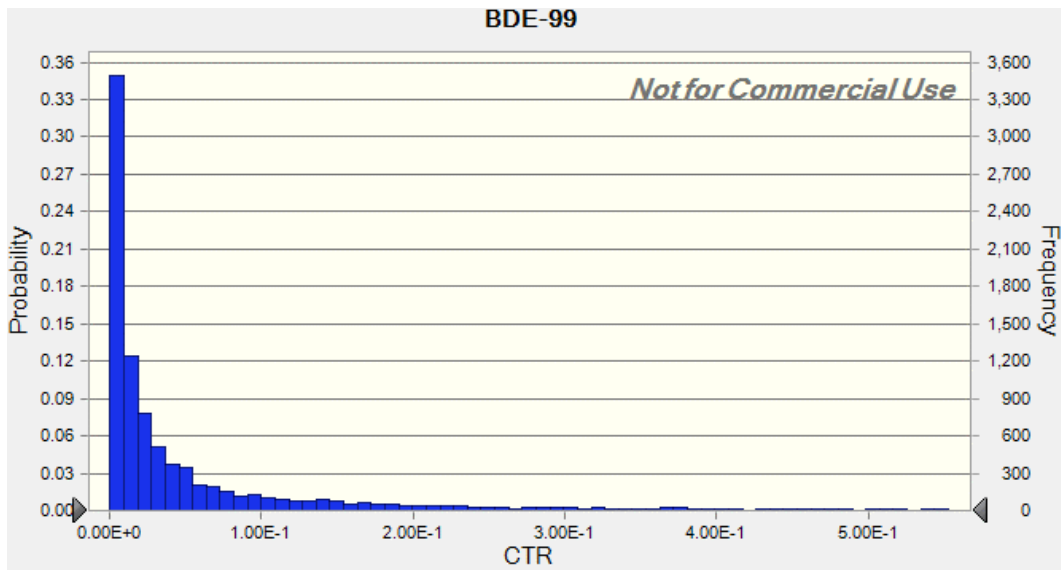


Figure SM 18. CTR levels of BDE-99 through dietary ingestion

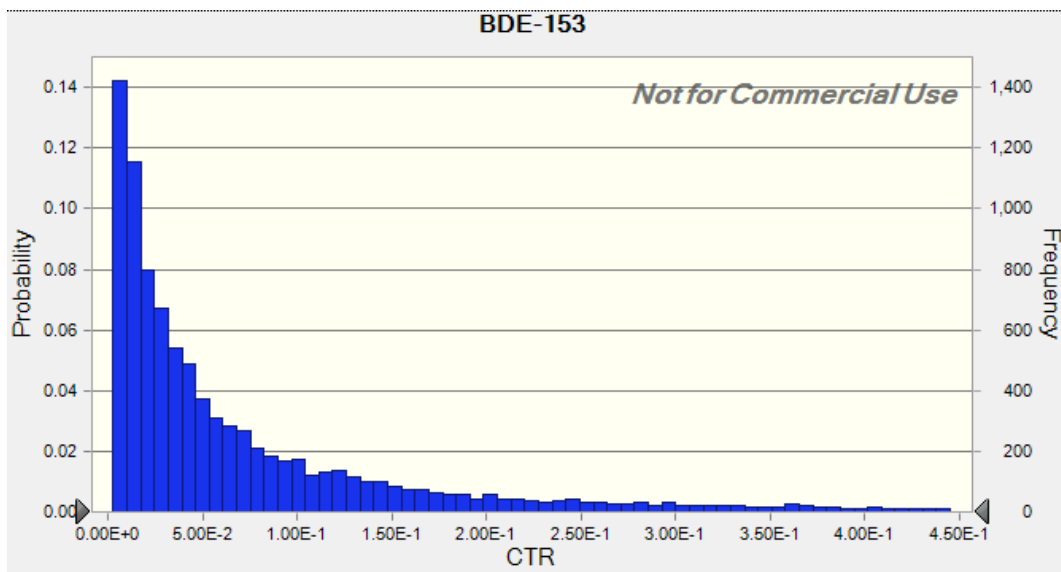


Figure SM 19. CTR levels of BDE-153 through dietary ingestion

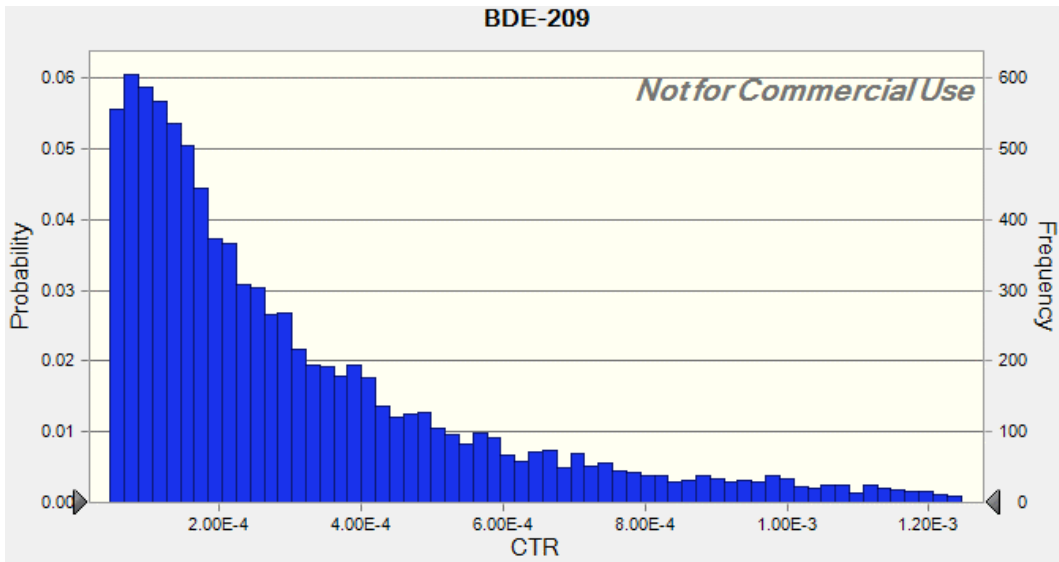


Figure SM 20. CTR levels of BDE-209 through dietary ingestion

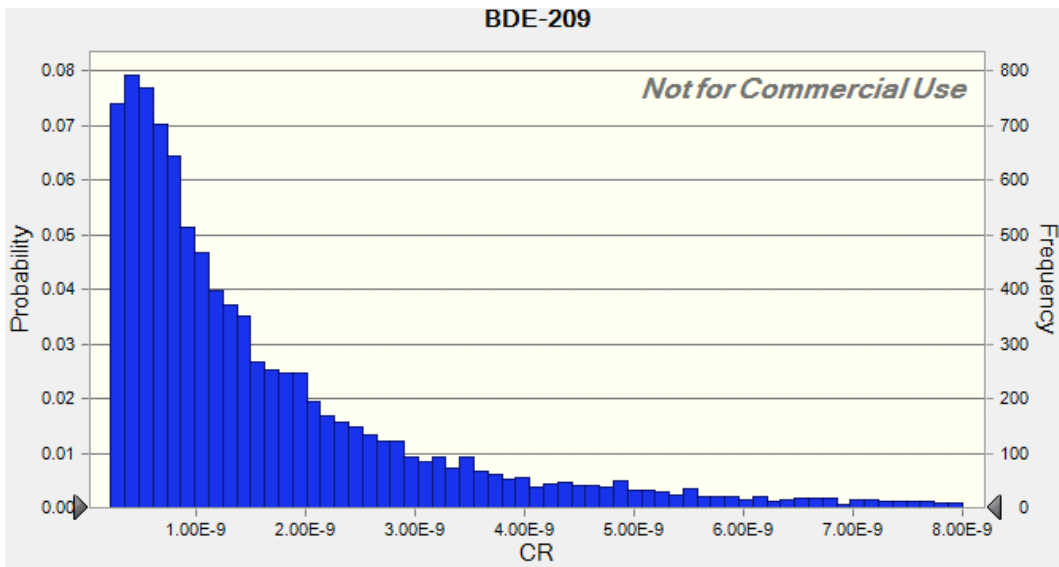


Figure SM 21. CR levels of BDE-209 through dietary ingestion

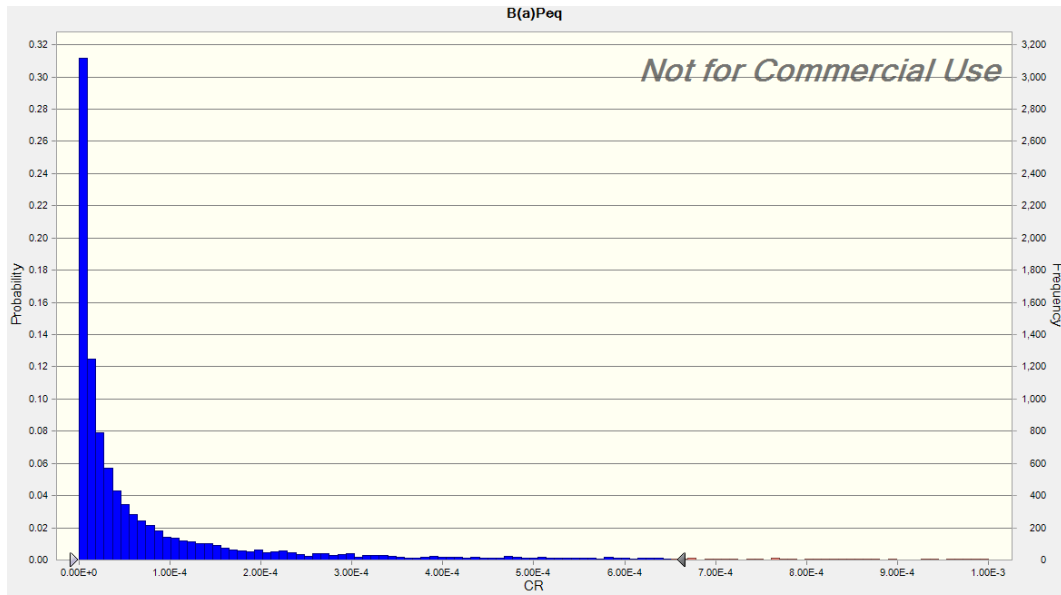


Figure SM 22. CR levels of PAHs through dietary ingestion

VITA

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- BSc, Department of Environmental Engineering, Suleyman Demirel University
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Work Experience

- Lecturer, Yalvaç Technical Vocational High School, Suleyman Demirel University, 2014
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Articles

- Synthesis and Characterization of Pumice Supported nZVI for Removal of Copper from Waters; Harman B.I. and **Genisoglu M.**; Advances in Materials Science and Engineering, 2016
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- Karbon Nanotüp Katkılı Polimerik İleri Ozmoz Membranların Geliştirilmesi ve Deniz Suyu Tuzsuzlaştırılması İçin Uygulanması (Development of carbon nanotube doped polymeric forward osmosis membranes and application for seawater desalination); TÜBİTAK 1001 Research Grants, **Genisoglu M.** (Project Scholar), 2012-2015
- Polimerik/Modifiye Seramik Hibrit Membran Prosesi ile Sensör Destekli Metal Giderimi ve Geri Kazanımı (Sensor-assisted metal removal and recovery with polymeric/modified ceramic hybrid membrane process - PMS-SEMEG); TÜBİTAK 1001 Research Grants, **Genisoglu M.** (Project Scholar), 2015-2017
- İzmir'de Kalıcı Organik Kirleticilere Maruziyetin ve İlişkili Sağlık Risklerinin Değerlendirilmesi (Evaluation of exposure to persistent organic pollutants and associated health risks in İzmir); TÜBİTAK 1001 Research Grants, **Genisoglu M.** (Project Scholar), 2018-2024

- İç Ortamlarda Ozon ve UV-C Dezenfeksiyonun PBDE'lerin Türleşmesine Etkisinin Belirlenmesi ve İlişkili Maruziyet ve Risk Seviyelerinin Modellenmesi ve İlişkili Sağlık Risklerinin Değerlendirilmesi (Determining the effect of ozonation and UV-C disinfection on the debromination of PBDEs in indoor environments and modeling the associated exposure and health risks); IYTE BAP Projects, **Genisoglu M.** (Researcher), 2021-2023
- İzmir'de kentsel, yarı-kentsel ve kırsal kesimlerde bulunan ev, okul ve kafe/bar/restoranlardan alınan çökeltmiş toz örneklerinde PCB düzeylerinin belirlenmesi (Determination of PCB levels in settled dust samples taken from houses, schools and cafes/bars/restaurants in urban, semi-urban and rural areas in İzmir); IYTE BAP Projects, **Genisoglu M.** (Researcher), 2021-2023
- UV dezenfeksiyon uygulamalarının, iç ortam havası ozon seviyelerine etkisinin belirlenmesi (Determination of the effect of UV disinfection on indoor air ozone levels); TÜBİTAK 2209/A - BSc Research Grants, **Genisoglu M.** (Advisor), 2022.
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Committee Membership of Scientific Events

- 5th International Environmental Chemistry Congress (ENVIROCHEM 2023, www.envirochem.org.tr), Antalya-TÜRKİYE– Congress Secretariat
- 6th International Environmental Chemistry Congress (ENVIROCHEM 2024, www.envirochem.org.tr), Trabzon-TÜRKİYE– Organizing Committee Member