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**DETERMINATION OF INDOOR AND OUTDOOR BIOGENIC AND
ANTHROPOGENIC VOLATILE ORGANIC COMPOUNDS IN
WORKPLACE AND HEALTH RISK ANALYSIS**

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ABSTRACT

DETERMINATION OF INDOOR AND OUTDOOR BIOGENIC AND ANTHROPOGENIC VOLATILE ORGANIC COMPOUNDS IN WORKPLACE AND HEALTH RISK ANALYSIS

MSC THESIS

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BOLU ABANT İZZET BAYSAL UNIVERSITY

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BOLU, JULY 2024

(xv + 118)

A group of pollutants, designated as volatile organic compounds (VOCs), is present in both indoor and outdoor environments. Some of these volatile compounds have been the subject of research interest due to their potential to cause adverse effects on human health. In this study, a total of 57 anthropogenic and biogenic volatile organic compounds (VOCs) were determined which were collected from six different dyeing and printing workplaces in Bolu, and their potential health effects on employees were evaluated. In the context of this study, both active and passive sampling techniques were employed, with samples being collected simultaneously at each sampling point. Air samples were collected from the photocopy center (7 days), painting class (7 days), print-making class-1 (3 days), print-making class-2 (3 days), tire shop, and car painter (2 days) between March 25 and April 26, 2022, respectively. Analyses were conducted using a TD-GC-MS (Thermal Desorption-Gas Chromatography-Mass Spectroscopy) device. The highest average VOC concentration was observed in the car painter, followed by the print-making class-2, the print-making class-1, the painting class, the tire shop, and the photocopy center. Upon examination of the lifetime cancer risk associated with the identified VOCs, a probable risk was determined for the carbon tetrachloride compound in the car painter. However, no cancer risk could be determined at any sampling point. The total hazard index was found to exceed the accepted limit at all sampling points.

KEYWORDS: Volatile Organic Compounds, Indoor and Outdoor Air, Active and Passive Sampling, Health Risk Assessment, Monte Carlo Simulation

ÖZET

İŞYERLERİNDE İÇ VE DIŞ ORTAM BİYOJENİK VE ANTROPOJENİK UÇUCU ORGANİK BİLEŞİKLERİN BELİRLENMESİ VE SAĞLIK

RİSKİ ANALİZİ

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Uçucu organik bileşikler (VOC'ler) olarak tanımlanan bir grup kirletici, hem iç hem de dış ortamlarda mevcuttur. Bu uçucu bileşiklerden bazıları, insan sağlığı üzerinde olumsuz etkilere neden olma potansiyelleri nedeniyle araştırma konusu olmuştur. Bu çalışmada Bolu'daki altı farklı boya ve baskı işyerinden toplanan örneklerde toplam 57 adet antropojenik ve biyojenik uçucu organik bileşik belirlenmiş ve bunların çalışanlar üzerindeki potansiyel sağlık etkileri değerlendirilmiştir. Bu çalışma kapsamında, her örnekleme noktasında eş zamanlı olarak numuneler toplanarak hem aktif hem de pasif örnek alma teknikleri kullanılmıştır. Hava örnekleri 25 Mart-26 Nisan 2022 tarihleri arasında sırasıyla fotokopi merkezi (7 gün), resim sınıfı (7 gün), özgün baskı sınıfı-1 (3 gün), özgün baskı sınıfı-2 (3 gün), lastik dükkanı (2 gün), ve kaportacı (2 gün) olmak üzere farklı alanlardan toplanmıştır. Analizler bir TD-GC-MS (Termal Desorpsiyon-Gaz Kromatografisi-Kütle Spektroskopisi) cihazı kullanılarak yapılmıştır. En yüksek ortalama VOC konsantrasyonu kaporta atölyesinde gözlemlenmiştir, bunu özgün baskı sınıfı-2, özgün baskı sınıfı-1, resim sınıfı, lastik dükkanı ve fotokopi merkezi izlemiştir. Tanımlanan VOC'lerle ilişkili yaşam boyu kanser riskinin incelenmesi üzerine, kaportacıdaki karbon tetraklorür bileşiği için olası bir risk belirlenmiştir. Ancak hiçbir numune alma noktasında kanser riski tespit edilememiştir. Toplam tehlike indeksinin tüm örnekleme noktalarında kabul edilen sınırı aştığı görülmüştür.

ANAHTAR KELİMELELER: Uçucu Organik Bileşikler, İç ve Dış Ortam Havası, Pasif ve Aktif Örnekleme, Sağlık Riski Analizi, Monte Carlo Simülasyonu

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LIST OF ABBREVIATIONS AND SYMBOLS

AER	: Air Exchange Rate
AT	: Average Time
AVOCs	: Anthropogenic Volatile Organic Chemicals
BTEX	: Benzene, Toluene, Ethylbenzene, and Xylene
BVOCs	: Biogenic Volatile Organic Chemicals
BW	: Body Weight
CA	: Contaminant Concentration
CDI	: Chronic Daily Intake
CNS	: Central Nervous System
CO	: Carbon Monoxide
COPD	: Chronic Obstructive Pulmonary Disease
CTC	: Carbon Tetra Chloride
CVD	: Cardiovascular Disease
ECD	: Electron Capture Detector
ED	: Exposure Duration
EF	: Exposure Frequency
EPA	: Environmental Protection Agency
ET	: Exposure Time
FID	: Flame Ionization Detector
HAPs	: Harmful
HI	: Hazard Index
IAQ	: Indoor Air Quality
IARC	: International Agency for Research on Cancer
IR	: Inhalation Rate
IRIS	: Integrated Risk Information System
IUR	: Inhalation Unit Risk
KI	: Potassium Iodide
LCR	: Lifetime Cancer Risk
MS	: Mass Spectrometer
MTs	: Monoterpenes

NO_x	: Nitrogen Oxide
O₃	: Ozone
OSF	: Oral Slope Factor
PAHs	: Poly Aromatic Hydrocarbons
Pb	: Lead
PCM	: Print-Making Class
PM	: Particulate Matter
RfC	: Reference Concentration
RfD	: Reference Dose
SBS	: Sick Building Syndrome
SIM	: Selected Ion Monitoring
SO₂	: Sulfur Dioxide
TCD	: Thermal Conductivity Detector
TD-GC-MS	: Thermal Desorption-Gas Chromatography-Mass Spectroscopy
VOCs	: Volatile Organic Chemicals
WHO	: World Health Organization

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1. INTRODUCTION

1.1 Air Pollution and Sources

According to the World Health Organization (WHO), air pollution is the pollution of the outdoor and indoor environment by biological, physical, or chemical events that cause a change in the properties of the atmosphere. Natural activities like vegetation, wildfire, or anthropogenic activities like vehicle exhaust, industrial factories, and fossil fuel combustion are the main sources of air pollution (1,2). Air pollution has negative effects on human health, such as respiratory disease, cardiovascular disease, and cancer, therefore causing much concern (1,3). Major air pollutants by the US Environmental Protection Agency (EPA) are divided into six groups mainly ozone (O_3), sulfur dioxide (SO_2), particulate matter (PM), nitrogen oxide (NO_x), lead (Pb), and carbon monoxide (CO) (4). Ozone is photochemical smog produced by the combination of nitrogen oxide (NO_x) emission and volatile organic compounds (VOCs) (5,6). Sulfur dioxide emissions are from fossil fuel use, and nitrogen oxides are substantially from vehicle emissions and form nitric acid and sulfuric acid (7). Particulate matter ($PM_{2.5}$ and PM_{10}) consists of tiny airborne particles emitted into the atmosphere from primary air pollutants such as diesel fuel or secondary air pollutants such as photochemical smog products. Particulate lead is the most common of the toxic metals and can cause significant health problems (1,4). Carbon monoxide is released from the emission produced by incomplete combustion in fossil fuel-powered engines (4,8).

1.1.1 Indoor Air Pollution and Their Sources

People spend most of their time in various indoor environments such as homes, schools, offices, shopping malls, cafes, and movie theaters (9,10). It is known that there are air pollutants such as microorganisms, NO_x, O₃, CO, SO₂, polycyclic aromatic hydrocarbons (PAHs) (such as naphthalene), semi-volatile, and volatile organic compounds (such as BTEX, formaldehyde), particulate matter (PM), and radon in indoor air (3,11). Indoor air pollution is generally at higher levels than outdoor air pollution (3,9,10,12). According to the World Health Organization, more than 2 billion people in the world cook food in their stoves by using dirty solids such as coal, manure, and waste wood or burn them in their fireplaces to heat their homes, so air pollutants such as NO_x, PM, and CO can also accumulate in the indoor environment (3,13). Nitrogen oxide (NO and NO₂) pollutants are mostly caused by vehicle emissions in the outdoor environment, and it is emitted from emissions from gaseous fuels such as cigarettes, stoves, ovens, and heaters in the indoor environment. In winter, NO₂ concentration can be observed at a higher level in indoor environments than in outdoor environments due to the use of heaters (11,14,15). Particulate matter in the indoor environment can leak into the indoor environment in different sizes such as PM₁₀, PM_{2.5}, or PM_{0.1} (ultrafine particulates). Particles can spread indoors from many different household activities; for example; smoking, burning candles and incense, and using a stove or oven (3,11). Sulfur dioxide pollutants arise as a result of the combustion of the fuels of vehicles using diesel as fuel in the outdoor environment and from the coal combustion, and thus can leak into the indoor environment. In addition, it is emitted from the combustion of sulfur-containing fuels such as coal, charcoal, and kerosine in the indoor environment (11,15). Polycyclic aromatic hydrocarbons (PAHs) with 2 or 3 rings are emitted from the gas phase, while PAHs with 5 or more 5 rings are emitted as particles; It is spread due to incomplete combustion such as wood burning, smoking, coal, and gas burning. PAHs are spread indoors by cooking, smoking, and using moth repellent (11,15,16). Naphthalene compound, which is both PAH and VOC, is abundant in indoor environments, and naphthalene spreads indoors from the use of deodorants, pesticides, cleaning materials, and cigarettes (11,17).

Volatile organic compounds (VOCs) are known to be the most common indoor air pollutant (9,10,12). Indoor VOCs are emitted in varying concentrations from biogenic (such as vegetation wildfire) and anthropogenic (such as traffic, and paints) sources (10,12). According to the EPA's research, the VOC pollutants inside the houses were found to be 2 to 5 times higher than the pollutants in the outdoor environment(18). Indoor environments are affected by a variety of VOC sources, and they are emitted from many places such as the use of solvents, wood preservatives, cleaning supplies, deodorants, hobby supplies, pesticides, furniture, paints, building materials, office supplies, automotive paint shops, and photocopy machine (3,10–13,18–20). Volatile formaldehyde is commonly found among indoor pollutants. Formaldehyde spreads from many different places, originating from building materials such as paints, wood products, plastics, furniture, cleaning materials, chipboards, carpets, adhesives, and plywood (11,14,15,21). Indoor VOCs generally include styrene, 1,4-dichlorobenzene, alpha-pinene, limonene, benzene, toluene, ethylbenzene, and xylenes (BTEX briefly stated), and BTEX is the most common of the indoor air VOCs (10,11,20). VOCs found indoors include benzene is carcinogenic and emitted from vehicle emissions, building materials, cigarettes, paints, household spray, barbecue charcoal, furniture, and self-care products; toluene is coming from vehicle emissions, carpets, paints, adhesives, printers, cleaning materials, household spray, wall coverings, textiles, barbecue, self-care products, and cooking processes. The other VOC, 1,4-dichlorobenzene, is emitted from cleaning materials and hawkmoth repellents. Perfumes, scented laundry products and cleaning supplies can be sources of limonene. The xylenes are emitted from adhesives, paints, cleaning supplies, household spray, textiles, wall covering, furniture, cooking processes, self-care products, and barbecue. Ethylbenzene, one of the other BTEX compounds, is emitted from self-care products, paint, adhesives, printers, textiles, wall covering, and vehicle emissions. The other VOC, naphthalene, is emitted from deodorant, window shades, and wall covering. Wood-based building products, cosmetics, barbecue, smoke, and furniture can be a source of benzaldehyde. The styrene emitted from essential oils, carpet, adhesives, paints, wall covering, printers, household spray, furniture, cleaning supplies, cooking processes, and

self-care products; and alpha-pinene from wood and wood-based products, perfumes, soaps, and self-care products (11,12,22–27).

In many studies in the literature, it has been stated that outdoor air affects indoor air (3,11,12,15,17,28). Outdoor air can enter the indoor environment in three different ways. The first is natural ventilation, air enters through the door or window. Secondly, outdoor air can enter inside with mechanical ventilation, a building central fan, or an air conditioner. The third is caused by the infiltration of outside air through the cracks in the building (3,11,15,17). Air exchange occurs in many different buildings such as open doors and windows, fans, air conditioners, fireplaces, ovens, bathroom and kitchen fans, and openings (cracks) in the building (17). Traffic-related pollutants enter the indoor environment more through open doors and windows in hot weather (3,17,29). The air exchange rate (AER) is expected to change with the wind speed and temperature differences between the indoor and outdoor environments (17). According to many studies, indoor VOCs' concentration is higher than outdoor VOCs (3,12,17,27,30), and indoor VOCs' concentration can be controlled in many ways such as ventilation quality, outdoor air quality, and air exchange rate (27). Indoor VOCs are known to have a higher concentration than outdoor VOCs when the ventilation quality is not sufficient (20).

According to the EPA, there are three ways to improve indoor air quality. The first and most effective way is source control, which can be implemented by identifying personal sources of pollution and reducing or eliminating their emissions. The second way is to improve ventilation, increasing the amount of outdoor air (e.g. using windows, and air conditioning) to reduce the concentration of pollutants indoors, thus reducing indoor pollutants and improving the IAQ. The third way is to use an air cleaner which removes the particulate matter in the environment but does not remove the pollutants that are usually in the gas phase. However, the EPA does not suggest that air cleaners reduce radon degradation products and radon levels (30).

1.2 General Information on Volatile Organic Compounds

Volatile organic compounds (VOCs) are among the most important pollutants and include several chemical groups. The EPA defines VOCs as organic compounds that contribute to ozone formation. VOCs are volatile carbon-based organic compounds that can evaporate with temperature and pressure (31,32). These volatile organic compounds include compounds with many functional groups such as aliphatic hydrocarbons, halogenated hydrocarbons, aromatic hydrocarbons, oxygenated hydrocarbons, aldehydes, ketones, esters, ethers, and alcohols (31,33,34).

VOCs are a group of compounds with different physical and chemical properties. In general, the boiling point of VOCs is lower (50-100 °C), and the upper boiling point is between 240-260 °C (31,32,35,36). VOCs are volatile due to their high vapor pressure and low boiling point. These compounds have a vapor pressure of over 0.01 kPa (0.01 mmHg) at 25 ° C room temperature (32,35). The chemical structures of 57 VOCs found in this thesis study are shown in Figure 1.1.

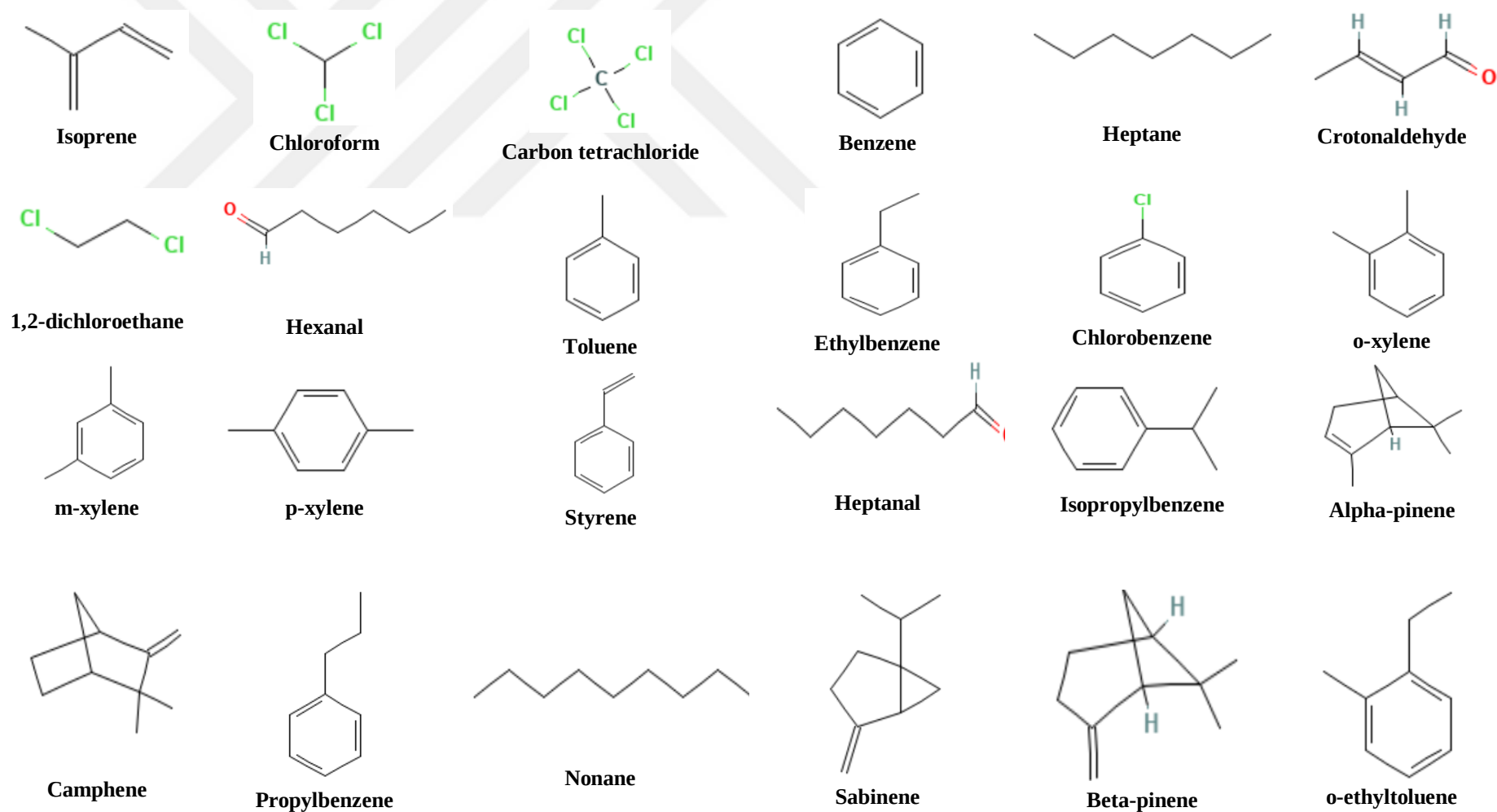
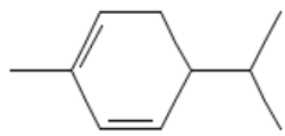
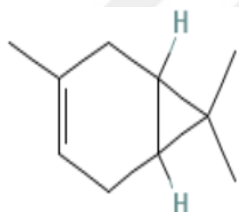


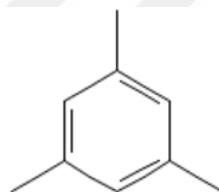
Figure 1.1. Chemical structure of VOCs in this thesis (37)



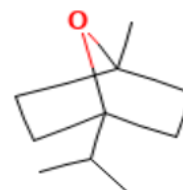
Alpha-phellandrene



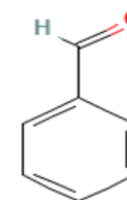
Delta-3-carene



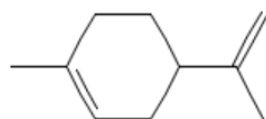
1,3,5-trimethylbenzene



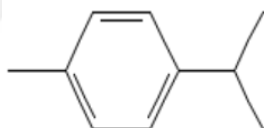
1,4-cineole



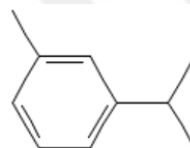
Benzaldehyde



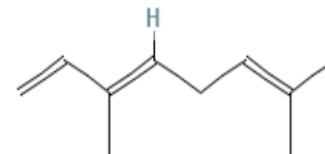
Limonene



p-cymene



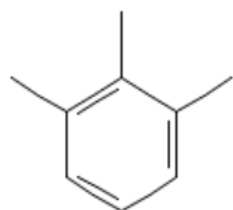
m-cymene



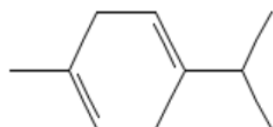
Ocimene



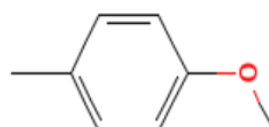
Eucalyptol



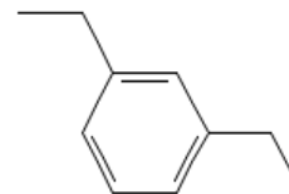
1,2,3-trimethylbenzene



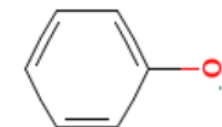
Gamma-terpinene



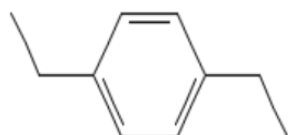
4-methylanisole



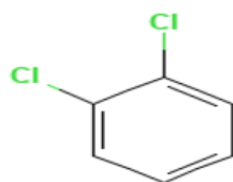
1,3-diethylbenzene



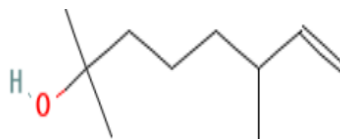
Phenol



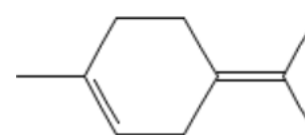
1,4-diethylbenzene



1,2-dichlorobenzene



Dihydromyrcenol



Alpha-terpinolene



1-octanol

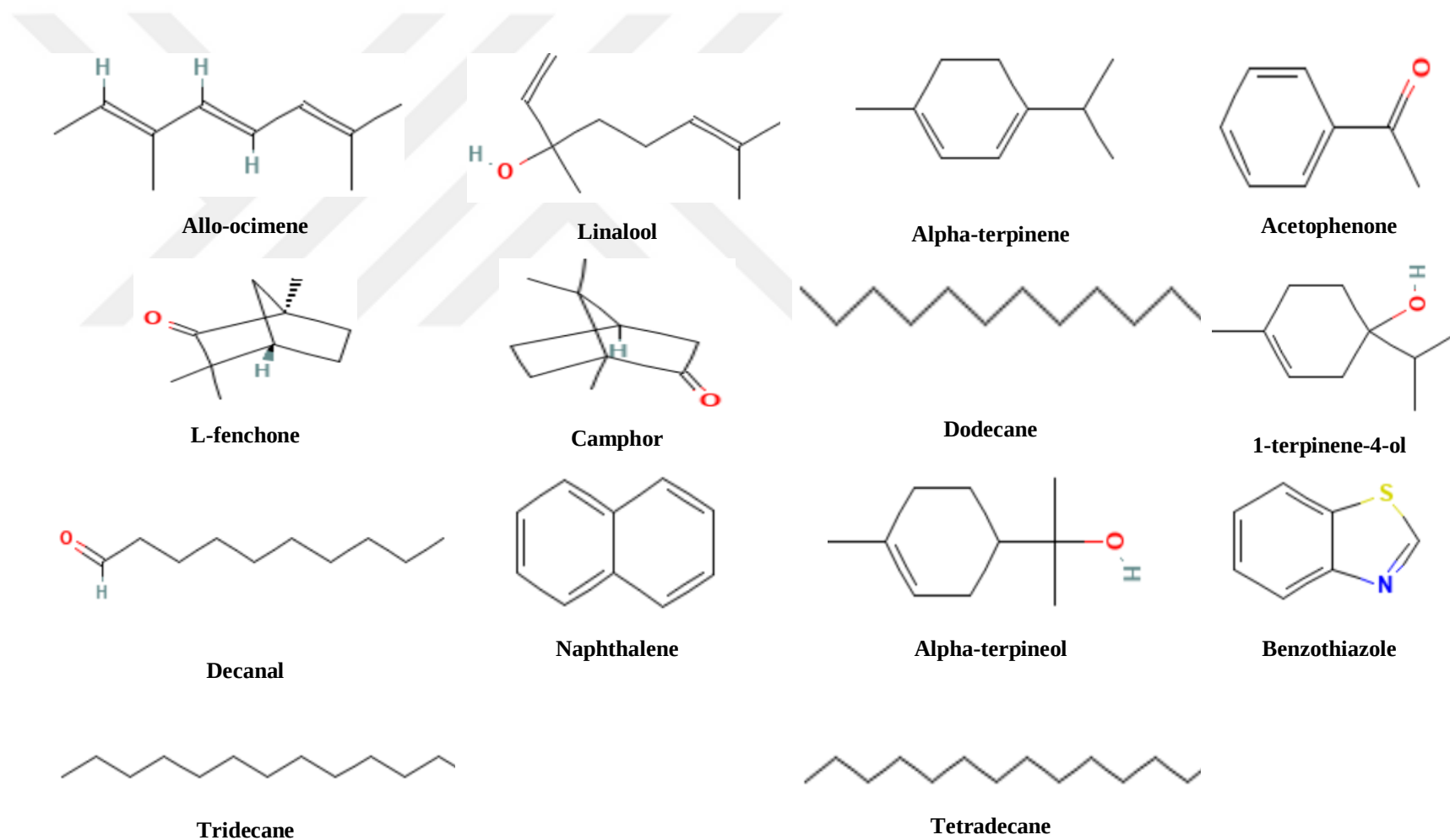


Figure 1.1 (continued) Chemical structure of VOCs in this thesis (37)

The chemical properties and chemical classes of the VOCs evaluated in this thesis are shown in Table 1.1.

Table 1.1. The chemical properties and chemical classes of the VOCs were evaluated in this thesis (37).

Chemical classes of VOCs		Chemical Formula	Molecular Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)	Pressure (mmHg) at 25 (°C)
Aromatic VOCs	Benzene	C ₆ H ₆	78.11	5.56	80.08	94.8
	Toluene	C ₇ H ₈	92.14	-94.9	110.6	28.4
	m+p-xylene	C ₈ H ₁₀	106.16	-47.85	139.1	8.29
	o-xylene	C ₈ H ₁₀	106.16	-25.16	144.5	6.65
	Ethylbenzene	C ₈ H ₁₀	106.16	-94.95	136.2	9.6
	Isopropylbenzene	C ₉ H ₁₂	120.19	-96.00	152.4	4.5
	Propylbenzene	C ₉ H ₁₂	120.19	-99.5	159.2	3.42
	1,3,5-trimethylbenzene	C ₉ H ₁₂	120.19	-44.8	164.7	2.48
	1,2,3-trimethylbenzene	C ₉ H ₁₂	120.19	-25.4	176.12	1.69
	Naphthalene	C ₁₀ H ₈	128.17	80.2	217.9	0.08
	Styrene	C ₈ H ₈	104.15	-30.65	145.3	6.4
	1,4-diethylbenzene	C ₁₀ H ₁₄	134.22	-42.83	183.7	1.03
	1,3-diethylbenzene	C ₁₀ H ₁₄	134.22	-83.9	181.1	1.2
	1,2-dichlorobenzene	C ₆ H ₄ Cl ₂	147	-16.7	180.1	1.36
	Benzothiazole	C ₇ H ₅ NS	135.19	2	231	0.014
	o-ethyltoluene	C ₉ H ₁₂	120.19	n.d	165.2	2.61
	4-methylanisole	C ₈ H ₁₀ O	122.17	-32	175.5	1.14
Aliphatic VOCs	Heptane	C ₇ H ₁₆	100.2	-90.55	98.38	46
	Nonane	C ₉ H ₂₀	129.26	-53.47	150.47	4.45
	Dodecane	C ₁₂ H ₂₆	170.33	-9.55	216.3	0.14
	Tridecane	C ₁₃ H ₂₈	184.36	-5.35	235.4	0.038
	Tetradecane	C ₁₄ H ₃₀	198.39	5.8	253.5	0.015
	Alloocimene	C ₁₀ H ₁₆	136.23	n.d	n.d	n.d
Oxygenated and Halogenated VOCs	Chloroform	CHCl ₃	119.38	-63.47	61.12	197
	Carbontetrachloride	CCl ₄	153.82	-22.2	76.7	115
	1,2-dichloroethane	C ₂ H ₄ Cl ₂	98.96	-35.6	83.4	78.9
	Chlorobenzene	C ₆ H ₅ Cl	112.56	-45.2	131.6	12
	Crotonaldehyde	C ₄ H ₆ O	70.09	-69	102.2	30
	Hexanal	C ₆ H ₁₂ O	100.16	-58.2	129.6	11.3
	Heptanal	C ₇ H ₁₄ O	114.18	-43.3	152.8	3.52
	Benzaldehyde	C ₇ H ₆ O	106.12	-57.12	178.7	1.27
	Decanal	C ₁₀ H ₂₀ O	156.27	-3.9	212	0.1
	1-octanal	C ₈ H ₁₈ O	130.23	-14.7	194.7	0.08
	Phenol	C ₆ H ₆ O	94.11	40.91	181.75	0.35
	Acetophenone	C ₈ H ₈ O	120.15	19.4	202.1	0.4

n.d: no data

Table 1.1 (continued) The chemical properties and chemical classes of the VOCs were evaluated in this thesis (37).

Chemical Classes of VOCs		Chemical Formula	Molecular Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)	Pressure (mmHg) at 25 (°C)
Terpenes	Camphene	C ₁₀ H ₁₆	136.24	52	161	2.5
	Camphor	C ₁₀ H ₁₆ O	152.23	179	209	0.65
	3-Carene	C ₁₀ H ₁₆	136.24	<25	170	n.d
	Limonene	C ₁₀ H ₁₆	136.24	-95.5	176	1.55
	Dihydromyrcenol	C ₁₀ H ₂₀ O	156.26	n.d	n.d	n.d
	beta-pinene	C ₁₀ H ₁₆	136.24	-61.50	166	2.93
	alpha-pinene	C ₁₀ H ₁₆	136.24	-62.5	156	4.75
	Isoprene	C ₅ H ₈	68.12	-145.95	34.07	550
	1,4-cineole	C ₁₀ H ₁₈ O	154.26	1	173.5	1.93
	alpha-phellendrene	C ₁₀ H ₁₆	136.24	n.d	172	1.4
	m-cymene	C ₁₀ H ₁₄	134.22	-63.8	175	1.72
	p-cymene	C ₁₀ H ₁₄	134.22	-68.9	177.1	1.5
	Ocimene	C ₁₀ H ₁₆	136.24	n.d	n.d	2.68
	Sabinene	C ₁₀ H ₁₆	136.24	n.d	163.4	n.d
	Eucalyptol	C ₁₀ H ₁₈ O	154.25	1.5	176	1.9
	gamma-terpinene	C ₁₀ H ₁₆	136.23	-10	183	1.09
	Terpinen-4-ol	C ₁₀ H ₁₈ O	154.25	n.d	209	0.04
	alpha-terpineol	C ₁₀ H ₁₈ O	154.25	37	219	0.04
	L-Fenchone	C ₁₀ H ₁₆ O	152.23	n.d	n.d	n.d
	alpha-terpinene	C ₁₀ H ₁₆	136.23	<25	175	n.d
	Linalool	C ₁₀ H ₁₈ O	154.25	<25	198	0.16
	alpha-terpinolene	C ₁₀ H ₁₆	136.23	<25	187	0.74

n.d: no data

1.3 Source of Volatile Organic Compounds

In urban and rural areas, volatile organic compounds are pollutants that are substantially gaseous in the ambient air. VOCs are emitted into the atmosphere primarily from anthropogenic (human-made) sources and biogenic (natural) sources and secondarily from chemical reactions occurring in the atmosphere (38,39). Anthropogenic sources include vehicle emissions, petroleum products, paints, household products, and solvent usage. Natural sources spread mainly

from forests, grasslands, grasslands in tropical woodlands, vegetation, and terrestrial plants. (19,40–42).

Biogenic (natural) volatile organic compounds (BVOCs) are VOC emissions due to the biosynthetic activities of plants (43). BVOCs commonly include oxygenated VOCs (e.g., ketones, aldehydes, alcohols, acids), isoprene, and terpenes (monoterpenes, diterpenes, triterpenes, tetraterpenes, polyterpenes, and sesquiterpenes) (44,45). Sources of BVOC emissions in the atmosphere include vegetation, biomass and organic substance burning, volcanic eruptions, and forest fires. Oxygenated VOCs, aliphatics, isoprene, terpenes, benzene, and toluene are emitted directly or indirectly from forest fires (39,46). Terpenes are a large group with a carbon skeleton of 5 carbon (C-5) units. For example, isoprene is a 5-carbon-containing hemiterpene and alpha-pinene is a 10-carbon-containing monoterpene. Compounds containing 15 carbons are classified as sesquiterpene, compounds containing 20 carbons as diterpene, compounds containing 30 carbons as triterpene, compounds containing 40 carbons as tetraterpene and compounds containing more than 45 carbons as polyterpenes (45). High amounts of isoprene are emitted from broadleaf trees such as Oriental Spruce and Nordmann Fir. Significant quantities of isoprene are also emitted from coniferous trees such as Eastern Cottonwood, Sessile Oak, Oriental Plane, European Aspen, Black Locust, and River Red Gum (43). Monoterpenes (MTs) are a large class that contains compounds like alpha-pinene, alloocimene, alpha-terpinene, camphene, beta-myrcene, beta-pinene, delta-3-carene, limonene, ocimene, m-cymene, p-cymene, sabinene, gamma-terpinene, phellandrene, terpinolene. MTs are most abundantly released from broad-leaved trees such as Turkish Red Pine, Black Pine, Maritime Pine, Aleppo Pine, Phenonicean Juniper, Greek Juniper, Foetid Juniper, Prickly Juniper, and Oriental Spruce. In addition, MTs are released in high amounts from coniferous trees such as Silver Lime and Sweet Chestnut (43). Alpha-pinene is most commonly emitted outdoors from trees such as Prickly Juniper, Black Pine, Phoenician Juniper, Radiata Pine, and Greek Juniper, while indoors from wood-based building products and self-care products (11,43). Limonene is mostly spread outdoors from trees such as Western Australian Golden Wattle, Oriental Plane, and Oriental Spruce, while

indoors from cleaning, laundry, and personal care products (11,27,43). Delta-3-carene spreads outdoors mostly from trees such as Mediterranean Cypress, Oriental Spruce, and Nordmann Fir, while indoors from personal care products (27,43). Beta-pinene is spread from the Turkish Red Pine tree outdoors, while it is spread from personal care products indoors (27,43). After terpenes, carbonyls are the most dominant group in the release of BVOCs, and biogenic carbonyls contain many compounds such as formaldehyde, hexanal, butanal, butenal, acetaldehyde, acetone, propanal, crotonaldehyde, nonanal, methyl-vinyl-ketone, and benzaldehyde (45). It is stated that the natural source of carbonyls is vegetation directly or indirectly, followed by microbial processes and forest fires are among the natural sources of carbonyls (45).

Anthropogenic (human-made) volatile organic compounds (AVOCs) are emitted from many sources such as solvent use, paints, fossil fuel combustion, vehicle exhausts (diesel vehicles and gasoline-powered), industrial activities, household products, and polishing and cleaning products (40,41,47). The sources mentioned cause the release of many AVOCs such as aromatic hydrocarbons, aliphatic hydrocarbons, aldehydes, alcohols, and ketones (48). Emissions of aromatic and aliphatic hydrocarbons are substantially due to evaporation and traffic emissions, industrial processes, and fuel combustion (49). BTEX (benzene, toluene, ethylbenzene, xylenes) compounds are often associated with vehicle emissions and home renovations (11,50). Toluene and benzene compounds are the most common compounds in indoor and outdoor environments. Toluene and benzene compounds are emitted from many sources such as paints, adhesives, furniture, personal care products, room fragrances, traffic emissions, and barbecue (27). Compounds such as acetone, acetaldehyde, isoprene, methyl vinyl ketone, benzene, toluene, and styrene are emitted from combustion process sources such as smoking, stove use, and barbecue use in indoor environments (12,27). Compounds such as decane, dodecane, nonane, trimethylbenzene, ethylbenzene isomers, and propylbenzene are emitted from wall and floor covering products such as wallpaper, carpet, concrete, and drywall (12).

1.4 The Effect of VOCs on Human Health

The Environmental Protection Agency has identified 189 compounds as HAPs (harmful air pollutants) due to adverse environmental effects and human health effects such as birth defects and cancer (51). The International Agency for Research on Cancer (IARC) has categorized VOCs in relation to human health. Accordingly, benzene and formaldehyde are classified as carcinogenic to humans (Group 1), styrene is classified as probably carcinogenic (Group 2A), ethylbenzene, naphthalene, 1,2-dichloroethane, carbon tetrachloride, and chloroform are classified as a possibly carcinogenic (Group 2B), and toluene, xylenes, phenol, chlorobenzene, and acetophenone are classified as not carcinogenic to humans (Group 3) (52).

High VOC concentration in the indoor environment causes many health problems such as long-term breathing, asthma, chronic obstructive pulmonary disease (COPD), allergic symptoms, cancer, headaches, cardiovascular disease (CVD), short-term inhalation, it has been observed that there is an irritation effect on the mucous membrane of the throat, and nose (3,9–12,26,53,54). These health effects cause Sick Building Syndrome (SBS), and when the ventilation of the environment is increased, SBS can be reduced, however, someone affected by SBS may develop the syndrome after leaving the environment (3,15,26).

Excessive exposure to benzene, which is known to be carcinogen, increases the risk of leukaemia, hematopoietic diseases, and lung cancer, and has been associated with CVD and diabetes. The risk of asthma is most strongly associated with benzene, followed by toluene and ethylbenzene (20,26,55). Toluene exposures occur in printing and painting workplaces such as automotive paint shops, nail salons, and printing houses. People working in such workplaces may be exposed to toluene by inhalation, ingestion, or splashing on the skin. Exposure to toluene can cause acute and chronic health problems such as tremors, dizziness/headaches, fatigue, nausea, upper respiratory tract irritation, confusion, and eye, nose, and throat irritation (56–58). Ethylbenzene, which is considered a possible carcinogen for humans,

causes acute or chronic health problems. Exposure to ethylbenzene can cause health problems such as difficulty in breathing, and eye and throat irritation (59). Exposure to xylenes (ortho-, meta-, para-xylene), which are not considered carcinogenic to humans, can occur in different ways such as inhalation, skin contact, and ingestion. Xylene exposure may cause short-term or chronic health problems such as headache/vertigo, tremors, throat, eye, and nose irritation, fatigue, irritability, and poor concentration (60,61). Exposure of humans to high levels of BTEX compounds causes many long-term or short-term adverse health effects (24,62). Short-term exposure to acetophenone, which is not carcinogenic to humans, causes temporary eye problems and skin irritation (63). Similarly, prolonged exposure of people to chlorobenzene, which is in group 3, causes health problems such as drowsiness and hyperesthesia (63). Non-carcinogenic to humans, phenol causes short-term or chronic health problems. Effects such as eye, skin, and mucous membrane irritation are observed with short-term exposure to phenol, while effects such as vertigo, diarrhea, and dark urine color are observed with long-term exposure to phenol (63). Carbon tetrachloride, which is considered a possible carcinogen for humans, causes chronic and acute health problems. Exposure to carbon tetrachloride disrupts the central nervous system (CNS) and causes health effects such as headaches, kidney and liver damage, and nausea/vomiting (63). Likewise, chloroform, which is considered a possible carcinogen for humans, causes short and long-term health problems. Exposure to chloroform causes health problems such as hepatitis, jaundice, and CNS deterioration (63). Similarly, high exposure to 1,2-dichloroethane, which is considered a possible carcinogen, has been reported to cause CNS disorders, lung effects, and kidney and liver disease in humans (63). Naphthalene, which is classified as a possible carcinogen for humans, can be exposed by skin contact, ingestion, and inhalation. It has been reported that exposure to naphthalene causes health problems such as neurological and liver damage, hemolytic anaemia, and cataracts (63). Styrene, which is considered a possible carcinogen to humans, causes acute or long-term health problems. Exposure to styrene has been linked to various health problems, including ligament pain, depression, eye irritation, and fatigue (63).

1.4.1 Assessment of the Health Risk of VOCs

There are four fundamental steps in the health risk assessment: dose-response assessment, hazard identification, risk assessment, and exposure assessment (10,29). Exposure to a variety of pollutants can cause long-term or short-term health problems. This risk assessment is very beneficial in identifying adverse health effects (10,64). According to the data from the World Health Organization (WHO), more than 19 million people were diagnosed with cancer in 2020 and approximately 10 million people died due to cancer (65). According to the classification made by the International Agency for Research on Cancer (IARC), benzene and formaldehyde compounds are classified as carcinogenic to humans, and it is known that these compounds have a cancer risk. According to IARC, some volatile organic compounds such as xylenes, chlorobenzene, 1,3,5-trimethylbenzene, nonane, and toluene are not carcinogenic (29,52).

The hazard ratio (HR) of each compound is determined to obtain the risk assessments for the non-carcinogenic compounds. For inhalation exposure, HR is determined by the ratio of the mean daily concentration (CDI in $\mu\text{g}/\text{m}^3$) to the corresponding reference concentrations (RfC in $\mu\text{g}/\text{m}^3$) (66) and is expressed by equation (1.1). For HR oral exposure, it is determined by the ratio of the mean daily concentration (CDI in $\mu\text{g}/\text{kg}\cdot\text{day}$) to the corresponding reference dose (RfD in $\mu\text{g}/\text{kg}\cdot\text{day}$) (67) and is expressed by equation (1.2). If HR values are less than or equal to 1, the risk is negligible. However, if the HR value is greater than 1, it indicates that there is a high probability of negative effects on human health, and it indicates that a non-carcinogenic but chronic health risk may occur (47,68,69). The RfC and RfD values are taken from the U.S.EPA - Integrated Risk Information System (IRIS) (63).

$$HR = CDI/RfC \quad (1.1)$$

$$HR = CDI/RfD \quad (1.2)$$

Reference concentrations (RfC) and reference dose (RfD) were used for toxic compounds in this study. The RfC indicates the daily exposure level at which a compound has no detrimental effects on health (10,47,66).

The risk assessment of carcinogenic compounds is indicated by the lifetime cancer risk (LCR), and the LCR exposure is calculated by multiplying the chronic daily intake (CDI) of each compound by the IRIS slope factor (64,66). Using Equation 1.3, the inhalation exposure estimate was obtained from the CDI point (mg/kg.day). This equation has been used to calculate health risks in many studies (10,20,29,53,64).

$$CDI = \frac{CA \times ET \times IR \times ED \times EF}{AT \times BW} \quad (1.3)$$

CDI: chronic daily intake (mg/kg.day)

CA: contaminant concentration in ambient (mg/m³)

ET: exposure time (hours/day)

IR: inhalation rate (m³/hour)

ED: exposure duration (years)

EF: exposure frequency (day/year)

AT: average time (day) (period of averaging exposure)

BW: body weight (kg)

The lifetime cancer risk (LCR) is determined by the evaluation of compounds with cancer risk using Equation 1.4.

$$LCR = CDI \times IUR \quad (1.4)$$

Cancer risk is defined as the probability that a person will develop cancer during their lifetime as a result of exposure to a potentially carcinogenic compound. The margin of risk for LCR is classified as, $1.0 \times 10^{-5} > LCR > 1.0 \times 10^{-6}$ as “negligible

risk”, $1.0 \times 10^{-4} > \text{LCR} > 1.0 \times 10^{-5}$ as “probable risks”, and $\text{LCR} > 1.0 \times 10^{-4}$ considered as “obvious risks” (29,47,66,70).

Monte Carlo simulation was developed in the 1940s to characterize the uncertainties and variables in health risk analysis as much as possible. Monte Carlo simulation has two main purposes. The first is to numerically find and characterize the variability of risk and exposure values. The second purpose is to determine the sources of the variables and to measure the effectiveness of the determined sources on the simulation results (29,64).

Monte Carlo analysis gives information about the input variables and their distribution of output variables. Parameters for each of the input variables are added to the simulation. Many input parameter data sets (for example 10,000 iterations) are generated by random sampling from their respective probability distributions. Random sampling generation is used by the simulation to combine the distribution. In this way, the analysis generates a precise output distribution of risk and exposure values, rather than a single estimate (64).

1.5 Sampling of VOCs

Many VOCs can be released from various sources in the indoor environment. VOC concentrations can be determined by various techniques and methods, such as real-time and online techniques, chemisorption, active sampling, and passive sampling (34,71). To perform a reliable and accurate sampling, parameters such as sampling environment, sampling point, sampling duration, analytical method, and control and reliability of the analysis method are very important (72). Passive sampling and active sampling techniques have mostly been used for the detection of VOCs (9,14,29,40,47,71,73–75).

1.5.1 Active Air Sampling

Active air sampling is based on collecting airborne compounds on the sampler with the help of a sampling pump. To ensure accurate results, sampling time and sampling rate are critical factors. Before sampling, calibration of the sampling pump to the determined flow rate is essential.

The volume of air sampled is obtained by multiplying the sampling duration by the pump flow rate (mL/min). The concentration of the compound is obtained by dividing the amount of substance obtained from the analysis (ng) by the volume of air sampled (L). For active air sampling, the concentration of VOCs is calculated using equation 1.5.

$$C = \left[\frac{m}{Q \times t} \right] \times 10^3 \quad (1.5)$$

where C is the amount of pollutant ($\mu\text{g}/\text{m}^3$), m is the mass of the target pollutant (ng), t is the sampling duration (min), and Q is the pump flow rate (mL/min).

Active sampling is suitable for short-term sampling. Active sampling has the advantage of collecting multiple samples in a short time, but it also has disadvantages such as the need for electricity and the need for expensive and large equipment. Equipment used to carry out active sampling reliably requires regular calibration and maintenance (42,71).

1.5.2 Passive Air Sampling

The procedure of collecting gaseous or vapor compounds from the ambient at a rate controlled by molecular diffusion is defined as passive sampling(34,71,76). The schematic representation of the passive sampling method is given in Figure 1.2.

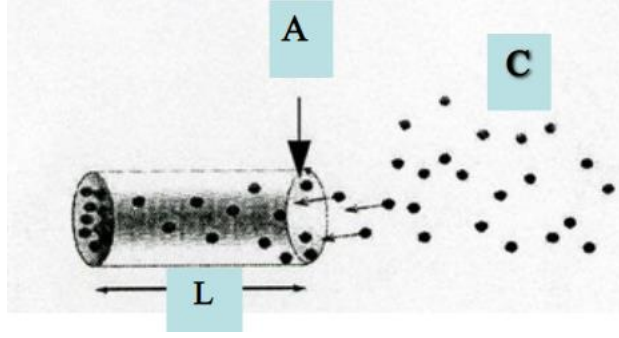


Figure 1.2. Diagram of the passive sampling method, A is the sampler surface area, L is the diffusion path, and C is the concentration of pollutants in the air (77)

This procedure is based on mass transport expressed by Fick's 1st law of diffusion. Fick's first law of diffusion is given in equation 1.6.

$$C = \left[\frac{m \times L}{D \times A \times t} \right] \times 10^3 \quad (1.6)$$

where C is the amount of pollutant ($\mu\text{g}/\text{m}^3$), m is the mass of the target pollutant (ng), L is the diffusion path length (cm), D is the diffusion coefficient (cm^2/s), t is the sampling duration (s), and A is the sampler surface field (cm^2).

The diffusion coefficient (D) situated in equation 1.6 is calculated individually for each compound using equation 1.7.

$$D_{298} = 10^{-3} \times \frac{T^{1.75} \times \left[\left(\frac{1}{m_i} \right) + \left(\frac{1}{m_{\text{air}}} \right) \right]^{\frac{1}{2}}}{P \times [V_i^{1/3} + V_{\text{air}}^{1/3}]^2} \quad (1.7)$$

where D_{298} is the diffusion coefficient of the compound (cm^2/s), T is the absolute temperature (298 K), m_i is the molar mass of the compound (g/mol), m_{air} is the average molar mass of ambient (28.97 g/mol), P is the gaseous phase pressure (1 atm), V_i is the molar volume of compound (cm^3/mol), and V_{air} is the average molar volume of gases in ambient ($\sim 20.1 \text{ cm}^3/\text{mol}$).

Equation 1.8 is used to arrange the diffusion coefficient to the mean temperature over the sampling period (34).

$$D_T = D_{298} \times T^{1.75} \times 298.15^{-1.75} \quad (1.8)$$

Passive air sampling is widely used in many different environments such as outdoor, indoor, personal sampling, and workplace environments. Passive samplers are very simple and easy to use and are suitable for long-term sampling (one day to four weeks). Passive samplers have many advantages such as the ability to operate at multiple sampling points simultaneously, not needing electricity, pumps, and large equipment, and being inexpensive. On the other hand, disadvantages of passive sampling include not being suitable for automation and variable environmental conditions such as humidity, temperature and wind speed (71,72).

1.6 Analysis of Volatile Organic Compounds: Thermal Desorption-Gas Chromatography-Mass Spectroscopy

A wide range of compounds may be present in air samples collected using passive or active methods. It is very substantial to work with highly sensitive analytical methods that can detect target compounds and low concentrations. The thermal desorption-gas chromatography-mass spectroscopy (TD-GC-MS) system is often preferred for VOC analysis and is a very advantageous analysis method. A diagram of the TD-GC-MS system is shown in Figure 1.3.

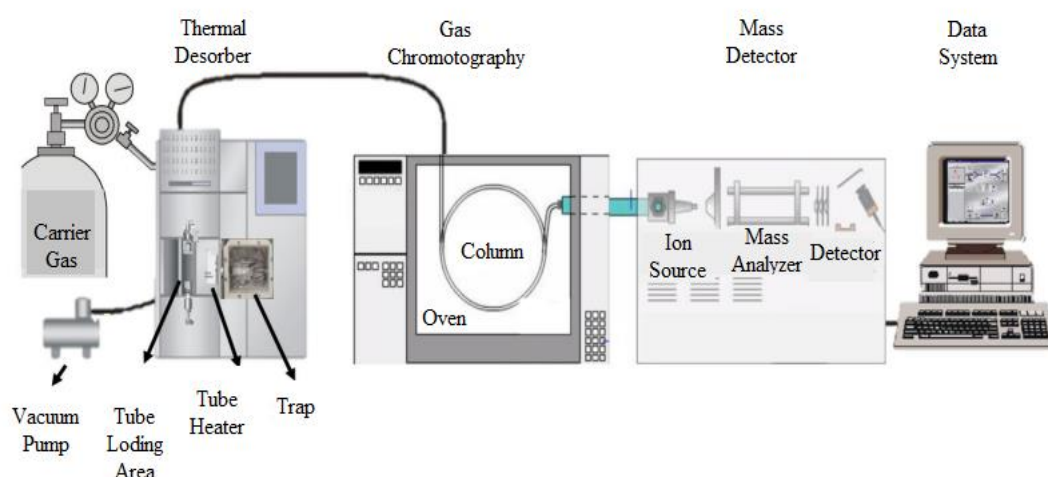


Figure 1.3. A Diagram of the TD-GC-MS system (34,72)

Thermal desorption (TD) is a Gas Chromatography pre-enrichment device used for the analysis of various VOCs collected by active sampling method. The

technique of the TD extracts volatiles by heating the sample with a flow of high-purity inert gas (78). Volatile compounds are concentrated on an electrically cooled, low thermal mass cold trap, and the compounds are transferred to the GC column by a heated transfer line. Thermal desorption has many advantages, the most important of which is that it minimizes interference for trace-level compounds and maximizes sensitivity for these compounds. It is very suitable for measuring VOCs at parts per billion (ppb) or less (34). Another advantage of this technique is that solvent-based sample preparation is not required. It also avoids sample loss through full automation of extraction/desorption, sample preparation, injection, and pre-concentration.

Chromatography is a technique based on the separation of the compounds in a mixture from each other according to the transport rate through the stationary phase with the help of the mobile phase(34,79). Gas chromatography is a selective and sensitive technique, as well as a quantitative and qualitative technique. In gas chromatography, the mobile phase is steam or gas. The vapor phase carries the compounds in the sample to the chromatographic column after thermal desorption. The compounds are separated by dispersion between the inert gas (mobile phase) and the stationary phase, which are retained in the column. Since the compounds in the sample have different boiling points, they leave the column at different times, and the exit time of the compounds from the column is determined by a suitable detector, and their quantities are measured (4). The gas chromatography instrument comprises six main parts: carrier gas system, sample injection system, column, column oven, detection system, and data system. A scheme of gas chromatography is shown in Figure 1.4.

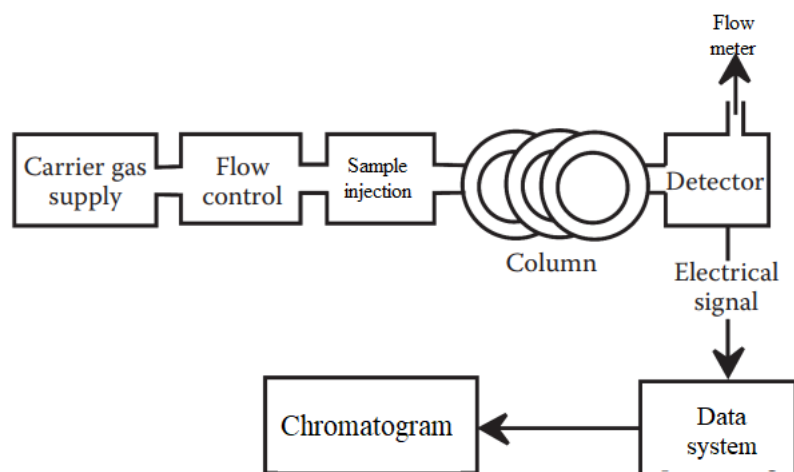


Figure 1.4. The scheme of gas chromatography (4)

Carrier gases are generally inert argon, hydrogen, helium, and nitrogen gases. The carrier gas transmits the compounds in the sample to the system with the help of a column (4). Some of the columns suitable for VOC analysis are HP-VOC, Rtx-VRX, Rtx-VMS, Rtx-VGC, HP-624, DB-624, and DB-VRX columns. Column lengths are highly variable and can range from 2 m and 60 m. These columns are usually made of pure copper, Teflon, glass, stainless steel, or fused silica (34,72).

The detector suitable for gas chromatography should have many features such as high selectivity, high sensitivity, wide temperature range (25°C to 400°C), ease of use and no sample degradation. Different detectors such as flame ionization detector (FID), electron capture detector (ECD), thermal conductivity detector (TCD), and mass spectrometer (MS) are used in gas chromatography. Among the detectors mentioned, mass spectrometry is the most widely used in VOCs analysis. Mass spectrometry converts the compounds in the sample into ions chemically or by electrical discharge, and then separates them according to the mass to charge (m/z) ratio. The mass spectrum is characteristic of each compound, and the spectra of each compound are stored in the libraries of computers with mass spectra (4). In the detector, two signals are obtained, the mass spectrum of each substance and the chromatogram containing all substances. The mass spectrum is used for qualitative analysis. On the other hand, the peak height or peak area of each compound in the chromatogram is used for quantitative analysis (34).

2. AIM AND SCOPE OF THE STUDY

Air pollution has become the greatest environmental health risk, and indoor air pollution is considered one of the most important risks to human health. The air in indoor environments is polluted by various natural and artificial sources. The most important group of pollutants in the indoor environment are volatile organic compounds (VOCs). VOCs are ubiquitous in the environment from many sources, and people spend a lot of time indoors. VOCs evaporate easily at room temperature and are often found indoors, so indoor air quality has a significant impact on human health. Among the VOCs within the scope of this study, chloroform, carbon tetrachloride, benzene, 1,2-dichloroethane, chlorobenzene, xylenes, ethylbenzene, styrene, phenol, toluene, naphthalene, and acetophenone are on the Environmental Protection Agency's list of harmful air pollutants and are frequently encountered in indoor air. Therefore, for the sake of human health, it is necessary to improve indoor air quality studies, ensure their continuity, identify possible sources and take the necessary measures to improve air quality.

Previous research on volatile organic compounds (VOCs) has predominantly focused on anthropogenic sources of VOCs. However, our study aimed to investigate both anthropogenic and biogenic VOCs. Moreover, to the best of our knowledge, no prior research has investigated indoor VOC air quality in Bolu. Therefore, our study represents a significant contribution to the field. The aim of this study is to determine the amount of biogenic and anthropogenic volatile organic compounds (VOCs) in both indoor and outdoor environments of dyeing and printing facilities, including a photocopy center, painting class, print-making class, tire shop, and car painter. The objective of this dissertation is to assess the indoor and outdoor air quality and the implications of this assessment from a human health perspective. The specific objectives of this study are:

- to perform a health risk analysis for individuals exposed to VOCs, especially biogenic ones, during their working hours,
- to evaluate the differences of VOCs in the sampling areas during day/night and weekday/weekend periods,
- to assess the indoor/outdoor ratio by comparing passive samples taken in both environments.

3. MATERIALS AND METHODS

3.1 Sampling Site and Sampling

The province of Bolu is located between 40° 06 minutes- 41° 01 minutes north latitudes and 30° 32 minutes- 32° 36 minutes east longitudes. The vegetation of Bolu is forested and 64% of its area is covered by forests. The most common trees in the forests are 44% larch, 18% scotch pine, 15% fir, 9% beech, 9% oak, 3% other leafy pine, and 3% red pine (80).

The province of Bolu is in the middle of two metropolitan cities, Istanbul and Ankara. In Bolu, the TEM and D-100 highways are the main highways of the city. There are many potentials in Bolu, including hunting tourism, winter tourism, sports tourism, health tourism, highland tourism, and seminar and meeting tourism (80).

In this thesis, two sampling techniques were used namely active sampling and passive sampling. A total of 217 air samples were collected from six different locations between March 2022 and April 2022. Air samples were taken from the photocopy center, painting class, two different print-making classes, tire shop, and car painter. The map of sampling points is shown in Figure 3.1. A more detailed table of the sampling strategy is presented in Table 3.1.



Figure 3.1. The map of Bolu, a) the map of sampling points in BAIBU, b) the map of sampling points in Bolu city center

The first sampling point is the copy center located in the Activity Center of Bolu Abant İzzet Baysal University (BAIBU) Gök   Campus at the 40°42'51.8"N, 31°30'46.9"E coordinates. The photocopy center is located in the building and operates an average of 12 hours per day. There is no ventilation system in the photocopier and its door is always open during the day. Air sampling was carried out between 25th March and 1st April 2022. A total of 47 air samples active and passive were collected from the copy center over seven days. 42 of the air samples were collected by active sampling. The optimum sampling time was determined to be four hours. Five passive samples were collected from the indoor and outdoor environments of the copy center. The active and passive sampling areas in the copy center are shown in Figure 3.2. The exposure time (ET) of the copy center workers was determined to be eight hours per day, the exposure frequency (EF) to be 240 days per year, the exposure duration (ED) during their working life to be 20 years, the average (AT) time spent in their life to be 4800 days, and their average weight to be 70 kg.



Figure 3.2. a) indoor active sampling, b) indoor passive sampling, and c) outdoor passive sampling in the copy center in the Activity Center of BAIBU

The second sampling point is the painting class at the BAIBU Fine Arts Faculty. The painting class is held on Mondays and Tuesdays, with an average of 10-15 students per class. During class hours (8 am to 5 pm), the classroom door is left open, and the classroom is ventilated through a window. Air samples were collected between 1st April and 8th April 2022. A total of 48 air samples were collected from the painting class over seven days. 42 of the air samples were collected by active sampling. The optimum sampling time was found to be four hours. Six passive samples were taken from the indoor and outdoor environments of the painting class. The active and passive sampling areas in the painting class are shown in Figure 3.3. The exposure time of the painting class teacher was determined to be four hours per day, the exposure frequency to be 60 days per year, the exposure duration during their working life to be 30 years, the average time spent in their life to be 1800 days, and their average weight to be 70 kg. The exposure time of the painting class students was determined to be four hours per day, the exposure frequency to be 60 days per year, the exposure duration during their student life to be 4 years, the average time spent in their life to be 240 days, and their average weight to be 70 kg.

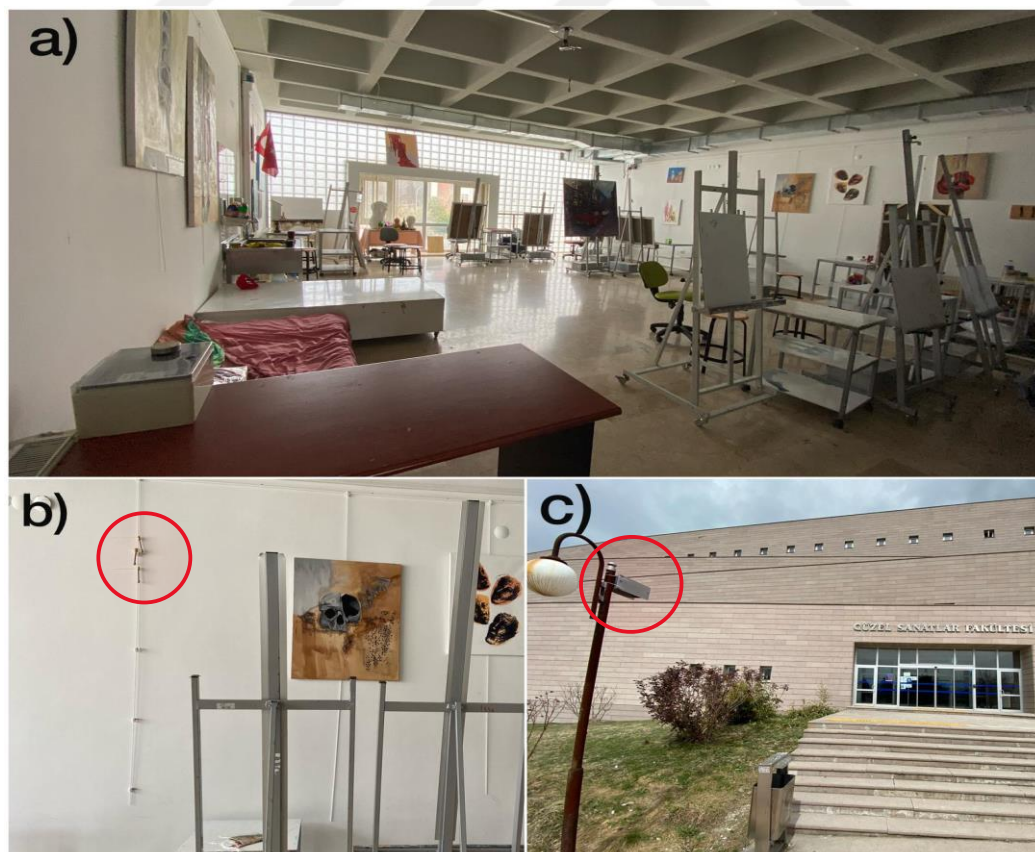


Figure 3.3. a) indoor active sampling, b) indoor passive sampling, and c) outdoor passive sampling in the painting class in BAIBU Fine Arts Faculty

The third sampling point is the printmaking class (I) at the BAIBU Fine Arts Faculty. The printmaking class has printmaking classes on Thursdays and painting classes on Fridays. The classes have an average of 15 students. The classroom is ventilated with an exhaust fan on Thursdays, and the door and window of the classroom are also used for ventilation. Air sampling was carried out between 14 and 17 April 2022. A total of 42 air samples were collected over three days from the printmaking classroom. 36 of the air samples were collected by active sampling. The sampling time was optimized to two hours. Six passive samples were taken from the indoor and outdoor environments of the print-making classroom. The active and passive sampling areas in the printmaking class are shown in Figure 3.4. The exposure time of the print-making class (I) teacher was determined to be four hours per day, the exposure frequency to be 60 days per year, the exposure duration during their working life to be 30 years, the average time spent in their life to be 1800 days, and their average weight to be 70 kg. The exposure time of the print-making class (I) students was determined to be four hours per day, the exposure frequency to be 60 days per year, the exposure duration during their student life to be 4 years, the average time spent in their life to be 240 days, and their average weight to be 70 kg.



Figure 3.4. a) active and passive sampling in the indoor environment, and b) outdoor passive sampling in the printmaking class in BAIBU Fine Arts Faculty

The fourth sampling point is in the printmaking class (II) of the Faculty of Education at BAIBU. Classes are held on Wednesdays and Thursdays, with an average of 10 students attending. The classroom has no ventilation system, relying instead on windows for ventilation. Air sampling was carried out between 19th and 22nd April 2022. A total of 41 air samples were collected during the printmaking course over a three-day period. 35 of the samples collected were active. The duration of 24 samples was two hours, while 11 samples were taken for one hour. The sampling duration was halved due to the strong odour in the classroom. Six passive samples were taken in the indoor and outdoor surroundings of the printmaking classroom. Figure 3.5 displays the active and passive sampling zones within the printmaking classroom. The exposure time of the print-making class (I) teacher was determined to be eight hours per day, the exposure frequency to be 60 days per year, the exposure duration during their working life to be 30 years, the average time spent in their life to be 1800 days, and their average weight to be 70 kg. The exposure time of the print-making class (I) students was determined to be four hours per day, the exposure frequency to be 60 days per year, the exposure duration during their student life to be 4 years, the average time spent in their life to be 240 days, and their average weight to be 70 kg.



Figure 3.5. a) indoor active sampling, b) indoor passive sampling, and c) outdoor passive sampling in the printmaking class in the BAIBU Faculty of Education

The fifth sampling location is the Albayraklar tire shop, located in the city center of Bolu, with coordinates at 40°44'16.1"N, 31°37'11.0"E. The tire shop has an average opening time of eleven hours per day and serves an average of one hundred customers per day. The shop is ventilated by air conditioning. Air sampling was conducted from 22nd to 25th April 2022. A total of twenty-one air samples were taken from the tire shop over a period of three days. Fourteen samples were taken during the working hours of the shop with active sampling lasting one hour. Meanwhile, seven passive samples were collected from both the indoor and outdoor environments of the tire shop. One of the passive samples was taken on a special day when the tire shop was closed. Figure 3.6 illustrates the active and passive sampling activities carried out in the tire shop. The exposure time of the tire shop workers was determined to be eleven hours per day, the exposure frequency to be 300 days per year, the exposure duration during their working life to be 30 years, the average time spent in their life to be 9000 days, and their average weight to be 70 kg.

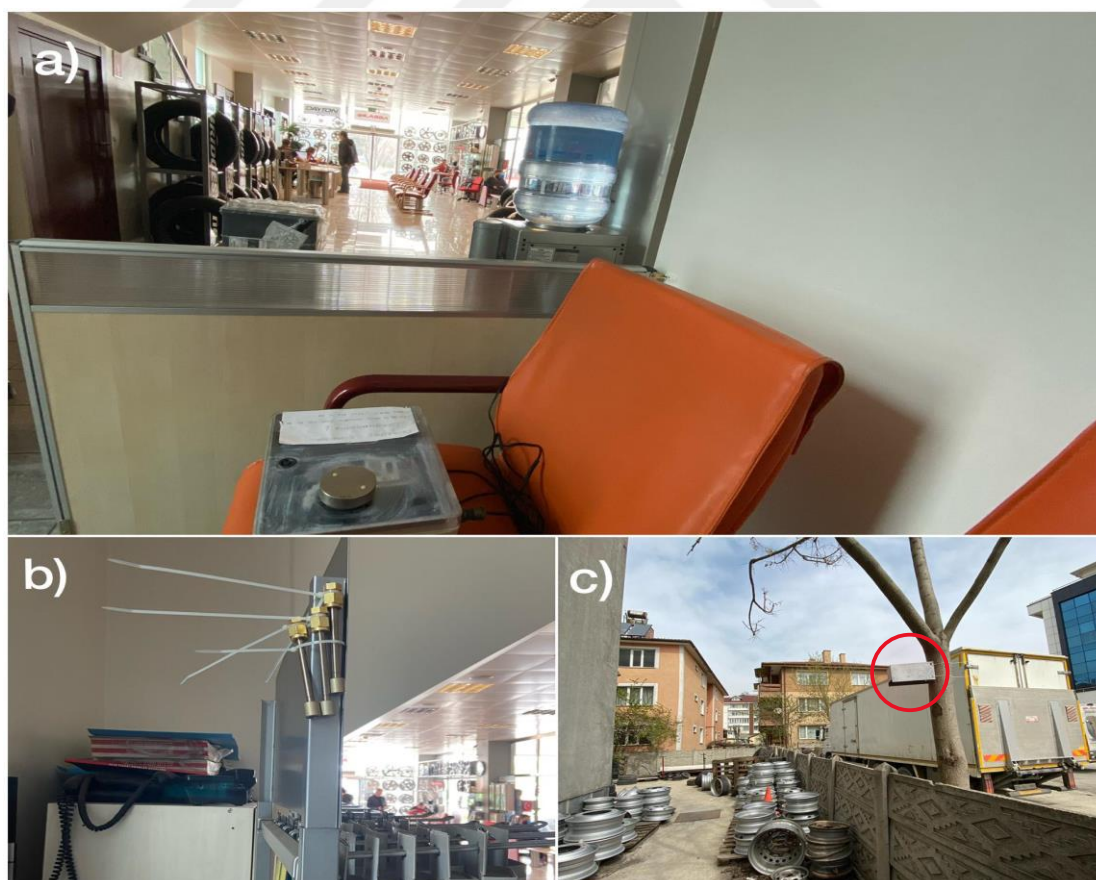


Figure 3.6. a) indoor active sampling, b) indoor passive sampling, and c) outdoor passive sampling in the tire shop

The final sampling site is the car painter located in Bolu Industrialists' Site on the coordinates 40°44'17.9"N, 31°37'42.4"E. The car painter works about ten hours a day and receives about five to seven visitors a day. There is no ventilation system in the workshop and the picket fence remains open during working hours. Air samples were collected between 25th and 26th April 2022. Nineteen air samples were collected over two days from the car painter's work environment. Of these, 14 air samples were collected by active sampling for five minutes during the car painter's working hours. A further five passive samples were taken from both the indoor and outdoor environments of the car painter. Figure 3.7 shows the results of the active and passive sampling in the car painter's work area. The exposure time of the car painter workers was determined to be ten hours per day, the exposure frequency to be 300 days per year, the exposure duration during their working life to be 40 years, the average time spent in their life to be 12000 days, and their average weight to be 70 kg.



Figure 3.7. a) indoor active sampling, b) indoor passive sampling, and c) outdoor passive sampling in the car painter

Within the scope of the study, the sampling time characteristics of the indoor and outdoor samples are given in Table 3.1.

Table 3.1. Properties of sampling points

Sampling points	Active Sampling (Duration)	Passive Sampling		Number of personnel	Ventilation
		Indoors (Duration)	Outdoors (Duration)		
Photocopy center	42 samples, 4 hours	2 samples, 7 days	3 samples, 7 days	4	Natural Ventilation
Painting class	42 samples, 4 hours	3 samples, 7 days	3 samples, 7 days	15	Natural Ventilation
Printmaking class (1)	36 samples, 2 hours	3 samples, 3 days	3 samples, 3 days	15	Exhaust fan, natural ventilation
Printmaking class (2)	Total 35 samples, 24 samples 2 hours, 11 samples 1 hour	3 samples, 3 days	3 samples, 3 days	10	Natural Ventilation
Tire shop	14 samples, 1 hour	3 samples, 3 days	3 samples, 3 days	3	Air Conditioning
Car painter	14 samples, 5 minutes	2 samples, 2 days	3 samples, 2 days	3	Natural Ventilation

3.2 The Compounds Determined

A total of 57 volatile organic compounds (LGC Standards, LOT No: D67574) were analyzed in this thesis study (Table 3.2). According to the literature, these VOCs are categorized as biogenic and anthropogenic (34,38,47,81–83).

Table 3.2. The CAS-Numbers of determined VOCs.

Anthropogenic VOC		Biogenic VOC
1,2,3-trimethylbenzene [CAS:526-73-8]	o-xylene [CAS:95-47-6]	1-octanol [CAS:111-87-5]
1,2-dichlorobenzene [CAS:95-50-1]	phenol [CAS:108-95-2]	4-methylanisole [CAS:104-93-8]
1,2-dichloroethane [CAS:107-06-2]	propylbenzene [CAS:103-65-1]	alloocimene [CAS:673-84-7]
1,3,5-trimethylbenzene [CAS:108-67-8]	styrene [CAS:100-42-5]	alpha phellandrene [CAS:99-83-2]
1,3-diethylbenzene [CAS:135-01-3]	tetradecane [CAS:629-59-4]	alpha pinene [CAS:80-56-8]
1,4-cineole [CAS:470-67-7]	toluene [CAS:108-88-3]	alpha terpinen [CAS:99-86-5]
1,4-diethylbenzene [CAS:105-05-5]	tridecane [CAS:629-50-5]	alpha terpineol [CAS:10482-56-1]
acetophenone [CAS:98-86-2]		alpha terpinolene [CAS:586-62-9]
benzaldehyde [CAS:100-52-7]		beta-pinene [CAS:127-91-3]
benzene [CAS:71-43-2]		camphene [CAS:79-92-5]
benzothiazole [CAS:95-16-9]		camphor [CAS:464-49-3]
carbon tetrachloride [CAS:56-23-5]		crotonaldehyde [CAS:123-73-9]
chlorobenzene [CAS:108-90-7]		delta 3 carene [CAS:13466-78-9]
chloroform [CAS:67-66-3]		dihyromyrcenol [CAS:18479-58-8]
decanal [CAS:112-31-2] *		dl-limonene [CAS:138-86-3]
dodecane [CAS:112-40-3]		eucalyptol [CAS:470-82-6]
ethylbenzene [CAS:100-41-4]		gamma-terpinene [CAS:99-85-4]
heptanal [CAS:111-71-7] *		hexanal [CAS:66-25-1]
heptane [CAS:142-82-5]		L-fenchone [CAS:7787-20-4]
isoprene [CAS:78-79-5] *		linalool [CAS:78-70-6]
isopropylbenzene [CAS:98-82-8]		m cymene [CAS:535-77-3]
m+p-xylene [CAS:108-38-3] [CAS:106-42-3]		ocimene [CAS:13877-91-3]
naphthalene [CAS:91-20-3]		p cymene [CAS:99-87-6]
nonane [CAS:111-84-2]		sabinene [CAS:3387-41-5]
o-ethyltoluene [CAS:611-14-3]		terpinen-4-ol [CAS:8000-41-7]

* VOCs with both biogenic and anthropogenic source

3.3 Preparation of Tenax-TA Tubes for Analysis

Active and passive volatile organic compound (VOC) sampling was performed using Tenax TA sampling tubes (Perkin Elmer, USA) (Figure 3.8). The Tenax TA tube has an outer diameter of 6.4 mm, an inner diameter of 5 mm, a length of 89 mm and a diffusion path length of 15 mm. The Tenax TA sorbent has a mesh size of 35/60. Tenax TA is a low-acid, porous polymer synthesised from 2,6-diphenyl-p-phenylene oxide (84).



Figure 3.8. Tenax-TA tube used in the active and passive sampling of VOCs (photo taken from our laboratory)

The sampling tubes were cleaned with a thermal desorber and the tubes were conditioned before starting the sampling. Conditioning of the tubes was carried out under high-purity helium gas (99.999% purity) at 320°C for 30 minutes. Conditioned tubes were stored in screw-cap plastic falcon tubes with activated carbon and silica gel packets folded into filter paper (Figure 3.9). The silica gel is used to prevent moisture and the activated carbon is used to avoid contamination problems.



Figure 3.9. Tenax-TA tube and packs of activated carbon and silica gel in falcon tube (photo taken from our laboratory)

3.4 Sampling Techniques

3.4.1 Active Sampling

The STS-25 sequential autosampler device (Perkin Elmer, USA) was used for active sampling (Figure 3.10). The flow rate of the vacuum pump connected to the sampler device was calibrated at 250 mL/min.

Since potassium iodide is used as an ozone scavenger during sampling, a filter impregnated with potassium iodide (KI) was used for active sampling. Ozone is decomposed ($\text{O}_3(\text{g}) + \text{H}_2\text{O}(\text{aq}) + 2\text{KI}(\text{s}) \rightarrow \text{O}_2(\text{g}) + 2\text{KOH}(\text{s}) + \text{I}_2(\text{g})$) so that it does not react with VOCs to change their concentrations.

The KI solution was prepared by dissolving 20 g of KI in 15 mL of deionized water. Glass microfibre filters were immersed in the KI solution and allowed to

stand until the filters had absorbed the solution. The glass-microfibre filters were then dried in an oven at 40°C for 45 minutes. KI filters were stored in petri dishes in a desiccator. Clearer and better signals were observed in samples with KI filters.

The different odour intensities at each of the sampling points, the presence or absence of ventilation, and the number of people entering and working vary. Optimization studies showed that the active sampling time should be 5 minutes and 4 hours to detect all compounds present in the indoor environment. Once the air sampling was complete, the samples were transferred to the laboratory in falcon tubes containing silica gel and activated charcoal and stored in a deep freezer at -18°C until analysis.

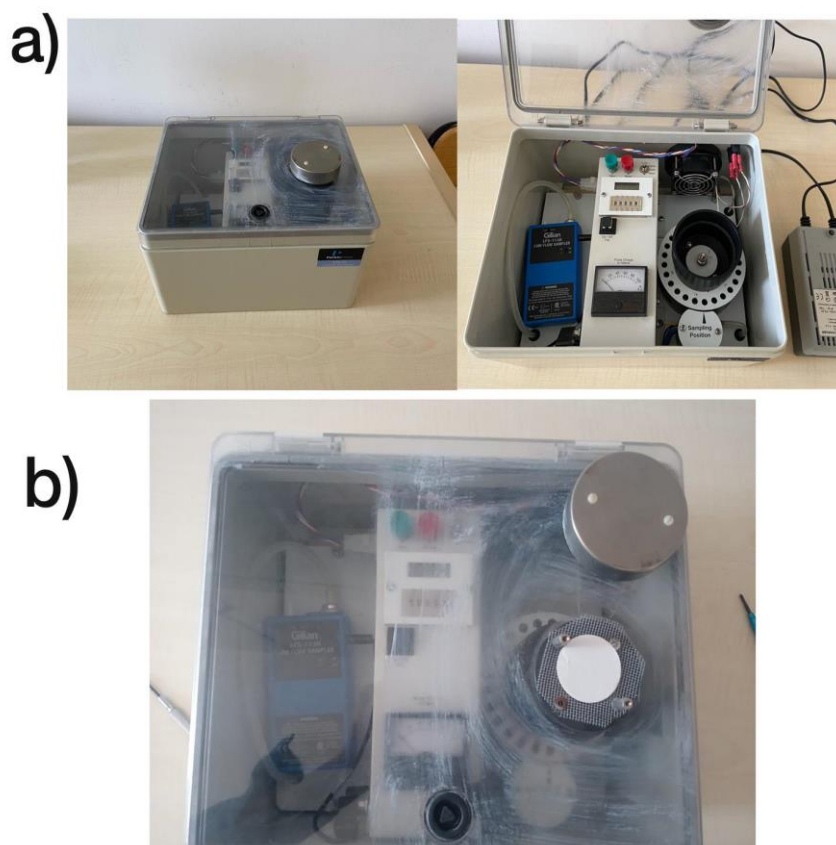


Figure 3.10. a) The STS-25 sequential autosampler device b) integration of the KI filter used in active sampling into the device (photo taken from our laboratory)

3.4.2 Passive Sampling

Passive sampling is a method based on molecular diffusion. At the sampling sites, Tenax-TA tubes are fixed to cables or poles at a height of 1.5-2 m above the ground in indoor environments, and the tubes are fixed to tree branches in outdoor environments. The fixed tubes were placed vertically in aluminium containers with the sorbent bed, that is the open end downwards (Figure 3.11). A diffusion bed was used to protect the sorbent bed from factors such as excessive wind, insects, and dust that may occur during the sampling. At the end of the the sampling period was over, the diffusion cap was removed, and the Tenax-TA tube caps were fitted. At the end of the air sampling period, the samples were transported to the laboratory in Falcon tubes containing silica gel and activated carbon and stored in a deep freezer at -18°C until analysis.

a)



b)



Figure 3.11. a) Diffusion cap, b) Tenax-TA passive sampler attached to a tree in a sampling point (photo from the field)

3.5 Analysis of Samples

A Gas Chromatography-Mass Spectrometry (Shimadzu, Japan) coupled Thermal Desorption (Perkin Elmer, USA) system was used for the analysis of VOC samples (Figure 3.12). VOC samples adsorbed from air onto the Tenax-TA tube were heat desorbed by thermal desorption and transferred to a Gas Chromatography-Mass Spectrum.



Figure 3.12. The TD-GC-MS system used for VOC analysis (Photo from our laboratory)

The VOCs were analysed using the RTX-624 column, which has a diameter of 0.25 mm, a length of 60.0 m and a thickness of 1.40 μm . The operating conditions for the thermal desorber and GC-MS throughout the analysis are given in Table 3.3.

The retention times of VOC compounds, target ions, and reference ions were determined using the SCAN mode, then after which the SIM (Selected Ion Monitoring) mode was selected in the GC-MS to enhance sensitivity and accuracy. VOCs are grouped in 9 different SIM windows. During group formation, the target ion and two reference ions of each compound were written to the MS detector according to the defined time intervals. The time intervals of the groups and the ions of the compounds in these intervals are shown in Table 3.4.

Table 3.3. TD-GC-MS operating parameters

TD	
Column flow	1.4 mL/min
Cycle time	20 min
Desorb time	10 min
High temperature	250 °C
Inlet Split flow	30 mL/min
Low temperature	-30 °C
Mode	2-stage-desorb
Outlet Split flow	30 mL/min
Purge time	2 min
Ratio	40 °C/sec
Split	Flow
Transfer temperature	250 °C
Tube temperature	250 °C
Valve temperature	230 °C
GC	SHIMADZU-QP2010SE
Carrier gas	Helium, High purity (%99.999)
Column flow	1.48 mL/min
Column oven temperature	30 °C
GC column	RTX-624 60.0 m x 0.25 mm x 1.40 µm
Injection mode	splitless
Injection temperature	100 °C
Injection volume	1 µL
Linear velocity	30.8 cm/sec
Oven temperature program	30 °C (5 min), 5 °C/min to 180 °C (5 min), 10 °C/min to 240 °C (3 min)
Pressure	155.9 kPa
Purge flow	3.0 mL/min
Sampling time	1 min
Split ratio	-1
Total flow	50 mL/min
MS	
Detector Voltage	0.3 kV
GC program time	49 min
Interface temperature	240 °C
Ion source temperature	230 °C
Mass spectrometer	Electron impact, 70 eV
Solvent cut time	1 min

Table 3.4. Selected Ion Monitoring parameters

SIM Windows	Time (min)	Monitored ions (m/z)
1	1.00- 11.00	67, 68, 53
2	11.00- 16.00	53, 52, 40, 57, 41, 82, 81, 83, 85, 47
	16.00- 19.00	97, 40, 99, 119, 117, 78, 77, 52, 62, 49, 64, 43, 41, 71, 39, 70
3	19.00- 26.70	91, 43, 92, 44, 41, 56, 112, 77, 114, 106, 51, 57, 105
4	26.70- 30.00	91, 106, 105, 104, 103, 78, 44, 70, 55, 93, 92, 120, 79, 121, 65, 57, 43
5	30.00- 32.75	105, 120, 93, 41, 69, 77, 91, 106, 43, 71, 111, 44, 68, 119, 67, 134, 79, 122, 121
6	32.75- 34.70	93, 91, 77, 105, 119, 134, 57, 43, 71, 146, 148, 111, 94, 66, 39, 121, 136, 59, 67, 41, 56, 55
7	34.70- 37.10	41, 71, 43, 121, 105, 136, 77, 81, 69, 44, 40, 57
8	37.10- 44.50	95, 81, 41, 71, 93, 43, 44, 57, 70, 59, 128, 127, 135, 108, 69
9		

Standards of 7 different concentrations were prepared for the calibration curve. A 10 ppm intermediate stock solution was prepared by taking 50 μ L of the 100 ppm main stock solution and diluting it with 500 μ L of methanol. 10 ng, 20 ng, 50 ng, 80 ng, 100 ng and 150 ng standards were obtained from the 10 ppm intermediate stock solution by injecting 1 μ L, 2 μ L, 5 μ L, 8 μ L, 10 μ L and 15 μ L into Tenax TA tubes, respectively. A 200 ng standard was prepared by taking 2 μ L of the main stock solution and injecting it into a Tenax TA tube. In this way a 7-point (10 ng, 20 ng, 50 ng, 80 ng, 100 ng, 150 ng and 200 ng) calibration curve was plotted. Figure 3.13 shows the calibration curve of the heptanal compound.

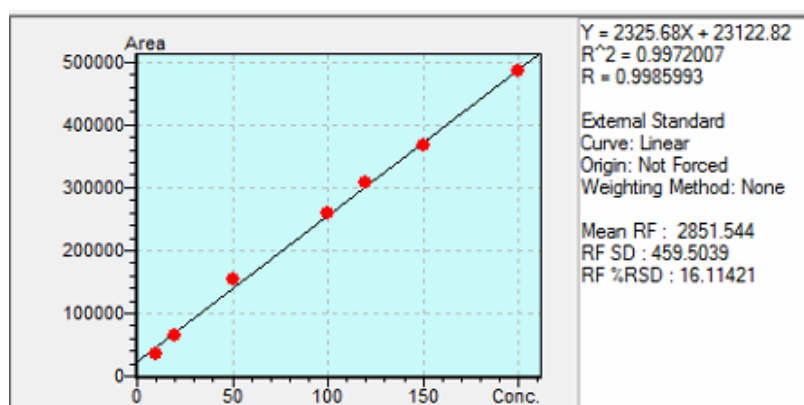


Figure 3.13. The calibration curve of the heptanal compound (without 80 ng standard) using TD-GC-MS

Chromatograms including 57 VOCs were plotted using by GC-MS software. Figure 3.14 shows the chromatograms of the 10 ng lowest standard and 3.15 shows the first active and passive samples from the photocopy center.

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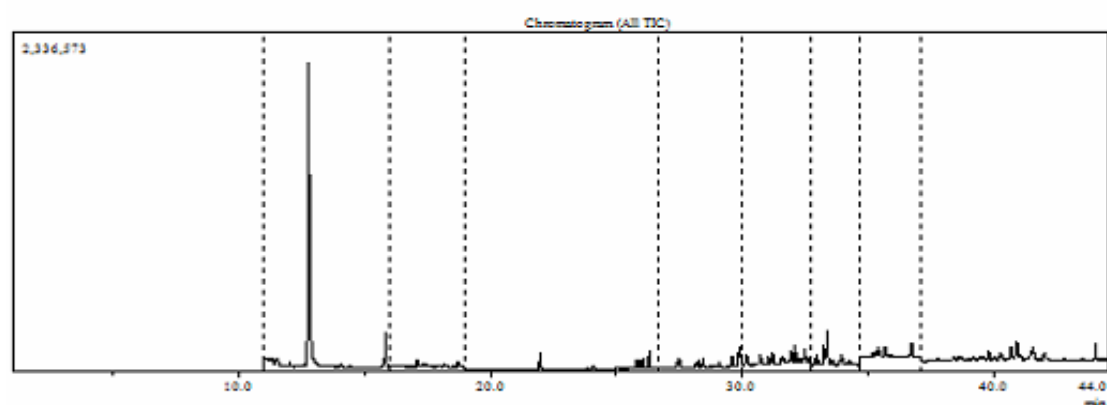


Figure 3.14. The chromatogram of the 10-ng standard (the lowest standard)

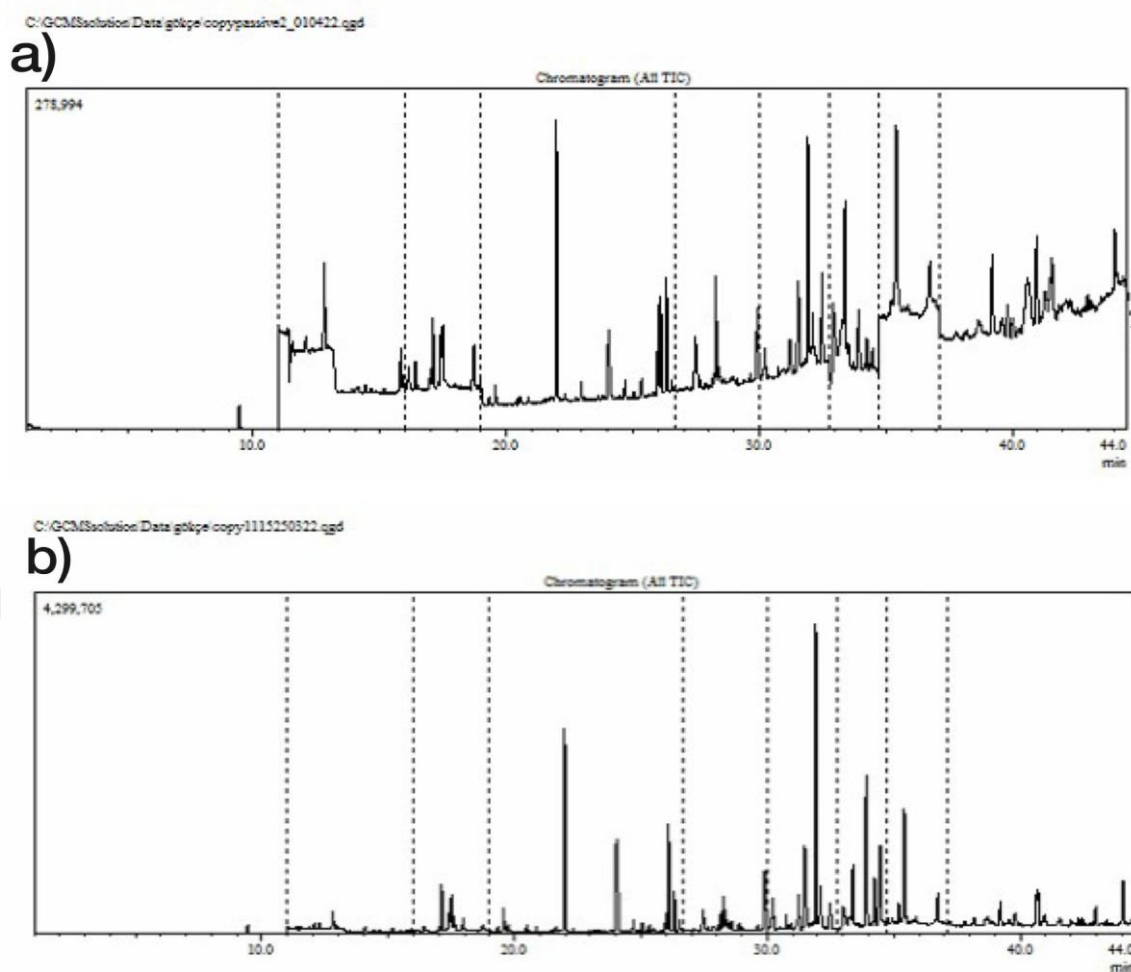


Figure 3.15. a) the first active sample and b) the first passive sample from the photocopy center

3.6 Calculation of Atmospheric Concentration

Atmospheric concentrations of each compound were determined in passive sampling with Fick's first law.

$$C = \frac{(m \times L)}{(D \times A \times t)} \times 10^3 \quad (3.1)$$

C: the amount of pollutant ($\mu\text{g}/\text{m}^3$)

L: diffusion path length (cm)

m: the mass of the target pollutant (ng)

t: sampling duration (sec)

D: diffusion coefficient (cm²/sec)

A: sampler surface field (cm²)

In the Tenax-TA sampling tubes used, L (diffusion path length) is 1.5 cm and A (sampler surface field) is 0.1963 cm². The D (diffusion coefficient) shown in equation 3.1 was calculated separately for each compound using equations 3.2 and 3.3, respectively.

$$D_{298} = 10^{-3} \times \frac{T^{1.75} \times \left[\left(\frac{1}{m_{air}} \right) + \left(\frac{1}{m_i} \right) \right]^{\frac{1}{2}}}{P \times \left[V_{air}^{1/3} + V_i^{1/3} \right]^2} \quad (3.2)$$

$$D_T = D_{298} \times T^{1.75} \times (298.15)^{-1.75} \quad (3.3)$$

For active sampling, on the other hand, atmospheric concentrations of VOCs were obtained by dividing the weight (ng) of each compound by the volume of air sampled (L). The volume of air sampled was determined by multiplying the sampling time (min) by the pump flow rate (mL/min).

Equation 3.4 was used to calculate the atmospheric concentrations (ng m⁻³) of the VOC analysis results for the active sampling.

$$A(ng/m^3) = \frac{A \text{ ng}}{\left(250 \frac{mL}{min} \times (4 \times 60) min \times \frac{1 L}{1000 mL} \times \frac{1 m^3}{1000 L} \right)} \quad (3.4)$$

3.7 Assessment of the Health Risk

VOC exposures to individuals actively working at sampling points were assessed by utilising IRIS, the risk evaluation guide as recommended by the US EPA. This assessment included the evaluation of the lifetime cancer risk (LCR) for VOCs that are considered to be carcinogenic, in addition to the hazard index (HI) health risks for non-carcinogenic VOCs (63). Table 3.5 gives the carcinogenic category (52), inhalation unit risk (IUR), oral slope factor (OSF), reference concentration (RfC), and reference dose (RfD) values for each VOC found in this study(63).

Table 3.5. The values for the RfC, the RfD, the OSP, the IUR, and the carcinogenic classification of the VOCs.

VOCs	RfC (mg/m ³)	RfD (mg/kg.day)	OSF (per mg/kg.day)	IUR (per µg/m ³)	Category of carcinogenicity (IARC)
isoprene	-	-	-	-	2B
chloroform	-	0.01	-	-	2B
carbon tetrachloride	0.1	0.004	0.07	6E-06	2B
benzene	0.03	0.004	0.015	2.2E-06	1
1,2-dichloroethane	-	-	0.091	2.6E-05	2B
heptane	-	-	-	-	-
crotonaldehyde	-	-	-	-	2B
toluene	5	0.08	-	-	3
hexanal	-	-	-	-	-
chlorobenzene	-	0.02	-	-	3
ethylbenzene	1	0.1	-	-	2B
nonane	-	-	-	-	-
m+p-xylene	0.1	0.2	-	-	3
o-xylene	0.1	0.2	-	-	3
styrene	1	0.2	-	-	2A
heptanal	-	-	-	-	-
alpha pinene	-	-	-	-	-
isopropylbenzene	0.4	0.1	-	-	-
camphene	-	-	-	-	-
propylbenzene	-	-	-	-	-
1,3,5-trimethylbenzene	0.06	0.01	-	-	-
beta pinene	-	-	-	-	-
o-ethyltoluene	-	-	-	-	-
alpha phellandrene	-	-	-	-	-
delta 3 carene	-	-	-	-	-

Table 3.5 (continued) The values for the RfC, the RfD, the OSP, the IUR, and the carcinogenic classification of the VOCs.

VOCs	RfC (mg/m ³)	RfD (mg/kg.day)	OSF (per mg/kg.day)	IUR (per µg/m ³)	Category of carcinogenicity (IARC)
1,2,3-trimethylbenzene	0.06	0.01	-	-	-
benzaldehyde	-	0.2	0.004	-	-
1,4-cineole	-	-	-	-	-
dl-limonene	-	-	-	-	3
p cymene	-	-	-	-	-
m cymene	-	-	-	-	-
sabinene	-	-	-	-	-
ocimene	-	-	-	-	-
eucalyptol	-	-	-	-	-
4-methylanisole	-	-	-	-	-
gamma terpinene	-	-	-	-	-
1,4-diethylbenzene	-	-	-	-	-
1,3-diethylbenzene	-	-	-	-	-
1,2-dichlorobenzene	-	0.09	-	-	-
phenol	-	0.3	-	-	3
alpha terpinolene	-	-	-	-	-
dihyromyrcenol	-	-	-	-	-
1-octanol	-	-	-	-	-
linalool	-	-	-	-	-
alloocimene	-	-	-	-	-
acetophenone	-	0.1	-	-	-
L-fenchone	-	-	-	-	-
alpha terpinene	-	-	-	-	-
dodecane	-	-	-	-	-
camphor	-	-	-	-	-
terpinen-4-ol	-	-	-	-	-
decanal	-	-	-	-	-
alpha terpinol	-	-	-	-	-
Naphthalene	0.003	0.02	-	-	2B
tridecane	-	-	-	-	-
benzothiazole	-	-	-	-	-
tetradecane	-	-	-	-	-

A health risk assessment was performed for both carcinogenic and non-carcinogenic VOCs in this study. Chronic daily intake (CDI) concentrations in

mg/kg/day were calculated for each compound using Equation 3.5 to assess the health risks related to oral exposure.

$$CDI_{oe} = \frac{CA(\frac{mg}{m^3}) \times IR(\frac{m^3}{day}) \times ET(\frac{hours}{1\ day} \times \frac{1\ day}{24\ hours}) \times ED(years) \times EF(\frac{day}{years})}{BW\ (kg) \times AT\ (day)} \quad (3.5)$$

where CA is the contaminant concentration in ambient (mg/m³); IR is the inhalation rate (m³/day); ET is the time of exposure in a day; ED is the exposure duration (years); EF is the exposure frequency (day/year); AT is the average time spent in a year (days); and BW is the body weight (kg).

To determine the health risks associated with inhalation exposure, we used Equation 3.6 to compute chronic daily intake (CDI) concentration in mg/m³ for each compound.

$$CDI_{ie} = \frac{CA(\frac{mg}{m^3}) \times ET(\frac{hours}{1\ day} \times \frac{1\ day}{24\ hours}) \times EF(\frac{day}{years}) \times ED(years)}{AT\ (day)} \quad (3.6)$$

where CA is a contaminant concentration in ambient air (mg/m³); ET is the time of exposure in a day; ED is exposure duration (years); EF is exposure frequency (day/year); and AT is the average time spent in a year (days).

The calculation of the lifetime cancer risk (LCR) for VOCs with oral carcinogenic properties involves the multiplication of the chronic daily intake (CDI in mg/kg.day) by the oral slope factor (OSF in per mg/kg.day), as given in equation 3.7. On the other hand, equation 3.8 demonstrates the calculation of the hazard index (HI) for non-carcinogenic compounds through the ratio of CDI and reference dose (RfD in mg/kg.day). A schematic representation of the calculation of lifetime cancer risk and hazard index for oral exposure is given in Figure 3.16.

$$LCR = CDI \times OSF \quad (3.7)$$

$$HI = CDI/RfD \quad (3.8)$$

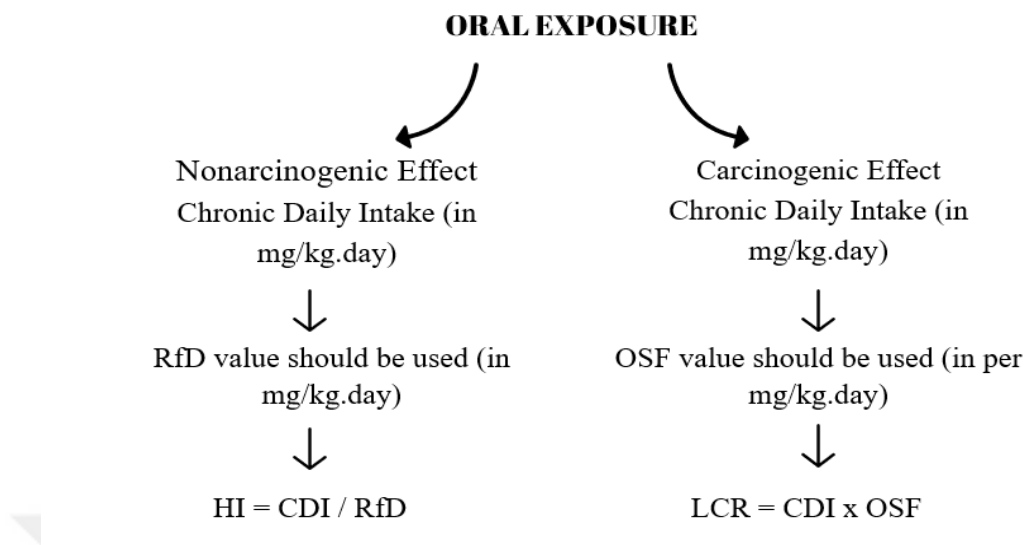


Figure 3.16. A schematic representation of the calculation of lifetime cancer risk and hazard index for oral exposure

The calculation of the lifetime cancer risk (LCR) for VOCs that can cause cancer through inhalation was done by multiplying the chronic daily intake (CDI in $\mu\text{g}/\text{m}^3$) with the inhalation unit risk (IUR in per $\mu\text{g}/\text{m}^3$) as given in equation 3.9. The hazard index (HI) for non-carcinogenic compounds was obtained by dividing the CDI by the reference concentration (RfC in mg/m^3) and is given in equation 3.10. A schematic representation of the calculation of lifetime cancer risk and hazard index for inhalation exposure is given in Figure 3.17.

$$LCR = CDI \times IUR \quad (3.9)$$

$$HI = CDI/RfC \quad (3.10)$$

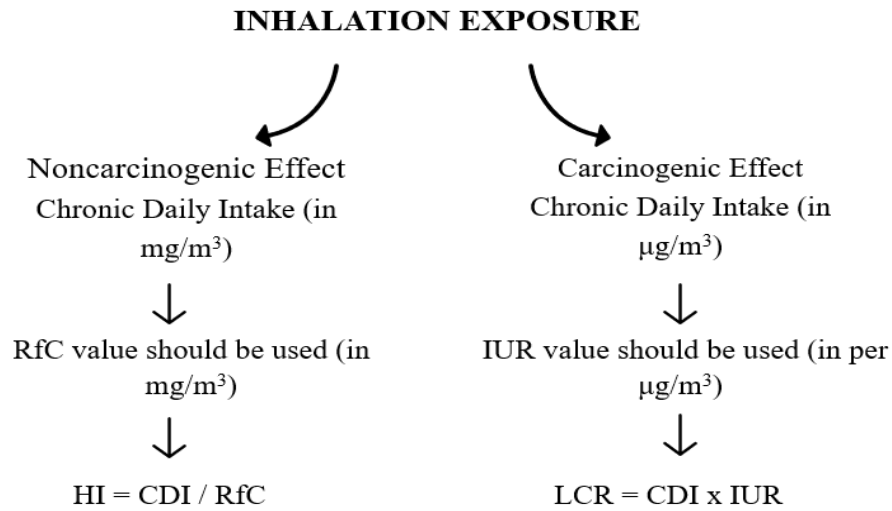


Figure 3.17. A schematic representation of the calculation of lifetime cancer risk and hazard index for inhalation exposure

In risk assessments, if the HI value is 1 or less than 1, the risk is negligible; if it is greater than 1, it is considered not to be carcinogenic to humans but to have adverse effects on human health (47,69). If the LCR value is greater than 1×10^{-4} , there is an obvious risk, if it is between 1×10^{-5} and 1×10^{-6} , there is a negligible risk, and if it is between 1×10^{-4} and 1×10^{-5} , there is possible risk (29,47,70).

4. RESULTS AND DISCUSSION

This dissertation study was carried out in the province of Bolu, located in the western Black Sea Region of Türkiye. Air samples were collected using active and passive sampling techniques. The data were collected from six different locations: a photocopy center, a painting class, two different printing classes, a tire shop and a car painter. A total of 217 air samples were collected using active and passive sampling techniques.

4.1 Active Sampling

4.1.1 Photocopy Center

Air samples were collected from the photocopy center inside the Activity Center at Bolu Abant İzzet Baysal University (BAIBU) Gököy campus on 25th March and 1st April 2022. Over seven days, 42 air samples were collected by active sampling. The trial at the photocopy center resulted in a four-hour sampling period. Air samples were collected in four-hour periods: 11.00 - 15.00, 15.00 - 19.00, 19.00 - 23.00, 23.00 - 03.00, 03.00 - 07.00, and 07.00 - 11.00. The photocopy center is open from 08:30 to 21:00 for twelve hours every day. As there is a lunch break between 12:00 and 13:00 on weekdays, it is very busy with an average of four to five hundred visitors a day. On the other hand, as the university is not busy with classes at weekends, the number of visitors is quite low. However, a Western Black Sea Regional Career Fair (BATIKAF) event took place at the University on 25th – 26th of March 2022, which resulted in a significant increase in the number of visitors to the activity center. An average of one thousand people visited the photocopy center during the BATIKAF event. The most emitted VOCs between the specified dates are, hexanal (15.1 $\mu\text{g}/\text{m}^3$); isoprene (9.7 $\mu\text{g}/\text{m}^3$); dl-limonene (7.73 $\mu\text{g}/\text{m}^3$); 1-octanol (6.4 $\mu\text{g}/\text{m}^3$) and toluene (5.69 $\mu\text{g}/\text{m}^3$).

The photocopy center does not have a ventilation system. The ventilation of the photocopy center, which is located inside the activity center, is provided naturally by leaving the door open as there is no window and therefore it has an inadequate ventilation system. The most abundant VOCs on average during the whole sampling at this sampling point are hexanal ($16.7 \mu\text{g}/\text{m}^3$); isoprene ($6.21 \mu\text{g}/\text{m}^3$); toluene ($6.19 \mu\text{g}/\text{m}^3$); and dl-limonene ($4.95 \mu\text{g}/\text{m}^3$). On the other hand, the VOCs with the lowest average concentration throughout the sampling are alpha terpinolene ($0.035 \mu\text{g}/\text{m}^3$); propylbenzene ($0.050 \mu\text{g}/\text{m}^3$); p-cymene ($0.057 \mu\text{g}/\text{m}^3$); o-ethyltoluene ($0.061 \mu\text{g}/\text{m}^3$); and isopropylbenzene ($0.068 \mu\text{g}/\text{m}^3$). Samples collected from the photocopier; 1,2-dichloroethane, chlorobenzene, 1,4-cineole, 4-methylanisole, gamma terpinene, 1,4-diethylbenzene, and alloocimene compounds were not found.

The biogenic organic compound hexanal released most during the BATIKAF event and throughout the sampling period, was released most between 19.00 and 23.00 on 26th March and 1st April, with concentrations of $36.9 \mu\text{g}/\text{m}^3$ and $36.6 \mu\text{g}/\text{m}^3$, respectively. The concentration versus daily hours graph of the hexanal compound is given in Figure 4.1. Hexanal, the most abundant compound in the copy center and of biogenic origin, is released from trees, but it is the compound most commonly released in indoor environments. The hexanal compound is also released from various sources such as air fresheners, synthetic resins, paints, scented cleaning products, paper products, adhesives, and cardboard (12,84,85).

The standard deviation, mean, and median values (in $\mu\text{g}/\text{m}^3$) for VOCs determined by active sampling at the copy center on 25th March 2022 and 1st April 2022 are given in Table 4.1.

Table 4.1. The standard deviation, mean, and median values obtained for VOCs determined at the photocopy center

VOCs	Arith. Mean	Median	Standard Deviation
isoprene	6.21	3.96	6.28
chloroform	0.384	0.118	0.435
carbon tetrachloride	0.724	0.716	0.0670
benzene	0.711	0.589	0.490
heptane	2.44	1.99	1.65
crotonaldehyde	0.584	0.287	0.965
toluene	6.67	6.00	3.12
hexanal	18.0	15.6	9.74
ethylbenzene	1.78	1.56	1.24
nonane	1.31	1.26	0.55
m+p-xylene	1.18	1.12	0.56
o-xylene	1.04	1.02	0.5
styrene	0.773	0.736	0.616
heptanal	0.834	0.703	0.371
alpha pinene	3.39	3.47	1.24
isopropylbenzene	0.0681	0.0791	0.0423
camphene	1.02	0.0399	2.52
propylbenzene	0.0503	0.0402	0.0452
1,3,5-trimethylbenzene	0.147	0.123	0.121
beta pinene	0.639	0.571	0.285
o-ethyltoluene	0.0612	0.0510	0.0575
alpha phellandrene	0.928	0.994	0.576
delta 3 carene	1.47	1.25	1.00
1,2,3-trimethylbenzene	0.542	0.481	0.237
benzaldehyde	2.36	2.27	0.605
dl-limonene	6.93	4.97	5.51
p cymene	0.0571	0.0539	0.0378
m cymene	0.316	0.213	0.277
sabinene	0.142	0.0633	0.283
ocimene	0.151	0.0658	0.315
eucalyptol	0.144	0.0951	0.177
1,2-dichlorobenzene	4.84	3.14	6.71
phenol	2.39	1.94	1.74
alpha terpinolene	0.0351	0.0351	0.0335
dihyromyrcenol	1.57	1.18	1.43
1-octanol	2.36	1.01	3.28
linalool	0.653	0.317	0.869
acetophenone	0.804	0.776	0.270
L-fenchone	0.344	0.331	0.247
alpha terpinene	1.14	1.11	0.303
dodecane	0.683	0.634	0.190
camphor	0.0867	0.0867	0.0358
terpinen-4-ol	0.288	0.280	0.221

Table 4.1 (continue). The standard deviation, mean, and median values obtained for VOCs determined at the photocopy center

VOCs	Arith. Mean	Median	Standard Deviation
decanal	0.919	0.921	0.695
alpha terpinol	0.071	0.0609	0.0197
naphthalene	0.215	0.212	0.0924
tridecane	0.638	0.602	0.23
benzothiazole	0.11	0.0659	0.106
tetradecane	1.19	1.17	0.366

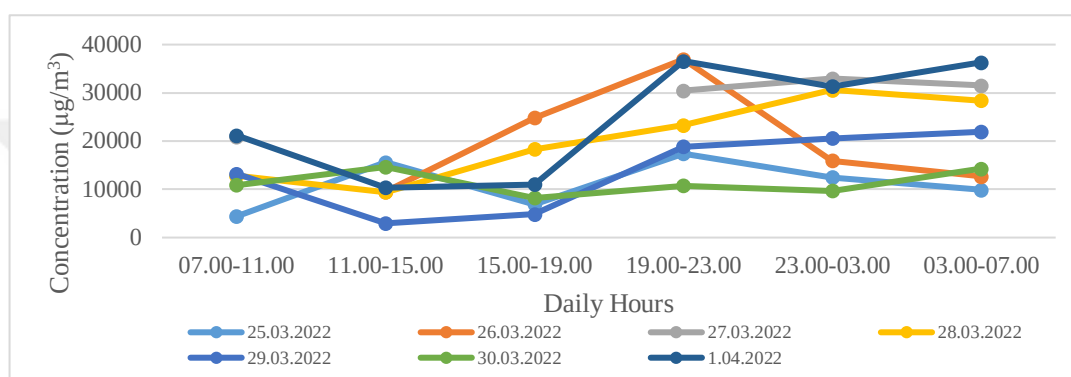
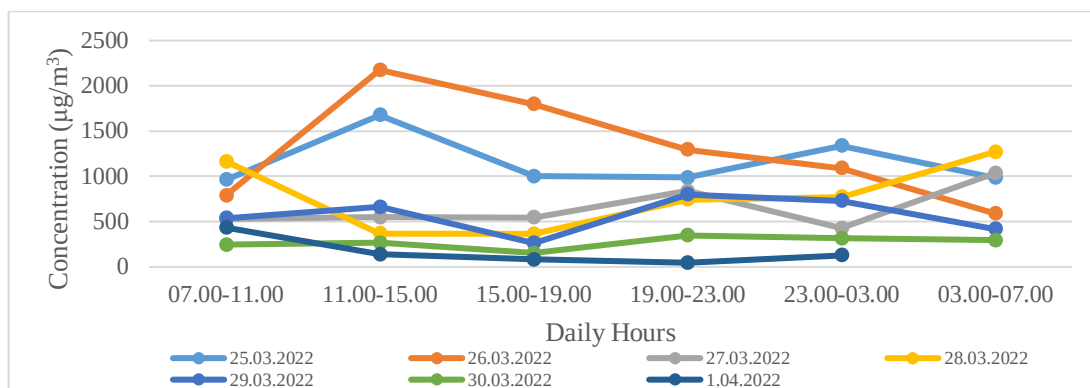


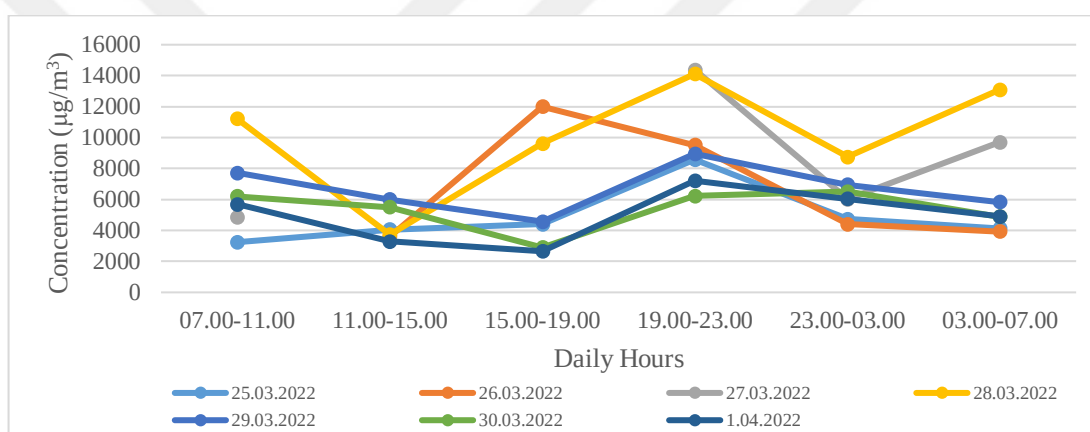
Figure 4.1. The concentration versus daily hours graph of the hexanal compound in the photocopy center

At the photocopy center, the average concentrations of benzene, toluene, ethylbenzene, m+p-xylene, and o-xylene (BTEXs) compounds were found to be $0.71 \mu\text{g}/\text{m}^3$, $6.67 \mu\text{g}/\text{m}^3$, $1.78 \mu\text{g}/\text{m}^3$, $1.18 \mu\text{g}/\text{m}^3$, and $1.04 \mu\text{g}/\text{m}^3$, respectively. The graph of concentration versus daily hours graph for benzene, toluene, and ethylbenzene compounds is shown in Figure 4.2. Examination of the BTEX compounds showed that their concentrations were generally high between 19.00 and 23.00. Benzene was most frequently released between 11.00 and 15.00 on 26th of March, with a concentration of $2.18 \mu\text{g}/\text{m}^3$. Benzene is used as a solvent for paints, resins, and inks (84). The highest release of toluene compound was between 19.00 and 23.00 on March 27 and 28, with concentrations of $14.4 \mu\text{g}/\text{m}^3$ and $14.1 \mu\text{g}/\text{m}^3$. Toluene is used as a solvent in a number of products, including coatings, paints, and inks. It is also an essential intermediate chemical in the production of benzene (86). The release of toluene at the photocopy center was increased due to the use of the compound as a solvent in toner in photocopiers. (87). The ethylbenzene compound had the highest concentration between 19.00 and 23.00

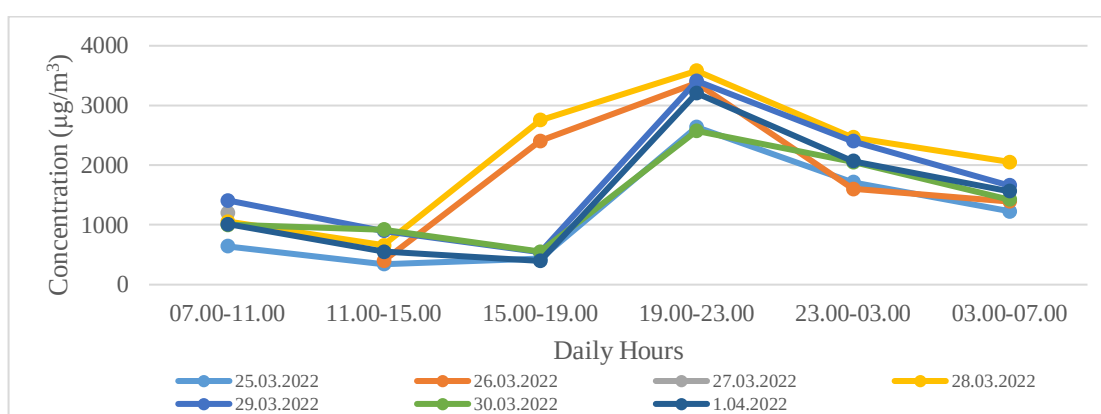
throughout the sampling period. The graph of ethylbenzene showed that it decreased during the day and increased during the evening and night hours.



(a)



(b)

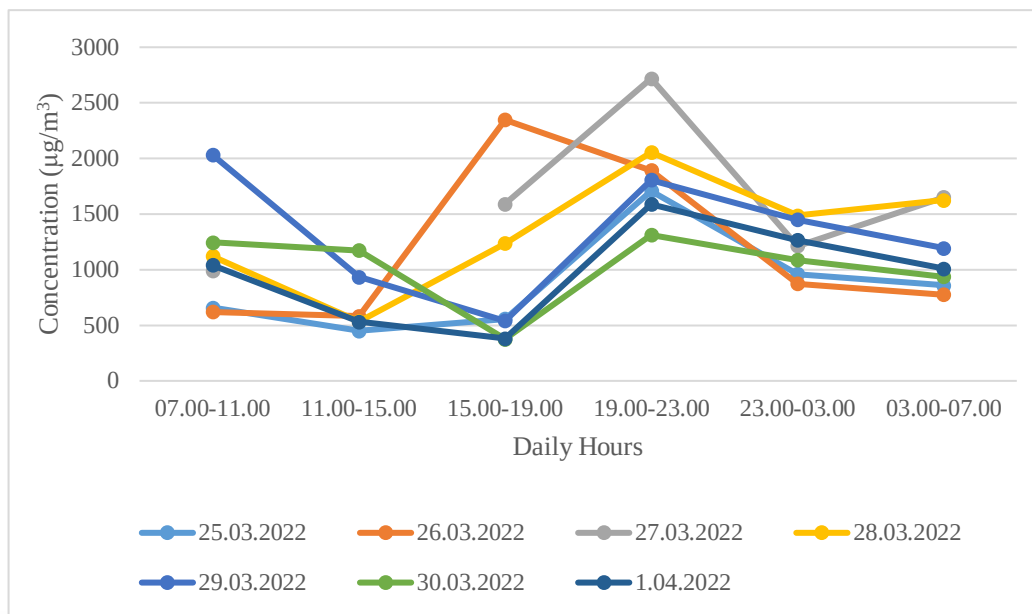


(c)

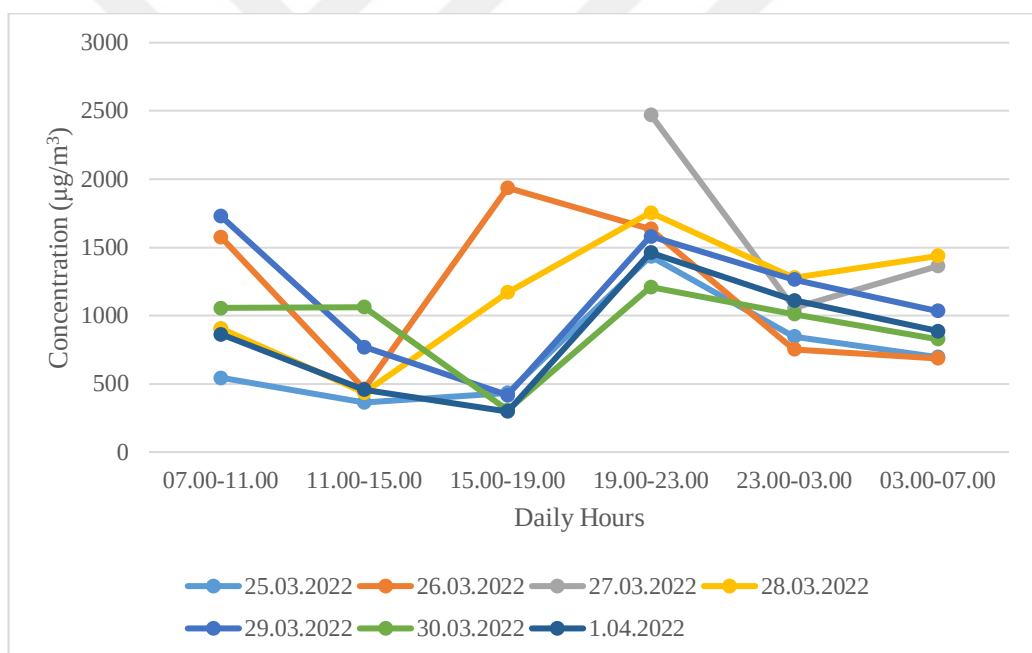
Figure 4.2. The concentration versus daily hours graph of (a) benzene compound, (b) toluene compound, and (c) ethylbenzene compound in the photocopy center

The compounds m+p-xylene and o-xylene were examined separately, and the concentration versus daily hours graphs of the xylene compounds are shown in Figure 4.3. The m+p-xylene compound was most released between 19.00 and 23.00 on March 27, with a concentration of $2.72 \mu\text{g}/\text{m}^3$. Then, it was determined that the highest release occurred between 15.00 and 19.00 on March 26, with a concentration of $2.35 \mu\text{g}/\text{m}^3$. For the o-xylene compound, the highest release was observed between 19.00 and 23.00 on 27th of March with a concentration with a concentration of $2.47 \mu\text{g}/\text{m}^3$. Then, on March 26, between 15.00 and 19.00, a high release was observed with a concentration of $1.94 \mu\text{g}/\text{m}^3$. The graph of the o-xylene compound showed that a similar result was obtained with m+p-xylene. Xylenes are used as solvents in a multitude of industrial applications, including those pertaining to the rubber, paint, printing, and leather industries. Conversely, xylenes are also utilized in the production of varnishes and paint thinners (88). It has been established that BTEX compounds are emitted from the inks of photocopiers.

In the absence of a ventilation system in the photocopy center, there is no ventilation from the time the workplace is closed until it is opened. As a result, volatile organic compounds remain suspended in the indoor air, increasing their concentration.



(a)



(b)

Figure 4.3. The concentration versus daily hours graph of (a) m+p-xylene compound, and (b) o-xylene compound in the photocopy center

4.1.1.1 Health Risk Assessment of Photocopy Center

Air samples collected from the photocopy center for seven days were evaluated separately for lifetime cancer risk (LCR) and hazard index (HI) of oral and inhalation exposure to carcinogenic and non-carcinogenic compounds. The results of the LCR and HI values of the photocopy center are given in Table 4.2.

Table 4.2. The LCR and HI values of the photocopy center

VOCs	LCR (Carcinogenic)		HI (Non-carcinogenic)	
	Inhalation	Oral	Inhalation	Oral
chloroform	-	-	-	3.62×10^{-3}
carbon tetrachloride	1.45×10^{-6}	4.78×10^{-6}	2.39×10^{-3}	1.71×10^{-2}
benzene	5.21×10^{-7}	1.01×10^{-6}	7.82×10^{-3}	1.68×10^{-2}
toluene	-	-	4.40×10^{-4}	7.86×10^{-3}
ethylbenzene	-	-	5.86×10^{-4}	1.67×10^{-3}
m+p-xylene	-	-	3.89×10^{-3}	5.56×10^{-4}
o-xylene	-	-	3.42×10^{-3}	4.89×10^{-4}
styrene	-	-	2.55×10^{-4}	3.64×10^{-4}
isopropylbenzene	-	-	5.62×10^{-5}	6.42×10^{-5}
1,3,5-trimethylbenzene	-	-	8.09×10^{-4}	1.39×10^{-3}
1,2,3-trimethylbenzene	-	-	2.98×10^{-3}	5.11×10^{-3}
benzaldehyde	-	8.89×10^{-7}	-	1.11×10^{-3}
1,2-dichlorobenzene	-	-	-	5.08×10^{-3}
phenol	-	-	-	7.52×10^{-4}
acetophenone	-	-	-	7.58×10^{-4}
naphthalene	-	-	2.37×10^{-2}	1.01×10^{-3}

The carcinogenic effects of the compounds carbon tetrachloride (CTC), benzene, and benzaldehyde were assessed in the photocopy center. The oral exposure VOCs were determined to be benzene, CTC, and benzaldehyde, and the LCR assessment of these compounds was found to be 1.01×10^{-6} , 4.78×10^{-6} , and 8.89×10^{-7} , respectively. According to the LCR risk assessment range, oral exposure to benzene and CTC compounds was found to be a “negligible risk” for photocopy center workers. The LCR evaluation of benzene and CTC compounds for inhalation exposure was 5.21×10^{-7} and 1.45×10^{-6} , respectively. According to the

LCR risk assessment range, inhalation exposure to benzene, CTC and benzaldehyde compounds was determined to be a “negligible risk” for workers.

The hazard index (HI) was calculated for oral and inhalation exposures of non-carcinogenic VOCs. Non-carcinogenic VOCs found in the photocopy center; chloroform, CTC, benzene toluene, ethylbenzene, m+p-xylene, o-xylene, styrene, isopropylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, benzaldehyde, 1,2-dichlorobenzene, phenol, acetophenone, and naphthalene. VOCs exposed by inhalation; CTC, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, styrene, isopropylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, and naphthalene. The HI evaluation results for inhalation exposure of these VOCs are respectively; 2.39×10^{-3} , 7.82×10^{-3} , 4.40×10^{-4} , 5.86×10^{-4} , 3.89×10^{-3} , 3.42×10^{-3} , 2.55×10^{-4} , 5.62×10^{-5} , 8.09×10^{-4} , 2.98×10^{-3} , and 2.37×10^{-2} . According to the risk assessment, since the HI values of the VOCs mentioned are less than 1, they are considered to pose a “negligible risk” to workers.

Oral exposed VOCs; chloroform, CTC, benzene toluene, ethylbenzene, m+p-xylene, o-xylene, styrene, isopropylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, benzaldehyde, 1,2-dichlorobenzene, phenol, acetophenone, and naphthalene. The average HI evaluation results for oral exposure were found to be 3.62×10^{-3} , 1.71×10^{-2} , 1.68×10^{-2} , 7.86×10^{-3} , 1.67×10^{-3} , 5.56×10^{-4} , 4.89×10^{-4} , 3.64×10^{-4} , 6.42×10^{-5} , 1.39×10^{-3} , 5.11×10^{-3} , 1.11×10^{-3} , 5.08×10^{-3} , 7.52×10^{-4} , 7.58×10^{-4} , and 1.01×10^{-3} , respectively. The risk assessment shows that the HI values of the specified VOCs are less than 1 and are therefore considered to present a negligible risk to employees.

The HI value of each VOC was calculated separately according to the sampling hours at the photocopy center of the VOCs exposed to the mouth. The HI values of the VOCs according to sampling hours and the total HI value for each compound are given in Table 4.3.

The hazard index chart for volatile organic compounds causing hourly oral exposure in the photocopy center by the hour is presented in Figure 4.4. The graph showed that benzene and CTC had the highest hazard indices.

Table 4.3. The HI values of VOCs and total HI value for each compound according to sampling hours at the photocopy center

VOCs	Hazard Index					
	07.00-11.00	11.00-15.00	15.00-19.00	19.00-23.00	23.00-03.00	03.00-07.00
chloroform	4.21×10^{-3}	1.24×10^{-3}	7.17×10^{-4}	3.91×10^{-3}	2.64×10^{-4}	1.16×10^{-2}
carbon tetrachloride	1.71×10^{-2}	1.72×10^{-2}	1.68×10^{-2}	1.66×10^{-2}	1.67×10^{-2}	1.80×10^{-2}
benzene	1.57×10^{-2}	1.97×10^{-2}	1.42×10^{-2}	1.70×10^{-2}	1.62×10^{-2}	1.80×10^{-2}
toluene	7.64×10^{-3}	5.14×10^{-3}	7.10×10^{-4}	1.16×10^{-2}	7.31×10^{-3}	7.82×10^{-3}
ethylbenzene	9.95×10^{-4}	5.94×10^{-4}	1.11×10^{-3}	3.43×10^{-3}	1.97×10^{-3}	1.62×10^{-3}
m+p-xylene	5.19×10^{-4}	3.30×10^{-4}	4.73×10^{-4}	8.81×10^{-4}	5.61×10^{-4}	5.42×10^{-4}
o-xylene	5.11×10^{-4}	2.79×10^{-4}	3.58×10^{-4}	7.78×10^{-4}	4.93×10^{-4}	4.67×10^{-4}
styrene	1.31×10^{-4}	1.01×10^{-4}	1.91×10^{-4}	7.84×10^{-4}	4.27×10^{-4}	4.56×10^{-4}
isopropylbenzene	4.71×10^{-5}	1.89×10^{-6}	5.47×10^{-5}	7.07×10^{-5}	8.49×10^{-5}	7.92×10^{-5}
1,3,5-trimethylbenzene	2.14×10^{-3}	1.19×10^{-3}	1.52×10^{-3}	1.74×10^{-3}	1.02×10^{-3}	1.04×10^{-3}
1,2,3-trimethylbenzene	5.96×10^{-3}	4.76×10^{-3}	5.51×10^{-3}	5.58×10^{-3}	4.46×10^{-3}	4.61×10^{-3}
benzaldehyde	1.00×10^{-3}	1.03×10^{-3}	1.23×10^{-3}	1.39×10^{-3}	1.03×10^{-3}	9.71×10^{-4}
phenol	1.13×10^{-3}	1.05×10^{-3}	6.75×10^{-4}	6.51×10^{-4}	5.70×10^{-4}	5.23×10^{-4}
acetophenone	6.19×10^{-4}	7.45×10^{-4}	8.91×10^{-4}	9.93×10^{-4}	7.17×10^{-4}	6.19×10^{-4}
naphthalene	8.44×10^{-4}	9.05×10^{-4}	9.76×10^{-4}	1.30×10^{-3}	1.03×10^{-3}	1.13×10^{-3}
Σ VOCs	5.85×10^{-2}	5.42×10^{-2}	5.17×10^{-2}	6.68×10^{-2}	5.28×10^{-2}	6.75×10^{-2}

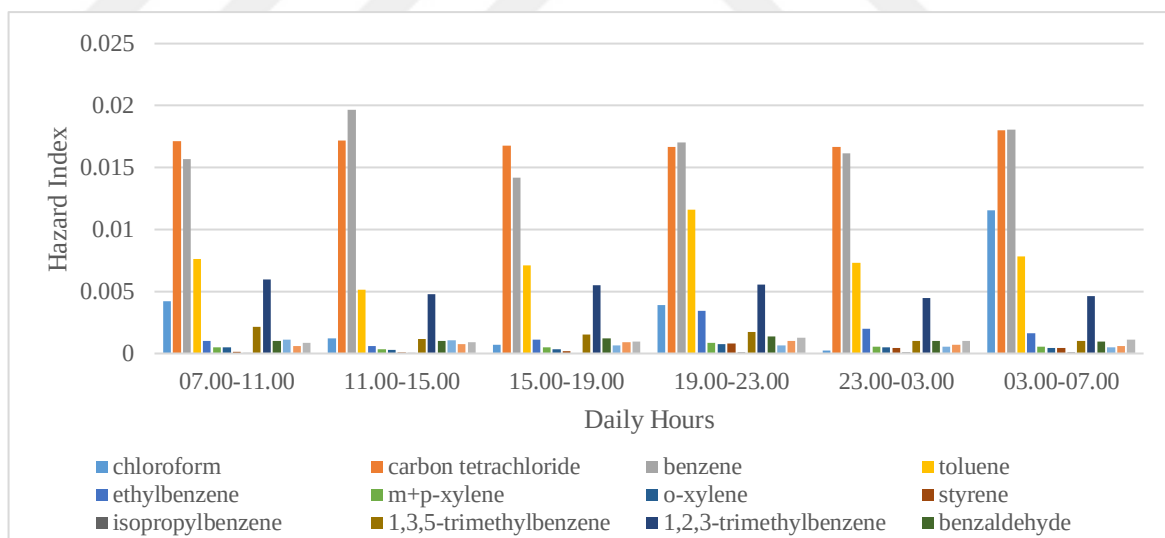


Figure 4.4. The Hazard Index versus daily hours graph for the photocopy center

The hours during which the photocopy center experiences the highest hazard index levels have been identified as 19:00–23:00 and 03:00–07:00. The hours when the hazard index (HI) value was relatively low were determined to be between 15:00 and 19:00. The graph of sampling hours versus total HI values is presented in Figure 4.5.

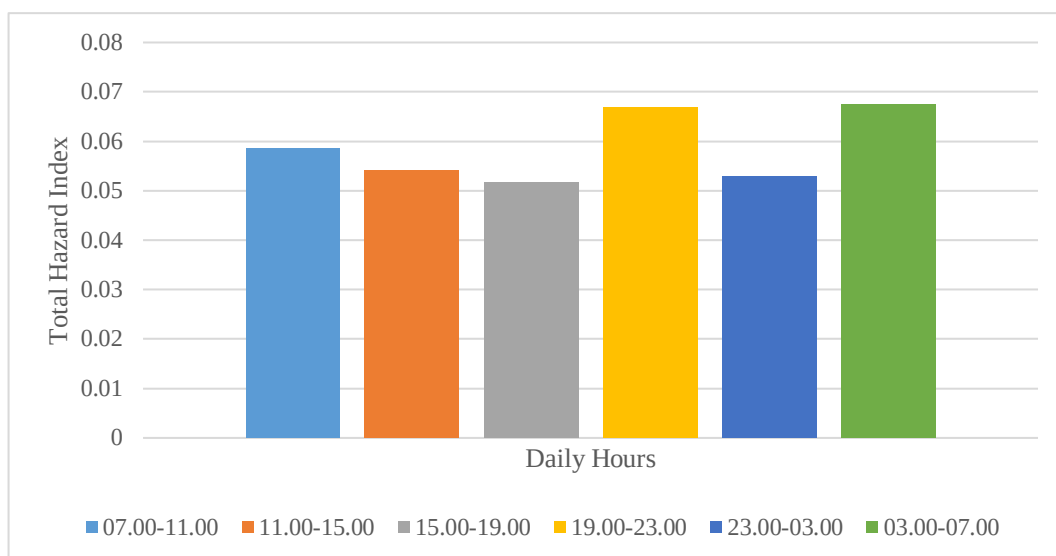


Figure 4.5. The total HI values versus sampling hours graph for the photocopy center

4.1.2 Painting Class

Air samples were collected from the painting class at the Faculty of Fine Arts of Bolu Abant İzzet Baysal University (BAIBU) between 1st of April 2022 and 8th of April 2022. Forty-two air samples were collected via active sampling over seven days. Sampling times were set at four hours as a result of experiments conducted in the art classes. Air samples were taken six times a day: 08.00 - 12.00, 12.00 - 16.00, 16.00 - 20.00, 20.00 - 00.00, 00.00 - 04.00, 04.00 - 08.00. Paint classes take place twice a week, on Mondays and Tuesdays between 8 a.m. and 5 p.m. The class size typically ranges from 10 to 15 students. In the air samples taken from the painting class, the VOCs with the highest average release throughout the sampling period were hexanal (42.6 $\mu\text{g}/\text{m}^3$); dodecane (9.52 $\mu\text{g}/\text{m}^3$); tridecane (8.86 $\mu\text{g}/\text{m}^3$); dl-limonene (7.42 $\mu\text{g}/\text{m}^3$); and alpha-pinene (6.58 $\mu\text{g}/\text{m}^3$). On the other hand, the VOCs with the lowest average concentration during the whole sampling period were crotonaldehyde (0.03 $\mu\text{g}/\text{m}^3$); benzothiazole (0.06 $\mu\text{g}/\text{m}^3$); and camphene (0.07 $\mu\text{g}/\text{m}^3$). During the sampling in the painting class, 1,2-dichloroethane, chlorobenzene, alpha-phellandrene, 4-methyl anisole, gamma-terpinene, alpha-terpinolene, and alloocimene compounds were not detected.

The mean, median and standard deviation values (in $\mu\text{g}/\text{m}^3$) of the VOCs determined in the air samples taken from the painting class on 1st and 8th of April 2022 are given in Table 4.4.

Table 4.4. The mean, median, and standard deviation values (in $\mu\text{g}/\text{m}^3$) of the VOCs determined in the air samples taken from the painting class.

VOCs	Arith. Mean	Median	Standard Deviation
isoprene	2.26	1.73	1.98
chloroform	0.763	0.469	0.862
carbon tetrachloride	0.604	0.638	0.122
benzene	0.332	0.300	0.224
heptane	0.609	0.329	0.972
crotonaldehyde	0.0287	0.00920	0.0621
toluene	5.93	4.87	3.94
hexanal	42.6	19.2	37.7
ethylbenzene	0.771	0.332	1.63
nonane	4.69	1.51	13.2
m+p-xylene	1.35	0.606	2.53
o-xylene	1.28	0.484	2.88
styrene	0.267	0.220	0.242
heptanal	0.765	0.718	0.504
alpha pinene	6.58	6.18	3.70
isopropylbenzene	0.617	0.591	0.618
camphene	0.0703	0.0679	0.0529
propylbenzene	0.900	0.111	2.97
1,3,5-trimethylbenzene	1.25	0.239	3.81
beta pinene	0.765	0.712	0.434
o-ethyltoluene	1.04	0.212	3.03
delta 3 carene	0.437	0.444	0.338
1,2,3-trimethylbenzene	3.71	1.16	9.56
benzaldehyde	2.31	2.15	1.71
1,4-cineole	4.41	3.17	4.18
dl-limonene	7.42	1.16	21.42
p cymene	0.773	0.0400	1.65
m cymene	0.271	0.0519	0.579
sabinene	0.424	0.184	0.611
ocimene	0.447	0.179	0.652
eucalyptol	1.91	0.38	5.63
1,4-diethylbenzene	1.23	0.202	2.03
1,3-diethylbenzene	2.49	0.404	7.37
1,2-dichlorobenzene	0.684	0.0971	1.24
phenol	1.52	1.19	1.15
dihyromyrcenol	0.570	0.389	0.514

Table 4.4 (continued). The mean, median, and standard deviation values (in $\mu\text{g}/\text{m}^3$) of the VOCs determined in the air samples taken from the painting class.

VOCs	Arith. Mean	Median	Standard Deviation
1-octanol	6.50	0.739	20.3
linalool	1.85	0.270	3.54
alloocimene	0.0758	0.0758	0.0769
acetophenone	0.700	0.628	0.519
L-fenchone	0.369	0.337	0.222
alpha terpinene	0.250	0.164	0.310
dodecane	9.52	3.28	16.8
camphor	0.675	0.675	0.844
terpinen-4-ol	0.912	0.470	0.992
decanal	1.72	1.68	0.916
alpha terpinol	0.439	0.281	0.570
naphthalene	0.305	0.179	0.422
tridecane	8.86	5.17	13.5
benzothiazole	0.0600	0.0307	0.0684
tetradecane	4.39	3.61	4.33

The compound hexanal, which is the most released in the painting class, is of biogenic origin, reaching the highest concentration at 20.00-00.00 on April 4 (Monday), with $122 \mu\text{g}/\text{m}^3$. Figure 4.6 shows the concentration versus daily hours graph of the compound hexanal. When the graph was examined, it showed a regular graph line with an average concentration of $73.3 \mu\text{g}/\text{m}^3$ on the 5th of April (Tuesday), the date of the lesson.

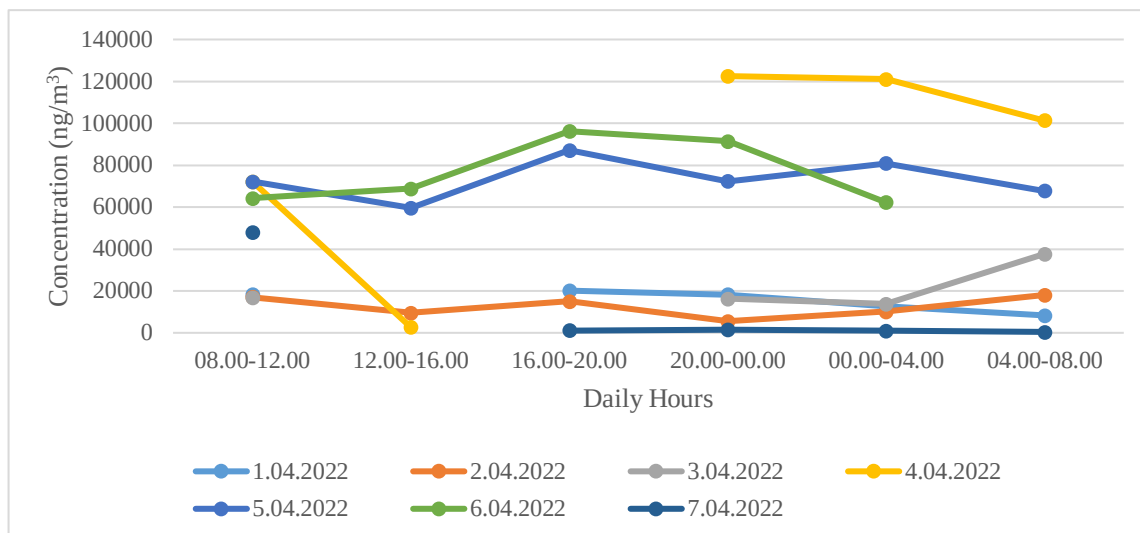


Figure 4.6. The concentration versus daily hours graph of the hexanal compound in the painting class

Figure 4.7 shows the concentration versus time graph of the dodecane compound, which is the second most released compound after the hexanal compound. Looking at the graph, the dodecane compound was mainly released on the 5th of April (the day of the lecture, Tuesday) between 16:00 and 00:00. Since the art class is naturally ventilated, the classroom is closed and cannot be ventilated after class. Therefore, it was observed that the concentration of the dodecane compound increases after class and decreases towards the morning. The dodecane compound is released from personal care products, including makeup and cosmetics (89).

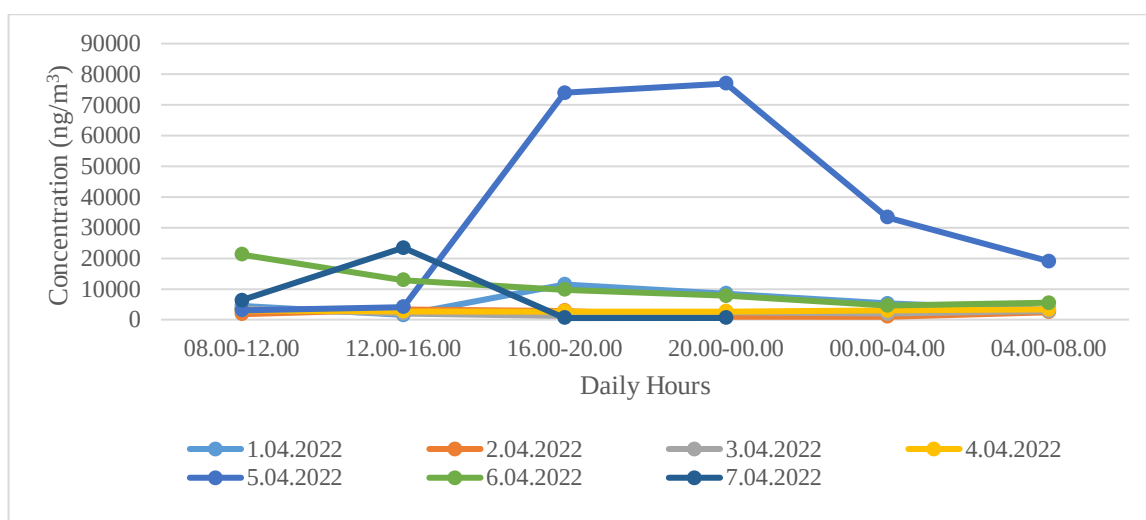


Figure 4.7. The concentration versus daily hours graph of the dodecane compound in the painting class

There is no ventilation system in the painting class, the ventilation of the classroom is done naturally. The classroom is ventilated by leaving the windows and doors open. After the class is over, there is no ventilation from evening to morning. For this reason, it has been observed that VOCs are concentrated in the evening hours.

4.1.2.1 Health Risk Assessment of Painting Class

The LCR values for the carcinogenic compounds and the HI values for the non-carcinogenic compounds were calculated and evaluated separately for oral and inhalation exposure using air samples collected from the painting class for seven days. Table 4.5 shows the results of the LCR and HI values of the painting class. When calculating the exposure times for teachers and students, the exposure times were the same, so the evaluations for teachers and students were made together.

Table 4.5. The LCR and HI values of the painting class

VOCs	LCR (Carcinogenic)		HI (Non-carcinogenic)	
	Inhalation	Oral	Inhalation	Oral
chloroform	-	-	-	3.63x10 ⁻³
carbon tetrachloride	6.04x10 ⁻⁷	2.01x10 ⁻⁶	1.01x10 ⁻³	7.17x10 ⁻³
benzene	1.22x10 ⁻⁷	2.37x10 ⁻⁷	1.85x10 ⁻³	3.96x10 ⁻³
toluene	-	-	1.98x10 ⁻⁴	3.53x10 ⁻³
ethylbenzene	-	-	1.28x10 ⁻⁴	3.67x10 ⁻⁴
m+p-xylene	-	-	2.25x10 ⁻³	3.22x10 ⁻⁴
o-xylene	-	-	2.13x10 ⁻³	3.05x10 ⁻⁴
styrene	-	-	4.44x10 ⁻⁵	6.35x10 ⁻⁵
isopropylbenzene	-	-	2.57x10 ⁻⁴	2.94x10 ⁻⁴
1,3,5-trimethylbenzene	-	-	3.47x10 ⁻³	5.95x10 ⁻³
1,2,3-trimethylbenzene	-	-	1.03x10 ⁻²	1.77x10 ⁻²
benzaldehyde	-	4.40x10 ⁻⁷	-	5.50x10 ⁻⁴
1,2-dichlorobenzene	-	-	-	3.62x10 ⁻⁴
phenol	-	-	-	2.41x10 ⁻⁴
acetophenone	-	-	-	3.33x10 ⁻⁴
naphthalene	-	-	1.70x10 ⁻²	7.27x10 ⁻⁴

For carcinogenic VOCs, the LCR value was calculated for inhalation and oral exposure. The VOCs exposed by inhalation were identified as benzene and carbon tetrachloride (CTC), and the LCR risk assessment was performed for these compounds. The result of LCR risk assessment results were found to be 1.22×10^{-7} and 6.04×10^{-7} , respectively. According to the LCR risk assessment range, the respiratory exposure to benzene and CTC compounds was determined to be a "negligible risk" for teachers and students in the painting class. Orally exposed VOCs were found to be CTC, benzene, and benzaldehyde, and LCR assessment was performed for these compounds. LCR assessment results were found to be 2.01×10^{-6} , 2.37×10^{-7} , and 4.40×10^{-7} , respectively. According to the LCR risk assessment range, the oral exposure to CTC, benzene, and benzaldehyde compounds was determined to be a "negligible risk" for teachers and students in the painting class.

For non-carcinogenic VOCs, HI values were calculated of respiratory and oral exposure. Non-carcinogenic VOCs in the painting class were CTC, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, styrene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, benzaldehyde, phenol, acetophenone, and naphthalene. VOCs exposed by inhalation were determined as CTC, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, 1,3,5-trimethylbenzene, and 1,2,3-trimethylbenzene. The HI values for VOCs for respiratory exposure were 1.01×10^{-3} , 1.85×10^{-3} , 1.98×10^{-4} , 1.28×10^{-4} , 2.25×10^{-3} , 2.13×10^{-3} , 4.44×10^{-5} , 2.57×10^{-4} , 3.47×10^{-3} , 1.03×10^{-2} , and 1.70×10^{-2} , respectively. According to the risk assessment, since the HI values of the above VOCs are less than 1, they are considered to pose a "negligible risk" to teachers and students. VOCs exposed orally were CTC, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, styrene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, benzaldehyde, phenol, acetophenone, and naphthalene. The HI values for oral exposure are respectively; They were found to be 3.63×10^{-3} , 7.17×10^{-3} , 3.96×10^{-3} , 3.53×10^{-3} , 3.67×10^{-4} , 3.22×10^{-4} , 3.05×10^{-4} , 6.35×10^{-5} , 2.94×10^{-4} , 5.95×10^{-3} , 1.77×10^{-2} , 5.50×10^{-4} , 3.62×10^{-4} , 2.41×10^{-4} , 3.33×10^{-4} , and 7.27×10^{-4} . According to the risk assessment, since the HI values of these VOCs are less than 1, they are considered to pose a "negligible risk" to teachers and students.

Total HI values of VOCs exposed orally were calculated according to the sampling hours in the painting class. The HI values and total HI values of VOCs according to sampling hours are given in Table 4.6.

Figure 4.8 shows the sampling hours versus the HI graph of the VOCs causing oral exposure in the painting class. When the graph was examined, the VOC with the highest hazard index was observed as 1,2,3-trimethylbenzene, followed by 1,3,5-trimethylbenzene.

Table 4.6. The HI values of VOCs and total HI value for each compound according to sampling hours in the printing class

VOCs	Hazard Index					
	08.00-12.00	12.00-16.00	16.00-20.00	20.00-00.00	00.00-04.00	04.00-08.00
carbon tetrachloride	7.50×10^{-3}	7.55×10^{-3}	7.02×10^{-3}	6.93×10^{-3}	7.23×10^{-3}	6.93×10^{-3}
benzene	3.71×10^{-3}	2.49×10^{-3}	4.15×10^{-3}	6.29×10^{-3}	4.80×10^{-3}	3.13×10^{-3}
toluene	3.22×10^{-3}	3.43×10^{-3}	4.32×10^{-3}	4.20×10^{-3}	3.33×10^{-3}	2.86×10^{-3}
ethylbenzene	1.31×10^{-4}	2.48×10^{-4}	8.55×10^{-4}	6.49×10^{-4}	2.18×10^{-4}	1.91×10^{-4}
m+p-xylene	1.48×10^{-4}	2.44×10^{-4}	6.89×10^{-4}	5.50×10^{-4}	2.23×10^{-4}	1.65×10^{-4}
o-xylene	1.14×10^{-4}	1.94×10^{-4}	7.61×10^{-4}	5.57×10^{-4}	1.80×10^{-4}	1.29×10^{-4}
styrene	5.36×10^{-5}	3.19×10^{-5}	3.14×10^{-5}	1.18×10^{-4}	8.76×10^{-5}	8.95×10^{-5}
1,3,5-trimethylbenzene	1.42×10^{-3}	2.54×10^{-3}	1.72×10^{-2}	1.36×10^{-2}	2.18×10^{-3}	1.41×10^{-3}
1,2,3-trimethylbenzene	7.01×10^{-3}	1.09×10^{-2}	3.84×10^{-2}	3.34×10^{-2}	1.03×10^{-2}	7.01×10^{-3}
benzaldehyde	4.88×10^{-4}	9.39×10^{-4}	5.39×10^{-4}	5.89×10^{-4}	4.81×10^{-4}	4.50×10^{-4}
phenol	2.30×10^{-4}	4.11×10^{-4}	2.78×10^{-4}	2.34×10^{-4}	1.66×10^{-4}	1.78×10^{-4}
acetophenone	2.85×10^{-4}	4.89×10^{-4}	3.48×10^{-4}	3.44×10^{-4}	2.22×10^{-4}	2.75×10^{-4}
naphthalene	5.93×10^{-4}	1.42×10^{-3}	7.71×10^{-4}	7.83×10^{-4}	4.60×10^{-4}	7.50×10^{-4}
Σ HI	2.49×10^{-2}	3.09×10^{-2}	7.53×10^{-2}	6.82×10^{-2}	2.99×10^{-2}	2.36×10^{-2}

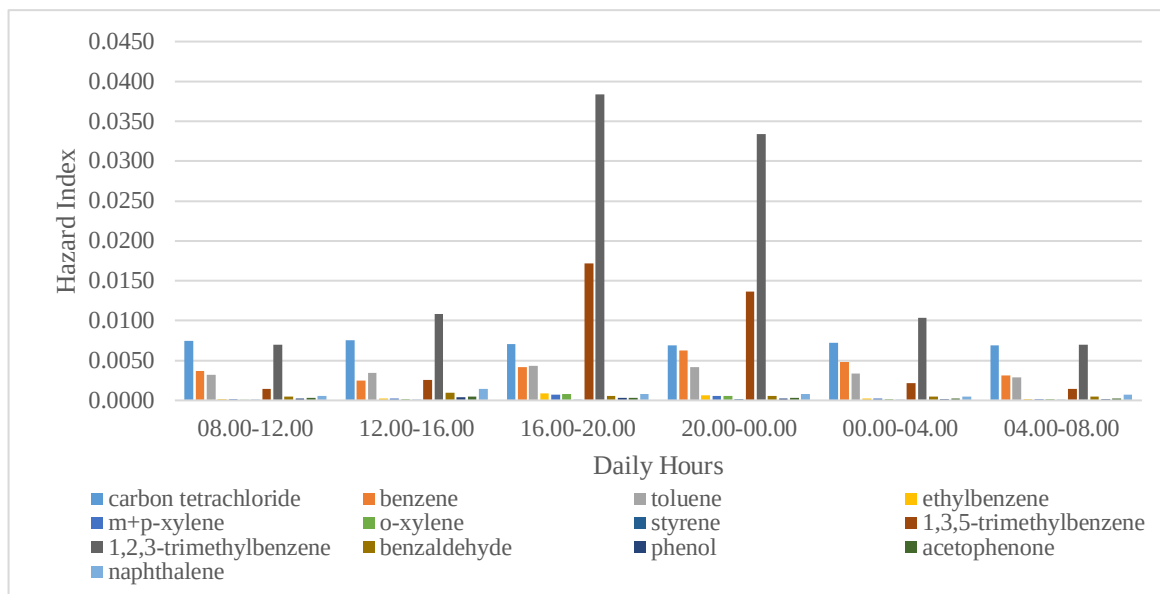


Figure 4.8. The sampling hours versus HI graph of VOCs in the painting class

The hours with the highest HI in the painting class were identified as 16:00 to 00:00. The hours with the lowest total HI values are identified as 04:00–08:00. The graph of total HI values versus sampling hours is shown in Figure 4.9.

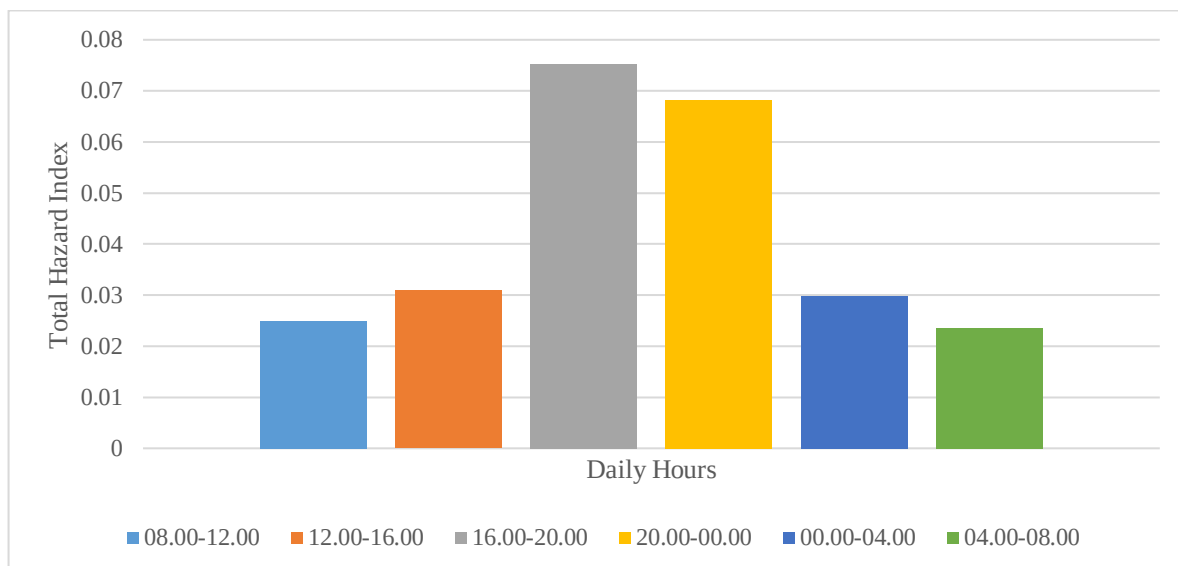


Figure 4.9. The total HI values versus daily hours graph for the painting class

4.1.3 Print-Making Class (I)

Air samples were collected from the print-making class at Bolu Abant İzzet Baysal University (BAIBU) Faculty of Fine Arts between 14th of April 2022 and 17th of April 2022. A total of 38 air samples were collected by active sampling over three days. The sampling period was determined to be 2 hours as a result of the trial experiments carried out in the print-making class. Sampling hours: 10.00 - 12.00, 12.00 - 14.00, 14.00 - 16.00, 16.00 - 18.00, 18.00 - 20.00, 20.00 - 22.00, 22.00 - 00.00, 00.00 - 02.00, 02.00 - 04.00, 04.00 - 06.00, 06.00 - 08.00, and 08.00 - 10.00 were selected and 12 air samples were collected per day. In the print-making class, printing lessons are held on Wednesdays and Thursdays, and painting lessons are held on Fridays. There are an average of 15 students in the class. The classroom has a ventilation system, but the ventilation system works only on Thursdays.

The VOCs with the highest average release in the print-making class were tridecane ($39.0 \mu\text{g}/\text{m}^3$); hexanal ($32.6 \mu\text{g}/\text{m}^3$); tetradecane ($28.5 \mu\text{g}/\text{m}^3$); and nonane ($16.9 \mu\text{g}/\text{m}^3$). Conversely, the VOCs with the lowest average release in the class are dihydromyrcenol ($0.15 \mu\text{g}/\text{m}^3$); dl-limonene ($0.16 \mu\text{g}/\text{m}^3$); acetophenone ($0.17 \mu\text{g}/\text{m}^3$); and phenol ($0.22 \mu\text{g}/\text{m}^3$). The standard deviation, mean, and median values (in $\mu\text{g}/\text{m}^3$) of the VOCs determined in the air samples taken from the print-making class between the specified dates are presented in Table 4.7.

The tridecane compound, which is the most prevalent in the print class, reached its highest concentration at $148 \mu\text{g}/\text{m}^3$ between 14:00 and 16:00 on April 14. Figure 4.10 presents a concentration versus daily hours graph of the tridecane compound. Upon examination of the graph, it was observed that the tridecane compound was released in the greatest quantity on Thursday, April 14, during the sampling period. Thereafter, the concentration decreased relatively on April 15. The tridecane compound is released from a variety of sources, including body cleansers, hair creams, and perfumes. It is also used as a solvent in inks. The tridecane compound has been identified as a constituent of personal care products and inks used in printing (90).

Table 4.7. The mean, median, and standard deviation values (in $\mu\text{g}/\text{m}^3$) of the VOCs determined in the print-making class (I)

VOCs	Arith. Mean	Median	Standard Deviation
carbon tetrachloride	0.868	0.860	0.0394
benzene	0.399	0.446	0.201
heptane	1.93	1.47	2.34
toluene	19.5	7.68	41.2
hexanal	32.6	32.0	11.2
ethylbenzene	1.54	0.518	3.35
nonane	16.9	8.66	27.5
m+p-xylene	3.03	1.14	6.89
o-xylene	2.75	1.15	5.74
styrene	0.305	0.305	0.102
heptanal	0.322	0.289	0.157
alpha pinene	5.41	4.63	2.32
isopropylbenzene	0.611	0.152	0.867
propylbenzene	2.08	1.13	3.04
1,3,5-trimethylbenzene	2.43	1.47	3.37
beta pinene	0.247	0.197	0.201
o-ethyltoluene	2.85	1.37	4.37
1,2,3-trimethylbenzene	8.72	5.51	10.8
benzaldehyde	0.919	0.936	0.261
1,4-cineole	1.69	1.03	2.42
dl-limonene	0.164	0.0628	0.166
p cymene	0.880	0.394	1.22
m cymene	0.405	0.145	0.526
eucalyptol	3.47	2.18	4.35
1,4-diethylbenzene	0.677	0.367	0.802
1,3-diethylbenzene	3.65	2.76	3.69
phenol	0.219	0.133	0.259
dihyromyrcenol	0.149	0.149	0.178
1-octanol	7.16	7.13	5.15
linalool	3.98	3.89	3.05
acetophenone	0.174	0.127	0.106
dodecane	9.72	7.13	6.52
terpinen-4-ol	4.07	4.07	0.0599
decanal	0.747	0.697	0.513
tridecane	39.0	24.2	32.4
tetradecane	28.5	21.0	18.2

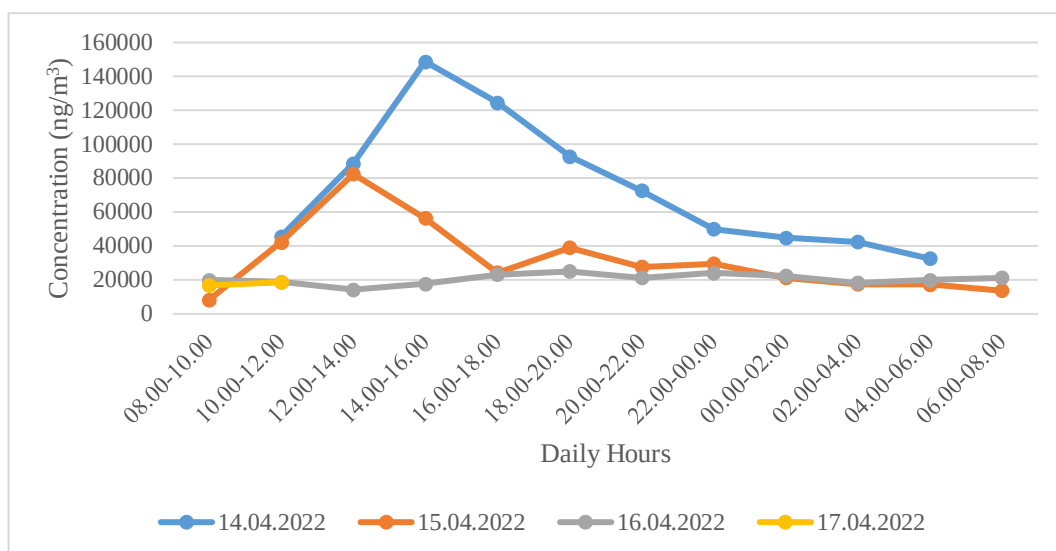


Figure 4.10. The concentration versus daily hours graph of the tridecane compound in print-making class (I)

The concentration versus daily hours graph of the tetradecane compound, another of the most released VOCs, is given in Figure 4.11. Upon examination of the graph, it can be seen that the greatest release occurred on Thursday, April 14, between 14.00 and 16.00, with a concentration of $73.6 \mu\text{g}/\text{m}^3$.

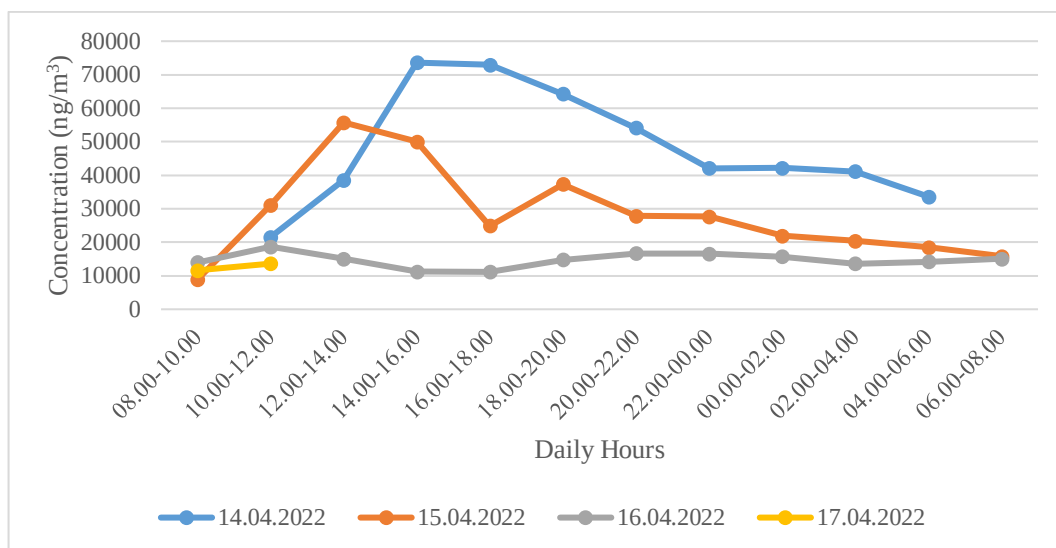


Figure 4.11. The concentration versus daily hours graph of the tetradecane compound in print-making class (I)

Looking at Figures 4.10 and 4.11, the day with the highest VOC release is the day when printing classes are held, and the ventilation system is open. When comparing the day of the printing class with the other days, it was observed that the VOC release was higher on the day of the printing class than on the other days, even though the ventilation system was open. Therefore, it was observed that the ventilation system is inadequate on the days when the printing classroom is in session.

4.1.3.1 Health Assessment of Print-Making Class (I)

Air samples collected from the print-making class for three days, LCR values for carcinogenic VOCs and HI values for non-carcinogenic VOCs were evaluated separately for oral and respiratory exposure. The results of LCR and HI values for VOCs in the print-making class are given in Table 4.8. Exposure calculations were performed separately for teachers and students. However, as a result of the calculations, the exposure time (ET) results for the teachers and students are the same. Therefore, risk assessments for teachers and students were made together.

Table 4.8. The LCR and HI values of the print-making class (I)

VOCs	Carcinogenic		Non-carcinogenic	
	Inhalation	Oral	Inhalation	Oral
carbon tetrachloride	8.68×10^{-7}	2.89×10^{-6}	1.45×10^{-3}	1.03×10^{-2}
benzene	1.46×10^{-7}	2.85×10^{-7}	2.22×10^{-3}	4.75×10^{-3}
toluene	-	-	6.51×10^{-4}	1.16×10^{-2}
ethylbenzene	-	-	2.56×10^{-4}	7.33×10^{-4}
m+p-xylene	-	-	5.05×10^{-3}	7.21×10^{-4}
o-xylene	-	-	4.58×10^{-3}	6.55×10^{-4}
styrene	-	-	5.08×10^{-5}	7.26×10^{-5}
isopropylbenzene	-	-	2.55×10^{-4}	2.91×10^{-4}
1,3,5-trimethylbenzene	-	-	6.74×10^{-3}	1.16×10^{-2}
1,2,3-trimethylbenzene	-	-	2.42×10^{-2}	4.15×10^{-2}
benzaldehyde	-	1.75×10^{-7}	-	2.19×10^{-4}
phenol	-	-	-	3.47×10^{-5}
acetophenone	-	-	-	8.31×10^{-5}

Inhalation and oral exposure to benzene, CTC, and benzaldehyde compounds, which are considered to be carcinogenic, were evaluated. The VOCs found to cause respiratory exposure were CTC and benzene, and LCRs were assessed for these VOCs. LCR values were found to be 8.68×10^{-7} and 1.46×10^{-7} , respectively. According to the LCR risk assessment range, the respiratory exposure to the specified VOCs for teachers and students in the classroom was evaluated as a "negligible" risk. Oral exposure to VOCs was identified for benzene, CTC, and benzaldehyde, and LCR assessment was performed for these compounds. LCR values were found to be 2.85×10^{-7} , 2.89×10^{-6} , and 1.75×10^{-7} , respectively. According to the LCR risk assessment ranges, the oral exposure to the specified VOCs for teachers and students in the classroom was evaluated as a "negligible" risk.

HI values were calculated for inhalation and oral exposure to non-carcinogenic VOCs. The VOCs that are in the print-making class that are considered non-carcinogenic are CTC; benzene; toluene; ethylbenzene; m+p-xylene; o-xylene; styrene; isopropylbenzene; 1,3,5-trimethylbenzene; 1,2,3-trimethylbenzene; benzaldehyde; phenol; and acetophenone. VOCs exposed by inhalation are CTC, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, styrene, isopropylbenzene, 1,3,5-trimethylbenzene, and 1,2,3-trimethylbenzene. The HI values for inhalation exposure of these VOCs were found to be 1.45×10^{-3} , 2.22×10^{-3} , 6.51×10^{-4} , 2.56×10^{-4} , 5.05×10^{-3} , 4.58×10^{-3} , 5.08×10^{-5} , 2.55×10^{-4} , 6.74×10^{-3} , and 2.42×10^{-2} , respectively. The HI values of the specified VOCs were found to be less than 1. According to the risk assessment range, inhalation exposure was evaluated as "negligible risk" for teachers and students due to HI values being less than 1. VOCs exposed orally were CTC, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, styrene, isopropylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, benzaldehyde, phenol, and acetophenone. The HI values for oral exposure were 1.03×10^{-2} , 4.75×10^{-3} , 1.16×10^{-2} , 7.33×10^{-4} , 7.21×10^{-4} , 6.55×10^{-4} , 7.26×10^{-5} , 2.91×10^{-4} , 1.16×10^{-2} , 4.15×10^{-2} , 2.19×10^{-4} , 3.47×10^{-5} , and 8.31×10^{-5} , respectively. The HI values of the specified VOCs were found to be less than 1. According to the risk assessment range, oral exposure was evaluated as "negligible risk" for teachers and students due to HI values being less than 1.

VOCs exposed orally the HI and total HI values were calculated according to the sampling hours in the print-making class. The HI and total HI values of VOCs according to sampling hours are given in Table 4.9. When considering the total HI values, no values exceeding the HI risk range were found during the sampling hours.

Figure 4.12 shows the graph of daily hours versus HI values of VOCs with oral exposure in the print-making class. Examining the graph, the VOCs with the highest HI values are determined as 1,2,3-trimethylbenzene and toluene.

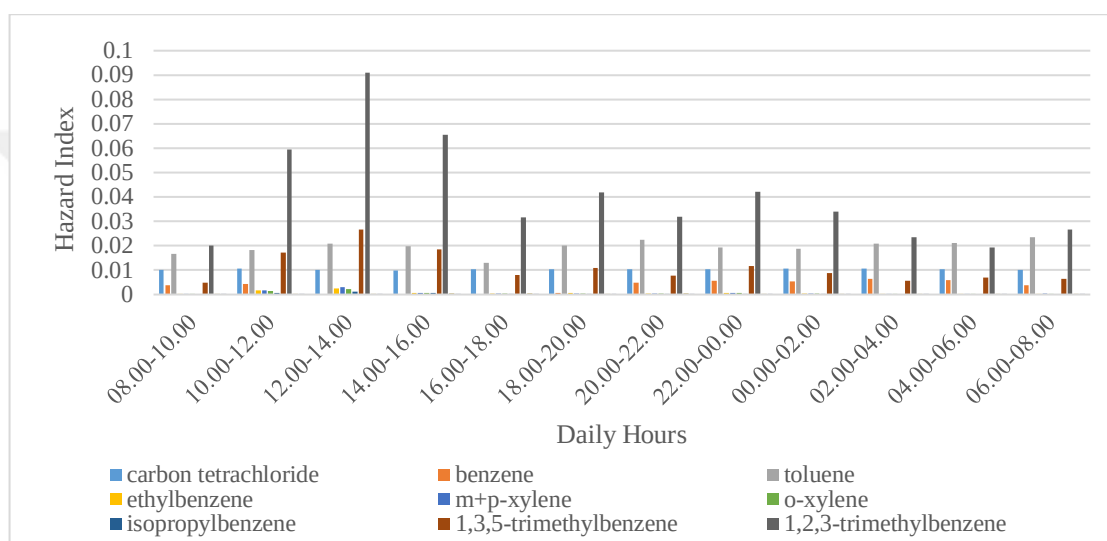


Figure 4.12. The sampling hours versus HI graph of VOCs in the print-making class (I)

Table 4.9. The HI values of VOCs and total HI value for each compound according to sampling hours in the print-making class (I)

VOCs	Hazard Index											
	08.00-10.00	10.00-12.00	12.00-14.00	14.00-16.00	16.00-18.00	18.00-20.00	20.00-22.00	22.00-00.00	00.00-02.00	02.00-04.00	04.00-06.00	06.00-08.00
carbon tetrachloride	9.99x10 ⁻³	1.06x10 ⁻²	9.99x10 ⁻³	9.95x10 ⁻³	1.05x10 ⁻²	1.03x10 ⁻²	1.03x10 ⁻²	1.03x10 ⁻²	1.06x10 ⁻²	1.06x10 ⁻²	1.04x10 ⁻²	1.02x10 ⁻²
benzene	3.76x10 ⁻³	4.38x10 ⁻³	-	-	-	5.48x10 ⁻⁴	4.90x10 ⁻³	5.71x10 ⁻³	5.43x10 ⁻³	6.55x10 ⁻³	5.93x10 ⁻³	3.86x10 ⁻³
toluene	1.68x10 ⁻²	1.81x10 ⁻²	2.08x10 ⁻²	1.99x10 ⁻²	1.30x10 ⁻²	2.01x10 ⁻²	2.25x10 ⁻²	1.93x10 ⁻²	1.87x10 ⁻²	2.09x10 ⁻²	2.12x10 ⁻²	2.34x10 ⁻²
ethylbenzene	2.25x10 ⁻⁴	1.72x10 ⁻³	2.59x10 ⁻³	6.33x10 ⁻⁴	3.74x10 ⁻⁴	5.71x10 ⁻⁴	3.35x10 ⁻⁵	7.86x10 ⁻⁴	4.22x10 ⁻⁴	2.20x10 ⁻⁴	1.75x10 ⁻⁴	2.47x10 ⁻⁴
m+p-xylene	2.53x10 ⁻⁴	1.58x10 ⁻³	2.93x10 ⁻³	6.38x10 ⁻⁴	3.48x10 ⁻⁴	4.89x10 ⁻⁴	3.07x10 ⁻⁴	6.09x10 ⁻⁴	3.62x10 ⁻⁴	2.28x10 ⁻⁴	1.94x10 ⁻⁴	2.72x10 ⁻⁴
o-xylene	2.25x10 ⁻⁴	1.44x10 ⁻³	2.33x10 ⁻³	6.60x10 ⁻⁴	3.37x10 ⁻⁴	2.85x10 ⁻⁴	3.32x10 ⁻⁴	6.17x10 ⁻⁴	3.92x10 ⁻⁴	2.28x10 ⁻⁴	1.82x10 ⁻⁴	2.44x10 ⁻⁴
isopropylbenzene	-	5.49x10 ⁻⁴	1.25x10 ⁻³	6.84x10 ⁻⁴	6.86x10 ⁻⁵	6.86x10 ⁻⁵	-	7.71x10 ⁻⁵	-	-	-	-
1,3,5-trimethylbenzene	4.80x10 ⁻³	1.71x10 ⁻²	2.68x10 ⁻²	1.85x10 ⁻²	7.94x10 ⁻³	1.09x10 ⁻²	7.79x10 ⁻³	1.17x10 ⁻²	8.87x10 ⁻³	5.75x10 ⁻³	6.99x10 ⁻³	6.49x10 ⁻³
1,2,3-trimethylbenzene	2.01x10 ⁻²	5.94x10 ⁻²	9.09x10 ⁻²	6.55x10 ⁻²	3.16x10 ⁻²	4.19x10 ⁻²	3.20x10 ⁻²	4.22x10 ⁻²	3.39x10 ⁻²	2.36x10 ⁻²	1.93x10 ⁻²	2.67x10 ⁻²
benzaldehyde	1.37x10 ⁻⁴	2.53x10 ⁻⁴	2.01x10 ⁻⁴	2.73x10 ⁻⁴	2.82x10 ⁻⁴	2.54x10 ⁻⁴	2.72x10 ⁻⁴	2.21x10 ⁻⁴	2.15x10 ⁻⁴	1.88x10 ⁻⁴	1.28x10 ⁻⁴	1.79x10 ⁻⁴
phenol	-	1.01x10 ⁻⁴	-	5.35x10 ⁻⁵	-	-	-	-	-	-	-	-
Σ HI	5.63x10 ⁻²	1.15x10 ⁻¹	1.58x10 ⁻¹	1.17x10 ⁻¹	6.45x10 ⁻²	8.54x10 ⁻²	7.87x10 ⁻²	9.15x10 ⁻²	7.89x10 ⁻²	6.82x10 ⁻²	6.45x10 ⁻²	7.17x10 ⁻²

In the print-making class, the hours with the highest hazard index were determined as 12.00 - 14.00, followed by 10.00 - 12.00, 14.00 - 16.00. The graph of daily hours versus total HI values is shown in Figure 4.13. The hours between 8 a.m. and 6 p.m. were determined as the hours when the HI values were highest.

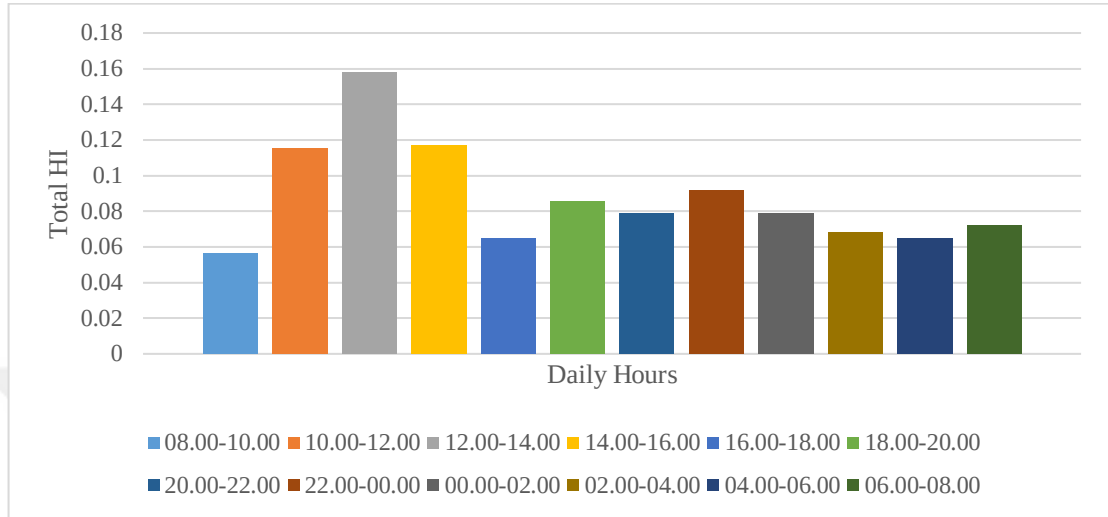


Figure 4.13. The Total HI values versus daily hours graph for the print-making class (I)

4.1.4 Print-Making Class (II)

A total of 35 active air samples were collected from the printing class of Bolu Abant İzzet Baysal University (BAIBU) Faculty of Education on 19th of April 2022 and 21st of April 2022. In the first two days of sampling, the sampling period was 2 hours, and 24 air samples were taken. Then, as the GC-MS instrument gave a detector-saturation warning for the toluene compound, the sampling period on the third day was reduced to 1 hour and a total of 11 air samples were taken on the third day. In the print-making class, classes are held only on Wednesdays and Thursdays and there are an average of 10 students in the class. The classroom does not have a ventilation system, it is only ventilated through the windows. On Wednesday (April 20), there were 16 students in the class and the lesson started at 09.00 and ended at 13.00. The windows were never opened, and the classroom was not ventilated during the lesson. In the lesson held on Thursday (April 21), there were five

students, the lesson continued throughout the day and the windows were opened only once during the lesson.

Table 4.10. The mean, median, and standard deviation values (in $\mu\text{g}/\text{m}^3$) of the VOCs determined in the print-making class (II)

VOCs	Arith. Mean	Median	Standard Deviation
isoprene	5.91	4.73	5.11
carbon tetrachloride	0.976	0.841	0.283
benzene	0.176	0.151	0.135
heptane	1.63	0.988	1.94
toluene	183	159	67.1
hexanal	15.6	15.2	6.99
ethylbenzene	6.20	4.16	7.19
nonane	110	124	74.1
m+p-xylene	12.1	8.74	12.5
o-xylene	34.7	30.1	32.3
styrene	0.776	0.426	1.04
heptanal	0.452	0.452	0.0908
isopropylbenzene	5.91	4.14	6.37
propylbenzene	19.0	16.1	19.9
1,3,5-trimethylbenzene	41.5	39.8	35.5
beta pinene	0.464	0.311	0.414
o-ethyltoluene	33.6	31.3	29.6
1,2,3-trimethylbenzene	77.2	93.3	48.7
benzaldehyde	1.09	0.787	0.678
1,4-cineole	3.24	2.57	2.89
dl-limonene	1.27	0.908	1.20
p cymene	13.7	10.3	16.2
m cymene	4.89	3.26	6.03
eucalyptol	41.3	41.9	35.3
1,4-diethylbenzene	6.95	4.53	8.37
1,3-diethylbenzene	42.0	33.4	42.3
phenol	0.861	0.549	0.682
1-octanol	39.1	29.1	40.3
linalool	14.8	10.1	15.3
acetophenone	2.04	1.45	1.78
dodecane	13.5	9.74	11.7
decanal	1.13	0.773	1.01
naphthalene	0.644	0.451	0.468
tridecane	38.6	26.6	37.5
tetradecane	27.2	26.7	17.8

The VOCs with the highest average release in the print-making class (II) are toluene ($183 \mu\text{g}/\text{m}^3$), nonane ($109 \mu\text{g}/\text{m}^3$), and 1,2,3-trimethylbenzene ($77.3 \mu\text{g}/\text{m}^3$). On the other hand, the VOCs with the lowest average emissions are benzene ($0.18 \mu\text{g}/\text{m}^3$), heptanal ($0.45 \mu\text{g}/\text{m}^3$), and beta-pinene ($0.46 \mu\text{g}/\text{m}^3$). The mean, median and standard deviation values (in $\mu\text{g}/\text{m}^3$) of the VOCs determined in the print-making class between 19th of April and 21st of April 2022 are given in Table 4.10.

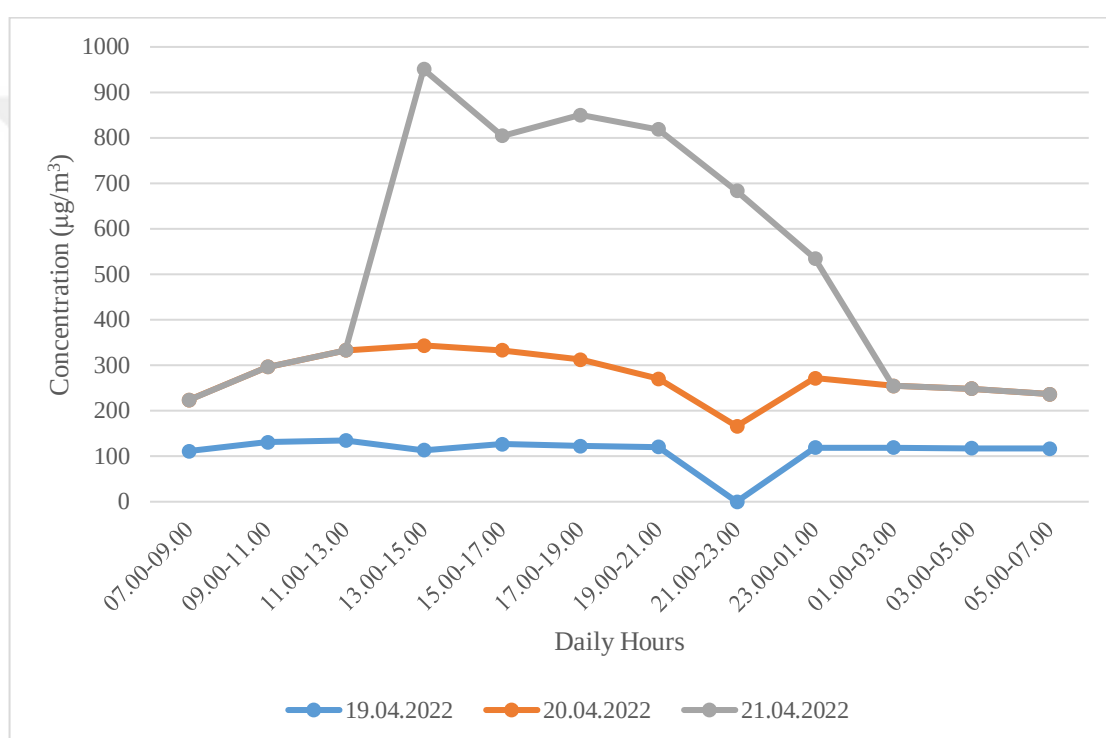


Figure 4.14. The concentration versus daily hours graph of the toluene compound in print-making class (II)

The toluene compound, which is the most released in the class, reached its highest concentration at 13.00-15.00 on April 21, with $606.9 \mu\text{g}/\text{m}^3$. Figure 4.14 shows the graph of the concentration versus daily hours of the toluene compound. It can be seen from the graph that the most intense release of the toluene compound occurred on 21st of April, due to the printing activities in the classroom. Thinner is

used to thin the paint in classroom printing processes, so toluene is the most emitted VOC in this class. The analysis revealed that the thinner contained toluene, ethylbenzene, and xylene compounds (72).

Although the windows were open during the lesson held on April 21, the toluene compound was found to be more concentrated in the classroom than on other days. In this case, it has been observed that ventilation through windows was found to be insufficient.

4.1.4.1 Health Assessment of Print-Making Class (II)

Air samples collected from the print-making class (II) for three days, the LCR value for carcinogenic VOCs, and the HI values for non-carcinogenic VOCs were evaluated separately according to inhalation and oral exposure. Since the chronic daily intake (CDI) amount of teachers and students is different, exposure calculations were performed separately. In Table 4.11, the results of the LCR and HI values of VOCs in the print-making class (II) are given for teachers.

For teachers, oral and respiratory exposures to carcinogenic and non-carcinogenic VOCs were evaluated separately. When the carcinogenic effect of VOCs is examined; VOCs exposed through inhalation were found to be benzene and CTC. VOCs that were exposed orally were found to be benzene, CTC, and benzaldehyde. When the LCR values of oral and respiratory exposures were examined, it was concluded that the specified VOCs did not pose a cancer risk as their exposures were outside the LCR risk range.

Table 4.11. The results of the LCR and HI values of VOCs in the print-making class (II) for teachers

VOCs	LCR		HI	
	Inhalation	Oral	Inhalation	Oral
carbon tetrachloride	1.95×10^{-6}	6.51×10^{-6}	3.25×10^{-3}	2.32×10^{-2}
benzene	1.29×10^{-7}	2.51×10^{-7}	1.95×10^{-3}	4.19×10^{-3}
toluene	-	-	1.22×10^{-2}	2.18×10^{-1}
ethylbenzene	-	-	2.07×10^{-3}	5.91×10^{-3}
m+p-xylene	-	-	4.04×10^{-2}	5.78×10^{-3}
o-xylene	-	-	1.16×10^{-1}	1.65×10^{-2}
styrene	-	-	2.59×10^{-4}	3.69×10^{-4}
isopropylbenzene	-	-	4.92×10^{-3}	5.63×10^{-3}
1,3,5-trimethylbenzene	-	-	2.30×10^{-1}	3.95×10^{-1}
1,2,3-trimethylbenzene	-	-	4.29×10^{-1}	7.36×10^{-1}
benzaldehyde	-	4.17×10^{-7}	-	5.21×10^{-4}
phenol	-	-	-	2.73×10^{-4}
acetophenone	-	-	-	1.94×10^{-3}
naphthalene	-	-	7.16×10^{-2}	3.07×10^{-3}

Regarding the non-carcinogenic effects of VOCs, the VOCs exposed by inhalation were found to be CTC, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, styrene, isopropylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, and naphthalene. The VOCs exposed orally CTC, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, styrene, isopropylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, benzaldehyde, phenol, acetophenone, and naphthalene. When the HI risk values of oral and respiratory exposure were examined, the HI values of the specified VOCs were found to be less than 1. According to the HI risk range, values less than 1 are considered "negligible risk". For this reason, the mentioned VOCs were considered to pose a "negligible risk" to teachers.

For teachers exposed to oral VOCs the HI and total HI values were calculated according to the sampling hours in the classroom. The HI and total HI values of VOCs according to sampling times are given in Table 4.12. When the total HI values are examined, it is seen that the total HI values are above 1 between 09.00 and 01.00. According to the HI risk ranges, this condition is not carcinogenic, but it causes a negative effect on human health.

Table 4.12. The HI and total HI values of VOCs according to sampling times in print-making class (II) for teachers

VOCs	Hazard Index for Teachers											
	07.00-09.00	09.00-11.00	11.00-13.00	13.00-15.00	15.00-17.00	17.00-19.00	19.00-21.00	21.00-23.00	23.00-01.00	01.00-03.00	03.00-05.00	05.00-07.00
carbon tetrachloride	1.94×10^{-2}	1.89×10^{-2}	1.90×10^{-2}	3.44×10^{-2}	3.47×10^{-2}	1.90×10^{-2}	3.41×10^{-2}	6.80×10^{-2}	1.95×10^{-2}	1.86×10^{-2}	1.93×10^{-2}	1.93×10^{-2}
benzene	-	-	-	9.00×10^{-3}	1.03×10^{-2}	2.14×10^{-3}	3.40×10^{-3}	4.33×10^{-3}	5.10×10^{-3}	4.40×10^{-3}	2.57×10^{-3}	1.83×10^{-3}
toluene	0.133	0.176	0.198	0.377	0.319	0.337	0.325	0.407	0.212	0.151	0.148	0.141
ethylbenzene	1.46×10^{-3}	4.13×10^{-3}	7.77×10^{-3}	1.60×10^{-2}	9.86×10^{-3}	9.83×10^{-3}	6.45×10^{-3}	1.10×10^{-2}	4.49×10^{-3}	2.24×10^{-3}	2.09×10^{-3}	1.68×10^{-3}
m+p-xylene	1.63×10^{-3}	3.98×10^{-3}	7.58×10^{-3}	1.34×10^{-2}	9.82×10^{-3}	1.01×10^{-2}	6.62×10^{-3}	1.11×10^{-2}	4.79×10^{-3}	2.51×10^{-3}	2.35×10^{-3}	1.88×10^{-3}
o-xylene	5.05×10^{-3}	9.74×10^{-3}	1.37×10^{-2}	3.56×10^{-2}	2.61×10^{-2}	2.94×10^{-2}	2.15×10^{-2}	3.85×10^{-2}	1.29×10^{-2}	7.89×10^{-3}	7.39×10^{-3}	5.77×10^{-3}
styrene	7.62×10^{-5}	2.03×10^{-4}	4.07×10^{-4}	9.78×10^{-4}	5.69×10^{-4}	5.36×10^{-4}	2.82×10^{-4}	5.27×10^{-4}	4.05×10^{-4}	2.10×10^{-4}	1.78×10^{-4}	1.08×10^{-4}
isopropylbenzene	2.10×10^{-3}	2.76×10^{-3}	5.85×10^{-3}	1.83×10^{-2}	1.16×10^{-2}	1.19×10^{-2}	7.32×10^{-3}	9.22×10^{-3}	6.82×10^{-3}	3.85×10^{-3}	3.57×10^{-3}	2.50×10^{-3}
1,3,5-trimethylbenzene	0.182	0.289	0.481	0.703	0.522	0.597	0.490	0.879	0.412	0.286	0.281	0.208
1,2,3-trimethylbenzene	0.443	0.629	0.730	1.223	0.868	1.079	1.078	1.704	0.555	0.507	0.505	0.468
benzaldehyde	5.26×10^{-4}	7.67×10^{-4}	3.04×10^{-4}	1.07×10^{-3}	8.17×10^{-4}	7.12×10^{-4}	2.64×10^{-4}	-	2.30×10^{-4}	2.01×10^{-4}	2.30×10^{-4}	5.13×10^{-4}
phenol	3.28×10^{-4}	4.96×10^{-4}	3.35×10^{-4}	1.17×10^{-4}	3.34×10^{-4}	4.43×10^{-4}	2.52×10^{-4}	4.31×10^{-4}	2.88×10^{-4}	2.85×10^{-4}	3.97×10^{-4}	3.39×10^{-4}
Σ HI	0.789	1.14	1.46	2.43	1.81	2.10	1.97	3.13	1.23	0.984	0.972	0.851

In the print-making class (II), the hours with the highest hazard index were determined as 21.00-23.00 and 13.00-15.00, and total HI values were found to be 3.13 and 2.43, respectively. Figure 4.15 shows the graph of daily hours versus total HI values for teachers. Looking at the graph, it can be seen that the total HI values for teachers are above 1 for most of the day.

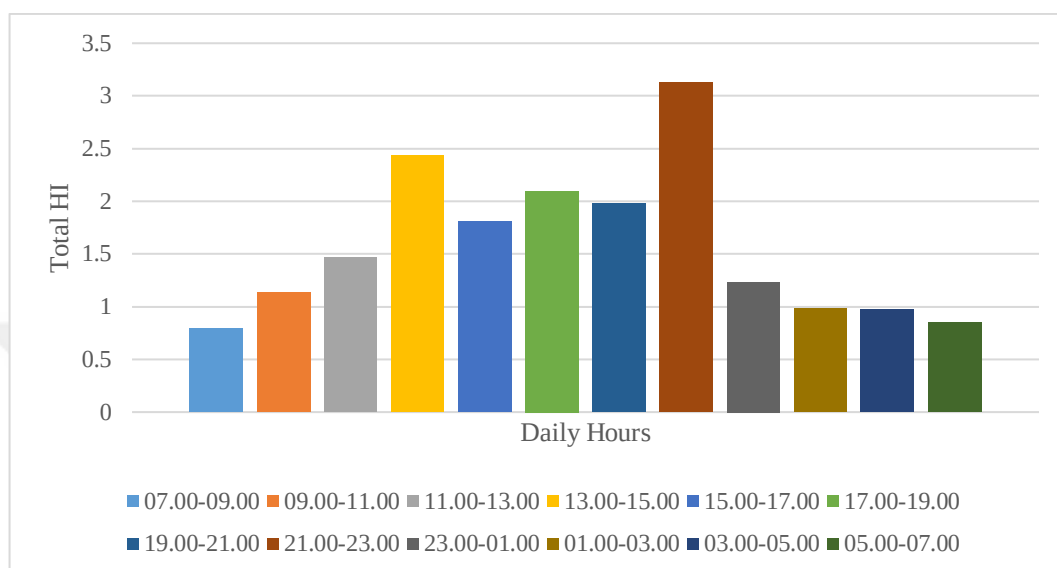


Figure 4.15. The total HI values versus daily hours graph in the print-making class (II) for teachers

For students, oral and respiratory exposures to carcinogenic and non-carcinogenic VOCs were evaluated separately. In Table 4.13, the results of the LCR and HI values of VOCs in the print-making class (II) are given for students. When the carcinogenic effect for students is examined, VOCs exposed through inhalation were found to be CTC and benzene. The VOCs exposed to the mouth were CTC, benzene, and benzaldehyde. It has been determined that respiratory and oral exposures do not carry a cancer risk since the LCR values are outside the risk range. Regarding the non-carcinogenic effect for students the VOCs exposed by inhalation were CTC, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, styrene, isopropylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, and naphthalene. The VOCs exposed to orally were CTC, benzene, and toluene, ethylbenzene, m+p-xylene, o-xylene, styrene, isopropylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, benzaldehyde, phenol, acetophenone, and naphthalene.

Table 4.13. The results of the LCR and HI values of VOCs in the print-making class (II) for students

VOCs	LCR		HI	
	Inhalation	Oral	Inhalation	Oral
carbon tetrachloride	9.76×10^{-7}	3.25×10^{-6}	1.63×10^{-3}	1.16×10^{-2}
benzene	6.45×10^{-8}	1.26×10^{-7}	9.77×10^{-4}	2.09×10^{-3}
toluene	-	-	6.11×10^{-3}	1.09×10^{-1}
ethylbenzene	-	-	1.03×10^{-3}	2.95×10^{-3}
m+p-Xylene	-	-	2.02×10^{-2}	2.89×10^{-3}
o-Xylene	-	-	5.78×10^{-2}	8.26×10^{-3}
styrene	-	-	1.29×10^{-4}	1.85×10^{-4}
isopropylbenzene	-	-	2.46×10^{-3}	2.81×10^{-3}
1,3,5-Trimethylbenzene	-	-	1.15×10^{-1}	1.97×10^{-1}
1,2,3-Trimethylbenzene	-	-	2.15×10^{-1}	3.68×10^{-1}
benzaldehyde	-	2.08×10^{-7}	-	2.61×10^{-4}
phenol	-	-	-	1.37×10^{-4}
acetophenone	-	-	-	9.71×10^{-4}
naphthalene	-	-	3.58×10^{-2}	1.53×10^{-3}

When the HI values of oral and respiratory exposures were examined, the HI values of the mentioned VOCs were found to be less than 1. According to the HI risk range, values less than 1 are considered as "negligible risk". Therefore, the mentioned VOCs were evaluated as "negligible risk" for students.

The VOCs exposed orally the HI and Total HI values were calculated for students according to the sampling hours in the classroom. In Table 4.14, the HI and total HI values of VOCs according to sampling hours are given. When examining the total HI values, the total HI values are greater than 1 at 21.00-23.00, 13.00-15.00, and 17.00-19.00 and the total HI values are found to be 1.57, 1.22, and 1.05, respectively. According to the risk ranges, this condition is not carcinogenic, but it causes a negative impact on the health of the students.

Table 4.14. The HI and total HI values of VOCs according to sampling times in print-making class (II) for students

VOCs	Hazard Index for Students											
	07.00-09.00	09.00-11.00	11.00-13.00	13.00-15.00	15.00-17.00	17.00-19.00	19.00-21.00	21.00-23.00	23.00-01.00	01.00-03.00	03.00-05.00	05.00-07.00
carbon tetrachloride	9.68x10 ⁻³	9.45x10 ⁻³	9.51x10 ⁻³	1.72x10 ⁻²	1.74x10 ⁻²	9.51x10 ⁻³	1.70x10 ⁻²	3.40x10 ⁻²	9.75x10 ⁻³	9.32x10 ⁻³	9.67x10 ⁻³	9.63x10 ⁻³
benzene	-	-	-	4.50x10 ⁻³	5.13x10 ⁻³	1.07x10 ⁻³	1.70x10 ⁻³	2.17x10 ⁻³	2.55x10 ⁻³	2.20x10 ⁻³	1.29x10 ⁻³	9.17x10 ⁻⁴
toluene	6.66x10 ⁻²	8.81x10 ⁻²	9.91x10 ⁻²	0.189	0.159	0.169	0.162	0.203	0.106	7.57x10 ⁻²	7.39x10 ⁻²	7.03x10 ⁻²
ethylbenzene	7.28x10 ⁻⁴	2.06x10 ⁻³	3.88x10 ⁻³	8.02x10 ⁻³	4.93x10 ⁻³	4.91x10 ⁻³	3.22x10 ⁻³	5.52x10 ⁻³	2.24x10 ⁻³	1.12x10 ⁻³	1.04x10 ⁻³	8.39x10 ⁻⁴
m+p-xylene	8.16x10 ⁻⁴	1.99x10 ⁻³	3.79x10 ⁻³	6.72x10 ⁻³	4.91x10 ⁻³	5.06x10 ⁻³	3.31x10 ⁻³	5.55x10 ⁻³	2.39x10 ⁻³	1.25x10 ⁻³	1.18x10 ⁻³	9.40x10 ⁻⁴
o-xylene	2.52x10 ⁻³	4.87x10 ⁻³	6.85x10 ⁻³	1.78x10 ⁻²	1.30x10 ⁻²	1.47x10 ⁻²	1.08x10 ⁻²	1.92x10 ⁻²	6.45x10 ⁻³	3.95x10 ⁻³	3.69x10 ⁻³	2.89x10 ⁻³
styrene	-	1.01x10 ⁻⁴	2.03x10 ⁻⁴	4.89x10 ⁻⁴	2.85x10 ⁻⁴	2.68x10 ⁻⁴	1.41x10 ⁻⁴	2.64x10 ⁻⁴	2.03x10 ⁻⁴	1.05x10 ⁻⁴	8.88x10 ⁻⁵	5.40x10 ⁻⁵
isopropylbenzene	1.10x10 ⁻³	1.38x10 ⁻³	2.93x10 ⁻³	9.13x10 ⁻³	5.82x10 ⁻³	5.97x10 ⁻³	3.66x10 ⁻³	4.61x10 ⁻³	3.41x10 ⁻³	1.92x10 ⁻³	1.79x10 ⁻³	1.25x10 ⁻³
1,3,5-trimethylbenzene	9.09x10 ⁻²	0.145	2.40x10 ⁻¹	0.351	0.261	0.299	0.245	0.439	0.206	0.143	0.140	0.104
1,2,3-trimethylbenzene	0.222	0.314	0.365	0.611	0.434	0.539	0.539	0.852	0.277	0.253	0.253	0.234
benzaldehyde	2.63x10 ⁻⁴	3.83x10 ⁻⁴	1.52x10 ⁻⁴	5.37x10 ⁻⁴	4.09x10 ⁻⁴	3.56x10 ⁻⁴	1.32x10 ⁻⁴	-	1.15x10 ⁻⁴	1.01x10 ⁻⁴	1.15x10 ⁻⁴	2.56x10 ⁻⁴
phenol	1.64x10 ⁻⁴	2.48x10 ⁻⁴	1.67x10 ⁻⁴	5.87x10 ⁻⁵	1.67x10 ⁻⁴	2.21x10 ⁻⁴	1.26x10 ⁻⁴	2.15x10 ⁻⁴	1.44x10 ⁻⁴	1.43x10 ⁻⁴	1.99x10 ⁻⁴	1.69x10 ⁻⁴
Σ HI	0.394	0.568	0.732	1.216	0.907	1.049	0.987	1.566	0.617	0.492	0.486	0.425

The graph of daily hours versus total HI values for students in the print-making class (II) is shown in Figure 4.16. The hours when the HI is highest for the students in the classroom were determined as 21.00-23.00 and 13.00-15.00. Classes are held in the classroom between 13.00 and 15.00, when the total HI value is high, and VOCs are concentrated at these hours due to the lack of ventilation system in the classroom.

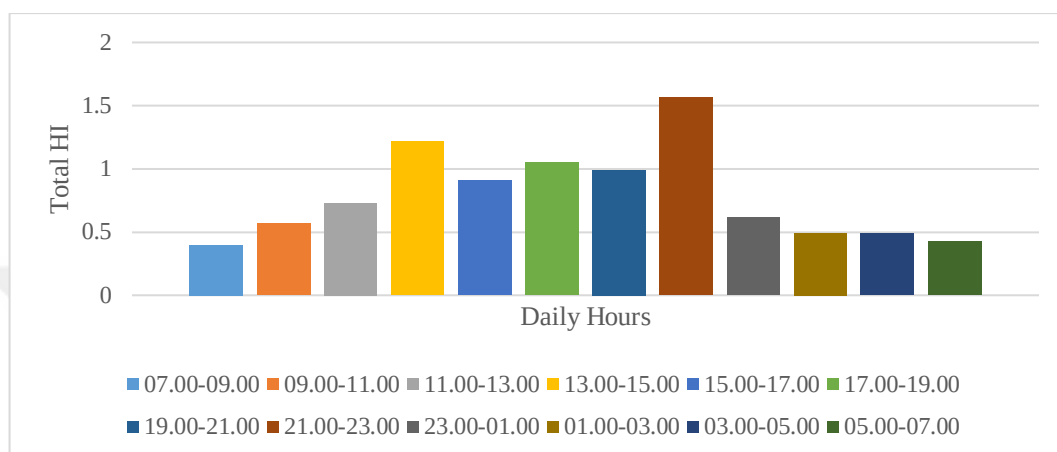


Figure 4.16. The Total HI values versus daily hours graph in the print-making class (II) for students

The health risk analysis was conducted separately for teachers and students. Teachers are exposed to VOCs for longer periods of their lives than students. In order to prevent VOC exposures from causing serious health problems for teachers throughout their working hours, the classroom should be frequently ventilated during the day and a ventilation system should be installed in the classroom. It is recommended that teachers' rooms be moved from their current location within the classroom to a more suitable location outside the classroom.

4.1.5 Tire Shop

A total of 14 air samples were collected from the tire shop located in the city center of Bolu on April 22-23, 2022. The sampling period was determined as one hour because of the optimization experiments carried out in the tire shop. The sampling hours were determined according to the working hours of the tire shop as 10.00 - 11.00, 11.00 - 12.00, 12.00 - 13.00, 13.00 - 14.00, 14.00 - 15.00, 15.00 -

16.00, and 16.00 - 17.00. At the time of sampling, the tire shop was busy due to the tire changing season and Ramadan Feast with an average of 100 people visiting the shop per day. An air conditioner is used for ventilation in the tire shop.

The VOCs with the highest average emissions in tire shops are toluene (49.9 $\mu\text{g}/\text{m}^3$); isoprene (17.8 $\mu\text{g}/\text{m}^3$); and benzothiazole (6.80 $\mu\text{g}/\text{m}^3$). On the other hand, the VOCs with the lowest average release in the tire shop were found to be nonane (0.18 $\mu\text{g}/\text{m}^3$) and acetophenone (0.32 $\mu\text{g}/\text{m}^3$). The mean, median and standard deviation values (in $\mu\text{g}/\text{m}^3$) of the VOCs determined in the air samples collected from the tire shop on April 22-23, 2022, are given in Table 4.15.

Table 4.15. The mean, median, and standard deviation values (in $\mu\text{g}/\text{m}^3$) of the VOCs determined in the tire shop

VOC	Arith. Mean	Median	Standard Deviation
isoprene	17.8	17.9	10.7
carbon tetrachloride	1.41	1.41	0.04
benzene	1.74	1.45	0.91
heptane	2.80	1.74	2.49
toluene	49.7	51.9	9.37
hexanal	6.32	3.78	9.49
ethylbenzene	0.977	0.811	0.734
nonane	0.180	0.181	0.0902
m+p-xylene	2.87	3.00	0.856
o-xylene	1.51	1.35	0.557
styrene	4.55	3.63	3.58
alpha pinene	0.684	0.851	0.471
1,2,3-trimethylbenzene	1.22	1.29	0.483
benzaldehyde	0.721	0.618	0.367
dl-limonene	2.00	1.35	1.90
phenol	2.05	2.15	0.566
1-octanol	0.912	0.841	0.695
linalool	2.09	2.49	1.09
acetophenone	0.319	0.354	0.233
tridecane	2.63	2.55	1.44
benzothiazole	6.80	7.31	2.33
tetradecane	2.14	1.99	1.13

The toluene compound, which is the most emitted in the tire shop, was released more intensely on Saturday, April 23 than on April 22. Figure 4.17 shows the

concentration versus daily hours graph of the toluene compound. The toluene compound reached its highest concentration of $60 \mu\text{g}/\text{m}^3$ on April 23, between 14.00 and 15.00 and 15.00.

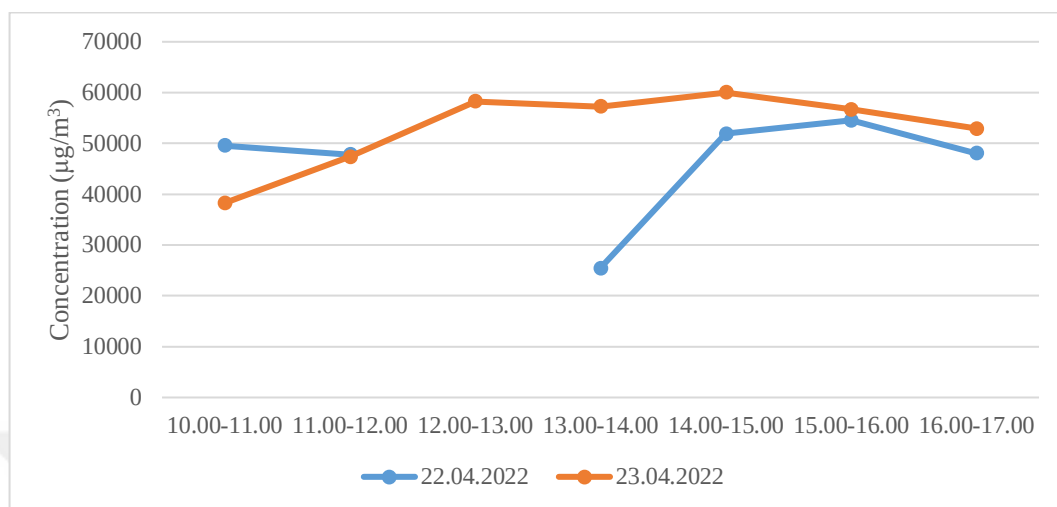


Figure 4.17. The concentration versus daily hours graph of the toluene compound in the tire shop

Figure 4.18 shows the concentration versus time of day plot for the isoprene compound, which is another of the VOCs with the highest emissions in the tire shop. The time when the isoprene compound is most released is between 16.00-17.00 on April 23. When Figures 4.17 and 4.18 are examined, it is seen that VOCs were released more on April 23 than on April 22. The tire shop is more crowded and busier on April 23, as it is both a weekend and before the Ramadan Feast.

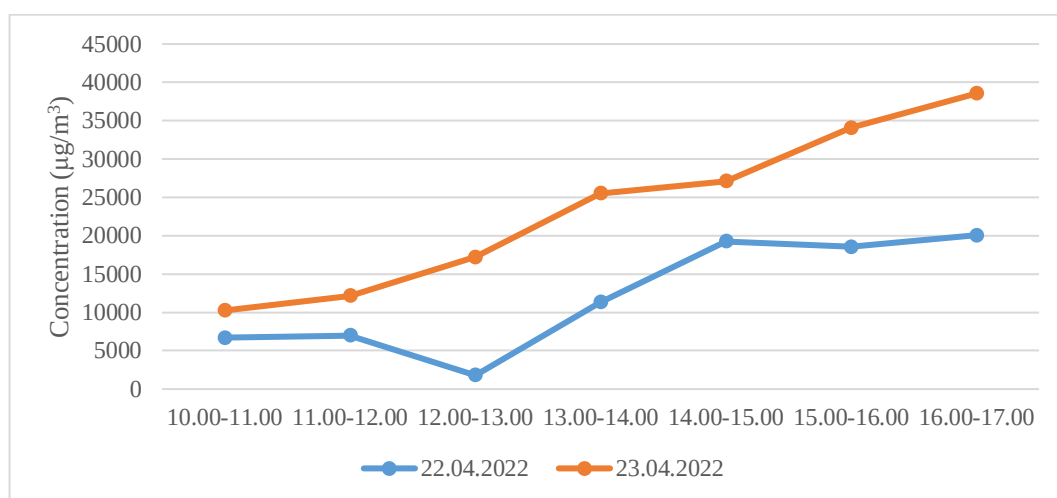


Figure 4.18. The concentration versus daily hours graph of the isoprene compound in the tire shop

4.1.5.1 Health Risk Assessment of Tire Shop

Air samples collected from the tire shop for two days, the LCR value for carcinogenic VOCs, and the HI values for non-carcinogenic VOCs were evaluated separately according to inhalation and oral exposure. The results of the LCR and HI values for VOCs in the tire shop are given in Table 4.18.

Table 4.16. The results of LCR and HI values for VOCs in the tire shop

VOCs	LCR		HI	
	Inhalation	Oral	Inhalation	Oral
carbon tetrachloride	3.87×10^{-6}	1.29×10^{-5}	6.45×10^{-3}	4.61×10^{-2}
benzene	1.75×10^{-6}	3.41×10^{-6}	2.65×10^{-2}	5.69×10^{-2}
toluene	-	-	4.57×10^{-3}	8.16×10^{-2}
ethylbenzene	-	-	4.48×10^{-4}	1.28×10^{-3}
m+p-xylene	-	-	1.32×10^{-2}	1.88×10^{-3}
o-xylene	-	-	6.91×10^{-3}	9.87×10^{-4}
styrene	-	-	2.09×10^{-3}	2.98×10^{-3}
1,2,3-trimethylbenzene	-	-	9.30×10^{-3}	1.59×10^{-2}
benzaldehyde	-	3.77×10^{-7}	-	4.72×10^{-4}
phenol	-	-	-	8.96×10^{-4}
acetophenone	-	-	-	4.18×10^{-4}

Inhalation and oral exposures of benzene, CTC, and benzaldehyde compounds, which are considered to be carcinogenic, were evaluated separately and LCR values were calculated. VOCs exposed through inhalation were determined as CTC and benzene, the LCR values were found to be 3.87×10^{-6} and 1.75×10^{-6} , respectively. As the LCR values obtained were outside the risk range, it was concluded that the respiratory exposure to the VOCs specified for tire shop workers did not carry a cancer risk. Orally exposed VOCs were determined as benzene, CTC, and benzaldehyde, and LCR values were found to be 1.29×10^{-5} , 3.41×10^{-6} , and 3.77×10^{-7} , respectively. When the obtained LCR values were examined, according to the LCR risk range, it was determined that the oral exposure to the CTC compound was considered a "negligible risk" to workers, while oral exposure of benzene and benzaldehyde compounds did not pose a cancer risk for employees as they were outside the risk range.

Non-carcinogenic VOCs from inhalation and oral exposure of the HI values were calculated. VOCs exposed by inhalation were determined as CTC, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, styrene, and 1,2,3-trimethylbenzene. VOCs exposed orally were determined as CTC, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, styrene, 1,2,3-trimethylbenzene, benzaldehyde, and phenol. When the HI values of the oral and inhalation exposures to the non-carcinogenic VOCs in Table 4.16 were examined, the HI values of the specified VOCs were found to be less than 1. According to the HI risk range, values less than 1 are considered "negligible risk". For this reason, the mentioned VOCs were considered to pose a "negligible risk" to tire shop workers.

The HI and total HI values of VOCs exposed to orally were calculated according to the sampling hours in the tire shop and are given in Table 4.17. When HI and total HI values were examined, no values exceeding the HI risk ranges were found during the sampling hours.

Table 4.17. The HI and total HI values of VOCs according to sampling times in the tire shop

VOCs	Hazar Index						
	10.00-11.00	11.00-12.00	12.00-13.00	13.00-14.00	14.00-15.00	15.00-16.00	16.00-17.00
carbon tetrachloride	4.68x10 ⁻²	4.64x10 ⁻²	4.65x10 ⁻²	4.47x10 ⁻²	4.74x10 ⁻²	4.60x10 ⁻²	4.51x10 ⁻²
benzene	9.04x10 ⁻²	6.84x10 ⁻²	1.03x10 ⁻¹	3.56x10 ⁻²	4.29x10 ⁻²	4.30x10 ⁻²	3.78x10 ⁻²
toluene	7.19x10 ⁻²	7.79x10 ⁻²	9.54x10 ⁻²	6.77x10 ⁻²	9.16x10 ⁻²	9.11x10 ⁻²	8.27x10 ⁻²
ethylbenzene	1.12x10 ⁻³	9.67x10 ⁻⁴	3.10x10 ⁻³	7.15x10 ⁻⁴	1.22x10 ⁻³	9.61x10 ⁻⁴	8.73x10 ⁻⁴
m+p-xylene	1.48x10 ⁻³	1.54x10 ⁻³	2.43x10 ⁻³	1.41x10 ⁻³	2.30x10 ⁻³	2.06x10 ⁻³	2.22x10 ⁻³
o-xylene	9.66x10 ⁻⁴	9.21x10 ⁻⁴	1.69x10 ⁻³	7.17x10 ⁻⁴	1.15x10 ⁻³	9.36x10 ⁻⁴	8.80x10 ⁻⁴
styrene	1.19x10 ⁻³	1.38x10 ⁻³	2.53x10 ⁻³	2.08x10 ⁻³	3.48x10 ⁻³	4.96x10 ⁻³	4.99x10 ⁻³
1,2,3-trimethylbenzene	1.11x10 ⁻²	1.25x10 ⁻²	1.89x10 ⁻²	1.44x10 ⁻²	1.97x10 ⁻²	1.78x10 ⁻²	1.89x10 ⁻²
benzaldehyde	3.3x10 ⁻⁴	3.65x10 ⁻⁴	6.41x10 ⁻⁴	6.64x10 ⁻⁴	5.81x10 ⁻⁴	5.44x10 ⁻⁴	5.89x10 ⁻⁴
phenol	9.49x10 ⁻⁴	9.21x10 ⁻⁴	1.03x10 ⁻³	5.84x10 ⁻⁴	8.23x10 ⁻⁴	1.01x10 ⁻³	9.58x10 ⁻⁴
Σ HQ	2.26x10 ⁻¹	2.11x10 ⁻¹	2.75x10 ⁻¹	1.68x10 ⁻¹	2.11x10 ⁻¹	2.08x10 ⁻¹	1.95x10 ⁻¹

Figure 4.19 shows the daily hours versus HI graph of VOCs with oral exposure in tire shop. On examination of the graph, toluene and benzene compounds were found to be the VOCs with the highest HI values.

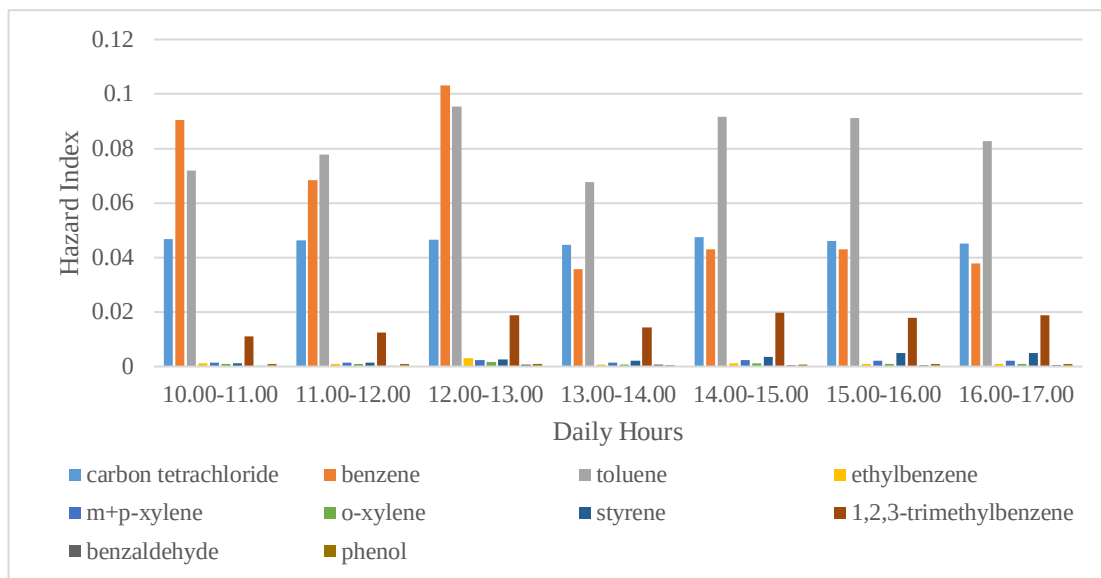


Figure 4.19. The sampling hours versus HI graph of VOCs in the tire shop

Figure 4.20 shows the daily hours versus total HI plot for the VOCs causing oral exposure in the tire shop. The hours when the hazard index is highest are determined as 12.00-13.00. The hours when the total HI value is relatively lower are determined as 13.00-14.00.

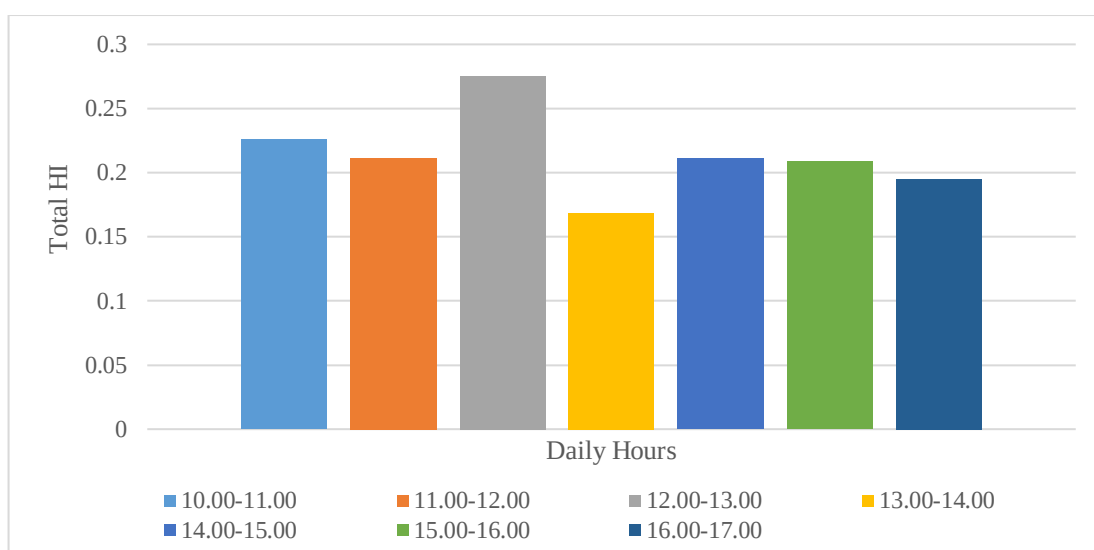


Figure 4.20. The total HI values versus daily hours graph in the tire shop

4.1.6 Car Painter

A total of 14 air samples were collected from the car painter located in the city center of Bolu on April 25 and April 26, 2022. The sampling period was determined on the basis of trial experiments carried out in the car painter. The GC-MS instrument gave a detector saturation warning for toluene, ethylbenzene, and xylene compounds if the sampling time exceeds 5 minutes. For this reason, the sampling time was set at 5 minutes. Six air samples were collected on April 25, 2022, and the sampling times were determined as 11.00-11.05, 11.05-11.10, 15.40-15.45, 15.50-15.55, and 15.55-16.00. Eight air samples were taken on April 26, 2022, and the sampling times were determined as 11.30-11.35, 11.35-11.40, 11.40-11.45, 11.45-11.50, 15.55-16.00, 16.00-16.05, 16.05-16.10, and 16.10-16.15. Two people work in the car painter, there is no ventilation system in the shop, ventilation is natural.

The most emitted VOCs on average in the car painter are toluene ($3571 \mu\text{g}/\text{m}^3$); hexanal ($238 \mu\text{g}/\text{m}^3$); and m+p-xylene ($163 \mu\text{g}/\text{m}^3$). In Table 4.18, the mean, median and standard deviation values (in $\mu\text{g}/\text{m}^3$) of VOCs determined in the car painter on April 25-26, 2022, are given.

The graph of concentration versus daily hours for the toluene compound with the highest release from the car painter is shown in Figure 4.21. The toluene compound had the highest release at 16.05-16.10 hours on April 25 with a concentration of $4701.5 \mu\text{g}/\text{m}^3$. When the graph is examined, it is observed that there is a very intense oscillation throughout the sampling. While the toluene concentration is at its highest, a part of the vehicle is being painted by the car painter. Since thinner is used as a paint thinner, toluene compound is quite abundant in the car painter.

Table 4.18. The mean, median, and standard deviation values (in $\mu\text{g}/\text{m}^3$) of the VOCs determined in the car painter

VOCs	Arith. Mean	Median	Standard Deviation
carbon tetrachloride	13.7	13.7	8.53×10^{-2}
toluene	3571	4034	1268
hexanal	238	82.8	449
ethylbenzene	81.1	30.5	154
m+p-xylene	163	67.5	290
o-xylene	95.2	37.9	171
styrene	159	117	145
1,2,3-trimethylbenzene	21.3	11.7	23.1
benzaldehyde	11.8	4.87	12.9

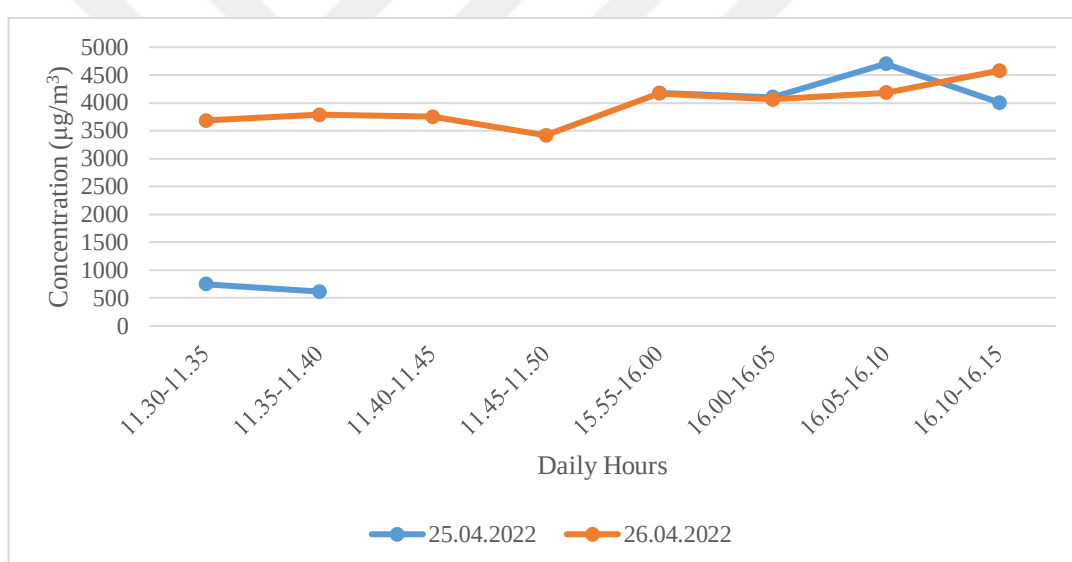
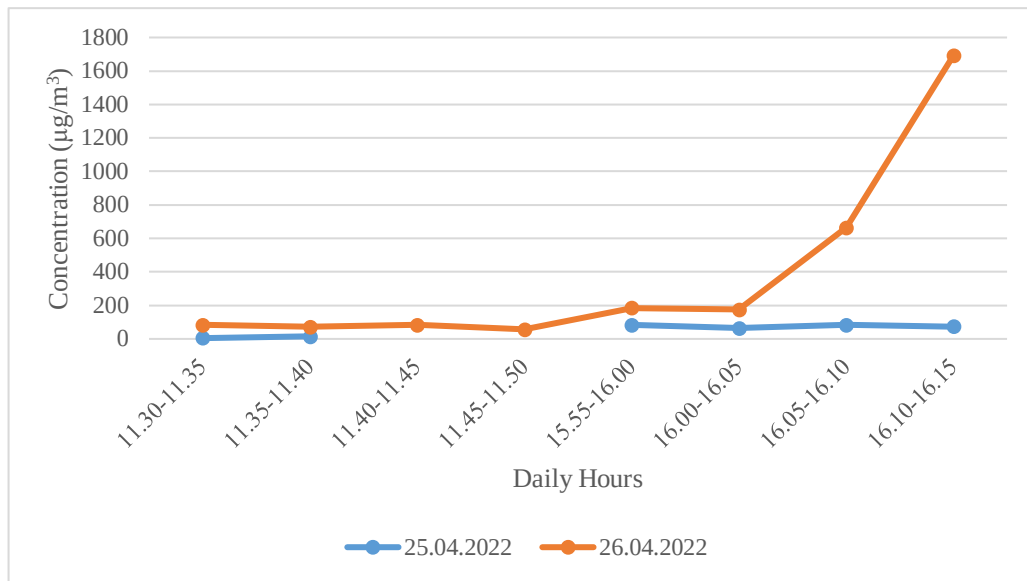
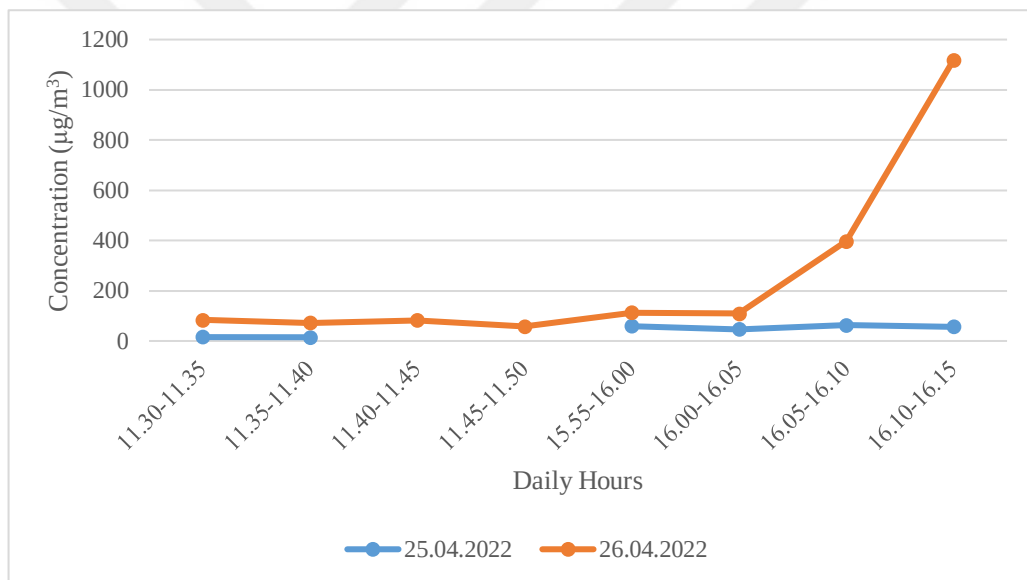


Figure 4.21. The concentration versus daily hours graph of the toluene compound in the car painter

The concentration versus daily hours graphs of hexanal (biogenic origin) and m+p-xylene compounds, which were the most released compounds after toluene, are shown in Figure 4.22. Looking at the graphs, both compounds have similar concentration slopes. It was seen that both compounds had more release on April 26, 2022. It was seen that the concentration increased between 16.00 and 16.15 on April 26, 2022, the reason for this is that the vehicle painting process was carried out at the specified hours.



(a)



(b)

Figure 4.22. The concentration versus daily hours graph of (a) hexanal compound, and (b) m+p-xylene compound in the car painter

The most prevalent compounds released in car paint shops are toluene and m+p-xylene, which are used in paint thinners. These compounds are released into the environment during the drying or coating process due to their high volatility (91).

4.1.6.1 Health Risk Assessment of Car Painter

Air samples collected from the car painter for two days, the LCR values for carcinogenic VOCs, and the HI values for non-carcinogenic VOCs were evaluated separately according to inhalation and oral exposure. The results of LCR and HI values for VOCs in the car painter are given in Table 4.19.

Table 4.19. The results of LCR and HI values for VOCs in the car painter

VOCs	LCR		HI	
	Inhalation	Oral	Inhalation	Oral
carbon tetrachloride	3.42×10^{-5}	1.14×10^{-4}	5.69×10^{-2}	0.407
toluene	-	-	0.298	5.31
ethylbenzene	-	-	3.38×10^{-2}	9.66×10^{-2}
m+p-xylene	-	-	0.681	9.73×10^{-2}
o-xylene	-	-	0.396	5.66×10^{-2}
styrene	-	-	6.62×10^{-2}	9.46×10^{-2}
1,2,3-Trimethylbenzene	-	-	4.99×10^{-2}	8.57×10^{-2}
benzaldehyde	-	5.6×10^{-6}	0.148	0.254

LCR values were calculated for respiratory and oral exposures of VOCs considered to be carcinogenic. The CTC compound was found to be exposed by inhalation. The LCR value of the CTC compound was found to be 3.42×10^{-5} . Respiratory exposure of the CTC compound is considered a "negligible risk" based on the LCR risk ranges. VOCs exposed orally were determined as CTC and benzaldehyde, and LCR values were found to be 1.14×10^{-4} and 5.6×10^{-6} , respectively. Looking at the LCR values of CTC and benzaldehyde compounds: According to the LCR risk range, oral exposure to the CTC compound is considered a "probable risk" for workers, while exposure to the benzaldehyde compound is considered not to pose a cancer risk since it is outside the risk range. Exposure to carbon tetrachloride has been associated with several adverse health effects, including damage to the kidneys and liver, as well as nausea and vomiting (63).

HI values were calculated for inhalation and oral exposure to non-carcinogenic VOCs. The VOCs exposed by inhalation were determined as CTC, toluene, ethylbenzene, m+p-xylene, o-xylene, styrene, and 1,2,3-trimethylbenzene. VOCs that were exposed to orally were determined as CTC, toluene, ethylbenzene, m+p-

xylene, o-xylene, styrene, 1,2,3-trimethylbenzene, and benzaldehyde. Looking at the HI values of the respiratory and oral exposures of non-carcinogenic VOCs in Table 4.19, none of the VOCs has an HI value greater than 1, except for the toluene, which is exposed orally. According to the HI risk range, values less than 1 are considered "negligible risk". Therefore, except for the toluene compound, the other VOCs were of "negligible risk" to workers. The HI value of the toluene compound was found to be greater than 1 for oral exposure. According to the HI risk range, it was evaluated that the toluene compound did not have a cancer risk but had a negative effect on the health of employees. Exposure to toluene had been associated with a number of adverse health effects, including dizziness/headache, fatigue, nausea, upper respiratory tract irritation, and eye, nose, and throat irritation (56,57).

The HI and total HI values of the VOCs exposed orally were calculated according to the sampling hours at the car painter and are present in Table 4.20. It appears that the toluene compound exceeds the HI risk ranges at all sampling hours. Therefore, total HI values exceeded the HI risk ranges for all sampling hours and posed a risk to the health of workers in the long-term exposure. It was known that a person working in the car painter had the occupational disease namely Chronic Obstructive Pulmonary Disease (COPD) at the time of the sampling.

Table 4.20. The HI and total HI values of VOCs according to sampling times in the car painter

VOCs	Hazard Index							
	11.30-11.35	11.35-11.40	11.40-11.45	11.45-11.50	15.55-16.00	16.00-16.05	16.05-16.10	16.10-16.15
toluene	3.30	3.28	5.58	5.09	6.22	6.08	6.61	6.39
ethylbenzene	2.50x10 ⁻²	2.08x10 ⁻²	4.28x10 ⁻²	2.95x10 ⁻²	4.94x10 ⁻²	4.44x10 ⁻²	0.134	0.367
m+p-xylene	2.97x10 ⁻²	2.57x10 ⁻²	4.90x10 ⁻²	3.44x10 ⁻²	5.14x10 ⁻²	4.64x10 ⁻²	0.137	0.349
o-xylene	1.66x10 ⁻²	1.35x10 ⁻²	2.64x10 ⁻²	1.81x10 ⁻²	2.83x10 ⁻²	2.50x10 ⁻²	0.126	0.199
styrene	2.59x10 ⁻²	0.0460	0.0569	0.0830	0.111	0.100	0.151	0.158
1,2,3-trimethylbenzene	0.121	7.35x10 ⁻²	0.130	9.30x10 ⁻²	0.270	0.232	0.366	0.604
benzaldehyde	1.32x10 ⁻³	1.34x10 ⁻³	3.86x10 ⁻³	1.48x10 ⁻³	8.26x10 ⁻³	4.75x10 ⁻³	1.28x10 ⁻²	1.22x10 ⁻²
Σ HI	3.42	3.32	5.77	5.17	6.60	6.41	7.53	8.06

Figure 4.23 shows the daily hours versus total HI graph for the VOCs causing oral exposure in the car painter. It appears from the graph that the times when the

total risk was highest were 16.00-16.15. The car painting process was carried out within the specified period and an intense odor occurred during this time.

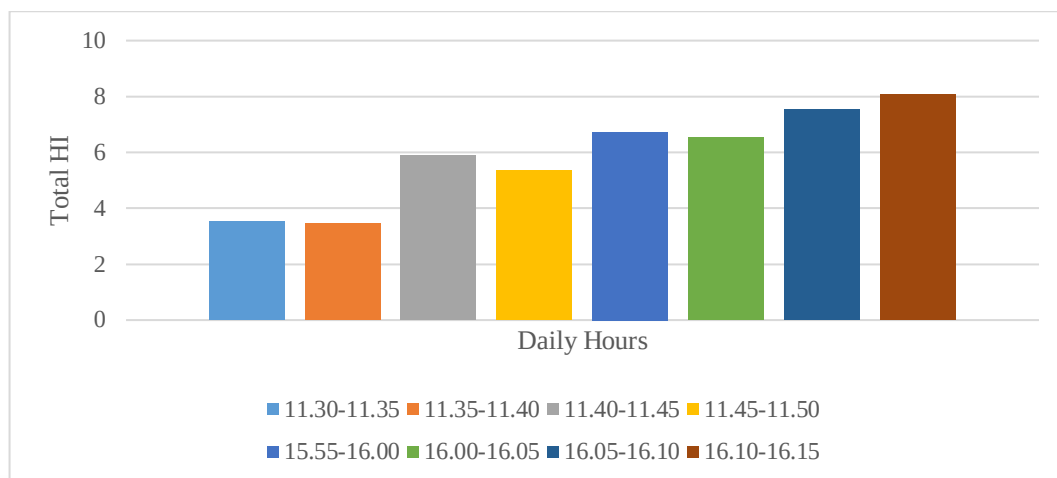


Figure 4.23. The daily hours versus total HI graph of VOCs in the car painter

4.2 Simulation of Monte Carlo

A probabilistic approach was employed in the health risk analysis conducted at the sampling sites. In the probabilistic approach, the variability of the data collected from the sampling points was quantified using the Monte Carlo simulation method, which was implemented with the Crystal Ball software. For the purpose of risk analysis, the assumptions pertaining to the compounds identified at the sampling points were obtained using the median, minimum, and maximum values, mean, and standard deviation. The probabilistic distributions for the risk analysis were derived from the obtained assumptions. The study was carried out with 10 000 iterations in the simulation for each compound.

The probability distribution graph resulting from the Monte Carlo simulation of the chronic daily intake (CDI) from oral exposure to toluene, the most common compound in the car painter, is depicted in Figure 4.24.

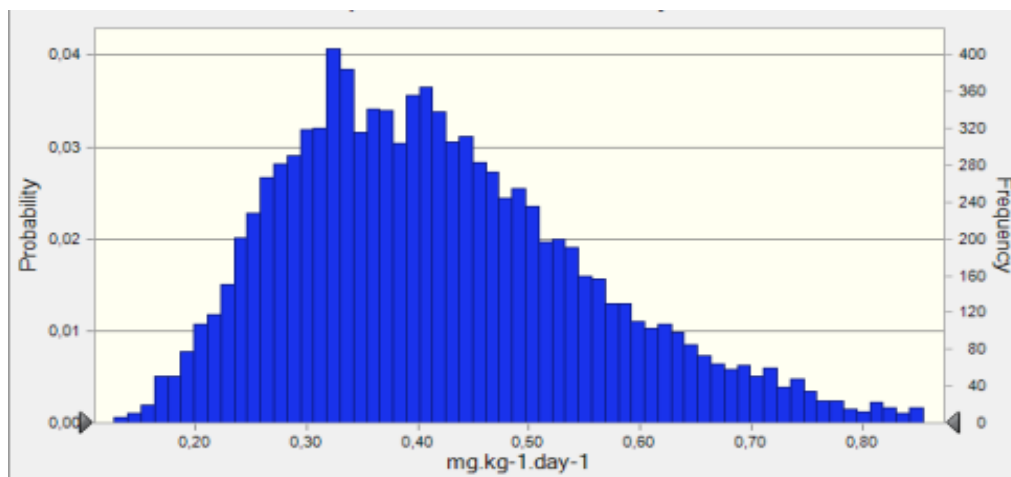


Figure 4.24. The probability distribution graph obtained from the Monte Carlo simulation of the CDI from oral exposure to the toluene in the car painter

Figure 4.25 presents the probability distribution graph of the hazard index for oral exposure to the toluene compound found in all car paints. Upon examination of the graphs in Figures 4.24 and 4.25, it was determined that the CDI distribution and the hazard index distributions of the toluene compound for oral exposure exhibited a high degree of similarity.

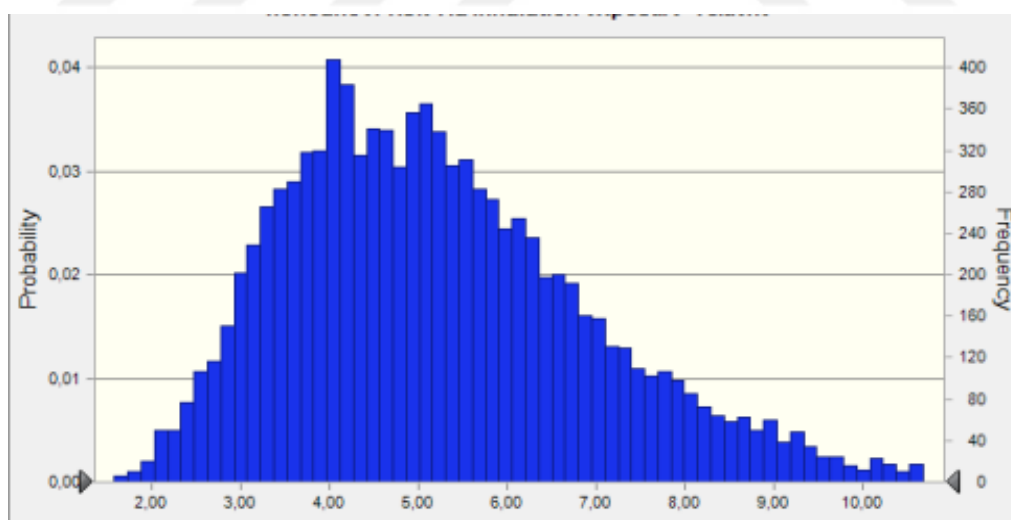


Figure 4.25. The probability distribution graph of the hazard index for oral exposure to the toluene compound found in the car painter

The simulation calculated the potential distributions of total LCR (TLCR) and total HI (THI) for inhalation and oral exposure at each sampling point. The results

of the simulation indicated that no human cancer risk was identified in humans at the sampling locations due to inhalation and oral exposure to VOCs.

The potential THI values of the sampling points were evaluated separately for oral and inhalation exposure. A simulation was conducted to assess the distribution of THI values for inhalation exposure at the sampling points. The minimum, maximum, and standard deviation values for the possible THI distribution of the inhalation exposure at the sampling points in the Monte Carlo simulation are presented in Table 4.21. Figure 4.26 illustrates the potential THI distributions of inhalation exposure at the sampling points. All plots generated by the simulation exhibit a log-normal distribution.

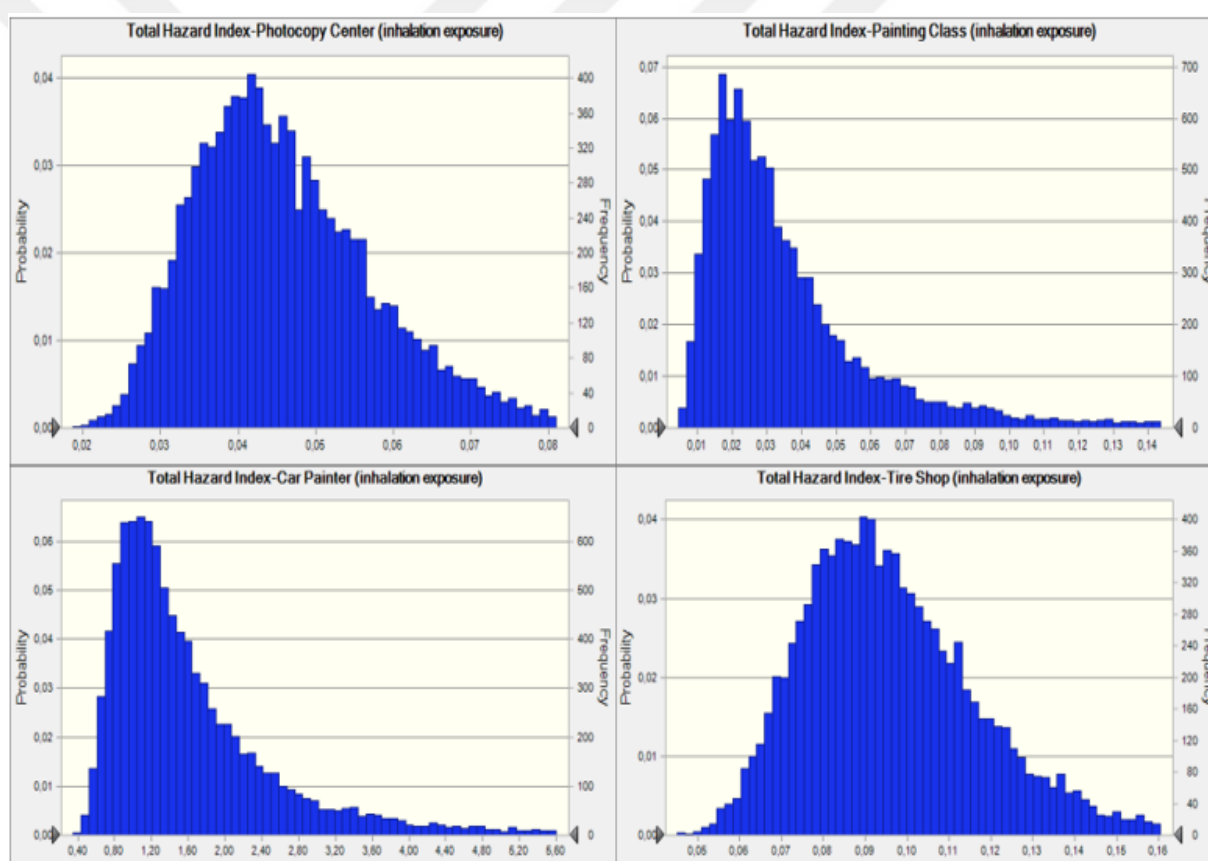


Figure 4.26. The possible THI distributions of the inhalation exposure at the sampling points

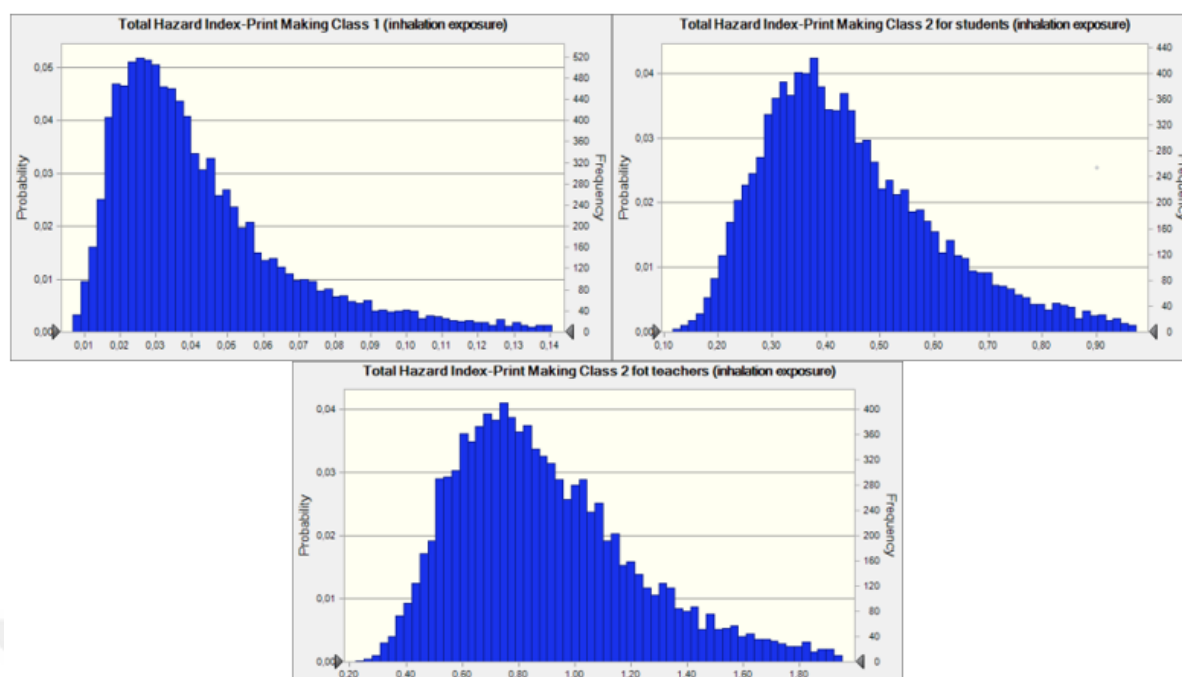


Figure 4.26 (continued) The possible THI distributions of the inhalation exposure at the sampling points.

Table 4.21. The minimum, maximum, mean, and standard deviation values for the possible THI distribution of the inhalation exposure at the sampling points.

Sampling Point	Minimum	Maximum	Arith. Mean	Standard Deviation
Photocopy center	0.02	0.13	0.05	0.01
Painting class	0	0.77	0.04	0.04
Print-making class-1	0.01	0.67	0.05	0.03
Print-making class-2 for students	0.12	1.94	0.46	0.18
Print-making class-2 for teachers	0.22	3.97	0.92	0.37
Tire shop	0.05	0.26	0.1	0.02
Car painter	0.35	28.93	1.74	1.38

A review of Table 4.21 reveals that the car painter exhibits the highest mean value among the sampling points, with a value of 1.74. As previously stated in Section 4.1.3.1, the exposure times for teachers and students in print-making class 1 (PCM-1) are identical. Hence, the possible THI for both teachers and students had to be evaluated together. The mean value for PCM-1 was found to be 0.05. In print-making class 2 (PCM-2), the mean value for students was 0.46, with a maximum

value of 1.94. The standard deviation value for teachers was 0.92, with a maximum value of 3.97. In PCM-2, the mean and maximum values for teachers are about twice as high as those for students. These data suggest that the hazard index was higher for teachers.

A comparison of the means for PCM-1 and PCM-2 showed that the mean for PCM-1 was 0.05, while the mean for students in PCM-2 was 0.46 and the mean for teachers was 0.92. In this case, the mean for students in PCM-2 was about nine times that of PCM-1, while the mean for teachers in PCM-2 was about eighteen times that of PCM-1. In PCM-1 there is a ventilation system, whereas in PCM-2 the classroom is naturally ventilated. The overall inhalation hazard index for teachers and pupils was higher than that observed in PCM-1.

A simulation was performed to assess the distribution of oral exposure from the sampling points for the THI. The minimum, maximum and standard deviation values for the possible THI distribution of oral exposure are presented in Table 4.22. Figure 4.27 illustrates the potential THI distributions of oral exposure at the sampling points. The results of the simulation indicated that all the plots obtained showed a log-normal distribution.

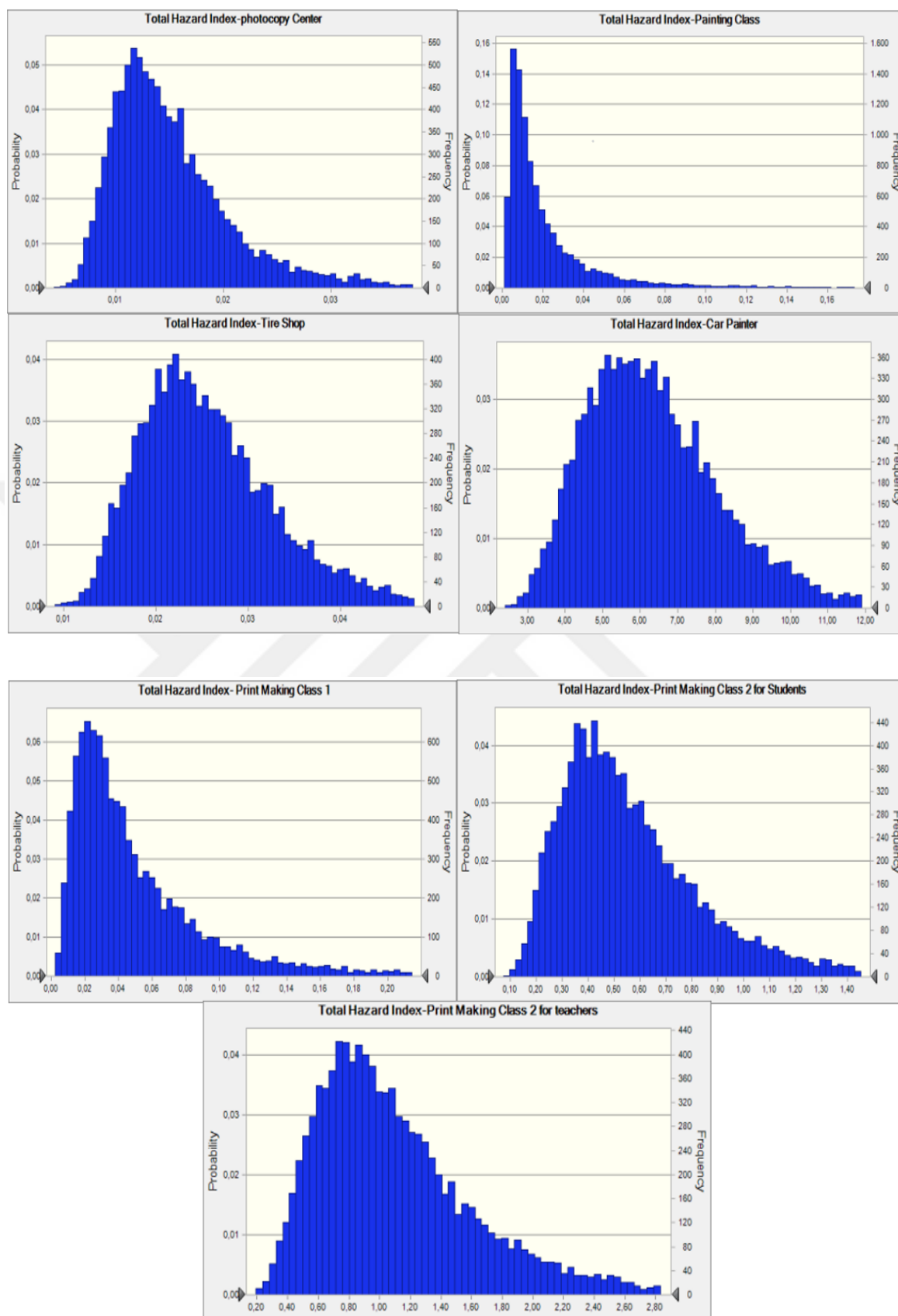


Figure 4.27. The possible THI distributions of the oral exposure at the sampling points

Table 4.22. The minimum, maximum, mean, and standard deviation values for the possible THI distribution of oral exposure

Sampling Point	Minimum	Maximum	Arith. Mean	Standard Deviation
Photocopy center	0	0.2	0.02	0.01
Painting class	0	2.72	0.03	0.05
Print-making class-1	0	0.88	0.06	0.06
Print-making class-2 for students	0.08	3.26	0.58	0.31
Print-making class-2 for teachers	0.19	5.85	1.14	0.6
Tire shop	0.01	0.09	0.03	0.01
Car painter	2.41	23.3	6.42	1.95

A review of Table 4.22 reveals that the car painter exhibits the highest value of the mean among the sampling points, with a value of 6.42. The mean value in PCM-1 was determined to be 0.06. In PCM-2, the mean value for students was 0.58, with a maximum value of 3.26. The mean value for teachers was 1.14, with a maximum value of 5.85. In PCM-2, the mean and maximum values of the teachers are approximately twofold higher than those of the students. In this case, although the risk of exposure during student life was relatively low in PMC-2, there was an observed increase in occupational exposure for teachers.

A comparison of PCM-1 and PCM-2 revealed that the mean value of PCM-1 was 0.06, while that of PCM-2 was 0.58 for students and 1.14 for teachers. In this instance, the mean value of students in PCM-2 was approximately 10 times higher than that of PCM-1, while the mean value of teachers in PCM-2 was approximately 19 times higher than that of PCM-1. The absence of a ventilation system in PCM-2 had the effect of increasing the overall hazard index and the risk of oral exposure for people in the classroom.

Upon examination of Tables 4.21 and 4.22, it was determined that the mean values for inhalation and oral exposure were 0.05 and 0.02, respectively, in the photocopy center. In the painting class, the mean values for inhalation and oral exposure were found to be 0.04 and 0.03, respectively. In PCM-1, the mean values for inhalation and oral exposure were found to be 0.05 and 0.06, respectively. In

PMC-2, the mean values of inhalation and oral exposure for students were found to be 0.46 and 0.58, respectively, with oral exposure approximately 1.2 times higher than inhalation exposure. In PMC-2, the mean values of inhalation and oral exposure for teachers were found to be 0.92 and 1.14, respectively, with oral exposure approximately 1.2 times higher than inhalation exposure. In the tire shop, the mean values for inhalation and oral exposure were found to be 0.1 and 0.03, respectively, with respiratory exposure being approximately three times higher than oral exposure. The mean values for inhalation and oral exposure in the car painter were found to be 1.74 and 6.42, respectively, with oral exposure approximately 3.6 times higher than inhalation exposure. While an increase in oral exposure relative to inhalation exposure was observed in the painting class, PCM-1, PCM-2, and the car painter, inhalation exposure was found to be higher in the tire shop.

4.3 Passive Sampling

In order to gain insight into the potential sources of indoor and outdoor air contamination, a total of 34 passive air samples were collected from six distinct locations. These locations included a photocopy center, a painting class, two print-making classes, a tire shop, and a car painter. The passive sampling technique was employed to collect the samples which were collected concurrently with the active air samples.

4.3.1 Indoor/Outdoor Ratio

A total of five air samples were collected by passive sampling at the copy center between March 25, 2022, and April 1, 2022. Two samples were collected indoors, and three samples were collected outdoors.

A total of six air samples, three of which were collected from the indoor environment and three from the outdoor environment, were obtained from the painting class by passive sampling between April 1 and April 8, 2022.

A total of six air samples were collected by passive sampling from the print-making class between April 14 and April 17, 2022. Three samples were collected from the indoor environment, and three were collected from the outdoor environment.

A total of six air samples were collected by passive sampling from the print-making class 2 between April 19 and April 22, 2022. Three samples were collected from the indoor environment, and three were collected from the outdoor environment.

A total of six air samples, three from the indoor environment and three from the outdoor environment, were collected by passive sampling from the tire shop between April 22 and April 23, 2022.

A total of five air samples were collected by passive sampling from the car painter between April 25 and April 26, 2022. Two samples were collected indoors and three were collected outdoors.

The indoor/outdoor (I/O) ratios and total I/O ratios were calculated by determining the indoor and outdoor concentrations at the sampling locations. The I/O ratios of the sample points and the total I/O ratios are presented in Table 4.23.

Table 4.23. The I/O ratios of the sample points and the total I/O ratios.

VOCs	Photocopy center	Printing class	Print making class-1	Tire shop	Car painter
carbon tetrachloride	0.168	0.350	0.290	0.465	-
heptane	-	0.278	0.754	0.394	0.69
toluene	-	-	-	2.98	4.80
hexanal	0.0132	-	-	-	17.4
ethylbenzene	-	-	-	-	17.4
m+p-xylene	-	-	-	-	14.0
o-xylene	-	-	-	-	17.0
styrene	-	-	-	-	217
alpha pinene	0.0716	-	-	-	-
benzaldehyde	0.172	0.149	0.0882	0.0273	2.01
phenol	0.240	-	-	-	-
tridecane	-	-	0.509	-	-
tetradecane	-	-	0.846	-	-
Total I/O ratio	0.664	0.776	2.49	3.87	290

In the photocopy center, the I/O ratios of the following compounds were calculated: CTC, hexanal, alpha-pinene, benzaldehyde, and phenol. The ratios were found to be 0.17, 0.013, 0.072, 0.17, and 0.24, respectively. The phenol compound exhibited the highest I/O ratio in the photocopy center.

In the painting class, the I/O ratios of the CTC, heptane, and benzaldehyde compounds were calculated to be 0.35, 0.28, and 0.15, respectively. The CTC compound had the highest I/O ratio in the painting class.

In PCM-1, the I/O ratios of CTC, heptane, benzaldehyde, tridecane, and tetradecane compounds were calculated to be 0.29, 0.75, 0.088, 0.51, and 0.85, respectively. In PCM-1, the tetradecane compound had the highest I/O ratio. In PCM-2, no similar VOCs were identified in the indoor and outdoor passive samples, thus precluding the determination of the I/O ratio.

In the tire shop, the I/O ratios of CTC, heptane, toluene, and benzaldehyde compounds were calculated to be 0.46, 0.39, 2.98, and 0.0273, respectively. The toluene compound had the highest I/O ratio in the tire shop.

In the car painter, the I/O ratios of heptane, toluene, hexanal, ethylbenzene, m+p-xylene, o-xylene, styrene, and benzaldehyde compounds were calculated as follows: 0.69, 4.80, 17.4, 17.4, 14.0, 17.0, 217, and 2.01, respectively.

The total I/O ratios of the copy center, painting class, PMC-1, tire shop, and car painter shop were calculated as 0.66, 0.78, 2.49, 3.87, and 290, respectively. When the total I/O ratios were examined, it was determined that the results for PCM-1, tire shop, and car painter shop were greater than 1. In this case, it was determined that the indoor VOCs at the specified sampling locations were more dominant than the outdoor VOCs. In the photocopy center, there was an interaction between outdoor and indoor air because the door of the photocopy center was always open.

4.4. Comparison with Literature

In the context of this study, the findings regarding VOCs in indoor and outdoor environments at six distinct sampling points were evaluated in comparison to analogous studies conducted globally. Table 4.24 presents a comparative analysis of the literature on the subject of photocopy centers. The VOC concentration levels observed in our study at the photocopying center are notably lower than those reported in studies conducted in Taiwan. The results demonstrated that the VOC concentrations reported in the study conducted in Kocaeli were slightly higher than those obtained in this study.

Table 4.24. A comparison of the values in the literature relating to photocopy centers (in $\mu\text{g}/\text{m}^3$)

Sampling Area	VOCs	Bolu, Türkiye	Tainan, Taiwan (92)	Kocaeli, Türkiye (10)
Photocopy Center	benzene	0.711	57.3	1.14
	toluene	6.67	409	11.6
	ethylbenzene	1.78	22.1	2.43
	m+p-xylene	1.18	61.1	1.58
	styrene	0.773	24.1	1.77
	o-xylene	1.04		1.08

Table 4.25 presents a comparative analysis of the literature on the painting class. The concentrations of VOCs obtained in our study conducted in the painting class are lower than those reported in the study conducted in Eskişehir.

Table 4.25. A comparison of the values in the literature relating to painting class (in $\mu\text{g}/\text{m}^3$)

Sampling Area	VOCs	Bolu, Türkiye	Eskişehir, Türkiye (93)
Painting Class	benzene	0.332	1.29
	toluene	5.93	90.2
	ethylbenzene	0.771	3.99
	m+p-xylene	1.35	7.08
	styrene	0.267	0.71
	o-xylene	1.28	4.71
	isopropylbenzene	0.617	3.04
	1,3,5-trimethylbenzene	1.25	8.14

A comparative analysis of the literature regarding print-making classes is presented in Table 4.26. The results of our study conducted in print-making classes indicated that the VOC concentrations were significantly lower than those observed in the study conducted in Brazil.

Table 4.26. A comparison of the values in the literature relating to print-making classes (in $\mu\text{g}/\text{m}^3$)

Sampling Area	VOCs	Bolu, Türkiye		Rio De Janerio, Brazil (94)
		PMC-1	PMC-2	
Print-making Classes	benzene	0.399	0.176	2.53
	toluene	19.5	183	7750
	ethylbenzene	1.54	6.2	
	nonane	16.9	110	1599
	o-xylene	2.75	34.7	
	p-cymene	0.88	13.71	162

Table 4.27 presents a comparative analysis of the literature on car painters. The results of our study conducted in the car painter indicated that the VOC concentrations were significantly lower than those observed in the study conducted in Spain. A comparison of the literature revealed that the VOC concentrations in this study were lower than those reported in previous studies.

Table 4.27. A comparison of the values in the literature relating to car painters (in $\mu\text{g}/\text{m}^3$)

Sampling Area	VOCs	Bolu, Türkiye	Cordoba, Spain (95)
Car Painter	toluene	3571	48371
	ethylbenzene	81.1	8024
	m+p-xylene	163	14312
	o-xylene	95.2	30460
	styrene	159	909

5. CONCLUSIONS AND RECOMMENDATIONS

The objective of this study was to identify the anthropogenic and biogenic volatile organic compounds present in the indoor and outdoor environments of six dyeing and printing facilities in Bolu. The study also assesses the potential health risks associated with these VOCs by evaluating their impact on human health. In the context of the thesis study, a total of 57 target VOCs were determined using passive and active sampling techniques. A total of 219 air samples were collected from the photocopy center, painting class, two different print-making classes, tire shop, and car painter.

A total of 42 air samples were collected daily over a four-hour period between March 25 and April 1, 2022, from the photocopy center located in the BAIBU activity center. These samples were collected using active sampling techniques. Additionally, five air samples were collected over the course of a week using passive sampling techniques. A total of 42 air samples were collected daily from April 1-8, 2022, from the painting class at the BAIBU Faculty of Fine Arts. These samples were collected in a four-hour period using active sampling. Additionally, six air samples were collected over the course of a week using passive sampling. From a print-making class (PCM-1) at the BAIBU Faculty of Fine Arts, a total of 38 air samples were collected daily over a two-hour period between April 14 and April 17, 2022, through an active sampling process, while six air samples were collected through passive sampling over a period of three days. A total of 35 air samples were collected by active sampling from the printmaking class (PCM-2) at the BAIBU Faculty of Education on a daily basis between April 19 and April 21, 2022. These samples were collected in two-hour and one-hour intervals. Three daily air samples were collected via passive sampling. A total of 14 air samples were collected via active sampling from the tire shop in the Bolu city center on 22–23 April 2022. Sampling was conducted daily and in a one-hour period. Two daily samples and six air samples were collected via passive sampling. A total of 14 air samples were collected on a daily basis over a five-minute period between April 25th and April 26th, 2022. These samples were collected from the car paint shop located in Bolu city center using active sampling techniques. Two daily and five air samples were collected via passive sampling.

In the photocopy center, hexanal, dl-limonene, toluene, and isoprene are the VOCs with the highest concentrations. The concentration of biogenic VOCs was found to be elevated in the photocopy center. The LCR values for carcinogenic VOCs and the HI values for non-carcinogenic VOCs were evaluated separately for inhalation and oral exposure. A review of the LCR values associated with inhalation and oral exposure to carcinogenic VOCs revealed that there was no appreciable risk of cancer for workers. Upon examination of the HI values associated with inhalation and oral exposure to noncarcinogenic VOCs, it was determined that the risk to workers was negligible.

Hexanal (biogenic origin), dodecane, and tridecane are the VOCs with the highest concentrations in the painting class. The carcinogenic VOCs and the non-carcinogenic VOCs were evaluated separately for inhalation and oral exposure. A review of the carcinogenic VOCs associated with inhalation and oral exposure revealed that there was no appreciable risk of cancer for workers. Upon examination of the HI values associated with inhalation and oral exposure to noncarcinogenic VOCs, it was determined that the risk to workers was negligible.

In the PMC-1, tridecane, hexanal, and tetradecane are the VOCs with the highest concentrations. The LCR values for carcinogenic VOCs and the HI values for non-carcinogenic VOCs were evaluated separately for inhalation and oral exposure. Upon calculation of the exposure times of teachers and students in PCM-1, it was found that they were identical. Consequently, a risk assessment was conducted for both educators and students. A review of the LCR values associated with inhalation and oral exposure to carcinogenic VOCs revealed that there was no appreciable risk of cancer for teachers and students. Upon examination of the HI values associated with inhalation and oral exposure to noncarcinogenic VOCs, it was determined that the risk to teachers and students was negligible.

In the PMC-2, toluene, nonane, and 1,2,3-trimethylbenzene are the VOCs with the highest concentrations. The LCR values for carcinogenic VOCs and the HI values for non-carcinogenic VOCs were evaluated separately for inhalation and oral exposure. Upon calculation of the exposure times of teachers and students in PCM-2, it was found that they differed. Consequently, risk assessments were conducted for teachers and students separately. A review of the LCR values associated with

inhalation and oral exposure to carcinogenic VOCs revealed that there was no appreciable risk of cancer for teachers and students. Upon examination of the HI values associated with inhalation and oral exposure to noncarcinogenic VOCs, it was determined that the risk to teachers and students was negligible.

In tire shop, toluene and isoprene are the VOCs with the highest concentrations. The LCR values for carcinogenic VOCs and the HI values for non-carcinogenic VOCs were evaluated separately for inhalation and oral exposure. A review of the LCR values associated with inhalation and oral exposure to carcinogenic VOCs revealed that there was no appreciable risk of cancer for workers. Upon examination of the HI values associated with inhalation and oral exposure to noncarcinogenic VOCs, it was determined that the risk to workers was negligible.

In the car painter, it was observed that toluene, hexanal, and m+p-xylene were the VOCs exhibiting the highest concentrations. The LCR values for carcinogenic VOCs and the HI values for non-carcinogenic VOCs were evaluated separately for inhalation and oral exposure. Upon examination of the LCR values associated with inhalation and oral exposure to carcinogenic VOCs, it was determined that workers exposed via inhalation did not exhibit an elevated cancer risk. However, when oral exposure was evaluated, the LCR value of the CTC compound was found to be 1.14×10^{-4} , indicating a “possible risk” for workers. Upon examination of the HI values associated with inhalation and oral exposure of noncarcinogenic VOCs, it was determined that the inhalation exposure of employees represented a negligible risk. However, when oral exposure was evaluated, the HI value of the toluene compound was found to be 5.31. It was determined that there was no cancer risk for employees, but that there was a negative health risk. It was known that one of the employees at the car paint shop suffered from chronic obstructive pulmonary disease at the time of the sampling.

A probabilistic approach was employed to calculate the health risk at the sampling points. In this probabilistic approach, cancer risk is calculated on numerous occasions for each sampling point. The results of the calculations indicated that the sampling points were not carcinogenic. Concurrently, an examination of the hazard index revealed that although the VOCs detected do not

pose a risk on their own, the total hazard index of the VOCs has a negative effect on human health.

It is recommended that the six sampling points from which air is taken are frequently ventilated. If there is no ventilation system in the PMC-2, it is advised that a ventilation system is installed and that teachers move their rooms outside the classroom. It is suggested that bodyshop workers carry out car painting in the open as much as possible and wear a protective mask.

It is recommended that the studies be extended and applied regularly by increasing the VOC components and sampling points in this study. By increasing cooperation between industry and universities, the health risk analysis for workers can be calculated by taking air samples from workplaces where painting and/or mass production takes place. It is advisable to develop company-specific strategies and to take the necessary precautions to reduce air pollution levels for workers to the limit values.

6. REFERENCES

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