DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

LINEAR AND CYCLIC VOLATILE METHYL SILOXANE LEVELS IN HOUSE DUST AND INDOOR AIR AND THEIR GAS-PARTICLE PARTITIONING

by

Ersan GÜNEL

February, 2024

İZMİR

LINEAR AND CYCLIC VOLATILE METHYL SILOXANE LEVELS IN HOUSE DUST AND INDOOR AIR AND THEIR GAS-PARTICLE PARTITIONING

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by

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THESIS EXAMINATION RESULT FORM

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LINEAR AND CYCLIC VOLATILE METHYL SILOXANE LEVELS IN HOUSE DUST AND INDOOR AIR AND THEIR GAS-PARTICLE PARTITIONING

ABSTRACT

Volatile methyl siloxanes (VMS) are added to several products (personal care, cleaning, and industrial) and they reach elevated levels in indoor air and atmosphere. In the present study, indoor air and dust samples were gathered from five different indoor environments (six from each) where people spend much of their time and having a high potential for VMS exposure (living rooms, bedrooms, offices, classrooms, cars, and hairdresser/barber shops). Concurrent atmospheric samples were also taken. Passive sampling was used to determine the indoor air concentrations with a sampling period of one week. Indoor dust samples were taken using a hand-held vacuum cleaner. All samples were analyzed for seven siloxane compounds (L3, L4, L5, D3, D4, D5 and D6). Indoor air ΣVMS concentrations ranged between 1526-449836 nanograms per cubic meter. Atmospheric concentrations were substantially lower (range: 236-9869 nanograms per cubic meter). Average indoor/outdoor concentration ratios were>1.0 (range: 16.8-183) indicating that VMS have significant indoor sources. Indoor dust ΣVMS concentrations ranged between 354-40852 nanograms per gram. The dominant VMS was D5 for indoor/ambient air and indoor dust samples. Highest average indoor air and indoor dust ΣVMS levels were measured in hairdresser and barber shops. However, lowest levels were observed for classrooms and homes for indoor air and dust, respectively. VMS partitioning between the gas-phase and indoor dust was also investigated. Predicted dust VMS concentrations correlated well with those measured (p<0.01, slope=0.97). However, on the average the predicted indoor dust VMS concentrations were 4.5 times lower than the measured values.

Keywords: Indoor dust, indoor air, VMS, passive sampling

EV TOZU VE İÇ ORTAM HAVASINDAKİ LİNEER VE HALKALI METİL SİLOKSAN SEVİYELERİ VE GAZ-PARTİKÜL FAZ DAĞILIMLARI

ÖZ

Uçucu Metil Siloksanlar (VMS) kişisel bakım, temizlik ve endüstriyel ürünlerde katkı maddesi olarak kullanılmakta, iç ortam havası ve atmosferde yüksek seviyelere ulaşabilmektedirler. Bu çalışmada, insanların en çok vakit geçirdiği beş farklı iç ortamdan (oturma/yatak odaları, ofisler, sınıflar, arabalar) ve siloksanlara maruz kalma olasılığı yüksek olan diğer ortamlardan (kuaför ve berber salonları) iç ortam havası ve toz örnekleri toplanmıştır. Eşzamanlı olarak dış hava örnekleri de toplanmıştır. İç ortam hava konsantrasyonlarının belirlenmesi için pasif örnekleme yöntemi kullanılmıştır (örnekleme süresi=1 hafta). İç ortam toz örnekleri elde taşınabilir bir elektrik süpürgesi kullanılarak toplanmıştır. Tüm örnekler yedi siloksan bileşiği (L3, L4, L5, D3, D4, D5 ve D6) için analizlenmiştir. İç ortam ΣVMS konsantrasyonları metreküpte 1526-449836 nanogram arasında değişmiştir. Dış havadaki konsantrasyonların ise önemli ölçüde daha düşük olduğu gözlenmiştir (aralık: metreküpte 236-9869 nanogram). Ortalama iç ortam havası/dış hava konsantrasyon oranları birden büyüktür (aralık:16,8-183). Bu sonuç VMS'nin önemli ölçüde iç ortamdan kaynaklandığını göstermektedir. İç ortam tozu ΣVMS konsantrasyonları gramda 354-40852 nanogram arasında değişmiştir. İç ortam havası, dış hava ve içortam tozu örneklerinde baskın VMS D5'tir. En yüksek ortalama iç ortam havası ve toz ΣVMS seviyeleri berber ve kuaför salonlarında ölçülmüştür. En düşük ortalama ΣVMS seviyeleri ise iç ortam havası için sınıflarda, iç ortam tozu için ise evlerde ölçülmüştür. VMS bileşiklerinin iç ortam havası ve tozu arasındaki faz dağılımları da incelenmiştir. Ölçülen ve model ile hesaplanan iç ortam tozundaki VMS konsantrasyonları arasında önemli ölçüde korelasyon olduğu gözlenmiştir (p<0.01, doğru eğimi=0.97). Hesaplanan iç ortam tozu VMS konsantrasyolarının ölçülen değerlerden ortalama olarak 4.5 kat daha düşük olduğu bulunmuştur.

Anahtar kelimeler: İç ortam havası, iç ortam tozu, VMS, pasif örnekleme

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CHAPTER ONE
INTRODUCTION

Volatile Methyl Siloxanes (VMS) are silicone and oxygen containing organic compounds (Wang et al., 2013). They are anthropogenic chemicals in a linear or cyclic structure. VMS are identified by their presence in linear (lVMS) and cyclic (cVMS) forms, with name for different oligomers based on the number of silicone and oxygen bonds (Horii & Kannan, 2008; Yucuis et al., 2013).

VMS are broadly used compounds in many industrial processes and products, including personal care products, protective coatings and furniture finishes (Chen et al., 2023; Horii & Kannan, 2008; Krogseth, Zhang, et al., 2013). In consumer applications, VMS are extensively included in personal care products including cosmetics, lotions, deodorants, shampoos, and antiperspirants (Coggon et al., 2018; Gkatzelis et al., 2021; Martellini et al., 2020). Besides the consumer products, VMS are also found in household products, like paints, varnishes, and furniture polishes (Katz et al., 2021; McDonald et al., 2018). VMS are utilized as solvents, lubricants, coatings, and sealants in industrial applications (Genualdi et al., 2011). They also take part in the production of antifoaming agents and coatings (Martellini et al., 2020).

VMS could be discharged into the environment during the production step, during their application and when they become waste. Studies have found that VMS exist in the outdoor air, sediment, soil, biota and wastewater (Brooke et al., 2009; Cheng et al., 2011; Li et al., 2016). VMS are transported in the environment via various mechanisms, such as dispersion/dilution in the atmosphere, dry and wet deposition, exchanging between water-air, soil-air, and plant-air interfaces (Kim et al., 2018). Numerous previous works investigated the levels of VMS in the atmosphere (Ahrens et al., 2014; Krogseth, Kierkegaard, et al., 2013; Ratola et al., 2016; Rauert et al., 2018; Yucuis et al., 2013).

Because of the general utilization of siloxane-containing products indoors and their volatile properties, VMS were detected in several studies conducted indoors (Hobson et al., 1997; Tran et al., 2015, 2019). Leung (2015) found that in over 65% of studies comparing indoor and outdoor air quality, indoor VMS concentrations surpassed

outdoor levels. Research shows that urban residents inhabit indoor spaces for over 90% of their daily life in indoor conditions. People pass much of their time not only in houses but also in offices, schools, automobiles, or various buildings (Klepeis et al., 2001; Mannan & Al-Ghamdi, 2021). This highlights the potential for higher exposure to VMS within homes and buildings. Siloxanes can remain in the air in gaseous form in indoor or settle and sorbed to dust particles (Lu et al., 2010). While people are indoors, they are exposed to siloxanes by inhaling both air and dust into their bodies.

The potential for environmental persistence, bioaccumulation and toxicity of VMS has generated significant concern regarding their impact on human health. Several studies have identified compelling link between the buildup of siloxanes in human body (Burns-Naas et al., 2002; Meeks et al., 2007). Studies suggests a strong relation between exposure to indoor dust and potential health risks due to the presence siloxanes. Inhalation, dermal contact, and ingestion have been identified as pathways for personal exposure to these contaminants within the indoor atmosphere (Norris et al., 2022; Pieri et al., 2013; Tran et al., 2015). The findings are consistent with the hypothesis that exposure to environmental pollutants, including siloxanes, can lead to cardiovascular diseases, endocrine disrupting, cancer, diabetes, and immune system health problems (Guo et al., 2019). Particularly, some of cVMS were categorized as very persistent and bio-accumulative in 2015 by the European Chemical Agency (ECHA) Member State Committee (MSC (ECHA Member State Committee), 2015). cVMS have direct and indirect toxicities across diverse biological pathways, including interference with reproductive function (Meeks et al., 2007; Quinn et al., 2007; Siddiqui et al., 2007).

The presence of VMS in the atmosphere and indoor was the subject of many studies in the literature (Ahrens et al., 2014; Chen et al., 2023; Fromme et al., 2019; Horii & Kannan, 2008; Krogseth, Kierkegaard, et al., 2013; Martellini et al., 2020). Studies at worldwide employing air sampling, including Arctic regions, have shown the distribution and transport of VMS (Genualdi et al., 2011; Krogseth, Kierkegaard, et al., 2013). Research on indoor air pollution has expanded to comprehend the presence and removal of VMS in residential environments (Molinier et al., 2022). Siloxane

compounds were found in indoor air, dust on the floor and dust on the surfaces such as furniture surface (Chen et al., 2023; L. Xu et al., 2015).

Active and passive air sampling methods are frequently utilized to determine VMS levels in both atmosphere and indoor air (Jaward et al., 2004; Krogseth, Zhang, et al., 2013; Rauert et al., 2018; Turk et al., 2007). This method involves deploying passive air sampling systems in different locations for a specific period to collect pollutants from the environment (Jaward et al., 2004; Krogseth, Zhang, et al., 2013). Their ease of use, low cost and ability to function independently make passive air samplers a preferred choice for large-scale air quality monitoring, especially in areas lacking reliable electricity (Krogseth, Zhang, et al., 2013). Sorbent-impregnated polyurethane foam (SIP) disks are generally used in passive air sampling to collect VMS in the air (Genualdi et al., 2011). Moreover, a passive air sampler (XAD-PAS) was calibrated and utilized to measure VMS (Krogseth, Zhang, et al., 2013). Additionally, a novel passive sampling technique was devised for VMS analysis (Okan et al., 2021). The collected samples can be prepared for analysis through a multi-step process, including solvent extraction, clean-up and volume reduction. Then, prepared samples are analyzed with a gas chromatograph-mass spectrometer (GC-MS).

The objective of the present study was to assess the siloxane levels in different indoor environments in Izmir, Türkiye. In this context, indoor air and dust samples were taken from 3 hairdressers, 3 barbers, 6 houses, 6 cars, 6 offices and 6 classrooms. Outdoor air samples were gathered simultaneously with indoor samples. Passive samplers were used for air samples, and a hand-held vacuum cleaner was utilized to take dust samples. The partition coefficient of siloxanes, considering the concentrations of indoor air and dust, was calculated and additionally predicted using a mathematical model (Wei et al., 2016; Weschler & Nazaroff, 2010a). The results obtained by calculation and modeling was compared.

The Stockholm Convention, which include many chemicals, is also evaluating new compounds that have the characteristics of being “persistent organic pollutants (POPs)” and the scope of the treaty is being expanded from time to time. Although siloxanes are not covered by this convention, research based on their physicochemical properties and toxicity suggest that they have the potential to be POPs. When

evaluating and incorporating new compounds into the convention, it is important to comprehensively monitor their levels and behaviors in various environmental compartments worldwide. This global monitoring is essential for ensuring the management and regulation of these chemicals, also for protecting environment and human health. This study will add to the literature on this subject and to the evaluation of siloxanes under the Stockholm Convention.

CHAPTER TWO
LITERATURE REVIEW

This chapter presents the chemical and physical properties, sources, and health impacts of VMS in indoor environments. Previous research on VMS emissions in indoor air and dust is also reviewed.

2.1 Chemical and Physical Properties of VMS

VMS are anthropogenic chemicals devoid of any natural sources consist of silicone and oxygen bounds with methyl branches (Fromme et al., 2019; Tran et al., 2019). Siloxanes can be categorized into two groups based on their structural characteristics: linear (L) and cyclic (D) siloxanes. Linear VMS are shown as Lx, where x represents the number of Si-O bonds. Similarly, cyclic VMS are shown as Dx (Lei et al., 2010). Table 2.1 and Table 2.2 present the molecular structures of siloxanes classified as cVMS (D3, D4, D5 and D6) and cVMS (L3, L4 and L5).

Table 2.1 Molecular structures of D3, D4, D5 and D6

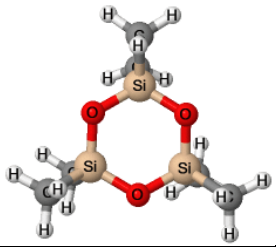
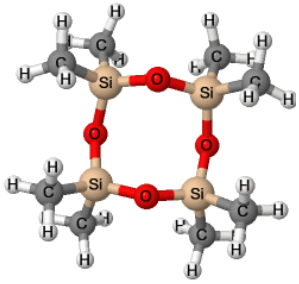
Compounds	**Molecular Formula**	**Molecular Structure**
D3 (Hexamethylcyclotrisiloxane)	$C_6H_{18}O_3Si_3$	
D4 (Octamethylcyclotetrasiloxane)	$C_8H_{24}O_4Si_4$	

Table 2.2 (Continued)

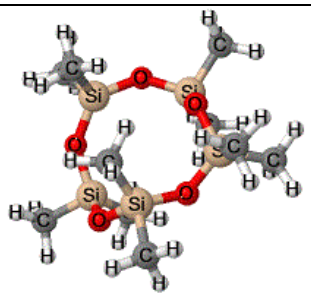
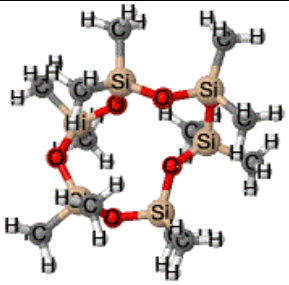
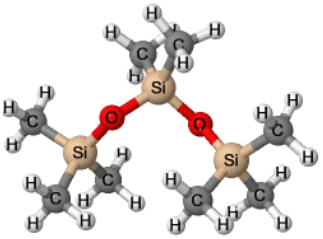
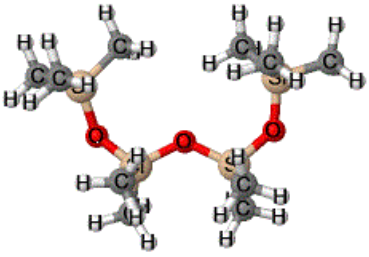
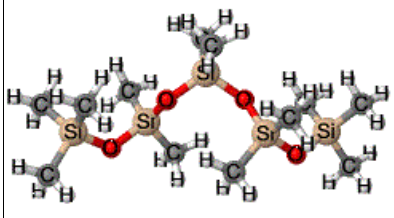
D5 (Decamethylcyclopentasiloxane)	$C_{10}H_{30}O_5Si_5$	
D6 (Dodecamethylcyclohexasiloxane)	$C_{12}H_{36}O_6Si_6$	

Table 2.3 Molecular structures of L3, L4 and L5

Compounds	**Molecular Formula**	**Molecular Structure**
L3 (Octamethyltrisiloxane)	$C_8H_{24}O_2Si_3$	
L4 (Decamethyltetrasiloxane)	$C_{10}H_{30}O_3Si_4$	
L5 (Dodecamethylpentasiloxane)	$C_{12}H_{36}O_4Si_5$	

The unusual physicochemical characteristics of VMS, such as their high molecular weight and high vapor pressure, are significant factors contributing to their extensive distribution in the environment (Ramos et al., 2016). These properties enable VMS to readily volatilize into the atmosphere and disperse over long distances. High vapor pressures of VMS facilitate their evaporation from diverse environmental compartments such as water, soil, and sediments. Siloxanes exhibit stability across a broad temperature spectrum (-100 to 250°C) and demonstrate resilience against atmospheric conditions, oxidation, UV radiation and moisture (Mojsiewicz-Pieńkowska & Krenczkowska, 2018). Table 2.3 presents a comparison of the physico-chemical properties of some linear and cyclic VMS (Ruiling et al., 2017; S. Xu et al., 2014; S. Xu & Kropscott, 2013).

Table 2.4 Some properties of linear and cyclic methyl siloxanes (Ruiling et al., 2017; S. Xu et al., 2014; S. Xu & Kropscott, 2013)

Compound	**Molecular weight (g/mol)**	**Saturated Vapor Pressure (Pa)**	**Octanol-air partitioning coefficient (log K_{OA})**	**Solubility in water (mg/L)**	**Air-water partitioning coefficient (log K_{AW})**
L3 (Octamethyltrisiloxane)	236	445.0	3.86	0.034	3.15
L4 (Decamethyltetrasiloxane)	310	50.0	4.76	0.00674	3.04
L5 (Dodecamethylpentasiloxane)	384	9.0	5.17	0.000309	NA
D3 (Hexamethylcyclotrisiloxane)	222	471.0	3.66	1.56	NA
D4 (Octamethylcyclotetrasiloxane)	296	132.0	4.43	0.056	2.48
D5 (Decamethylcyclopentasiloxane)	370	23.2	5.00	0.0017	2.38
D6 (Dodecamethylcyclohexasiloxane)	444	4.0	5.86	0.005	1.95

2.2 Sources of VMS

VMS are derived from a various consumer products and industrial practices which has caused to increase their global production years by years. In 20 years, the world's

siloxane production capacity was grown by 6 million tons, exceeding the 2 million tons in 2002 (Mojsiewicz-Pienkowska et al., 2016). Besides, siloxane containing material production in Europe was reported as 480000 tons, and just in China, annual production of VMS was approximately 800000 tons (Rücker & Kümmerer, 2015). They are extensively utilized in the production of consumer goods such as shampoo, lotions, deodorants, and antiperspirants, thereby contributing to their environmental distribution (Coggon et al., 2018). Studies have delved into the emission of VMS from the utilization of personal care products, uncovering diurnal changes and emission trends in urban settings (Coggon et al., 2018). Furthermore, VMS have been identified in indoor environments, including museums, and have been detected in outdoor air in urban areas characterized by diverse industrial influences (Martellini et al., 2020). cVMS are especially found in personal care products, while lVMS are generally found in paints, varnishes, and furniture polishes. High amounts of linear siloxanes are also included in facial creams (Horii & Kannan, 2008). The study by Pieri et al. (2013) reported the presence of lVMS and cVMS in indoor air samples in England and Italy, suggesting that indoor environments serve as reservoirs for VMS. The study also highlighted that the ∑VMS concentrations could reach up to 940 $\mu g/m^3$. The research conducted in urban areas of India determined the level of volatile organic compounds, including siloxanes, both inside and outside homes. The study demonstrated that household products, electronic devices, furniture, and cooking utensils are common sources of VMS in indoor environments (Norris et al., 2022).

Additionally, VMS have been recognized as substantial pollutants in biogas, leading to operational complications in biogas utilization (McBean, 2008; Zhang et al., 2017). In wastewater plants, VMS presence has been found, signifying their occurrence in such areas (Bletsou et al., 2013; L. Xu et al., 2013). In their recent study, Okan et al. (2021) and Słupek et al. (2021) investigated to identify the primary sources of VMS. The results of Okan et al. (2021) research emphasized the importance of reducing VMS emissions, as the concentrations of ∑VMS varied from 41.4 to 981 ng/m^3 from urban areas, wastewater treatment plants and landfill. This highlights the critical need to address VMS emissions from these sources in order to effectively manage and reduce their environmental impact.

Moreover, the levels of VMS in the Arctic region have been the subject of scientific research. VMS have been discerned in various environmental media, encompassing Arctic soils, vegetation, phytoplankton, and krill, thereby indicating their pervasive prevalence in the air (Sanchís et al., 2015). A comprehensive study on the worldwide variation of linear and cyclic VMS in the atmosphere, including five locations in the North Pole, has been conducted. Research has utilized passive air samplers with sorbent-impregnated polyurethane foam (SIP) disks to assess the presence of VMS in the North Pole air. The study has offered valuable knowledge on the spatial variation of VMS, shedding light on potential sources and transport mechanisms in the Arctic region. The levels of cVMS differ between urban, background and high-altitude areas. Urban areas, which are significantly affected by industrial activities, are led by D5 and D6, with levels varying from below the detection limit to 280 ng/m^3 (Genualdi et al., 2011).

Based on the studies, siloxanes deserve closer research in terms of indoor air quality. Since people pass a significant part of their time indoors, exposure to pollutants in indoor environments contributes to the intake of these pollutants into the body (Jones-Otazo et al., 2005). While we often focus on outdoor air pollution, the air inside could be more contaminated (Byun et al., 2010; Shuai et al., 2013).

Due to widespread usage of products containing siloxanes in indoor environments, the likelihood of finding siloxanes in samples such as indoor air and dust is quite high (Fendinger et al., 1997). Scientists have attempted to determine which exposure routes pose the utmost danger to humans and have investigated the probability of siloxane uptake through different paths, namely, respiratory (Pieri et al., 2013; Tran et al., 2015), ingestion (Lu et al., 2010) and dermal exposure (Horii & Kannan, 2008). Overall, scientists have concluded that exposure is related to environmental pollution from siloxanes (surface waters like rivers, lakes, and sea, sediments, wastewater, soils, air, and dust). However, exposure is largely associated with the use of different cosmetics and personal care products (deodorants, lipsticks, makeup, body-lotions and creams) (Biesterbos et al., 2015; Lu et al., 2011). The tendency of siloxanes to bind to particulate matter has led to dust in indoor environments becoming an environmental issue (McKim, 2001).

2.3 Health Effects

Widespread utilization of VMS in personal care products and industrial applications has raised concerns about their potential health effects (Alton & Browne, 2020; Genualdi et al., 2011). Several studies have reported both direct and indirect harmful impacts of VMS on both aquatic and terrestrial ecosystems (Xu et al., 2013). Additionally, the occurrence of VMS in indoor air and dust have indicated the possibility of exposure to these substances in indoor settings (Pieri et al., 2013). The likely health impacts of VMS are currently being investigated, and their effects on human health is not completely comprehended. Nevertheless, it is known that VMS are synthetic compounds produced in large quantities and are widely present in the environment (Sanchís et al., 2015).

The environmental behavior of VMS has been explored in municipal wastewater treatment systems, but the precise health impacts of these substances have not been completely delineated (Parker et al., 1999). The existing literature provides limited information on the health effects of siloxanes, which complicates the ability to make comprehensive assessments and comparisons of the toxicity of VMS based on the available data (De Arespacochaga et al., 2015). Further study is required to fully characterize the health effects of VMS and their potential implications for human health.

2.4 Studies on VMS in the Literature

Researchers reviewed articles on VMS from several studies (Capela et al., 2017; Tran et al., 2019; Wang et al., 2013; Xu et al., 2014). The concentrations of VMS varied across different studies. The levels of VMS in various countries and environments were compared based on the literature.

In Sweden, the concentrations of D4, D5 and D6 in university rooms, offices and homes were observed as 1280, 1700 and 2200 ng/m^3, respectively (Sha et al., 2018). Yucuis et al. (2013) reported concentrations in offices and laboratories in United States, with D4, D5 and D6 ranging from 1020 to 59300 ng/m^3. In the United States again, commercial buildings had a concentration of D5 ranging from 1300 to 120000 ng/m^3 (Wu et al., 2011). In Italy, concentrations were measured higher, with

bathrooms, bedrooms, living rooms and offices had D3-D6 and L2-L5 concentrations varying from 18000 to 230000 ng/m^3 (Pieri et al., 2013). Similarly, in the UK, Pieri et al (2013) measured high concentrations in bathrooms, supermarkets, living rooms, bedrooms, and offices, ranging from 78000 to 340000 ng/m^3.

Siloxanes with smaller molecular weights were predominantly found at greater concentrations in the gas-phase. Contrarily, larger molecular weight VMS exhibited a larger preference for partitioning to the particulate phase (Chng & Sholl, 2023). VMS occurrence in indoor dust was a subject of studies since the 2000s. Based on the study in China had the D4-D6 and L4-L16 concentrations, with barbershops showing the highest with 43126 ng/g, followed by homes with 2449 ng/g and university dormitories with 2091 ng/g (Liu et al., 2018). In Vietnam, hair salons had a mean D4-D6 concentration of 671 ng/g, ranging between 178 and 1240 ng/g (Tran et al., 2018). Tran et al (2015) measured the levels of D3-D7 and L4-L14 compounds in homes in Greece and in homes and cars in Kuwait varied from 384 to 30100 ng/g and from 476 to 42800 ng/g, respectively.

CHAPTER THREE
MATERIALS AND METHODS

3.1 Sampling Study

Indoor air and dust samples were gathered from five distinct indoor settings where individuals typically pass a significant portion of their time, namely living rooms, bedrooms, offices, classrooms, and automobiles. Additionally, samples were collected from a sixth indoor environment, namely hairdressers and barbershops, where the likelihood for exposure to VMS is particularly high. Within each category of indoor environment, six indoor air and dust samples were obtained. Simultaneously, ambient air samples were also collected, with one sample corresponding to each category of indoor environment. Sampling program is given in Table 3.1.

Table 3.1 Sampling program

Indoor Environments	Number of Sampler	Sampling Period (days)
Living rooms	6	7.30
Bedrooms	6	7.30
Offices	6	7.19
Classrooms	6	7.13
Cars	6	6.99
Hairdressers and barbers	6	7.04

3.2 Preparation for Sampling and Analysis

3.2.1 Indoor air sampling

Passive air sampling (PAS) is an appropriate method for the determination of VMS in indoor settings. PAS has been extensively used for monitoring a variety of air pollutants, including VMS (Zabiegala et al., 2009).

A commercially available air sampler (Raidello® Code 130) for volatile organic compounds (VOCs) was adapted and utilized (Figure 3.1). The sampler contains a mesh cylinder packed with granulated activated carbon (GAC). The sampler was adapted by substituting XAD-2 resin for the activated carbon (Okan et al., 2021). Upon closer examination, a porous cylinder fabricated from stainless steel, measuring 60 millimeters in height and 5.8 millimeters in diameter, was packed with approximately 440 milligrams of XAD-2 resin. The cylinder exhibited a mesh size of 165, resulting in an open area of 47%. Following the preparation of the cylinder, it is carefully inserted into a commercially obtainable, white Radiello® diffusive body. The diffusive body, produced from high-density polyethylene, features a porous section (height=47 millimeters), a porous barrier (thickness=1.7 millimeters), and has a diameter of 16 millimeters (McLagan et al., 2016). The diffusive body is fastened to the supporting plate (Figure 3.2 and Figure 3.3).

The stainless-steel mesh cylinders packed with XAD-2 utilized for indoor air sampling underwent a cleaning process involving three cycles of immersion in acetone-hexane (1:1) for 10 minutes for sonication. Subsequently, they were subjected to drying via passing through high purity N_2 for duration of 45 minutes (Figure 3.4).

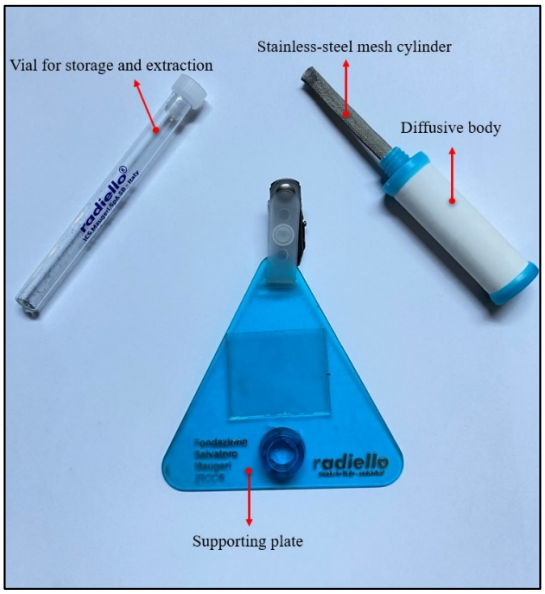


Figure 3.1 The passive air sampler

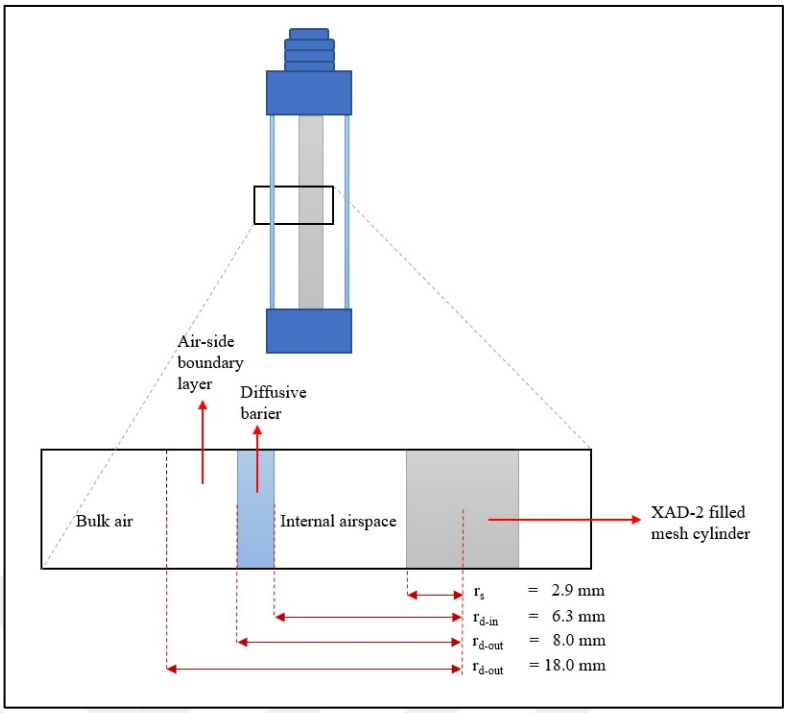


Figure 3.2 A passive air sampler: A comprehensive overview (McLagan et al., 2016)



Figure 3.3 Ready-to-sampling passive air sampler

Following the sampling, mesh cylinders packed with XAD-2 were immersed in 2 ml of hexane overnight. Subsequently, they were supplemented with 20 microliters of surrogate standard comprising 2000 ng tetrakis(trimethylsilyloxy)silane (M4Q) and subjected to ultrasonic extraction for 10 minutes. Then, 1 ml portion of sample extracts were transferred to 2 ml gas chromatography vials for subsequent analysis.

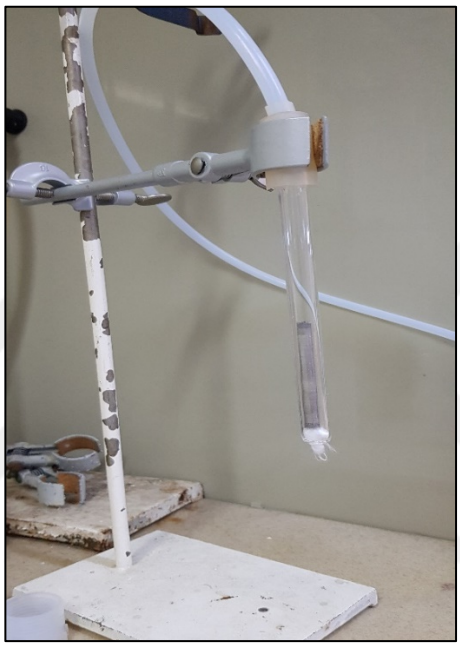


Figure 3.4 Sampler subjecting to drying process by using N_2

3.2.2 Sampling of dust

Dust samples were gathered from each indoor site using a hand-held vacuum cleaner at the beginning (Figure 3.5), three days after and at the end of passive sampling period and they were combined. The samples have been stored in aluminum foil in the refrigerator until they are analyzed (Figure 3.5).

The collected indoor dust samples were filtered through a 212 µm sieve. Then, approximately 0.5 g sieved dust sample was transferred to a vial for extraction (40 ml, amber). Then, 5 ml extraction solvent (hexane, spiked with 5000 ng of M4Q) was added, and it was immersed for 12 hours. Sample extraction was done by sonication for 10 minutes. Then, a portion of sample extract (approximately 1 ml) was filtered

utilizing a 0.45 µm PTFE syringe filter and transferred to a 2 ml gas chromatography vial for analysis (Figure 3.6).

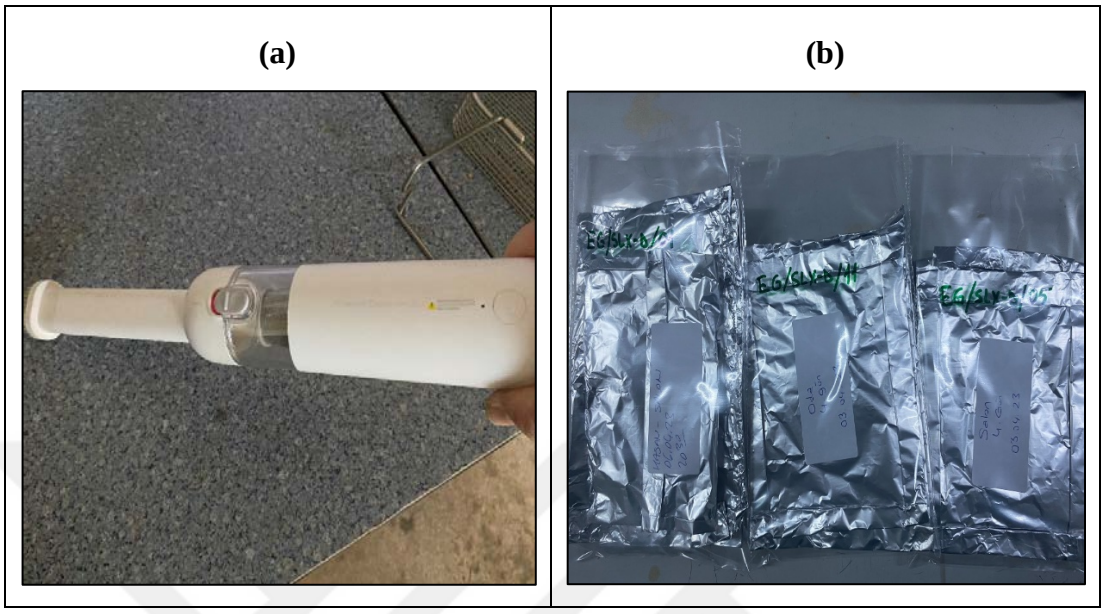


Figure 3.5 (a) Handheld vacuum cleaner, (b) Dust samples stored in aluminum foil after collection

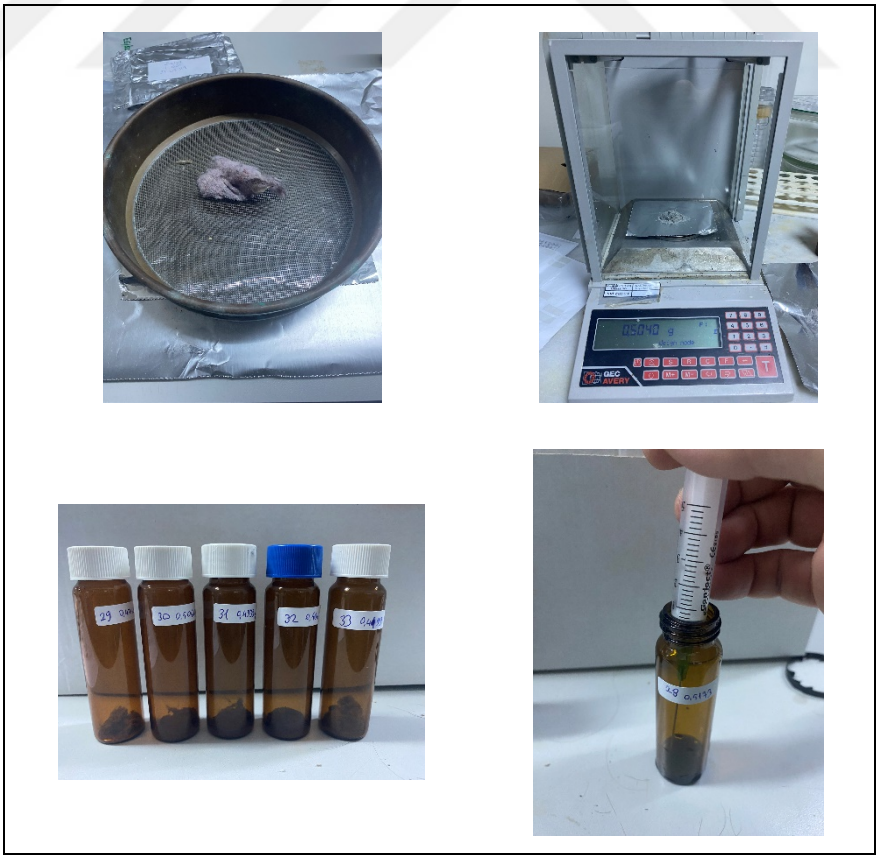


Figure 3.6 Transferring dust samples into amber vials

3.2.3 Instrumental analysis

All indoor air, atmospheric, and dust samples were analyzed for 7 cyclic and linear siloxanes (D3, D4, D5, D6, L3, L4 and L4). A Gas Chromatography (Agilent 6890N)-Mass Spectrometry (Agilent 5973 inert MSD) system was used at electron impact ionization (EI) and selected ion monitoring mode (SIM) for analysis (Figure 3.7). Helium was the carrier gas utilized to transport the sample through the HP5-MS-UI capillary column (diameter=0.25 mm, length=30 m, and stationary phase thickness=0.25 µm). Initially, the oven temperature was at 40°C for 3 minutes then increased to 160°C step up 10°C per minute, final temperature was increased to 300°C at a rate of 30°C per minute and held at the 300°C for 3 minutes. The temperatures of the injector, ion source and quadrupole were 150, 230 and 150°C, respectively.



Figure 3.7 GC-MS used in analysis (Personal archive, 2023)

3.3 Quality Control

During sampler preparation, field sampling, sample preparation for analysis, and analysis the materials (e.g. silicone septa) and use of personal care products have been avoided to minimize VMS contamination. All glass and metal materials used in analysis were rinsed with solvents (acetone and hexane), and then dried in oven at

105°C. Both before and after sampling, the samplers were placed within desiccator with their container until analysis.

The recovery efficiency of M4Q was determined as 98.5 ± 13.6% for air samples and 90.2 ± 9.1% for dust samples. The method detection limit (MDL) can be expressed as sum of the mean blank value and three times the standard deviation. Moreover, instrumental detection limits (IDL) obtained from the calibration curve, which was depended on the area of a peak having a minimum signal to noise ratio of three (Table 3.2).

Table 3.2 Method and instrumental detection limits for indoor air and indoor dust samples

Compound	**Air Samples**			**Dust Samples**		
	IDL (ng/ml)	**MDL (ng/sample)**	**MDL (ng/m^3)**	**IDL (ng/ml)**	**MDL (ng/sample)**	**MDL (ng/g)**
D3	1.46	50.9	106	1.18	42.8	85.2
L3	0.16	0.16	0.43	0.06	0.30	0.6
D4	0.11	7.51	19.2	0.18	11.3	22.4
L4	0.15	0.15	0.45	0.07	0.35	0.7
D5	0.15	2.81	8.24	0.13	8.73	17.4
L5	0.15	0.15	0.48	0.13	0.65	1.3
D6	0.17	1.47	4.65	0.16	12.7	25.2

Okan et al (2021) extracted and analyzed the samples taken from supporting plate and diffusive body for their VMS contents. It was found that the values were below the MDL, proving that the supporting plate and diffusive body do not cause contamination of VMS.

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Indoor Air VMS Concentrations

Indoor air samples collected from living rooms, bedrooms, offices, classrooms, cars, barber shops and hairdressers and ambient air were analyzed for concentrations of 4 cyclic (D3, D4, D5, and D6) and 3 linear (L3, L4, and L5) VMS compounds. The total of 36 samples were collected to determine indoor air VMS concentrations, and ∑VMS concentration was measured as 52612 ± 92684 ng/m^3 (Average ± SD) (Table 4.1). Minimum ∑VMS level was 1526 ng/m^3 while the maximum was 449836 ng/m^3. The average ∑VMS concentration in indoor air in Italy was measured by Pieri et al (2013) 994000 ng/m^3. The same study found that the average ∑VMS in indoor air in United Kingdom was 1544000 ng/m^3 (Pieri et al., 2013). These indoor air levels were substantially higher than ones measured in the present study. However, the ∑VMS concentration of 56800 ng/m^3 found in a research conducted in the United States was similar to the results of this study (Hoang et al., 2017). Overall, the highest-level VMS compound was D5. It was followed by D3 and D4, having average levels of 37007, 13581, 746 ng/m^3, respectively.

Table 4.1 Summary of indoor air VMS concentrations (ng/m^3)

Compound	**Indoor Air**				
	Minimum	**Maximum**	**Median**	**Average**	**Standard Deviation**
D3	746	49560	9025	13581	13994
D4	84	2841	459	746	736
D5	498	403862	10479	37007	88320
D6	78	2076	361	497	491
∑cVMS	**1492**	**428591**	**27553**	**51832**	**90119**
L3	0.7	3731	1.9	121	621
L4	1.1	2488	10	167	468
L5	1.8	15027	22	492	2502
∑lVMS	**4**	**21245**	**34**	**780**	**3533**
∑VMS	**1526**	**449836**	**27570**	**52612**	**92684**

VMS were found in samples collected from cosmetics products such as moisturizers, toilet soaps, body gels, shampoos, deodorants, shaving products. The highest average ∑VMS concentrations were measured in moisturizers. D3-D6 compounds were found in 94% of all cosmetics (nd-1203 ng/g, D3 dominant), and L2-L5 compounds were found in 54% of them (nd-7.85 ng/g, L5 dominant) (Capela et al., 2016). Thus, the highest level of ∑VMS in indoor air were measured in hairdressers and barber shops, followed by houses and cars (Figure 4.1). Indoor air average concentrations of ∑cVMS were measured as 9937, 26838, 44969, 70588 and 88070 ng/m^3 for classrooms, offices, cars, homes and hairdressers, respectively. Moreover, ∑lVMS concentrations were measured as 37, 48, 64, 285 and 2123 ng/m^3 for hairdressers, classrooms, cars, offices and homes, respectively.

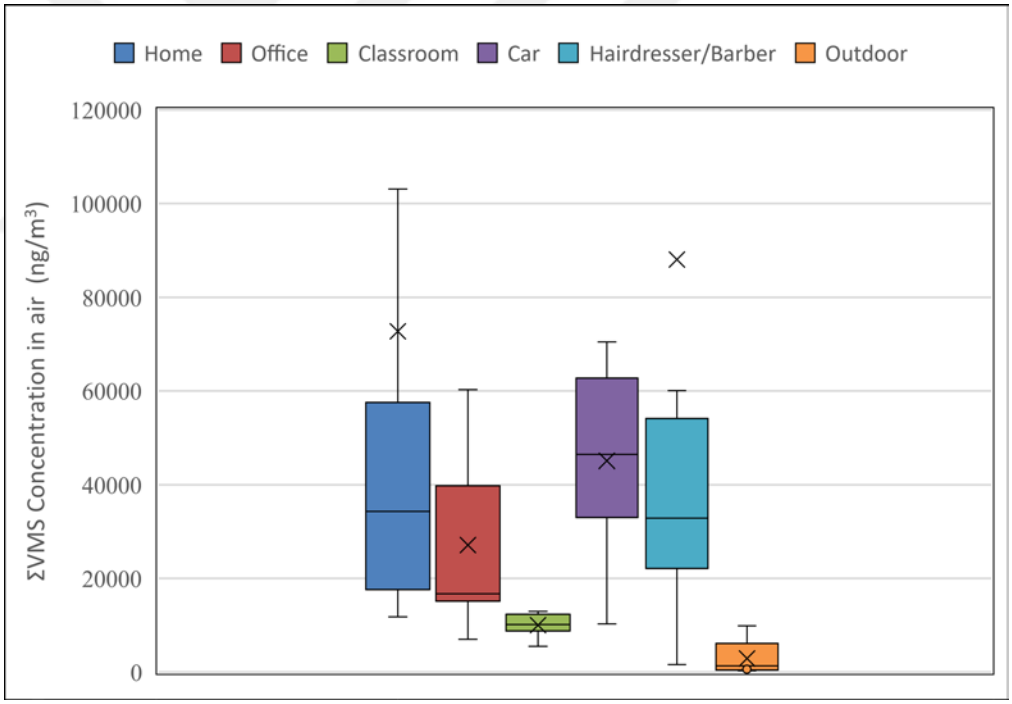


Figure 4.1 Indoor air ∑VMS concentrations

In the present study, the measured indoor air results are given in the Table 4.2. When comparing the studies, high concentrations were measured where personal care products and cosmetics were used intensely. In Turkey, the highest concentrations

were found in hairdressers and barbers. In studies conducted in Italy and United Kingdom, higher concentrations were measured in bathrooms. In all the studies examined, homes, including bedrooms, living rooms, etc. contained higher concentrations compared to offices or public buildings. This indicated that the main sources were the use of cosmetic products.

Table 4.2 Comparison of VMS in indoor air concentrations with the literature

Country	**Year**	**Environments**	**Compound**	**Concentrations (ng/m^3)**	**References**
Turkey	2023	Hairdresser/Barber Home Car Office Classroom	D3-6, L3-5 D3-6, L3-5 D3-6, L3-5 D3-6, L3-5 D3-6, L3-5	88106 (1526-381670) 72711 (11753-449836) 45034 (10239-70458) 27123 (6945-60294) 9984 (5436-12911)	This study
Sweden	2016	Homes Offices University rooms	D4-6 D4-6 D4-6	2200 (570-3600) 1700 (550-3600) 1280 (110-2600)	Sha et al., 2018
US	2010 2010	Commercial buildings Offices and laboratories	D5 D4-6	24900 (1300-120000) 14000 (1020-59300)	Wu et al., 2011 Yucuis et al., 2013
Italy	2011	Bathrooms Bedrooms Living rooms Offices	D3-6, L2-5 D3-6, L2-5 D3-6, L2-5 D3-6, L2-5	230000 (17000-820000) 200000 (2100-940000) 100000 (26000-300000) 18000 (14000-21000)	Pieri et al., 2013
UK	2011	Bathrooms Supermarkets Living rooms Bedrooms Offices	D3-6, L2-5 D3-6, L2-5 D3-6, L2-5 D3-6, L2-5 D3-6, L2-5	340000 (17000-820000) 330000 (130000-630000) 320000 (28000-520000) 187000 (56000-430000) 78000 (16000-220000)	Pieri et al., 2013

In total, 12 samples were taken from 6 different houses including bedrooms and living rooms. ∑VMS concentrations ranged from 11753 to 449836 ng/m^3. Average ∑VMS concentrations in bedrooms were higher than living rooms. The reason for this may be that personal care products such as perfumes and deodorants are stored and used/applied in the bedrooms. The most dominant compound was D5 with an average concentration of 48009 ng/m^3, followed by D3 with 20678 ng/m^3 and L5 with 1400 ng/m^3. The contributions to ∑VMS based on the compounds was given in Figure 4.2. According to research in Vietnam, the concentrations found in houses varied between 80.5 and 532 ng/m^3 (Tran et al., 2015). In a different study in Italy, the concentration values also varied between 26000 and 300000 ng/m^3 (Pieri et al., 2013). Although the

concentrations based on the measurement in homes in the present study were higher than the levels observed in Vietnam, they were similar to the study conducted in Italy.

A total of 6 air samples were taken from 6 offices, including 2 teacher's office, 2 headmaster's office, 1 administrative office and 1 research assistant's office. In comparison to houses lower concentrations values were measured in offices. ∑VMS concentrations were ranged between 6945 and 60294 ng/m^3. The most dominant compound was D5 again with average concentrations of 20890 ng/m^3. D3 and D6 followed D5 with levels of 5002 and 587 ng/m^3, respectively (Figure 4.2). Researchers in Sweden measured VMS concentrations in offices as a mean value of 1700 ng/m^3 ranged between 550 and 3600 ng/m^3 (Sha et al., 2018). The VMS levels measured in offices included in the present study were higher than ones reported in Sweden. On the other hand, concentration values ranging from 1020 to 59300 ng/m^3 were measured in offices in the United States and these were comparable to the values measured in the present study, unlike Sweden (Yucuis et al., 2013).

The lowest levels measured in the present study were observed in classrooms. ∑VMS concentrations measured in 6 classrooms ranged between 5436 and 12911 ng/m^3. Total concentration of the dominant compound, D5, was 6002 ng/m^3. The second most dominant VMS was D3 with an indoor air concentration of 3522 ng/m^3 and the compound with the lowest concentration was L3, measured as 4 ng/m^3 (Figure 4.2). Tran & Kannan (2015) measured the ∑VMS concentration as 1240 ng/m^3 in United States and this was lower than ones observed in the present study.

VMS levels in samples collected from 6 cars were measured in the range of 10239 to 70458 ng/m^3. The leading compound was D3, with a level of 26865 ng/m^3. D5 and D4 followed D3 with levels of 16727 and 845 ng/m^3, respectively (Figure 4.2). In a study in China, the levels of D4, D5 and D6 compounds were measured within the range of 200-5300 ng/m^3 (Meng & Wu, 2015). In another study in the literature, total siloxane concentrations were measured between 283 and 639 ng/m^3 by researchers from Vietnam (Tran et al., 2017). The VMS levels measured in the present study were higher than those two previous studies. This may be due to the differences in the amounts of cosmetics used and the personal care products used by people traveling in vehicles.

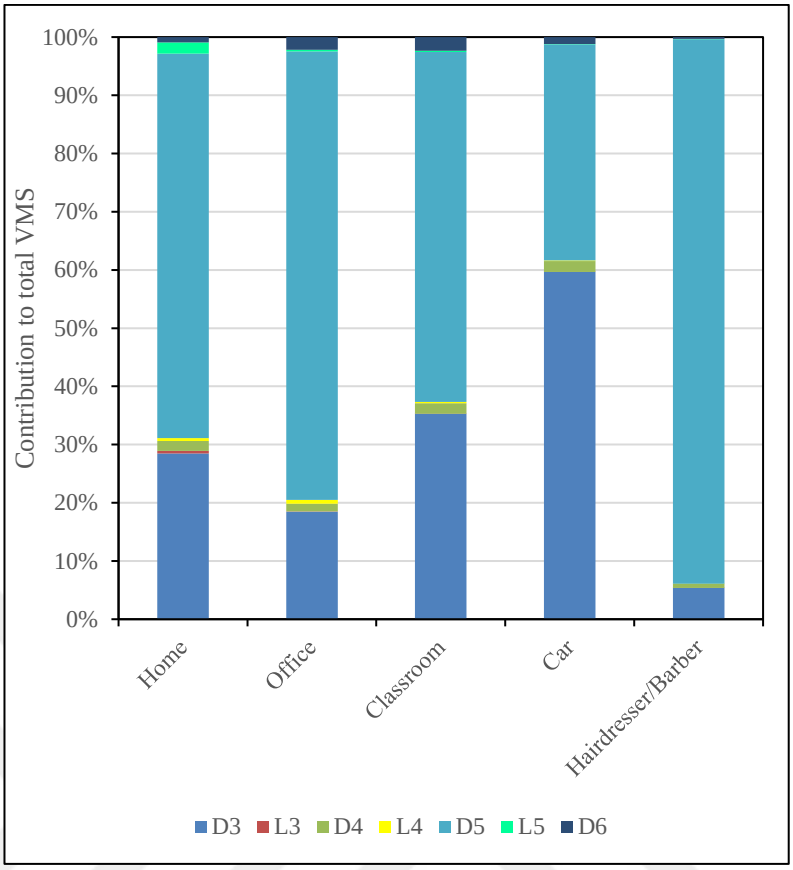


Figure 4.2 VMS profiles for indoor air.

The highest ∑VMS levels were observed in hairdressers and barber shops with the concentration values from 1526 to 381680 ng/m^3. In hairdressers and barbers, the leading compound was D5 again with an average level of 82404 ng/m^3. D3 and D4 followed D5, with the concentrations of 4726 and 642 ng/m^3, respectively (Figure 4.2). Tran et al (2017) also measured the concentration levels of siloxanes in the hairdressers' indoor air in Vietnam. They found that the average level of D4-D6 siloxanes was 1030 ng/m^3, with a range of 415 to 2610 ng/m^3. The average level of D3-D6 and L4-L9 siloxanes was 1320 ng/m^3, with a range of 289 to 1950 ng/m^3 (Tran et al., 2018). The number of customers coming in, differences in the personal care products and cosmetics they use may be the reason for relatively lower concentrations reported in the literature.

4.2 Indoor/Outdoor Concentrations Ratios

In total, 5 ambient air samples were collected concurrently with indoor air (one for each category). ∑VMS concentration was measured as 2827 ± 4010 ng/m^3 (Average ± standard deviation). The leading VMS was D5 with a level of 2298 ng/m^3. The concentrations for all VMS were given in the Table 4.3. ∑VMS concentration in ambient air representing house was measured as 1257 ng/m^3. ∑VMS ambient concentrations were 9869 ng/m^3 for offices, 2228 ng/m^3 for classrooms, 546 ng/m^3 for cars and 236 ng/m^3 for hairdressers/barbers.

Table 4.3 Summary of atmospheric VMS concentrations (ng/m^3)

Compound	**Ambient Air**				
	Minimum	**Maximum**	**Median**	**Average**	**Standard Deviation**
D3	107	681	324	380	247
D4	27	206	56	84	75
D5	89	8830	828	2298	3689
D6	7,6	130	24	52	54
∑cVMS	**233**	**9847**	**1231**	**2813**	**4006**
L3	0,5	4,0	1,6	1,9	1,3
L4	1,2	3,6	2,5	2,4	0,9
L5	1,2	19	6,6	10	8,1
∑lVMS	**3**	**26**	**10**	**14**	**10**
∑VMS	**236**	**9869**	**1257**	**2827**	**4010**

Average indoor/outdoor concentrations ratios were higher than 1.0 and ranged between 16.8 (D4) and 183 (D5) (range: 2 D4 in classroom-921 D5 in hairdresser/barber) indicating that VMS had significant indoor sources (Figure 4.3).

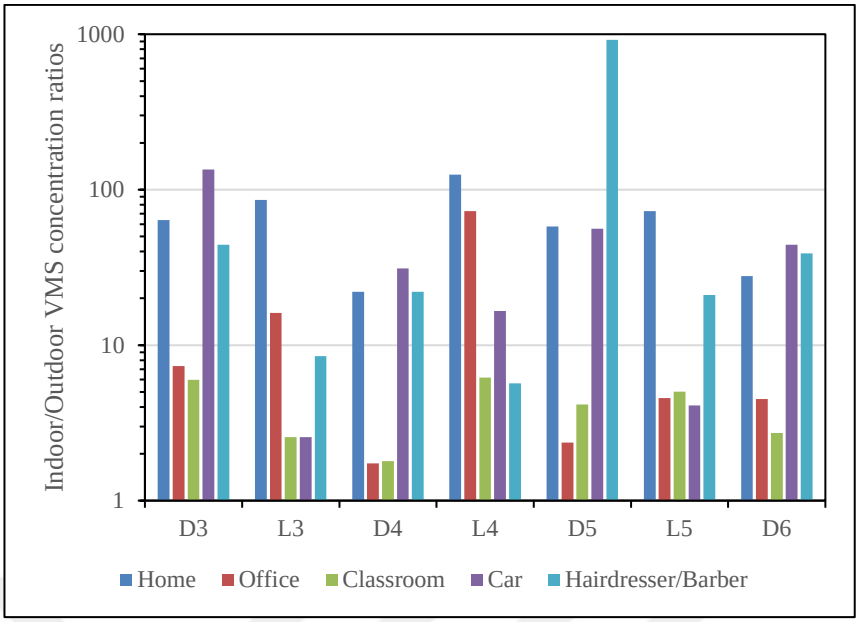


Figure 4.3 Indoor/outdoor VMS concentration ratios

4.3 Indoor dust VMS concentrations

Indoor dust samples collected from living rooms, bedrooms, offices, classrooms, cars, barber shops and hairdressers using a hand-held vacuum cleaner at the beginning, three days after and at the end of indoor air sampling period and they were combined. They were analyzed for concentrations of four cyclic (D3, D4, D5, and D6) and three linear (L3, L4 and L5) VMS compounds. A total of 36 samples were collected to determine indoor dust VMS concentrations, and ∑VMS concentration was measured as 3096 ± 7138 ng/g (Average ± Standard deviation) (Table 4.4). Minimum ∑VMS level was 354 ng/g and the maximum level was 40852 ng/g. Studies were conducted on indoor dust samples in Greece, Kuwait, Japan, Pakistan and South Korea and the average VMS concentrations were measured as 5590, 4780, 4240, 2690 and 2620 ng/g, respectively (Tran et al., 2015). Indoor dust VMS levels measured by Tran et al (2015) were almost similar to those measured within the present study. The leading VMS was D5. D6 and D3 followed D5, with average levels of 1775, 916 and 305 ng/g, respectively.

Table 4.4 Summary of indoor dust VMS concentrations (ng/g)

Compound	Indoor Dust				
	Minimum	**Maximum**	**Median**	**Average**	**Standard Deviation**
D3	143	758	232	305	151
D4	25	653	45	88	112
D5	85	38925	231	1775	6484
D6	76	14948	292	916	2499
∑cVMS	**351**	**40836**	**1061**	**3083**	**7137**
L3	0.7	2.7	1.7	1.6	0.7
L4	0.8	40	2.2	3.6	6.9
L5	1.4	94	4.1	8.8	16
∑lVMS	**1.5**	**137**	**6.1**	**13**	**23**
∑VMS	**354**	**40852**	**1067**	**3096**	**7138**

The highest concentration of ∑VMS in indoor dust was measured in hairdressers and barber shops, followed by houses and cars (Figure 4.4). Indoor dust average concentrations of ∑cVMS was measured as 635, 2649, 1889, 1413 and 11278 ng/g for homes, offices, classrooms, cars and hairdressers, respectively. Moreover, ∑lVMS concentrations were measured as 9, 19, 31, 8 and 11 ng/g for homes, offices, classrooms, cars and hairdressers, respectively.

Indoor dust VMS levels obtained in the present study were compared to the ones observed in previous similar studies in Table 4.5. Indoor dust collected in hairdressers again had the highest siloxane concentrations. The dust VMS concentrations in hairdressers in China were almost four times higher than the concentrations observed in the present work while lower concentrations were measured in Vietnam. Samples were gathered from homes and cars in Greece and Kuwait, and concentrations were higher than the ones observed in homes and cars in Turkey. Differently, for the levels observed in indoor air samples, the lowest dust VMS levels were measured in homes.

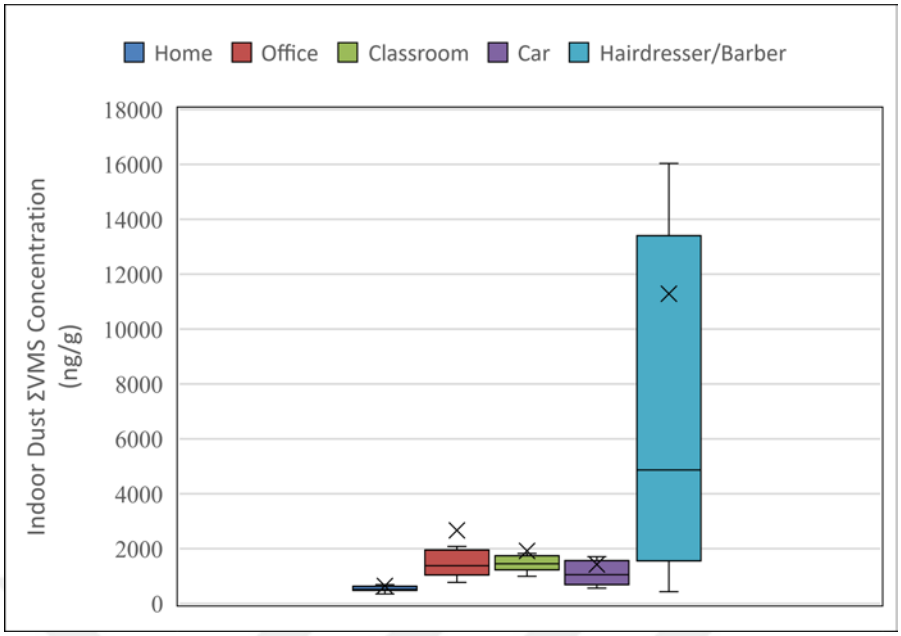


Figure 4.4 Indoor dust ΣVMS concentrations

In total, 12 samples were collected from 6 different houses including bedrooms and living rooms. ∑VMS concentrations were measured within the range from 354 to 1307 ng/g, as the lowest dust VMS levels in this study. Average ∑VMS concentrations in bedrooms were higher than living rooms. The reason for this could be that personal care products like perfumes and deodorants are stored and used in the bedrooms. The most dominant compound was D5 with average concentrations of 220 ng/g, followed by D3 with 218 ng/g and D6 with 156 ng/g. The contribution to ∑VMS based on the compounds was given in Figure 4.5. According to research in China, the concentrations were measured in houses ranged between 250 and 8678 ng/g (mean 2449 ng/g) (Liu et al., 2018). The levels observed in China were appreciably higher than the concentrations found in the present study. In another research in Colombia, the concentrations were ranged between 102 and 2370 ng/g (mean 502 ng/g) (Tran et al., 2015). The VMS levels measured in Colombia were similar to the concentrations measured in the present study.

Table 4.5 Comparison with literature-∑VMS in indoor dust

Country	Year	Environments	Compound	Concentrations (ng/g)	References
Turkey	2023	Hairdresser/Barber Office Classroom Car Home	D3-6, L3-5 D3-6, L3-5 D3-6, L3-5 D3-6, L3-5 D3-6, L3-5	11288 (435-40852) 2666 (772-9397) 1917 (993-4622) 1420 (563-3545) 642 (354-1307)	This study
Vietnam	2017	Hair salon	D4-6	671 (178-1240)	Tran et al., 2018
China	2012	Barbershop Home	D4-6, L4-16 D4-6, L4-16	43126 (5293-132599) 2449 (250-8678)	Liu et al., 2018
Greece	2014	Home	D3-7, L4-14	5590 (384-30100)	Tran et al., 2015
Kuwait	2013	Home, car	D3-7, L4-14	4780 (476-42800)	Tran et al., 2015

A total of 6 dust samples were collected from 6 offices, including 2 teacher's office, 2 headmaster's office, 1 administrative office and 1 research assistant's office. In comparison to houses lower concentrations were measured in offices. ∑VMS levels varied between 772 and 9397 ng/g. The leading compound was D5 again with an average concentration of 1205 ng/g followed by D6 and D3 with concentrations of 848 and 492 ng/g, respectively (Figure 4.5). In South Korea, the indoor dust concentration was measured to be approximately 2000 ng/g in offices, while in the US, concentration of 423 ng/g was detected (Tran et al., 2015). The results observed in South Korea were similar with those in the present study.

∑VMS dust concentrations were measured in 6 classrooms ranged between 5436 and 12911 ng/g. The concentration of dominant compound, D6 was 973 ng/g. The second-high level VMS was D5 with the concentration of 446 ng/g and the compound with the lowest concentration was L3, measured as 2 ng/g (Figure 4.5).

The VMS levels in samples gathered from 6 cars were measured in the range of 563 to 3545 ng/g. The leading compound was D5, with the concentration of 645 ng/g. D5 was followed by D6 and D3 with 478 and 222 ng/g, respectively (Figure 4.5).

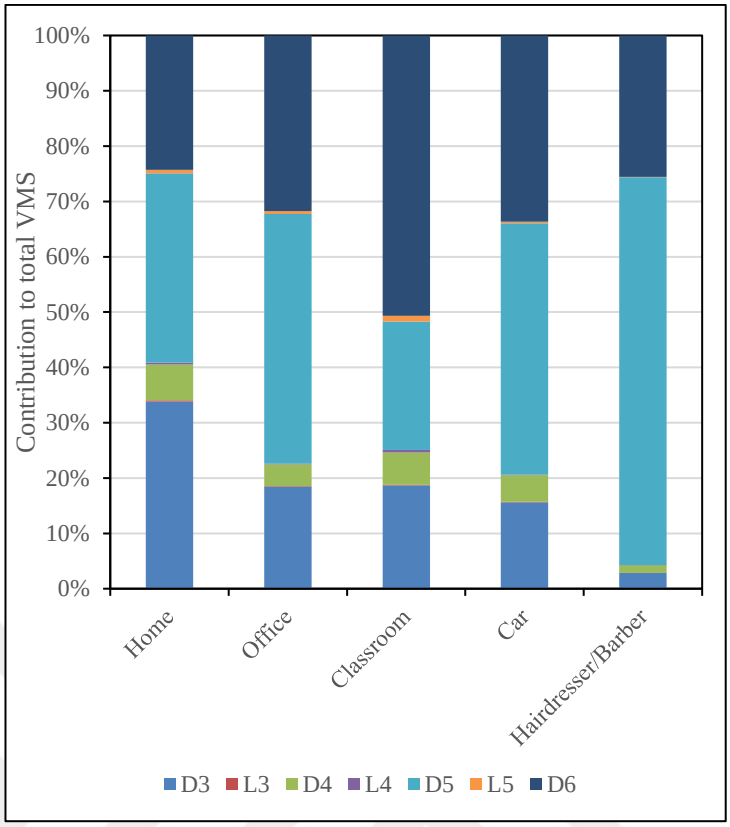


Figure 4.5 VMS profiles for indoor dust

The highest ∑VMS concentrations were measured in hairdressers and barber shops with the concentrations from 435 to 40852 ng/g. In hairdressers and barbers, as in other environments, the leading VMS was D5 again with the average concentration of 7916 ng/g followed by D6 and D3 with the concentrations of 2883 and 320 ng/g, respectively (Figure 4.5). Liu et al (2018) measured the levels of siloxanes in the hairdressers' indoor dust in China. They reported that the average level of D4-D6 and L4-L16 siloxanes was 43126 ng/g, with a range of 5293 to 132599 ng/g (Liu et al., 2018). The levels observed in China were similar to concentrations in this study. However, another study in Vietnam concentrations were measured much lower with an average of 671 ng/g (range 178-1240 ng/g), in contrast to the levels measured in this study (Tran et al., 2018). The reason for the lower levels found in this study could be because of the differences in the contents and usage amounts of personal care products.

4.4 Estimation of Dust-Indoor Air Partitioning of VMS

The partitioning of VMS between the gas-phase and indoor dust was explored using the simple modeling approach suggested by Weschler and Nazaroff (2010). While chemicals also partition to inorganic matter, the affinity of chemicals for the organic fraction is substantially higher (Salthammer & Schripp, 2015). Assuming that the main mechanism is sorption to organic matter, the partitioning of an organic compound to indoor dust may be estimated by Equation (4.1) (Weschler and Nazaroff, 2010).

$$X_{dust,predicted} = \frac{f_{om-dust}\ K_{OA}\ C_g}{\rho_{dust}} \quad (4.1)$$

Under equilibrium conditions, $X_{\text{dust, predicted}}$ expresses the estimated mass fraction of the VMS in the dust (µg/g), K_{OA} is the octanol-air partitioning coefficient, $f_{\text{om-dust}}$ is the organic matter fraction of indoor dust and ρ_{dust} is the dust density (g/m^3).

The relationship between indoor gas-phase VMS concentrations (log C_g, µg/m^3) and measured VMS concentrations in indoor dust (log $X_{\text{dust,measured}}$, µg/g) is illustrated in Figure 4.6.

log C_g and log $X_{\text{dust,measured}}$ correlated well (r^2=0.59, p<0.01) indicating that gas-phase VMS concentration is an important parameter in determining indoor dust concentrations.

Equation (4.1) was utilized to estimate the indoor dust VMS levels along with the measured gas-phase concentrations, f_{om} values, and temperature-adjusted K_{OA} values. Organic matter fraction of indoor dust ranged between 0.13-0.93 (0.46±0.24, average±SD). Measured indoor temperatures varied between 17.5-24.4°C (21.7±2.1°C, average±SD). K_{OA} values were taken from Whelan and Kim (2022) and adjusted for measured temperatures using the enthalpies of octanol-air exchange. Dust density was not measured in the present study. ρ_{dust} was assumed as 1x10^6 g/m^3, based on the recommendation by Salthammer and Schripp (2015).

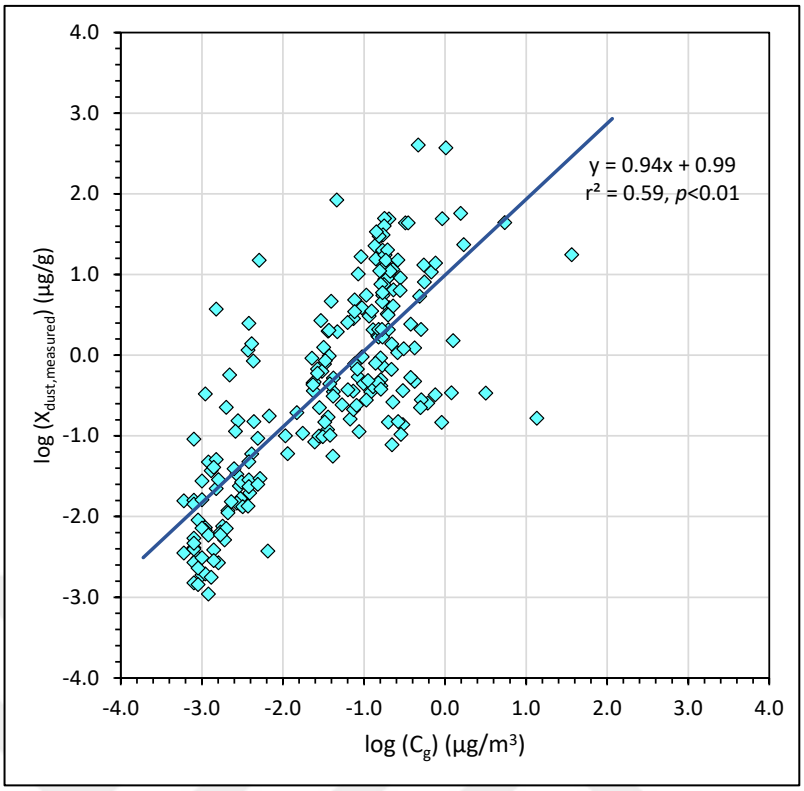


Figure 4.6 Relationship between indoor air and dust VMS concentrations

Figure 4.7 compares predicted and measured indoor dust VMS concentrations. Predicted dust VMS concentrations correlated well with the measured ones (r^2=0.56, p<0.01) having a slope close to 1.0 (0.97) and an intercept of -0.65. The intercept shows that, on average, the estimated indoor dust VMS concentrations are 4.5 times lower (=$10^{0.65}$) than the experimental values. It is implausible that this difference could be due to the assumed dust density value. Other factors might elucidate the observed discrepancies between estimated and experimental VMS content of indoor dust.

As the K_{OA} increases, the equilibrium partitioning is reached at a slower speed, and the mass fraction of a semi-volatile organic compound in indoor dust may not find adequate time to equilibrate with the gas-phase. This results in overestimated $X_{dust,\ predicted}$ values for chemicals having high log K_{OA} values (>11.5) (Cetin and Odabasi, 2008; Weschler and Nazaroff, 2010). However, VMS have relatively low log K_{OA} values (3.77-5.77) (Whelan and Kim, 2022) and could reach to equilibrium quickly. Measured indoor gas-phase VMS levels in the present study represent the average values over the sampling period (≈7 days). Although indoor dust samples were taken

at the beginning, three days after and at the end of passive sampling period and they were combined, they could be considered as instantaneous samples. Therefore, measured gas-phase and indoor dust VMS concentrations are not essentially concurrent. This may be one of the factors contributing to the discrepancy between the measured and estimated indoor dust VMS concentrations.

The discrepancy between the measured and estimated indoor dust concentrations was also attributed to the dissimilarities between octanol and indoor dust organic matter (Weschler and Nazaroff, 2010). The relationship expressed by Equation (4.1) assumes that the solubility of a chemical in the organic matter fraction of indoor dust is anologous to its solubility in octanol. Weschler and Nazaroff (2010) suggested that this assumption may not be valid for all organics based on the modelling results for several different classes of chemicals.

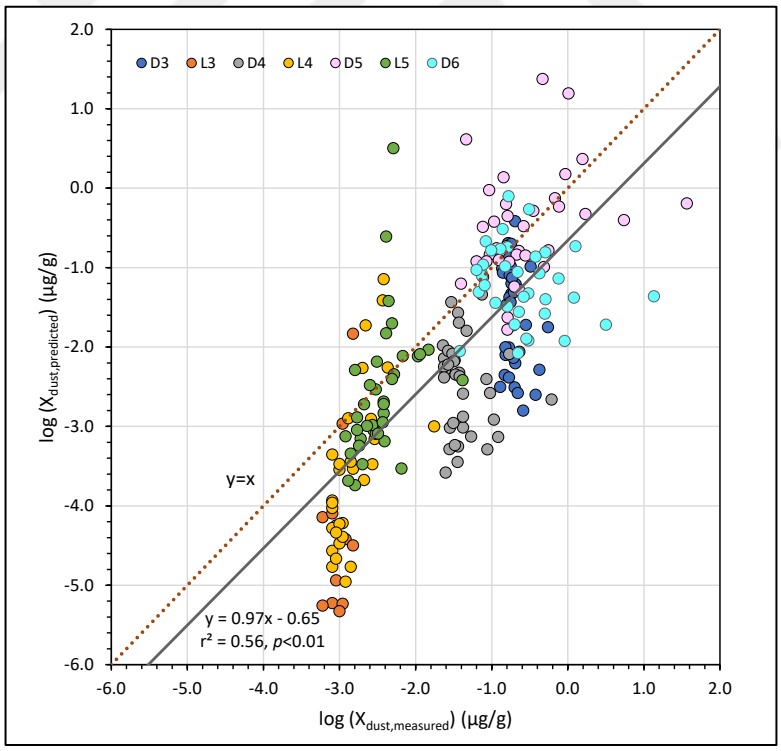


Figure 4.7 Relationship between log ($X_{dust,predicted}$) and log ($X_{dust,measured}$)

Shoeib et al. (2005) postulated another reason for the discerned difference between experimental and estimated partitioning is that some of the chemicals in indoor dust

may be derived from indoor abrasion or wear processes forming highly contaminated particles. Such circumstances could result in underestimation of measured values as observed in the present study (Figure 4.7).

CHAPTER FIVE
CONCLUSIONS AND RECOMMENDATIONS

This study presented the levels of VMS in indoor and ambient air, as well as indoor dust in Izmir. The dominant VMS compounds in both indoor and ambient air samples were D5 while following compounds were D3 and D4. This suggested that D5 was the most prevalent VMS in indoor and ambient air. Furthermore, the average indoor/outdoor concentrations ratios were calculated to be greater than 1.0, indicating that VMS had significant indoor sources. The ratios ranged between 16.8 (D4) and 183 (D5), highlighted the influence of indoor sources on VMS levels.

Moreover, the analysis of indoor dust showed that the leading VMS was D5, followed by D6 and D3. This provided information about the composition of VMS in indoor dust and underscored the prevalence of D5 in indoor environments.

Additionally, the study determined hairdressers and barbers as having the highest average indoor air and indoor dust ∑VMS levels. These findings suggested that VMS concentrations are elevated, potentially due to the use of personal care products containing VMS.

Furthermore, the study's findings contributed to the previous literature by demonstrating that indoor air and dust VMS concentrations were similar the ranges reported in previous studies. Additionally, the study suggested that indoor dust levels could be predicted using a gas-indoor dust partitioning model to compare these predictions with the concentrations measured in this study.

In summary, a comprehensive analysis about the determination of VMS concentrations in indoor air and ambient air samples, as well as indoor dust, provided valuable information about the prevalence, sources and variability of VMS in indoor environments. The findings not only contributed to the current understanding of VMS exposure in indoor environments, but also provided a basis for future research aimed at explaining the factors that influenced VMS concentrations and their potential impacts on human health and indoor air quality.

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