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Passive sampling-based characterization of volatile organic compounds in Skopje: seasonal trends and source identification

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Abstract

Volatile organic compounds (VOCs) are key contributors to urban air pollution, photochemical smog, and associated health risks. Skopje, one of Europe's most polluted capitals, faces significant VOC emissions from traffic, industry, and domestic heating. This study presents a year-long monitoring of 82 VOCs at five urban sites in Skopje, assessing concentrations, seasonal variability, emission sources, and ozone formation potential (OFP). Aliphatic hydrocarbons dominated, followed by aromatics (notably BTEX (benzene, toluene, ethylbenzene and xylenes)), terpenes, and hydrocarbon derivatives. Winter showed higher VOC levels due to heating, traffic, and industrial activity, while summer levels declined due to photochemical degradation and atmospheric dispersion. BTEX analysis, diagnostic ratios of toluene/benzene (T/B), and correlation patterns indicated traffic as the primary source, with industrial and waste-related contributions at specific sites. Principal component analysis identified six source-related factors: mixed traffic, solvent/industrial emissions, biogenic sources, fuel evaporation, personal care products, and industrial/petroleum-related VOCs. Meteorological factors also influenced VOC dynamics: aromatics and aliphatics correlated negatively with temperature, UV radiation, and ozone, while $PM_{2.5}$ correlated positively with aromatics and terpenes, linking VOC emissions to fine particulate matter. OFP analysis revealed that highly reactive species – toluene, xylenes, C_6-C_3 substituted benzenes, and *n*-tetradecane – disproportionately drive ozone formation, despite lower abundance. This work provides the first comprehensive VOC dataset for Skopje, revealing source contributions, seasonal patterns, and compounds with the greatest OFP. Findings support targeted air quality management, emphasizing control of high-OFP VOCs and integrated strategies considering both emissions and atmospheric chemistry to reduce urban pollution and associated health risks.

Keywords Volatile organic compounds · Air pollution · Passive sampling · GC–MS · Skopje ambient air

Introduction

Air pollution has been a major global environmental issue due to its severe impacts on human health, climate change, and the deterioration of air quality (Von Schneidemesser et al. 2015; Almetwally et al. 2020; Fan et al. 2022), and it is now the leading environmental risk factor (World Health Organization 2016). This challenge is particularly pronounced in large cities, where rapid industrialization and urbanization created pollution hotspots.

Urban populations worldwide are increasingly affected, and capital cities in the Balkan are known for poor air quality (Belis et al. 2019). Skopje, the capital of North Macedonia, frequently ranks among the most polluted cities globally, especially regarding particulate matter (PM) concentrations. Reports by the United Nations Environment

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Programme (United Nations Development Programme 2020) and World Health Organization (World Health Organization 2023) ranked Skopje, along with Bitola and Tetovo, among Europe's top ten most polluted cities in 2017, with air quality worsening over the preceding five years. The WHO Ambient Pollution Database (2018) also identified Skopje as the most polluted European capital (World Health Organization; UNEP (United Nations Environment Programme) 2018).

VOCs play a key role in urban air pollution in large cities, both as direct pollutants and as precursors of fine particulate matter ($PM_{2.5}$) and photochemical smog driven by elevated ozone (O_3) levels (Marć et al. 2014b; Fan et al. 2022), often causing frequent urban haze. They are emitted from diverse natural and anthropogenic sources, including fuel and biomass combustion, transport, industrial processes, solvent usage, building materials, landfill sites, biogenic emissions etc. (He et al. 2019; Duan et al. 2023). VOC emissions comprise various chemical classes, including alkanes, alkenes, alkynes, aromatics, alcohols, aldehydes, ketones, esters, halocarbons, and sulfur/nitrogen-containing compounds (He et al. 2019; Duan et al. 2023), while aromatic hydrocarbons like benzene, toluene, ethylbenzene, and xylene (BTEX) are of particular concern due to their carcinogenic and neurotoxic effects (Akash And Rehman 2021).

City geography and meteorology, including topography, climate, wind patterns, temperature, humidity, and UV radiation, strongly influence VOC levels and dispersion (Elminir 2005; Von Schneidemesser et al. 2015). Higher temperatures increase VOC volatilization and atmospheric dispersion, while cooler conditions can trap them locally. UV radiation drives photochemical reactions, affecting VOC formation and degradation, with different compounds showing varying persistence in the atmosphere (George et al. 2015). Understanding these interactions is essential for effective urban air quality management and pollution control strategies.

Continuous monitoring of VOCs from urban sources is vital for understanding their distribution, guiding mitigation measures, and reducing their health and environmental impacts. Passive sampling has emerged as a key methodological advancement for detecting VOCs in urban ambient air. Literature shows that passive sampling is widely used and well-established in urban air quality monitoring (Król et al. 2010; Marć et al. 2014b; Huang et al. 2018), allowing simultaneous sampling at multiple sites and providing time-weighted average concentrations of target analytes. Comparing to active sampling it offers similar accuracy (Yamada et al. 2004; Hayward et al. 2010) while being cost-effective, easy to operate, and not requiring external power. Moreover, passive sampling supports green analytical chemistry by minimizing or eliminating solvent use during sample preparation (Seethapathy et al. 2008).

In light of these considerations, this study aimed to monitor volatile organic compounds (VOCs) in ambient air in Skopje using passive air sampling at five locations from January to December 2022. The study focused on assessing the spatial and temporal distribution of VOCs, identifying their chemical types, estimating monthly concentrations, and examining seasonal variations. It also aimed to determine potential emission sources, including traffic, industry, and biogenic contributions, and to explore how meteorological factors such as temperature and UV radiation influence VOC levels and their relationship with $PM_{2.5}$ and ozone. By addressing these goals, the study provides essential data to support urban air quality management and mitigation of related health and environmental impacts.

Materials and methods

Site characteristics

Passive air sampling of VOCs was conducted in Skopje, the capital and largest city of North Macedonia, located in the Skopje Valley along the Vardar River (1818 km^2, elevation 245 m). The urban population is 422,540 residents, with 526,502 in the broader city area (MakStat database 2021). The climate is moderately continental, with an average temperature of 13.5 °C, and annual rainfall of 940 mm (Grad Skopje 2023).

Skopje is situated in a mountain-enclosed basin, which restricts air circulation and traps emissions from traffic, households, and industry, often leading to poor air quality, especially during winter fog events. Skopje receives most of its electricity from a lignite-fired thermal power plant in Bitola, over 100 km to the south of the city. Since 2010, a natural gas–fueled combined heat and power plant supplies heat to the district heating system, covering about 40% of the city's demand (Ministry of Economy 2010). The remaining demand is mainly met by firewood and heating oil. The primary heating oils used in Skopje are mazut (heavy fuel oil, M-1 NS) and extra light heating oil (EL-1). Mazut, a residual heavy oil with relatively high sulfur content, is primarily used in industrial and institutional heating systems, while EL-1, a lighter and cleaner fuel, is mostly employed for residential applications (ERC MK EWS and MWMSRC 2023). Key industrial activities in the Skopje region include production of steel (5 km west), cement and concrete (5 km south), and an oil refinery (20 km southeast of the city center) (Anttila et al. 2016). An industrial lindane landfill is located at the former OHIS factory, about 5.5 km southeast from the city center. Skopje has an organized bus-based public transport system, but a high number of private vehicles contributes to traffic congestion.

To investigate the potential impact of sources on VOC distribution patterns in the ambient air, five representative locations in Skopje were selected (Fig. 1), where the monitoring of VOCs was carried out from January to December 2022:

- Organized municipal waste landfill (41.93256° N, 21.45340° E)
- One location near landfills of former OHIS Factory (41.96026° N, 21.48605° E)
- Macedonian Academy of Arts and Sciences (MANU) (41.99654° N, 21.44151° E)
- Institute of Chemistry (42.00139° N, 21.45337° E)
- Novo Lisiche (41.97937° N, 21.47718° E)

It was considered different areas of the city to be covered: a municipal landfill in an area of the city with low traffic intensity, industrial landfill (OHIS), two urban locations along roads with higher traffic intensity (MANU and Novo Lisiche) and one near the Institute of Chemistry with low traffic intensity and an area with vegetation nearby. The preliminary measurements of VOCs at seven locations all over Skopje in 2020 (Sofronievska et al. 2022) showed that the most polluted locations are MANU and Novo Lisiche, which is why they were also selected as part of the locations where VOCs were monitored.

Standards and reagents

Dichloromethane was used as the extraction solvent (purity ≥ 99.8% stabilized with amylene, Fisher Chemical, USA). BTEX stock solution in hexane containing benzene, toluene, ethylbenzene and *o*-, *m*-, and *p*-xylene, each at a concentration of 200 mg/L was purchased from CPAChem Ltd, Bulgaria. Trichloroethylene (≥99.5%), tetrachloroethylene (≥99.0%), butyl acetate (≥99.7%), chlorobenzene (≥99.5%), α-pinene (≥97.0%), β-pinene (≥99.0%), 1,2,4-trimethylbenzene (≥98.0%), *p*-cymene (≥99.5%) and *R*-(+)-limonene (≥98.0%) were obtained from Sigma-Aldrich, USA. Anisole was used as an internal standard (≥99.7%, Sigma Aldrich, USA).

Passive VOCs sampling

VOCs sampling was performed using Radiello passive air samplers (Fondazione Salvatore Maugeri, Padova, Italy), as described in our previous work (Sofronievska et al. 2022).

Samplers were positioned 1.5–2 m above the ground, either under a protective polypropylene shelter or in a covered area to shield them from atmospheric conditions and were exposed to ambient air for one month, since it was previously concluded that this is the optimal sampling time (Sofronievska et al. 2022). Average ambient air temperature was recorded during sampling, as it influences the sampling rate (Q) for each compound and the calculation of average VOC concentrations. After collection, sorbents were sealed in glass tubes and either analyzed immediately or stored below 4 °C for up to three days.

One sample was collected monthly at each of the five sites, resulting in 60 samples analyzed over the study period.

Sample preparation and analysis

Sample preparation and analysis were performed as described in a previous work (Sofronievska et al. 2022, 2024). Anisole was added as an internal standard, and VOCs were extracted

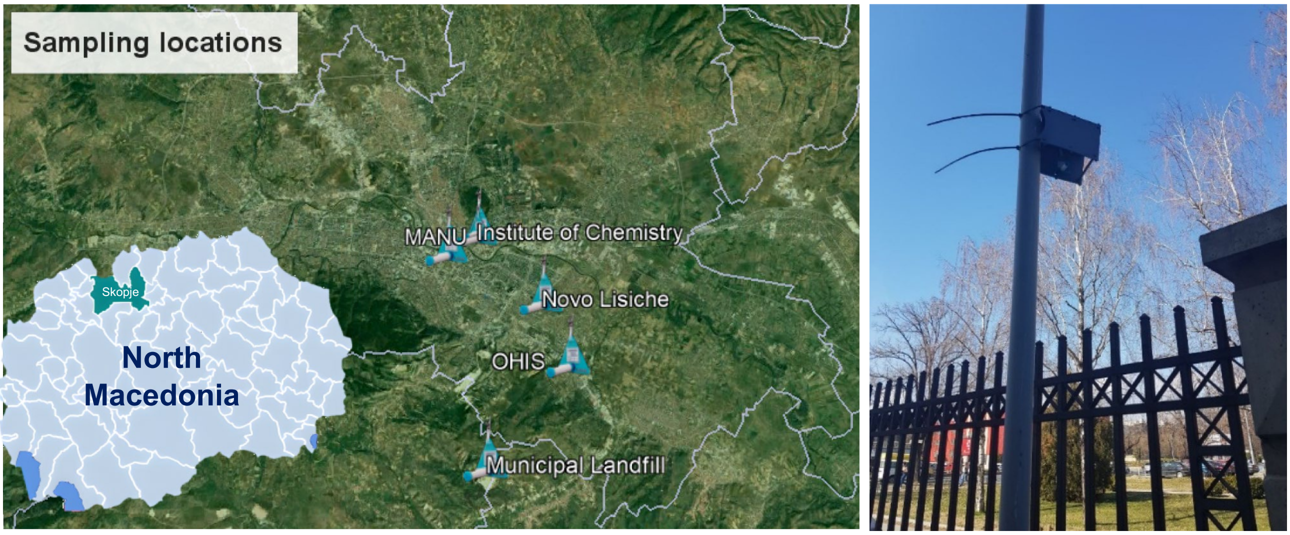


Fig. 1 Locations of the sampling points

at room temperature by adding 2 mL of dichloromethane to the glass tube with the adsorbent during 45 min with occasional shaking. Analyses were performed using gas chromatography coupled with mass spectrometry (GC–MS) under conditions described in previous studies (Sofronievska et al. 2022, 2024). An Agilent 8890N gas chromatograph coupled to a 5977B mass spectrometer as a detector was used with an HP-5 capillary column (30 m × 0.25 mm ID, film thickness 0.25 μm) with a (5%-phenyl)-methylpolysiloxane stationary phase. Helium (purity > 99.999%) was the carrier gas at a constant flow of 1 mL/min. The injection volume was 2 μL with a split ratio of 1:2. The injector temperature was set to 240 °C. Separations were performed in a temperature-programmed mode starting at 80 °C (2-min hold), ramping to 150 °C at 15 °C/min, then to 250 °C at 5 °C/min, and finally to 300 °C at 2 °C/min (5-min hold).

Compounds were identified based on retention times compared to standards, target and qualifier ions, and using the NIST Library of mass spectra (NIST MS Search 2.0).

Quality control and statistical analysis

Quality control involved laboratory and transportation blanks. A control sampler was kept unopened in a cool, dark place and one unopened sampler was transported during each testing period to assess potential transportation effects. Blanks were analyzed alongside the samples and values were mostly below detection limits.

Statistical analysis was performed using Microsoft Excel, while the Wilcoxon Signed-Rank Test and Principal Component Analysis (PCA) were conducted in Python.

The Wilcoxon test, a non-parametric method, was used to compare paired VOC concentrations at different locations without assuming normality.

PCA, widely applied in air pollution studies (Yang et al. 2013; Chen et al. 2020), was used to explore relationships between VOCs and their primary sources. PCA reduces data dimensionality by identifying principal components that capture the most variance. Since variables may load on multiple components, varimax rotation was applied to simplify the structure, maximizing the variance of squared loadings and producing clearer, more interpretable components linked to underlying factors.

Results and discussion

VOCs detected, seasonal trends, spatial differences, and health relevance

A total of 82 VOCs were identified across five monitoring locations during the study period, categorized into four groups: aromatic hydrocarbons, aliphatic hydrocarbons, terpenes, and hydrocarbon derivatives (Table S1 and Figs. 2 and 3). Total VOC concentrations varied considerably across sites and seasons, being lowest in summer and highest in spring. The estimated total VOC concentrations ranged from 14 μg/m^3 (in July at OHIS) to 189 μg/m^3 (in April at OHIS). The April peak at OHIS is probably related to intensified cleanup activities at the lindane landfill, including machinery operation and increased traffic in the area. Aliphatic and aromatic VOCs were consistently higher in winter than summer at all sites (Figs. 2 and 3), driven by emissions from residential heating, industrial activities, traffic and unfavorable meteorology (Elminir 2005; Giakoumi et al. 2009; He et al. 2017). Winter use of firewood, heating oil, and gas likely adds to VOC levels, while low temperatures, reduced sunlight, and frequent inversions slow degradation and trap pollutants near the surface (George et al. 2015; Von Schneidemesser et al. 2015). In contrast, summer's clear, warm, and turbulent conditions (Stafilov et al. 2003), enhance photochemical breakdown by oxidants such as hydroxyl radicals ($^{\bullet}$OH) (George et al. 2015) promoting dispersion and lower concentrations. These seasonal patterns align with other urban studies (McCarthy et al. 2007; Yoshino et al. 2012; Ibragimova et al. 2021; Huang et al. 2023), but were not observed for terpenes and hydrocarbon derivatives.

Aliphatic hydrocarbons were the most abundant VOC class at all sites (Figs. 2, 3 and 4), especially in spring (from 66 to 121 μg/m^3) and winter (from 58 to 100 μg/m^3). *n*-Alkanes with 11 to 14 carbons (*n*-undecane to *n*-tetradecane) dominated. Springs levels were influenced by both anthropogenic and biogenic sources such as leaf growth and pollen release (Kang et al. 2018), while winter concentrations reflected fossil fuels combustion, traffic, industrial activity. The diagnostic carbon maximum number (C_{max}) indicated mixed sources, but the prevalence of low-carbon (C_7–C_{20}) alkanes across seasons suggests strong anthropogenic input, mainly vehicular emissions (Chen et al. 2014; Lyu et al. 2017). Spatial contrasts also emerged among alkanes: *n*-heptane was more abundant at MANU, while *n*-nonane and *n*-decane were elevated at OHIS (Fig. S1), consistent with gasoline and diesel evaporation and combustion emissions (Huang et al. 2015).

Aromatic hydrocarbons were the second most abundant group (9–29 μg/m^3), dominated by BTEX and C_6–C_3 substituted benzenes, with concentrations (17–29 μg/m^3) highest in winter, 1.3–3.1 times higher than in other seasons. BTEX compounds (benzene, toluene, ethylbenzene, *o*-xylene, *p* + *m*-xylene) were elevated at urban sites relative to the Municipal Landfill (Fig. S1), reflecting traffic, industrial activities, and residential heating (Huang et al. 2015). OHIS exhibited particularly high BTEX due to traffic and

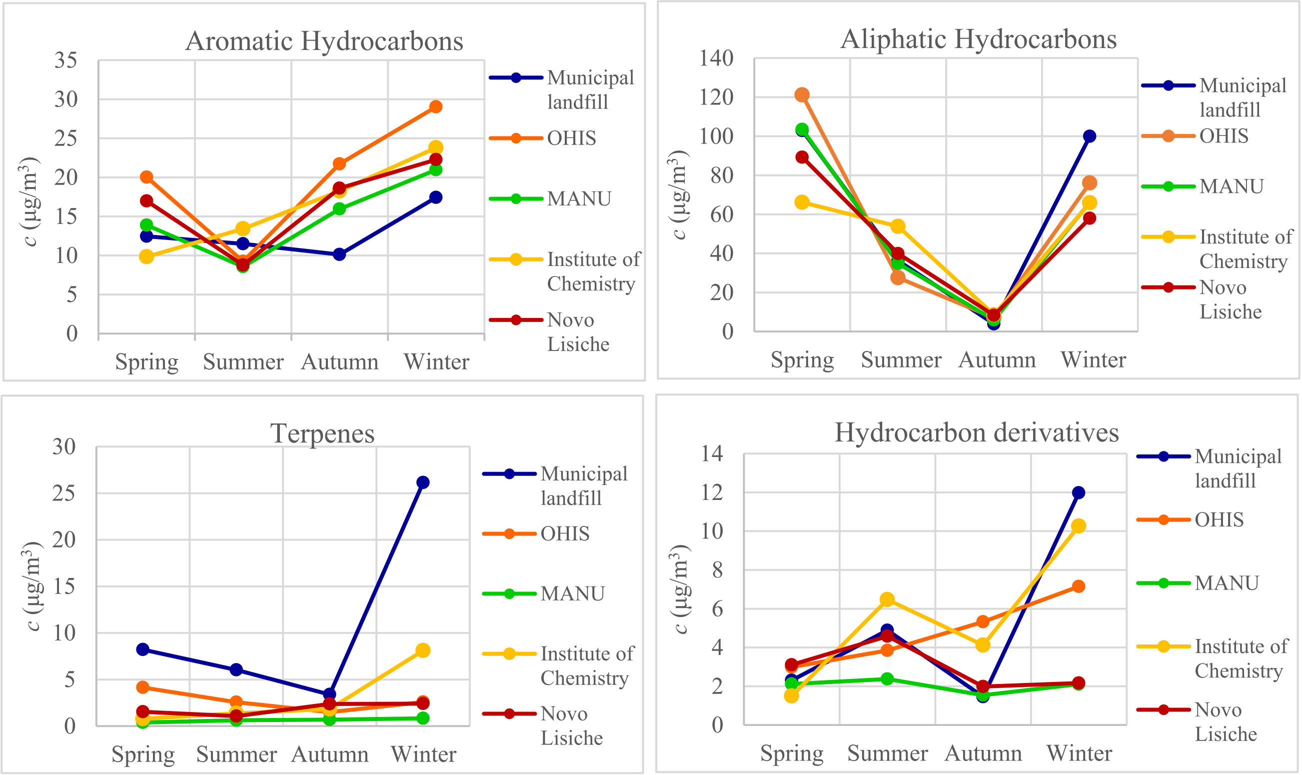


Fig. 2 Seasonal variations of the 4 different groups of VOCs in air at the five locations

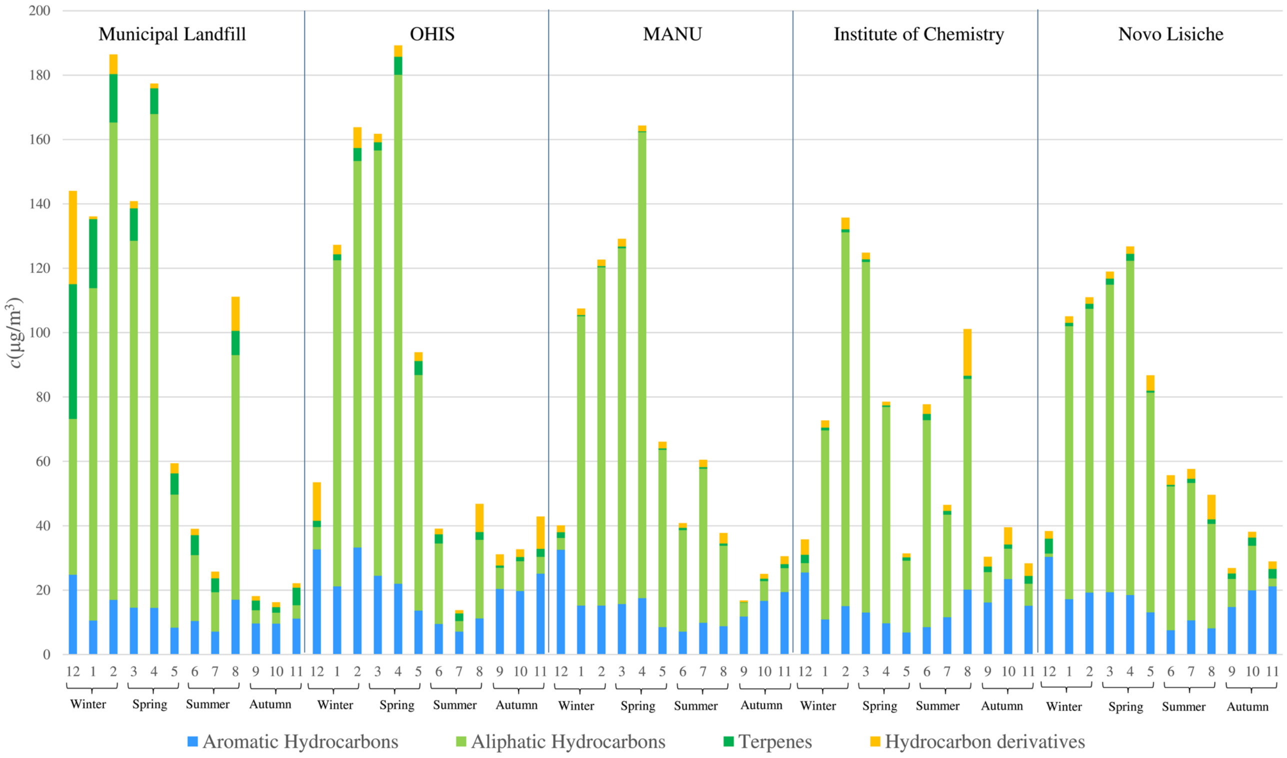


Fig. 3 Monthly variations (µg/m^3) of different VOCs groups at the five locations. Numbers 1–12 represent months (January-December 2022) of the monitoring period (numerical values are provided in Supplementary Table S2

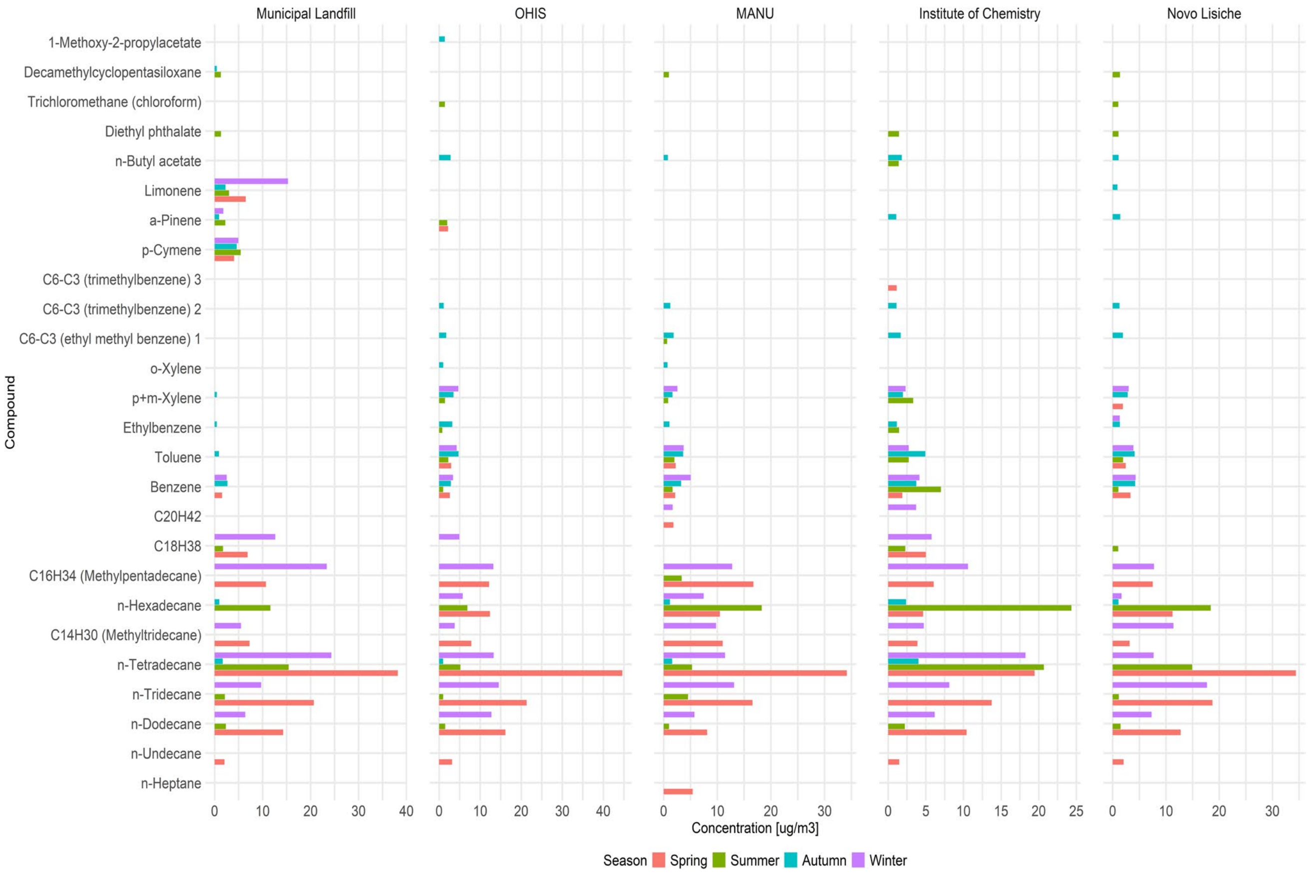


Fig. 4 Most abundant compounds (μg/m^3) at different locations during different seasons

remediation activities at the lindane landfill. Elevated benzene and trimethylbenzenes at Novo Lisiche, MANU, and OHIS suggest diesel-related emissions (Huang et al. 2015). In contrast,

higher *n*-propylbenzene at the landfill was likely linked to organic waste burning and leachate processes (Liu et al. 2016).

In Skopje, BTEX accounted for 29–47% of aromatic compounds at the landfill, and 43–72% at urban sites. The lower BTEX percentages at the Municipal landfill might indicate a more diverse mix of aromatic compounds or less influence from sources typically associated with BTEX emissions, such as vehicle exhaust or industrial processes. Conversely, the higher BTEX levels at other sites could reflect significant contributions from such sources. The relatively high BTEX proportion observed at the Institute of Chemistry, despite its location in a low-traffic area, can likely be attributed to local sources, including emissions from heating systems, dispersion of pollutants from nearby roads and parking areas and minor solvent use in laboratories. Seasonal ratios indicated higher BTEX concentrations in autumn–winter compared to spring–summer: average benzene in winter was 1.3–2.3 times higher than spring and 2.6–4.8 times higher than summer; toluene, 1.5–5.5 times higher than spring and 1.1–2.0 times higher than summer; ethylbenzene, 1.6–2.3 times higher than spring; and o-xylene and *p*+*m*-xylene similarly elevated. These values were below the United States Environmental Protection Agency (EPA) reference concentrations for non-carcinogenic effects (benzene 0.03 mg/m3; toluene 5.0 mg/m3; ethylbenzene 1.0 mg/m3; xylenes 0.1 mg/m3) (U.S. Environmental Protection Agency (EPA) 2023). Chronic benzene exposure at 0.03 mg/m3 increases leukemia risk to 1 in 10,000 (Montero-Montoya et al. 2018). Maximum estimated concentrations in the study were 0.020 mg/m3 for benzene, 0.008 mg/m3 for toluene, 0.006 mg/m3 for ethylbenzene, and 0.009 mg/m3 for xylenes, indicating safe levels but justifying continuous monitoring.

Terpenes, including α-pinene, β-pinene, limonene, and 3-carene, were detected at all sites, originating from vegetation and consumer products such as air fresheners and detergents. Limonene and α-pinene were most frequent, with elevated landfill levels attributable to fresh and green waste emissions and biodegradation (Sadowska-Rociek et al. 2009; Nair et al. 2019). *p*-Cymene was also enriched at the landfill, likely formed through microbial transformation of monoterpenes under anaerobic conditions (Carriero et al. 2018; Nair et al. 2019).

Hydrocarbon derivatives most frequently detected included *n*-butyl acetate, *n*-propyl acetate, tetrachloroethylene, and decamethylcyclopentasiloxane. Esters likely originated from biomass burning and solvent use, with relatively low toxicity (Gao et al. 2021). Tetrachloroethylene, a common solvent, was enriched at OHIS due to historical industrial activity, with moderate levels at Novo Lisiche from local solvent use (Gulyas And Hemmerling 1990). Volatile methyl siloxanes (octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, and hexamethyldisiloxane) were detected at low concentrations (<0.03 µg/m^3), with decamethylcyclopentasiloxane occurring most frequently. While far below landfill gas values reported elsewhere (up to 50 mg/m3; Ghorbel et al. 2014), their persistence and bioaccumulation potential pose environmental concerns (Okan et al. 2021). Butyl acetate was highest at the Institute of Chemistry, reflecting solvent use, while OHIS values likely originated from traffic or industrial emissions.

The most abundant VOCs across all sites and seasons included alkanes (C_{11}–C_{16}), BTEX, C_6–C_3 substituted benzenes, *p*-cymene, α-pinene, limonene, *n*-butyl acetate, diethyl phthalate, and decamethylcyclopentasiloxane (Fig. 4, Figs. S2 and S3, Supplementary). Spring and winter top ten VOCs were dominated by *n*-alkanes and aromatics, with *n*-tetradecane, *n*-tridecane, and *n*-hexadecane consistently among the most abundant. Aromatic VOCs were generally less abundant than aliphatics, except in autumn, when their contribution increased.

Overall, the non-parametric Wilcoxon Signed-Rank test showed that 20 of 82 VOCs exhibited statistically significant spatial variation (Supplementary Fig. S1). Toluene, *o*-xylene, *p*+*m*-xylene, and ethylbenzene were higher at urban sites relative to the landfill, reflecting traffic, industry, and residential heating (Huang et al. 2015). Alkanes and terpenes showed site-specific differences: *n*-heptane at MANU, *n*-nonane and *n*-decane at OHIS, α-pinene and limonene at the landfill (Sadowska-Rociek et al. 2009; Nair et al. 2019)). Tetrachloroethylene was markedly higher at OHIS, *p*-cymene was enriched at the landfill, and butyl acetate peaked at the Institute of Chemistry. This indicates that while some compounds are tied to localized sources, many VOCs are more evenly distributed, reflecting regional background or common urban emissions.

Source appointment

Source apportionment was performed using PCA and toluene-to-benzene ratios (T/B). The results are presented in the following sections.

BTEX diagnostic ratios, particularly the toluene-to-benzene (T/B) ratio, are commonly used to identify VOC sources and photochemical age (Miller et al. 2011; Marć et al. 2014a; Marčiulaitienė et al. 2017; Hajizadeh et al. 2018). The toluene-to-benzene (T/B) ratio of 1.5–3.0 typically indicates traffic emissions, with regional variations reflecting vehicle and fuel differences (Hoque et al. 2008; Marć et al. 2014a). In Skopje, summer T/B ratios fell within this range at all sites except the Municipal Landfill (Fig. 5 and Table S3 indicating traffic as the primary source of benzene and toluene in summer and near OHIS in autumn. These results are consistent with other studies that reported a higher T/B ratio in summer (Marčiulaitienė et al. 2017; Hajizadeh et al. 2018). Lower ratios in other seasons suggest additional sources, such as domestic heating and industrial activities using coal, wood, or heavy fuel oil. At the landfill, lower T/B values likely reflect open burning practices rather than traffic.

Correlation analysis further helps identify shared VOC sources. The results are summarized in Table 1. At the Municipal Landfill, benzene showed weak correlations with other BTEX (benzene-toluene: 0.22; benzene-*o*-xylene: 0.09), suggesting distinct sources like waste management, while toluene correlated strongly with ethylbenzene (0.79) and xylenes (0.76–0.88), indicating common sources. At OHIS, strong correlations among toluene, ethylbenzene, and *o*-xylene (0.70–0.84) suggest shared industrial or traffic-related emissions. MANU showed very high correlations across BTEX (toluene-*o*-xylene: 0.98; ethylbenzene-o-xylene: 0.99), reflecting dominant common sources, likely industrial or vehicular. At the Institute of Chemistry, benzene correlations with other BTEX were near zero (0.03–0.10), indicating distinct sources, while ethylbenzene and xylenes showed very strong correlations, pointing to local point sources. Novo Lisiche exhibited high correlations across all BTEX (toluene-ethylbenzene: 0.98; ethylbenzene-*o*-xylene: 0.99), consistent with shared traffic or industrial sources.

Overall, benzene is mainly vehicular, whereas other BTEX compounds derive from both traffic and industrial sources (Miri et al. 2016). High correlations at MANU, OHIS, and Novo Lisiche indicate shared sources, while weaker correlations at the landfill and Institute of Chemistry reflect more diverse or isolated sources. The consistently strong correlations between toluene and xylene isomers suggest frequent co-emission from industrial or vehicular activities.

Principal component analysis (PCA)

To identify potential sources of VOCs, 35 of the 82 detected compounds were selected for PCA, representing 82.5–99.2% of total VOC concentrations (the factor loadings are presented in Table S4).

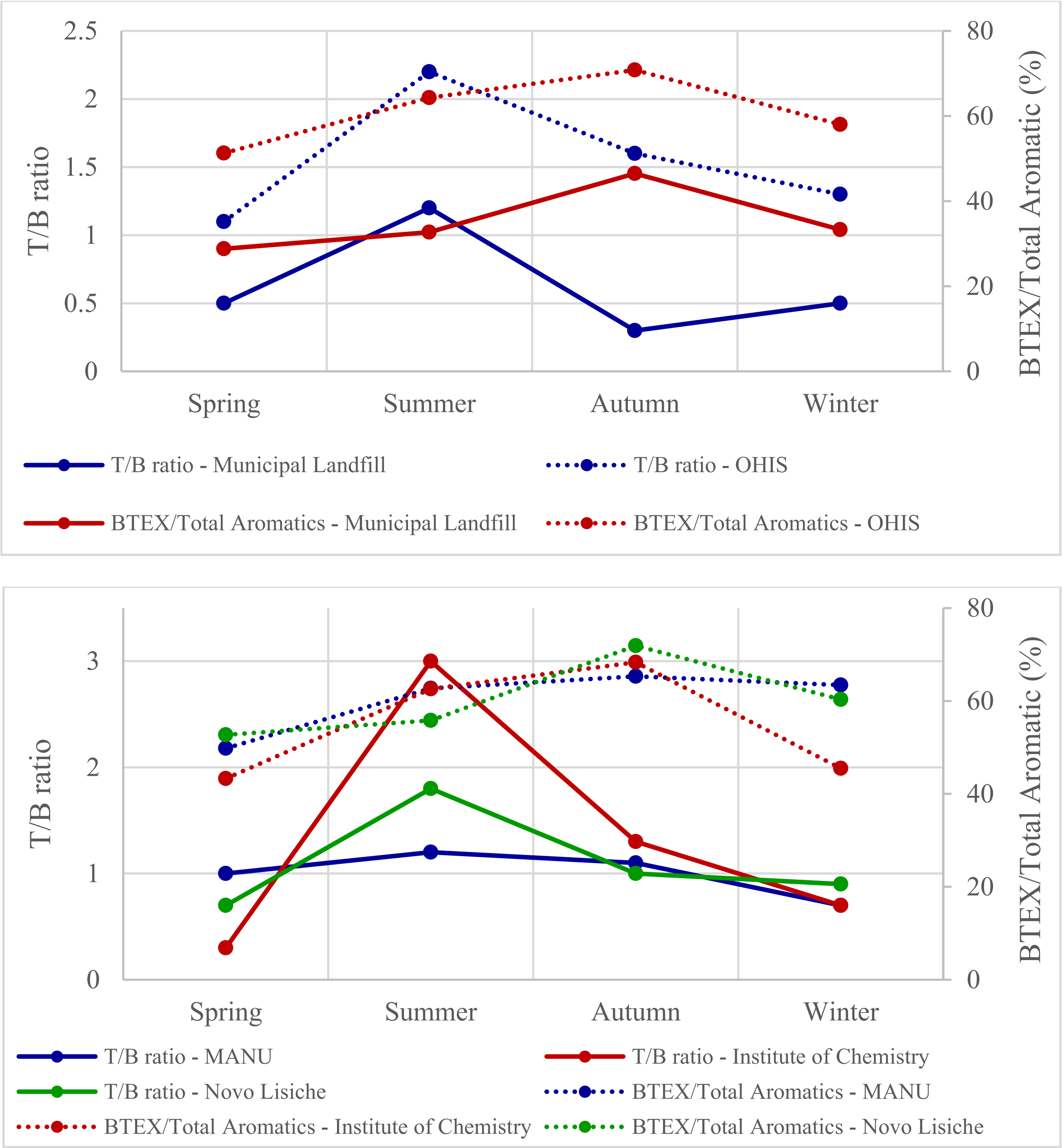


Fig. 5 T/B ratio and % BTEX in Total Aromatics at the five locations

The number of principal components was determined using the Kaiser criterion, where only components with eigenvalues greater than 1 were considered (Yang et al. 2013) and the requirement that each factor had at least one variable with a loading of 0.7 or higher. As a result, a 6-factor solution was selected for the VOC dataset, accounting for 72% of the total variance. Factor 1 accounted for 23.2% of the total variance, while Factor 6 contributed 5.44%. Figure 6 presents a heatmap of the PCA loadings for the VOCs, helping to identify which compounds contribute most to each principal component in order to reveal potential sources behind the VOC profiles.

Factor 1 (23.2%) is dominated by *n*-alkanes (C_{11}–C_{16}) and C_6–C_3 substituted benzenes, markers of diesel and

Table 1 Correlation analysis of BTEX

	Municipal Landfill	OHIS	MANU	Institute of Chemistry	Novo Lisiche
Correlation	*r*	*r*	*r*	*r*	*r*
Benzene-Toluene	0.22	0.36	0.81	0.55	0.89
Benzene-*p*+*m*-xylene	0.30	0.57	0.82	0.04	0.87
Benzene-*o*-xylene	0.09	0.44	0.87	0.03	0.86
Benzene-ethylbenzene	0.12	0.14	0.82	0.10	0.87
Toluene-Ethylbenzene	0.79	0.70	0.97	0.61	0.98
Toluene-*p*+*m*-xylene	0.76	0.77	0.80	0.43	0.88
Toluene-*o*-xylene	0.88	0.81	0.98	0.57	0.96
Ethylbenzene-*p*+*m*-xylene	0.60	0.50	0.75	0.96	0.91
Ethylbenzene-*o*-xylene	0.65	0.84	0.99	0.99	0.99
o-xylene-*p*+*m*-xylene	0.75	0.72	0.81	0.95	0.92

gasoline exhaust (Liu et al. 2008; Dumanoglu et al. 2014), indicating traffic emissions. **Factor 2** is characterized by toluene, ethylbenzene, and xylenes, linked to vehicle exhaust, fuel evaporation, and industrial solvents (Huang And Hsieh 2019), consistent with T/B ratios and BTEX correlations that indicate a common source for these compounds. **Factor 3** (10.05%) includes limonene, α- and β-pinene, *p*-cymene, and propyl acetate, reflecting biogenic emissions from vegetation.

Factor 4 (7.58%) features aliphatic hydrocarbons (*n*-heptane, methylcyclohexane, C_{14}–C_{16} alkanes), indicating fuel evaporation from refueling, storage, or petroleum infrastructure rather than combustion (Chin And Batterman 2012). **Factor 5** (6.62%) comprises decamethylcyclopentasiloxane, diethyl phthalate, and n-propyl acetate, representing personal care products and plasticizers (Cao 2010; Gouin et al. 2013). **Factor 6** includes ethylbenzene, isopropylbenzene, tetrachloroethylene, and C_8–C_{10} alkanes, pointing to industrial solvent use, refinery emissions, and petroleum-related activities (Liu et al. 2008).

PCA provides insight into VOC sources, though factors may represent mixed rather than pure sources due to overlapping emissions and atmospheric transformations (Hopke 2016). Combined with T/B ratio analysis, results confirm that traffic and industrial activities, particularly vehicle exhaust, fuel evaporation, and domestic/industrial combustion of low-quality fuels, are the primary contributors to VOC levels in Skopje.

Published data from the State Statistical Office, Ministry of Interior, and Ministry of Environment and Physical Planning indicate that the total number of registered vehicles in the Skopje region grew from 161,474 in 2014 to 436,502 nationwide by 2015, with a 15.3% increase in Skopje between 2012 and 2016 (Dodovski And Temjanovski 2020). Passenger cars dominated the fleet (88% in 2016), and diesel vehicles increased sharply: diesel passenger cars rose from 25 to 38% (77% growth), diesel freight vehicles by 62%, and diesel buses from 83 to 90%. This growth, combined with the high share of diesel vehicles and a mix of older cars, likely sustains elevated urban VOC levels, consistent with the *n*-alkane concentrations observed in this study.

Household energy data show that most of the 161,841 households in Skopje were built before 1991, with 38% using electricity and 29% connected to district heating; wood remains widely used for heating (33%), alongside coal and heavy fuel oil in smaller amounts (Ministry of Environment And Physical Planning 2016). Biomass burning accounts for nearly 99% of VOC emissions from domestic heating, contributing both aliphatic hydrocarbons (including *n*-alkanes) and aromatic compounds (BTEX) (Sun et al. 2019). Heavy fuel oil (HFO), used mainly in industrial and institutional heating, contains complex mixtures of long-chain alkanes, aromatics, sulfur- and nitrogen-containing compounds, making its combustion emissions more polluting than lighter fuel oils (ERC MK EWS and MWMSRC 2023, McKee et al. 2014).

Relationship between average concentrations of each VOCs class and $PM_{2.5}$, ozone, UV index and temperature

Seasonal variations in VOC concentrations in Skopje are influenced not only by emission sources but also by meteorological conditions such as temperature, UV radiation, and ozone. Pearson correlation analysis ($p=0.05$) was used to assess relationships between $PM_{2.5}$, ozone, UV index, temperature, and the average monthly concentrations of each VOC class (Table 2). Correlation strength was interpreted as strong (0.60–0.85), weak (0.00–0.30), moderate negative (−0.30 to −0.50), or strong negative (−0.50 to −0.85).

During the monitoring period, average air temperatures ranged from 2.15 to 24.12 °C (Table S5), and $PM_{2.5}$ and ozone data were obtained from the Ministry of Environment and Physical Planning of Macedonia (Ministry of environment and physical planning – Republic of North Macedonia 2022). $PM_{2.5}$ showed strong positive correlations with aromatic hydrocarbons ($r=0.71$) and terpenes ($r=0.63$), but no significant correlation with aliphatic hydrocarbons or hydrocarbon derivatives ($p>0.05$), indicating that emissions of aromatics and terpenes are accompanied by fine particle formation.

Ozone exhibited a strong negative correlation with aromatic hydrocarbons ($r=-0.74$), reflecting photochemical reactions of aromatics that produce ozone (Giakoumi et

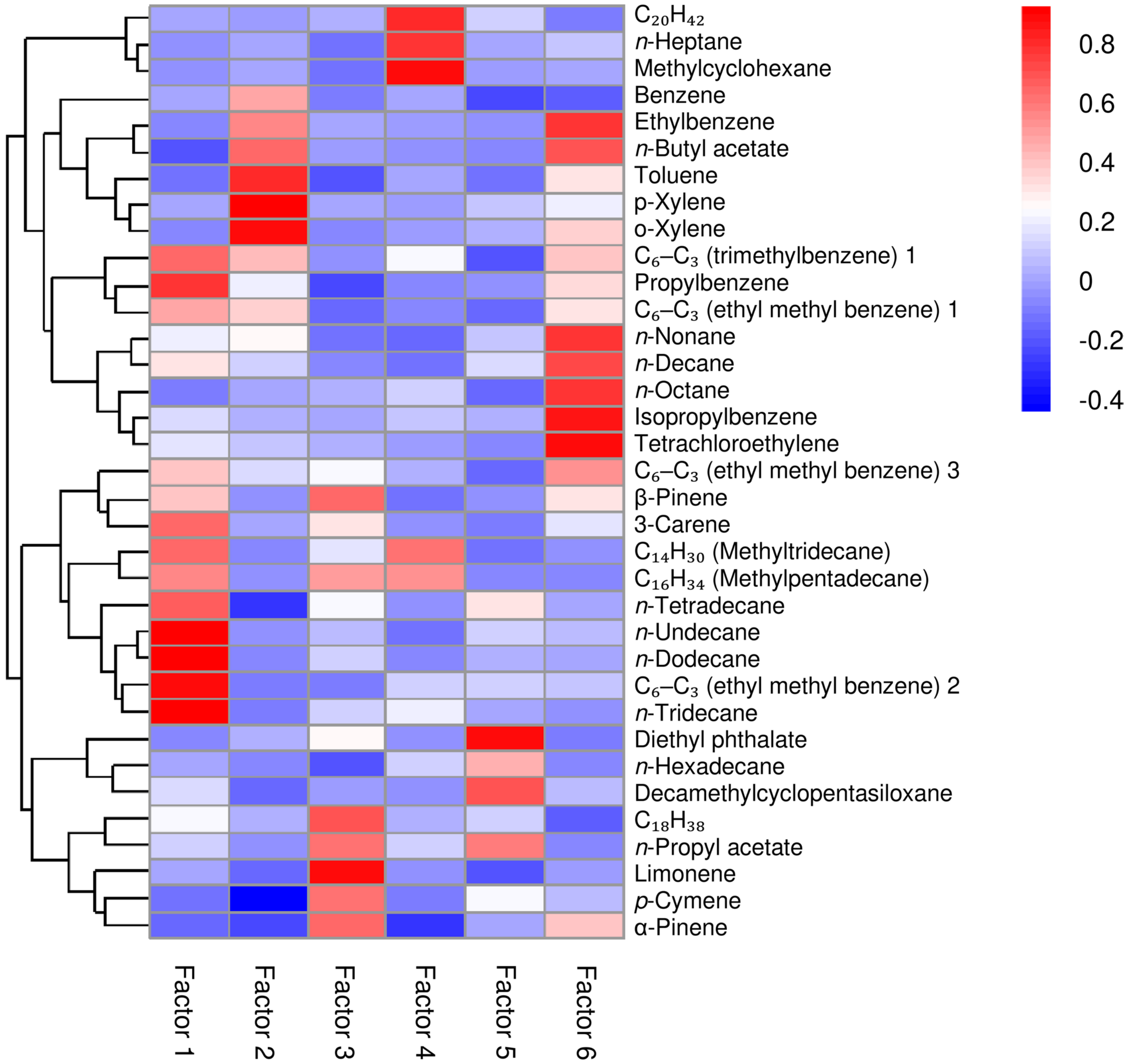
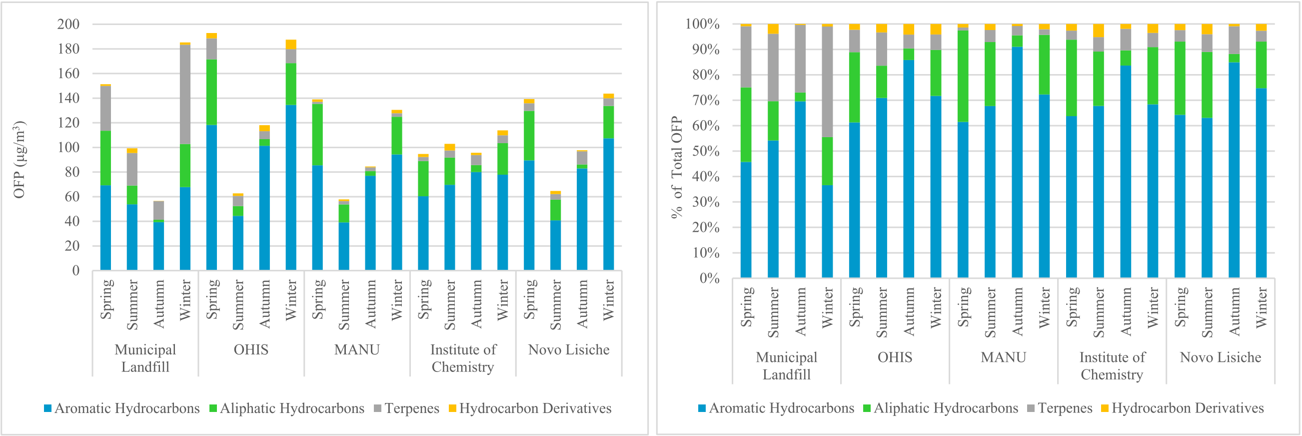


Fig. 6 Heatmap of PCA Loadings for VOC Source Apportionment

Table 2 Pearson correlation coefficients between $PM_{2.5}$, O_3, monthly temperature and UV and average concentrations of VOCs classes ($p < 0.05$) (strong positive, strong negative correlation)

	Pearson correlation coefficients							
Compound class	$r(PM_{2.5})$	p-value	$r(O_3)$	p-value	r(temp.)	p-value	r(UV)	p-value
Aromatic Hydrocarbons	0.71	0.01	−0.74	0.01	−0.65	0.02	−0.80	0.00
Aliphatic Hydrocarbons	0.00	1.00	−0.27	0.40	−0.58	0.05	−0.09	0.78
Terpenes	0.63	0.03	−0.47	0.12	−0.56	0.06	−0.57	0.05
Hydrocarbon Derivatives	0.23	0.48	−0.19	0.55	−0.03	0.93	−0.20	0.53

al. 2009). Similarly, UV radiation was strongly negatively correlated with aromatic hydrocarbons ($r = -0.80$), consistent with UV-driven degradation (Słomińska et al. 2014). Temperature also negatively correlated with aromatic ($r = -0.65$) and aliphatic ($r = -0.58$) VOCs, suggesting accelerated photochemical breakdown in summer under higher temperatures and stronger sunlight (Xiong et al. 2021). In the troposphere, aliphatic VOCs react with ˙OH, ˙NO_3, ˙Cl,



a)

b)

Fig. 7 **a** Total ozone formation potentials and **b** fraction of the total ozone formation potential for different classes of VOCs across seasons at the five locations

or O₃ to form alkyl radicals, while aromatic VOCs form ring-adducts that further generate phenols, carbonyls, and organic nitrates (Atkinson And Arey 2003). These transformations reduce parent VOC concentrations, explaining lower summer levels compared to winter.

Overall, VOC pollution in Skopje is shaped by both emissions and seasonal atmospheric processes, with temperature, UV radiation, and ozone modulating concentrations in addition to $PM_{2.5}$-associated source contributions.

Ozone formation potentials

VOCs contribute to ozone formation through reactions with free radicals, though their contribution is not proportional to ambient ozone levels due to differences in reactivity with NO_x and $^{\bullet}OH$ radicals (Luo et al. 2020; Zulkifli et al. 2022). In this study, the ozone formation potential (OFP) of VOCs was calculated using the maximum incremental reactivity (MIR) method (Carter 2008, 2010):

$$\mathrm{OFP}\,(\mathrm{VOC}) = C\,(\mathrm{VOC})\,\mathrm{MIR}\,(\mathrm{VOC})$$

where C(VOC) is the VOC concentration (μg/m^3) and MIR is the reactivity coefficient (g O_3/g VOC). This approach accounts for mechanistic reactions and VOC/NOx ratios in ozone formation (Carter 2008).

The total OFPs across seasons ranged from 57 to 193 μg/m^3 (Fig. 7 and Table S7), averaging 116 μg/m^3, with seasonal values of 144 μg/m^3 in spring, 78 μg/m^3 in summer, 91 μg/m^3 in autumn and 152 μg/m^3 in winter. The seasonal variation in OFP in this study does not completely match the pattern of the observed ozone levels. While OFP was higher in spring and winter, the observed O₃ concentrations were highest in summer and autumn. This discrepancy can be attributed to the reaction between NO and O₃, which forms NO₂ and reduces ambient ozone concentrations. Meteorological factors, such as sunlight, temperature, and atmospheric mixing, may also influence ozone formation. These findings are in agreement with previous studies (Wang et al. 2022; An et al. 2024), which also reported that high OFP does not necessarily lead to high ozone levels due to such reasons.

The average OFP was highest at OHIS (140 μg/m^3), followed by the landfill (123 μg/m^3), MANU (103 μg/m^3), Institute of Chemistry (102 μg/m^3), and Novo Lisiche (111 μg/m^3).

Although aromatic VOCs represented only 10–26% of total VOCs (Fig. 7; except in autumn: 59%), they contributed the largest fraction of total OFP (37–91%) across all locations and seasons, except in winter at the landfill, where terpenes contributed more (44% vs. 37%). This reflects the high reactivity (MIR) of aromatics such as toluene, xylenes, and C_6–C_3 substituted benzenes, despite lower ambient concentrations compared to aliphatic VOCs. Contributions from aromatics were highest in winter and lowest in summer, consistent with observed seasonal VOC patterns.

The top 10 VOCs contributing to OFP at each location are presented in Fig. S4 and Table S7. Across all seasons and sites, excluding the landfill, key contributors were toluene, *p*+*m*-xylene, C_6–C_3 substituted benzenes, *n*-tetradecane, and *n*-hexadecane. At the landfill, terpenes (limonene, α-pinene) and *p*-cymene dominated OFP. Interestingly, these high-OFP species often differ from the most abundant VOCs. For example, in spring, the top ten VOCs account for 25–53% of total OFP, increasing to 32–61% in summer and 57–82% in autumn, while in winter their contribution declines to 25–66%, reflecting seasonal photochemical activity and emission patterns.

These results indicate that VOCs with the highest OFP, particularly xylenes, toluene, C_6–C_3 substituted benzenes, and *n*-tetradecane, play a disproportionately large role in ozone formation in Skopje and should be prioritized in air quality control strategies.

Conclusion

This study provides the first comprehensive, year-long assessment of VOCs in ambient air in Skopje, using a validated passive sampling method at five strategically selected urban sites identified in a prior city-wide survey as representative of highly polluted and relevant areas in the city (Sofronievska et al. 2022). However, it must be acknowledged that the study focuses on selected representative locations rather rather than covering the entire city of Skopje.

A total of 82 VOCs were detected, encompassing aliphatic hydrocarbons, aromatic hydrocarbons (BTEX and C_6–C_3 substituted benzenes), terpenes, and hydrocarbon derivatives. Seasonal variations revealed markedly higher concentrations of both aliphatic and aromatic VOCs in winter, reflecting the combined impact of traffic density, domestic heating with coal, wood, and heavy fuel oil, industrial activities, and meteorological conditions that favor pollutant accumulation. In contrast, summer exhibited lower VOC levels due to enhanced photochemical degradation and atmospheric dispersion.

Aliphatic hydrocarbons, dominated by C_{11}–C_{16} *n*-alkanes, were the most abundant compounds across all sites, while aromatic VOCs, despite lower concentrations, contributed the largest fraction of ozone formation potential due to their high reactivity, highlighting their role in secondary pollution.

Terpenes, including limonene and α-pinene, were present year-round, with elevated levels near the municipal landfill, while hydrocarbon derivatives such as *n*-butyl acetate, diethyl phthalate, and decamethylcyclopentasiloxane indicate additional sources including personal care products and industrial emissions.

Source apportionment through T/B ratios and PCA identified six principal factors: mixed traffic (gasoline + diesel), solvent/industrial emissions, biogenic emissions, fuel evaporation, personal care products/plasticizers, and industrial/solvent-related sources. Traffic and fuel-related VOCs dominated areas with high vehicle density, while localized industrial operations and waste degradation contributed to elevated VOC levels at specific sites. Many VOCs originated from overlapping sources, underscoring the complexity of urban air pollution in Skopje. Correlation analyses showed strong associations between $PM_{2.5}$ and aromatics/terpenes, and significant negative correlations between VOC concentrations and temperature, UV radiation, and ozone, emphasizing the role of photochemical reactions in seasonal variability. Ozone formation potential analysis revealed that highly reactive species—particularly toluene, xylenes, C_6–C_3 substituted benzenes, and *n*-tetradecane—disproportionately drive ozone production across locations and seasons, regardless of abundance.

Overall, this study provides critical baseline data on VOC concentrations, sources, and atmospheric transformations in Skopje, offering an evidence-based foundation for air quality management and targeted emission control strategies. The findings highlight the importance of addressing both mobile and stationary sources and are relevant to other cities in North Macedonia and the Western Balkans, where traffic, domestic heating, and industrial activities remain major contributors to urban air pollution. Future research should expand monitoring efforts, include additional urban and industrial areas, and assess the health impacts associated with chronic VOC exposure.

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Author contributions All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Ivona Sofronievska and Marina Stefova. Ivona Sofronievska wrote the first draft of the manuscript and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability Data generated or analyzed during this study are included in this published article and its supplementary information files. Additional information is available from the corresponding author on reasonable request.

Declarations

Ethics approval This study did not involve human participants, animals, or any personally identifiable or protected data, and therefore did not require ethical approval.

Consent to participate Not applicable, as the study did not involve human participants.

Consent to publish Not applicable, as the study did not involve human participants or any individual data requiring consent.

Competing interests The authors declare that they have no competing interests and have no relevant financial or non-financial interests to disclose.

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