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Wintertime VOC concentration measurements in a Northern traffic supersite demonstrate the strong role of anthropogenic terpene emissions in VOC chemistry

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Abstract. Volatile organic compounds (VOCs) are key drivers of urban atmospheric chemistry, acting as precursors to ozone and secondary organic aerosol (SOA). Terpenes, typically considered biogenic, may also have important anthropogenic sources in cities, although distinguishing these contributions remains challenging.

We measured terpenes and other VOCs (C_6–C_{15}) using in situ TD-GC-MS at a traffic supersite in Helsinki during winter 2022, when biogenic emissions were minimal. Additional offline measurements of lighter hydrocarbons (C_2–C_5) were conducted at residential and urban background sites. Most VOCs, including benzene, furfural, naphthalene, and p-cresol, showed higher concentrations at the residential and background sites, indicating a strong influence from wood combustion. In contrast, terpenes were elevated at the traffic site, suggesting emissions from other anthropogenic activities.

At the traffic site, terpenes had a mean concentration of 164 ng m^{-3}, contributing less than 1% of total measured VOC mass. Despite their low abundance, they played a significant role in atmospheric chemistry due to high reactivity, accounting for 7% of hydroxyl radical reactivity, 59% of ozone reactivity, and 65% of nitrate radical reactivity among the measured VOCs. Combined with their strong SOA formation potential, this highlights the importance of anthropogenic terpene emissions for urban air quality.

Intermediate-volatility VOCs (IVOCs, C_{11}–C_{15}) were present at low concentrations and generally had minor contributions, although undetected compounds may still be relevant. Among them, sesquiterpenes showed notable ozone reactivity (23%) despite concentrations below 3 ng m^{-3}.

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1 Introduction

Volatile organic compounds (VOCs) play a central role in urban atmospheric chemistry, serving as precursors to tropospheric ozone and secondary organic aerosol (SOA) formation, both of which significantly affect air quality, climate forcing, and human health (Atkinson, 2000). In most cities, traffic emissions were long regarded as the dominant VOC source, but their contribution has decreased substantially across many developed countries following the implementation of stricter vehicle emission standards, improved exhaust after-treatment technologies, and the increasing use of electric vehicles (EEA, 2019). As a result, relative importance of other anthropogenic VOC sources, such as volatile chemical products (VCPs), which include cleaning agents, solvents, coatings, paints, adhesives and personal care products have increased (McDonald et al., 2018; Coggon et al., 2021; Gkatzelis et al., 2021). VCPs are released by evaporation during use, application, and storage. Eddy covariance measurements, ambient observations, and inventories have shown that VCP-related emissions can be comparable in magnitude to traffic emissions in many cities, and in some cases exceed them (Karl et al., 2018; Gkatzelis et al., 2021). This shift has important implications for ozone and SOA formation because VOCs emitted by the VCPs often exhibit different chemical reactivities and oxidation pathways than combustion-related compounds.

Among non-traffic related VOCs, terpenes are of particular interest. Globally, vegetation is the dominant source of terpene emissions (Guenther et al., 2012). However, increasing evidence indicates that anthropogenic activities also emit significant amounts of terpenes (Katz et al. 2025; Coggon et al. 2021; Gkatzelis et al. 2021). Terpenes are commonly classified as VCPs and used in fragrances, cleaning agents, disinfectants and released during cooking, making them ubiquitous indoors (Steinemann et al. 2011; Kelin et al. 2016; You et al. 2022). Indoor terpene concentrations are typically higher than outdoors (Sheu et al., 2021), suggesting that indoor–outdoor exchange could be an important source of ambient terpenes in cities. Furthermore, human-related activities, such as consumer product use, building ventilation, and direct emissions from gatherings of people, have been identified as potential contributors (You et al., 2022). Although emissions from these pathways are often small individually, their cumulative contribution in densely occupied urban environments may be non-negligible.

Despite their often low abundance compared to other VOCs, terpenes can dominate the reactivity of the urban atmosphere due to their rapid oxidation by OH, O_3, and NO_3 radicals (Atkinson and Arey, 2003). Their oxidation products contribute to SOA formation, influencing particulate matter concentrations and hence urban air quality (Zhao et al., 2015). Therefore, understanding the magnitude, variability, and chemical role of anthropogenic terpene emissions is crucial for improving air quality assessments and chemical transport models.

Distinguishing between biogenic and anthropogenic terpene sources in urban areas is challenging, particularly in warmer seasons when vegetation emissions dominate. Green urban infrastructure such as parks, roadside trees, and green roofs further complicates this attribution by adding local biogenic inputs. Several approaches have been applied, including weekday–weekend ratios (Katz et al., 2025; Peron et al., 2024), tracer compounds such as limonene (Gkatzelis et al., 2021), emission inventories (Katz et al., 2025), and source-apportionment methods (Peng et al. 2022; Hellén et al., 2012). However, overlapping emission signatures, chemical transformations, and turbulent mixing often limit the precision of source separation.

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Wintertime observations offer an opportunity to bypass many of these difficulties. Under sub-zero low-light conditions in northern latitudes, biogenic terpene emissions are minimal, allowing anthropogenic signals to be isolated with greater confidence. In this study, we investigate the contribution of anthropogenic terpene emissions to urban VOC chemistry using wintertime measurements from a street canyon in Helsinki, Finland. The in situ VOC measurements were conducted during a winter aerosol characterization campaign (Teinilä et al., 2025) and capture conditions in which biogenic emissions are negligible. This setting provides a unique opportunity to isolate anthropogenic terpene sources, examine their temporal variability, and assess their influence on atmospheric reactivity under low-temperature, low-light conditions. Our results provide new insight into the chemical role of anthropogenic terpenes in northern European cities during winter and highlight their importance for urban air quality management and future emission inventory development.

The headings of all sections, including introduction, results, discussions, or conclusions must be numbered. Three levels of sectioning are allowed, e.g. 3, 3.1, and 3.1.1. The abbreviation "Sect." should be used when it appears in running text and should be followed by a number unless it comes at the beginning of a sentence. Footnotes should be avoided in the text, as they tend to disrupt the flow of the text. If absolutely necessary, they should be numbered consecutively. Footnotes to tables should be marked by lowercase letters.

2 Methods

1.1 Measurement sites

Traffic supersite: The principal measurement site of the winter campaign was the traffic supersite station, an urban air quality station operated by the Helsinki Region environmental Services Authority (HSY). It is located in a street canyon on Mäkelänkatu street in Helsinki (60.1964° N, 24.9521° E). The site has continuous monitoring of urban air pollutants and particle properties, and during the campaign, an additional container was installed to accommodate intensive in situ VOC and other measurements.

Mäkelänkatu is a busy six-lane street with tram lines, rows of trees, and sidewalks, with a total width of approximately 42 m near the station. The site is strongly influenced by traffic emissions, with an average weekday traffic volume of about 17,000 vehicles, including ~10% heavy-duty vehicles (City of Helsinki). A more detailed description of the site can be found e.g. from Teinilä et al. (2025).

Urban background (UB) supersite: The SMEAR III station, located at the University of Helsinki Kumpula campus (60.2029° N, 24.9612° E) approximately 0.9 km from the traffic supersite, served as the urban background supersite (Järvi et al., 2009). The station is situated ~150 m from a main road with ~50,000 vehicles per weekday, including a significant fraction of heavy-duty traffic. However, due to the greater distance from the road, the site is less directly affected by traffic than the traffic supersite. During winter, local residential wood combustion also contributes to emissions at the site. The UB supersite hosts continuous monitoring of aerosol and trace gas properties, and during the campaign, additional instruments were installed to provide complementary data on urban background air.

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Residential site: Tapanila station (60.2638° N, 25.0241° E) run by the Helsinki Region Environmental Services Authority (HSY) is located in a densely constructed detached housing area of Helsinki 8.5 km from the traffic supersite. Traffic volumes are low, and wood combustion appliances are used in several houses.

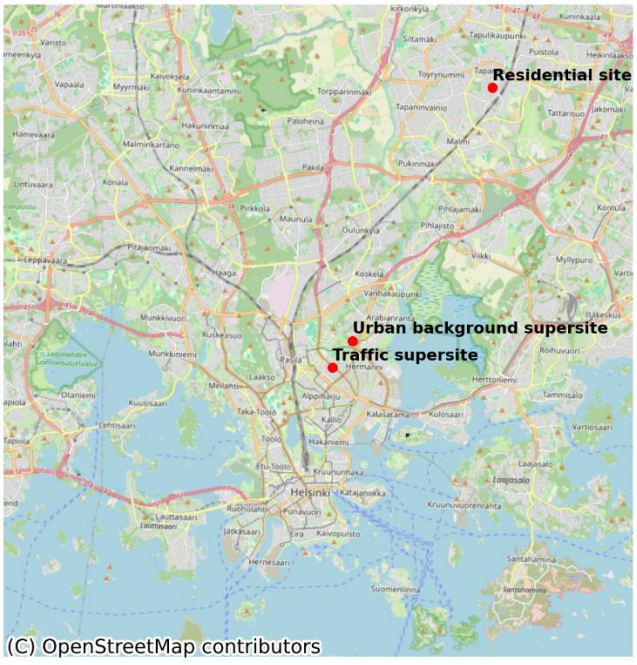

Figure 1: Map of the measurement sites in Helsinki, Finland

2.2 VOC measurements

Volatile organic compounds (VOCs) and intermediate volatile organic compounds (IVOCs) with 6 to 15 carbon atoms were monitored at one-hour intervals using an in situ thermal desorption-gas chromatograph-mass spectrometer (TD-GC-MS) at the traffic supersite. The quantified compounds comprised 10 terpenoids, 15 alkanes, 20 aromatic hydrocarbons, 4 oxygenated aromatic hydrocarbons, and 8 polycyclic aromatic hydrocarbons (PAHs) (see Table S1). The measurement system included a TurboMatrix 350 thermal desorption (TD) unit equipped with an online sampling accessory, Clarus 680 gas chromatograph (GC), and Clarus SQ 8 T mass spectrometer (MS), all procured from PerkinElmer. The GC column employed was an Elite-5MS with dimensions of 60m x 0.25mm (i.d.) and a film thickness of 0.25µm (PerkinElmer). Samples were directed to the TD's Tenax-TA & Carbopack B dual absorbent cold trap maintained at 20°C. Sampling occurred approximately 3 meters above street level at the traffic supersite. The inlet, a 1/8-inch FEP line, had its exterior heated to around 30°C. Ozone was eliminated from the sample flow by passing it through a 1/8-inch stainless steel tube heated to 120 °C. The inlet flow of 300-800 ml/min

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was used, with the TD collecting samples of 30-45 minutes at a flow rate of 40 ml/min. A more detailed description of the system and methodology is available in (Helin et al., 2020).

Additional tube samples were obtained from the UB supersite and the residential site. Sampling involved the use of Tenax-TA & Carbopack B dual absorbent tubes via a modified sequential tube sampler (STS 25 Unit, PerkinElmer). Key modifications included upgrading the sampling pump and replacing the stainless steel rain cover with PFA. The carousel, holding 24 tubes at a time, operated with a sampling time set for 4 hours, resulting in sampling sets lasting 4 days. The sampling flow was 80-100 ml min^{-1}, and the tubes were subsequently analyzed in the laboratory using a TD-GC-MS setup similar to the one described for in situ samples.

Non-methane hydrocarbons (NMHCs) were sampled in silcosteel-coated stainless steel vacuum canisters. The flow from ambient air to the canisters was controlled by a critical orifice, limiting the sampling time to 24 h. Before analysis, the canisters were overpressurized with pure nitrogen (99.9999%). From the pressurized canisters, samples were directed to the cold trap of the Markes International Unity 2 via the AirServer add-on. The system featured a deans switch with a dual-column and detector setup. The first column was a DB-5MS with dimensions of 60m x 0.25mm (i.d.) and a film thickness of 1µm (Agilent). Subsequently, the lighter compounds were directed to a second column, CP-Al2O3/KCl with dimensions of 50m x 0.32mm (i.d.) and a film thickness of 5µm (Agilent), via the deans switch. Lighter compounds (2-5 carbon atoms) were analyzed using a flame ionization detector (FID), while the rest were analyzed using the MS. The GC/FID setup was Agilent 7890A, and the MS setup was Agilent 5975C.

2.3 Measurements of other air pollutants

Data for other air pollutants i.e. nitrous oxide (NO), nitrogen dioxide (NO_2), particulate matter < 2.5 µm ($PM_{2.5}$), ozone (O_3) and black carbon (BC) was produced by Helsinki Region Environmental Services Authority (HSY) as a part of their continuous air quality monitoring. Description of the instrumentation used to acquire data can be found for example in Teinilä et al. (2025).

2.4 Reactivity and SOA formation potential calculations

The total VOC reactivity (R_x) was calculated by combining the measured concentrations of individual VOCs ([VOC_i]) with their corresponding reaction rate coefficients ($k_{i,x}$). This provides an approximate assessment of the relative contributions of specific compounds or compound classes to local OH, nitrate radical (NO_3), and O_3 chemistry.

$$R_x = \sum[VOC_i] \times k_{i,x} \quad (1)$$

The reaction rate coefficients used in this study are provided in Supplementary Table S3.

The relative SOA formation potentials (SOAP) of measured VOCs were calculated as follows:

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$$SOAP_i = [VOC_i] \times Y_i \quad (2)$$

where $SOAP_i$ represents the SOAP of the VOC_i, $[VOC_i]$ is the concentration of the VOC_i and Y_i represents the SOA yield of VOC_i.

To show the relative impact of studied compounds for local SOA production, reactivity of the VOCs were used:

$$SOAP\_X_i = [VOC_i] \times k_{i,x} \times Y_i \quad (3)$$

where $SOAP\_X_i$ is reactivity-based SOAP (X_i=OH, NO_3 or O_3).

3 Results and discussion

3.1 VOC concentrations at the traffic supersite

While alkanes were the major compound group for the low masses (C_2-C_5), compounds with 6 to 9 carbon atoms (C_6-C_9) were mostly aromatic hydrocarbons and for higher masses (C_{10}-C_{15}) alkanes and terpenes had 84 % contribution (Fig. 2a). The contribution of PAHs was very low. Compounds with lower masses are mainly contributing to the ozone formation while higher ones (C_6-C_{15}) are also expected to contribute to secondary organic aerosol (SOA) formation.

As indicated by the time series in supplement Fig. S1, strong variations of the C_6-C_{15} VOC concentrations were detected over the campaign. In general, concentrations were higher on weekdays than on weekends, consistent with increased anthropogenic activity, particularly road traffic, during weekdays. Elevated weekday concentrations of NO and NO_2 further indicate that traffic emissions were an important source of these compounds (Table 1). Among the VOCs, the largest weekday increases were observed for higher molecular weight and more reactive species, whose concentrations in urban air are expected to be dominated by local emissions. Diurnal variation generally followed the variation of traffic/human activity.

During the campaign, three distinct air pollution episodes (E1–E3) with elevated particulate and gaseous pollutant concentrations were observed in Helsinki. These episodes are described in detail by Teinilä et al. (2025). The results indicate that the episodes were driven by a combination of long-range transported pollution, particularly from biomass burning, and locally accumulated traffic emissions, leading to degraded air quality in the Helsinki metropolitan area. Higher concentrations of most VOCs were also detected during E1 and E2, whereas VOC levels during E3 were comparable to the campaign mean (Table 1, Fig. S1). The cold conditions during E1 and E2 likely favoured also the accumulation of local pollutants.

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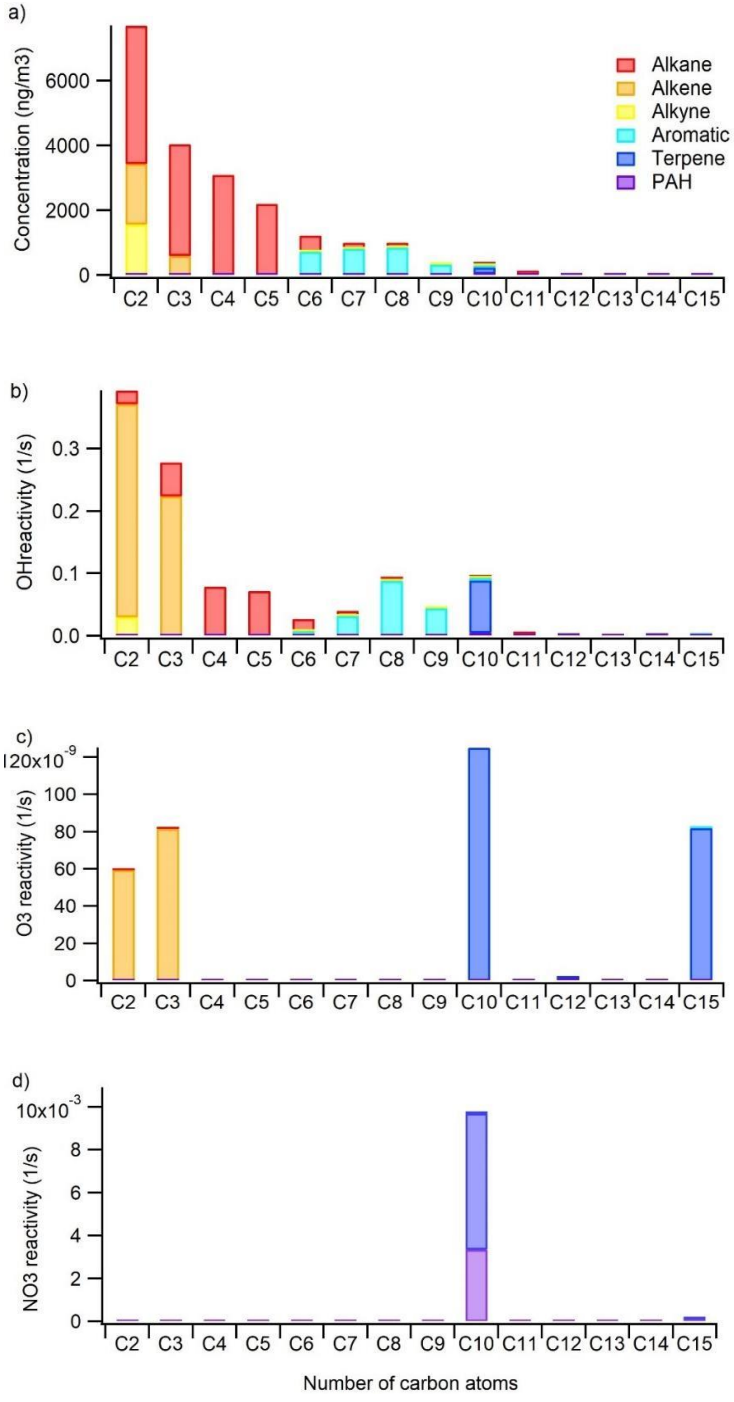

Figure 2: Carbon-scale of a) concentrations, b) OH reactivity, c) ozone reactivity and d) NO_3 reactivity of VOCs at Mäkelänkatu traffic supersite in during the 2022 intensive campaign. Only periods with additional offline-canister sampling are included.

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Table 1: Limit of detection (LOD), mean concentrations of C_6-C_{15} VOCs, NO, NO_2, $PM_{2.5}$, O_3 and black carbon measured at Mäkelänkatu traffic supersite from 17 Jan 19:20 to 22 Feb 14:00 in 2022 for the whole campaign (ALL), weekdays, weekends, and episodes (E1 from 22 Jan 15:00 to 23 Jan 10:00, E2 from 31 Jan 7:00 to 5 Feb 16:00 and E3 from 13 Feb 12:00 to 17 Feb 23:00). N=number of samples. Values of other air pollutants have been averaged to the VOC sampling times.

	LOD	ALL	weekday (non-episode)	weekend (non-episode)	weekend/ weekday	E1	E2	E3
N		609	325	122		18	73	76
Terpenes (ng m^{-3})								
α-pinene	6.0	47	33	29	0.87	86	152	40
camphene	1.3	12	11	11	0.92	27	24	9
Myrcene	1.9	13	11	12	1.14	33	29	9
β-pinene	0.7	9	3	12	3.53	71	35	4
Δ3-carene	3.0	15	13	11	0.85	27	26	19
p-cymene	2.2	18	18	20	1.07	57	19	12
limonene	3.7	35	37	19	0.52	75	64	31
1,8-cineol	3.1	9	11	10	0.84	23	2	9
terpinolene	4.2	3	3	2	0.75	2	2	2
β-caryophyllene	4.5	3	3	3	0.99	2	2	3
Terpene SUM		164	145	128	0.89	404	354	137
Aromatic HCs (ng m^{-3})								
benzene	3.5	550	432	452	1.05	992	1274	563
toluene	12.0	685	624	602	0.96	852	1225	603
ethylbenzene	1.8	134	120	109	0.92	175	271	117
p/m-xylene	2.7	372	347	308	0.89	504	698	302
styrene	7.4	35	31	31	1.02	100	77	22
o-xylene	1.0	141	127	113	0.89	173	285	116
propylbenzene	5.7	20	19	15	0.78	28	41	13
3-ethyltoluene	0.2	59	70	57	0.81	151	37	44
4-ethyltoluene	0.4	27	32	23	0.71	51	19	23
1,3,5-TMB	0.5	23	31	22	0.72	52	0.5	20
2-ethyltoluene	1.0	19	24	18	0.75	45	1	17

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1,2,4-TMB	0.6	98	97	84	0.87	156	158	81
1,2,3-TMB	0.6	24	24	21	0.89	43	39	19
1,3-diethylbenzene	1.7	4	5	3	0.69	3	4	5
1,4-diethylbenzene	1.2	22	24	16	0.66	30	25	19
2-propyltoluene	1.3	5	5	3	0.71	6	7	4
2-ethyl-p-xylene	0.5	6	7	4	0.64	7	7	6
1,2,4,5-TEMB	1.1	5	6	4	0.58	9	8	5
1,3,5-triethylbenzene	1.2	1	1	1	0.96	1	1	1
1,4-dibutylbenzene	2.0	2	2	2	0.88	1	2	2
Aromatic HC SUM		2232	2027	1890	0.93	3381	4168	1981
Alkanes (ng m^{-3})								
Hexane	1.2	425	455	730	1.60	1255	135	136
Heptane	0.7	197	205	251	1.22	816	222	75
Octane/2-octene	0.6	151	165	152	0.92	302	150	100
Nonane	0.2	43	48	31	0.64	56	54	35
Decane	0.5	99	114	70	0.62	79	79	109
Undecane	3.6	88	108	45	0.41	91	92	80
Dodecane	2.8	56	75	27	0.36	47	49	38
Tridecane	3.0	46	62	20	0.32	34	38	33
Tetradecane	2.6	31	42	13	0.30	22	26	20
Pentadecane	2.9	23	30	11	0.35	23	28	15
Alkane SUM		1159	1304	1350	1.03	2725	873	642
Others (ng m^{-3})								
Furfural	10.4	12	12	12	1.03	20	9	15
Benzylalcohol	16.1	27	32	13	0.39	25	8	22
o-cresol	8.4	6	6	4	0.72	4	5	6
p-cresol	7.6	8	8	5	0.59	4	4	13
Others SUM		53	58	34	0.58	53	26	56
PAHs (ng m^{-3})								
Naphthalene	1.0	25	22	22	1.03	65	38	35
Acenaphthylene	1.4	1	1	1	0.67	1	2	2
Acenaphthene	1.6	1	1	1	0.97	1	1	1
Fluorene	1.5	3	3	3	1.01	1	1	5

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Anthracene	1.8	3	3	2	0.75	2	3	4
Phenanthrene	1.7	1	1	1	0.89	1	1	1
Fluoranthene	1.6	2	2	1	0.52	1	1	2
Pyrene	1.4	2	2	1	0.49	1	1	2
PAH SUM		38	35	32	0.92	72	47	52
Air pollutants (µg m^{-3})								
NO		16	16	6	0.36	5	39	12
NO_2		24	25	16	0.63	22	38	23
$PM_{2.5}$		5.4	3.5	4.1	1.18	7.4	12	10
Ozone		42	45	50	1.11	32	14	42
Black carbon		0.6	0.5	0.4	0.78	1.0	1.5	0.9

TMB = trimethylbenzene, TEMB = tetramethylbenzene

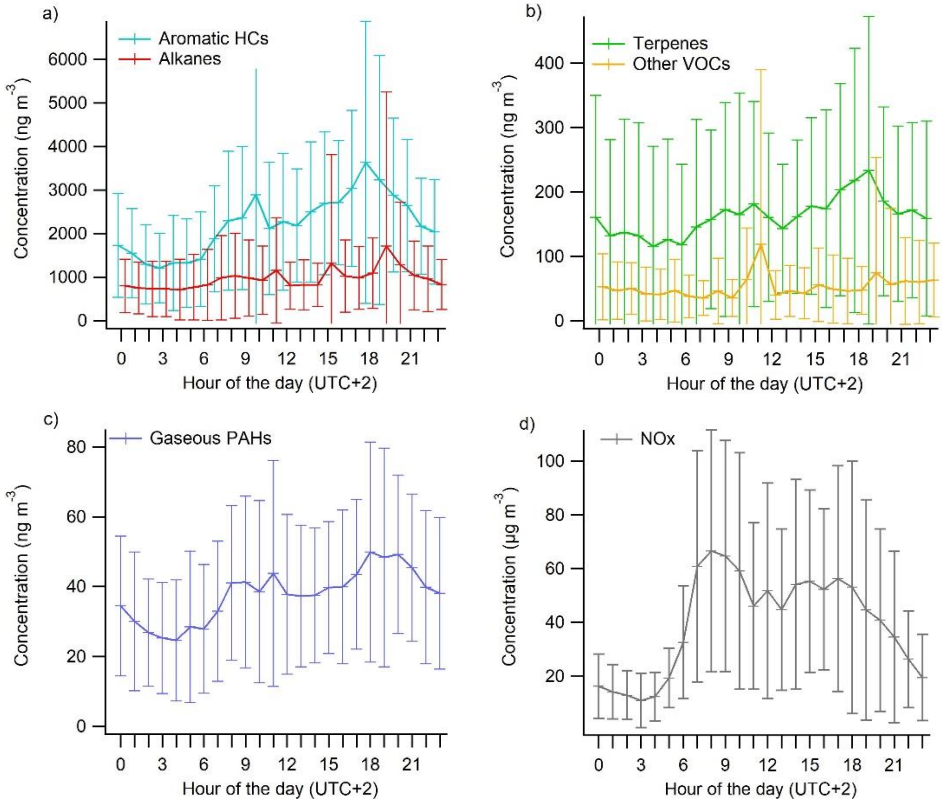

Figure 3: Mean diurnal variation (±standard deviation) of a) aromatic HCs and alkane, b) terpene and other VOC, c) gaseous PAH and d) NOx concentrations.

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3.1.1 Aromatic hydrocarbon concentrations

Aromatic hydrocarbons were the dominant VOC group detected at the site (Fig. 2a), contributing substantially to the pool of reactive SOA precursors among the measured C_6–C_{15} VOCs (Table 1, Fig. 2). Toluene and benzene showed the highest concentrations within this group. Most aromatic hydrocarbons exhibited clear diurnal patterns aligned with traffic activity (Fig. 3) and higher concentrations during weekdays (Table 1), consistent with traffic being their primary source at the street canyon site. However, benzene deviated from this with slightly higher concentrations during weekends, suggesting an additional source contribution. Elevated residential wood combustion, which is more common on weekends in the Helsinki region, likely explains this behaviour. Long-term monitoring of benzene and toluene at the site further supports this interpretation, indicating that while the role of traffic has declined in recent years, the relative role of residential wood combustion and long-range transport has increased (Timonen et al., 2026).

During the air pollution episodes E1 and E2, the concentrations of more reactive C9-C10 aromatic hydrocarbon were higher than during the non-episode periods indicating a contribution from the local sources (e.g. traffic, Table1). During the third episode (E3), concentrations of less reactive benzene were clearly higher than during the non-episode periods, while more reactive aromatic hydrocarbons were lower, indicating the long-range transported pollution or local/regional residential wood combustion as a source. Gaseous PAH concentrations were also higher during E3 (0.05 µg m-3) than during the non-episode periods or other episodes (0.03 µg m-3) indicating also the impact from the wood combustion.

3.1.2 Terpene concentrations

The mean terpene concentration during the campaign was 164 ng m^{-3}. Although terpenes contributed less than 1% to the total measured VOC mass, they represented 4.4 % of the C_6–C_{15} SOA precursors. The detected terpenes are typically emitted by common boreal tree species in Finland, such as Scots pine, Silver and Downy birches, and Norway spruce. However, their emissions during cold winter conditions are negligible (Hellén et al., 2018 & 2021; Hakola et al., 2022), indicating that the observed concentrations originated from other sources. Among individual species, α-pinene and limonene showed the highest concentrations. Limonene comprises a much larger fraction of the total monoterpene mass than typically observed in boreal forest environments, where it usually accounts for only a minor share (Hellén et al., 2018; Hellén et al., 2020).

Several of the measured terpenes are known to be emitted from anthropogenic activities, particularly from cleaning agents, hygiene products, and other volatile chemical products (You et al., 2022). Terpenes with highest observed ambient concentrations, α-pinene and limonene, are well-established constituents of cleaning and hygiene products (You et al. 2022). The weekday dependence of concentrations supports their anthropogenic origin, with higher levels observed on weekdays compared to weekends, coinciding with higher human activity. This trend was especially evident for limonene, which is strongly associated with consumer product use (You et al., 2022). Because of their short atmospheric lifetimes (e.g., Hellén et al., 2012), terpenes are unlikely to be transported over long distances, further suggesting that the observed compounds originated from local or regional sources.

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The diurnal variability of terpene concentrations (Fig. 3) followed traffic patterns, with peaks during rush hours. This pattern is likely linked to increased human activity and associated product use rather than direct traffic emissions. However, the terpene concentrations also correlated well with CO_2 concentration, which is a strong tracer for road traffic emissions, suggesting potential impact of road traffic on the terpenes at the traffic supersite (Savolainen et al., 2026).

Concentrations of terpenoids were higher than the mean of whole campaign, especially during episodes E1 and E2. Although Teinilä et al. (2025) concluded that these episodes were influenced by long-range transport, the elevated levels of short-lived terpenoids (lifetimes of only a few hours) suggest a strong local contribution. In forested environments, terpenoid concentrations are highly dependent on the mixing layer height (Hellén et al., 2018), and low mixing conditions were also observed during the cold episodes E1 and E2, when the highest concentrations were measured. A shallow mixing layer would accumulate locally emitted pollutants. This effect is less evident for compounds with higher background concentrations, making terpenoids particularly sensitive indicators of local influence under stagnant weather conditions.

Monoterpene concentrations at the traffic supersite were comparable to those measured in an earlier campaign in January–February 2011 at the rooftop station of the Finnish Meteorological Institute, located approximately ~1 km away and representing urban background (Hellén et al., 2012). In summertime, when strong impact from biogenic emissions was expected, three times higher concentrations were measured in July 2011.

In addition to monoterpenes, the highly reactive sesquiterpene, β-caryophyllene, was also detected. Anthropogenic sources of sesquiterpenes include e.g. fragrances, cooking and essential oils (Klein et al., 2016). β-caryophyllene concentration remained very low (mean 3 ng m^{-3}) throughout the campaign. Given its extremely short atmospheric lifetime (generally on the order of minutes; Atkinson and Arey, 2003), the presence of β-caryophyllene points to very local sources.

3.1.3 C_6-C_{15} alkane concentrations

Hexane had the highest concentrations of the C_6-C_{15} alkanes. While other alkanes were clearly related to weekday activities, hexane and heptane had higher concentrations during weekends. Higher alkanes (>C_{10}) had low concentrations and a minor impact on OH reactivity. However, they may still be important for the SOA formation due to their high SOA formation potentials (Gu et al., 2021).

During the air pollution episode E1, higher than average concentrations of C_6-C_9 alkanes were detected, but higher alkanes remained at the same level (Table 1). During other episodic periods C6-C9 alkane levels remained at lower or at the same level as during non-episode times.

3.1.4 Gaseous PAH concentrations

For PAHs, traffic and regional residential wood combustion are expected to be their main sources (Hellén et al., 2017; Barreira et al., 2023). However, PAH concentrations remained very low during the whole campaign, naphthalene being the major PAH. The campaign mean for the sum of all PAHs was 38 ng m^{-3}. For naphthalene and fluorene, the ratio between weekend and weekdays was 1.0, but for other PAHs higher weekday concentrations were measured indicating higher contribution of traffic

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compared to wood combustion, which is expected to be higher during the weekends. PAH concentrations also correlated well with CO2 concentration, which is a strong tracer for road traffic emissions (Savolainen et al., 2026).

3.1.5 Concentrations of other VOCs

Other detected C_6-C_{15} VOCs included furfural, benzylalcohol, *o*-cresol and *p*-cresol. Their mean concentrations were between 6 and 27 ng m^{-3} and therefore they had only a minor contribution to the total VOC mass.

3.1.6 C_2-C_5 NMHC concentrations

Highly volatile NMHCs with two to five carbon atoms were measured only over four days using 24-hour Silcosteel-coated canister sampling. These additional offline samples indicated the strong contribution of these highly volatile to the total measured VOC mass (Fig. 2a). Due to low reactivity and long atmospheric lifetimes, these compounds are accumulated and long-range transported in the atmosphere. High concentrations have been detected even in remote air in Northern Finland (Hellén et al. 2015). In an earlier study in Helsinki, traffic related sources and the use of commercial natural gas were found to be major sources for these compounds (Hellén et al., 2006).

3.2 Comparison of traffic supersite concentrations to residential and urban background sites

To compare different urban areas, additional 4-hour offline sorbent tubes were collected at a residential site (Tapanila) and at an urban background site (SMEAR III) over four days.

Higher concentrations of most VOCs (Fig. 4) and especially benzene, furfural, naphthalene and *p*-cresol (Table S2) were observed at the residential site and at the urban background site, indicating wood combustion as a stronger source at these sites. Furfural is a tracer for biomass burning (Stutz et al., 2021) and wood combustion emissions are known to also contain PAHs and cresols (Shauer et al., 2001; Hartikainen et al., 2018). Furfural concentrations at the residential site, where wood is used for heating in many houses, were five times higher than at the traffic supersite.

While most other VOC groups were lower at the street canyon site, terpenes and especially limonene showed clearly higher concentrations. This might be explained by human activity (e.g. cleaning, cooking, vaping and personal care products), which is expected to be higher at the traffic site with higher population density. The difference was highest for limonene, which is used in many cleaning and hygiene products. On average limonene had 7 times higher concentrations at the traffic site compared to the residential site.

Larger C_8-C_{15} alkanes also had higher concentrations at the traffic site. For higher alkanes, indoor activities are a possible source (Mai et al., 2024), and higher population density around the traffic site could explain this.

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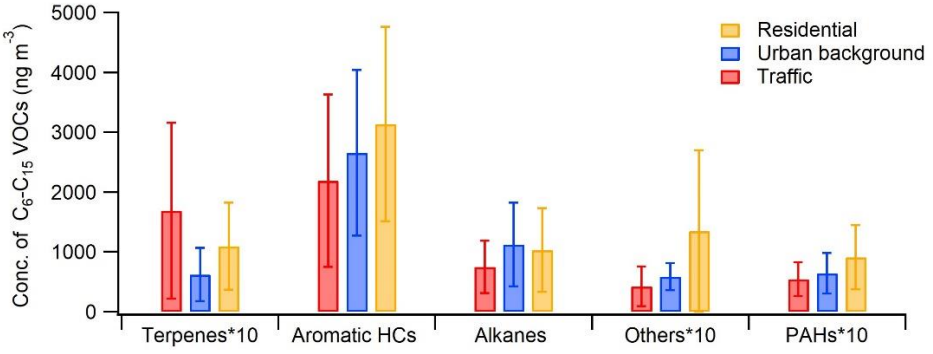

Figure 4. Mean concentrations (± standard deviation) of C_6-C_{15} VOC groups measured at the residential site, urban background site and at traffic site in Helsinki on 14th – 18th of February 2022. For better figure presentation, concentrations of terpenes (Terpenes*10), other VOCs (Others*10) and gaseous PAHs (PAHs*10) were multiplied by 10.

3.3 Importance of the studied VOCs and IVOCs for local chemistry

3.3.1 Reactivity of studied VOCs and IVOCs

Based on the calculated OH radical reactivity, light alkenes (ethene and propene) are the most important compounds related to local OH radical chemistry (Fig. 2b), but also C_4-C_5 alkanes, aromatic hydrocarbons and monoterpenes have major contribution at the traffic site. VOCs are also oxidized by ozone and nitrate radicals. Ozone reactivity calculations show that main VOCs/IVOCs for ozone oxidation in traffic environment are mono- and sesquiterpenes with some contributions also from light alkenes (ethene and propene, Fig. 2c). Nitrate radical reactivity is dominated by the monoterpenes and PAHs (Fig. 2d).

Terpenoids have a significant role in OH chemistry, and they are major contributors in ozone and nitrate radical reactivity (Fig. 2). This clearly shows the important role of terpenes in urban air. Due to reduced OH production by the photolysis of ozone, OH radical concentrations are expected to be lower during these dark winter months (Hakola et al., 2003) increasing the importance of ozone and nitrate radical reactivity. However, especially in urban areas, production of OH radicals is partly sustained also in wintertime by reactions of unsaturated hydrocarbons with ozone (Heard et al. 2004).

Concentrations of detected IVOCs with 10 to 15 carbon atoms remained low, and reactivity calculations indicated that they did not have strong impacts on local chemistry either. However, there could be more highly reactive IVOCs, which were not included into selected ion monitoring method and whose low concentrations are not detected in the Scan-mode of the instrument. These compounds may still have strong impacts on local air chemistry, like sesquiterpenes, which were included in selected ion monitoring method and had strong impacts on ozone reactivity even with very low concentrations (few ng m^{-3}).

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3.3.2 Secondary organic aerosol formation potentials

SOA formation potentials (SOAP) of the studied compounds were estimated by multiplying both ambient concentrations (Fig. 2a) and reactivity-scaled concentrations (Fig. 2b-d) with SOA yields reported in Gu et al. (2021). These values should be interpreted only as rough estimates, as SOA yields can vary substantially depending on environmental conditions and the presence of other pollutants.

Based on SOAP calculated directly from measured concentrations (Fig. 5a), aromatic hydrocarbons with some contribution also from higher (C_{11}-C_{15}) alkanes appear to be the dominant contributors to SOA formation at the site. However, ambient concentrations do not necessarily reflect local emissions or local chemical processing. Highly reactive compounds are typically under-represented in ambient air because they are emitted and oxidized rapidly, whereas longer-lived compounds may be transported over long distances and thus have a smaller influence on local chemistry and SOA formation than their concentrations would suggest. Thus, if the SOAP of emissions from individual source is needed, the more comprehensive evaluation method could be the measurement of SOA precursors directly from emission source or, alternatively, using e.g. oxidation flow reactors designed for the determination of maximum SOAP of aerosol sample, i.e., exhaust or flue gas (see e.g. Timonen et al. 2017).

To better capture the local situation and the relative contributions of individual compounds to SOA production, we therefore used reactivity-scaled concentrations. For SOA formation via OH-initiated oxidation (Fig. 5b), aromatic hydrocarbons still play a major role, but monoterpenes (C_{10}) become much more important than indicated by their ambient concentrations alone. For SOAP based on O_3 reactivity (Fig. 5c), mono- and sesquiterpenes dominate. For SOAP based on NO_3 reactivity (Fig. 5d), monoterpenes and naphthalene are the key contributors. During the dark winter period, O_3- and NO_3-initiated oxidation may be even more important than in summer, further increasing the significance of terpenes as local SOA precursors.

This interpretation is consistent with our earlier study at the site (Saarikoski et al. 2023), where we found that ozone oxidation of terpenes was the primary pathway producing VOC oxidation products. The study was conducted in late summer to early autumn, when biogenic emissions are still substantial and OH radical production remains relatively efficient due to higher light levels.

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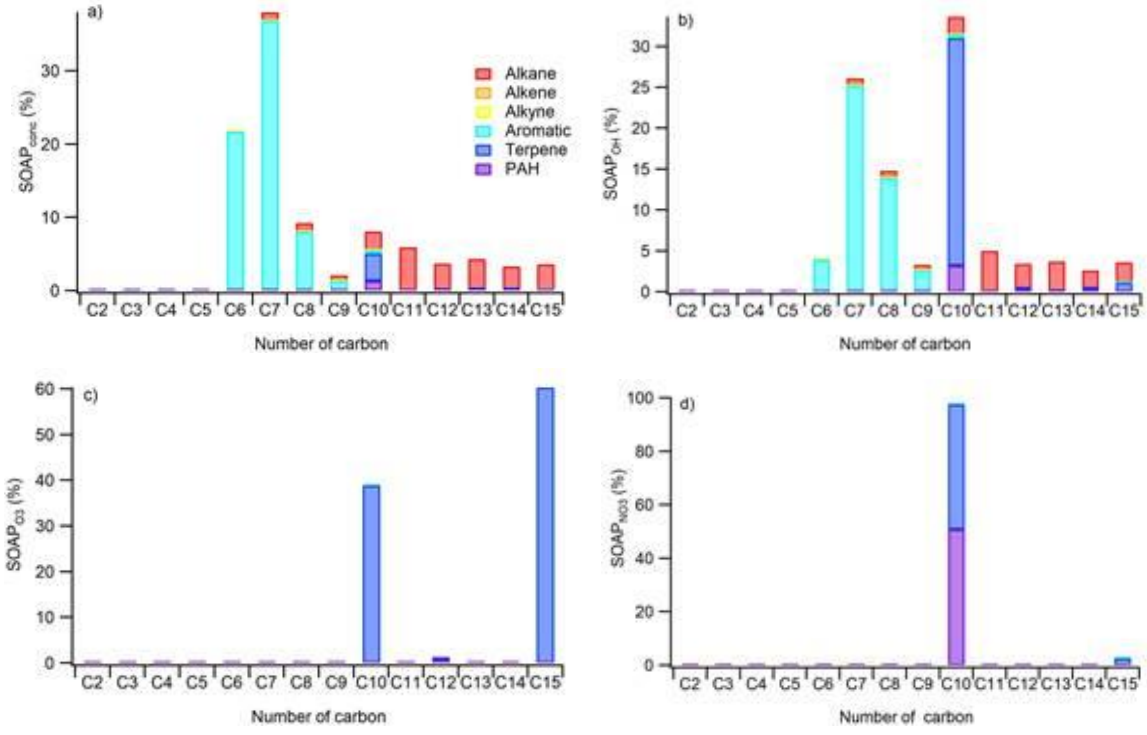

345 **Figure 5. Carbon-based contributions (%) of different compound classes to secondary organic aerosol formation potentials (SOAP) at the Mäkelänkatu traffic supersite in January–February 2022. Contributions are estimated from a) measured concentrations (SOAP$_{conc}$), b) OH reactivity scaled concentrations (SOAP$_{OH}$), c) ozone reactivity scaled concentrations (SOAP$_{O3}$) and d) NO3 reactivity scaled concentrations (SOAP$_{NO3}$). Only periods with additional offline-canister sampling are included.**

350

4 Conclusions

Our results indicate that in urban street canyon environment, traffic is no longer the dominant source of many VOCs. Lower concentrations were observed at the traffic site compared to the residential site, where wood combustion from house and sauna heating have strong contribution to VOC concentration. In contrast, higher terpene concentrations were measured in the traffic
355 environment, particularly on weekdays, highlighting the strong influence of human activities on terpene concentrations. Under the cold winter conditions of this campaign (mean T < 0 °C), biogenic emissions were negligible, confirming the importance of anthropogenic terpene sources.

Reactivity calculations indicated that terpenes have a major contribution to the oxidative potential at the site. Terpenes were dominating, especially ozone and nitrate radical oxidation of VOCs. If the importance of SOA precursors were estimated only
360 based on the concentrations, aromatic hydrocarbons appeared to be the most important compound group. However, when

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compound reactivity was also taken into account, our results indicated that terpenes are equally important and in some cases more important SOA precursors, even during the cold winter period.

Detected IVOCs (C_{11}–C_{15}) were present at low levels and showed limited influence on atmospheric reactivity, but may still have some more impact for SOA production. Undetected reactive IVOCs may also affect local chemistry. In particular, sesquiterpenes demonstrated strong contributions to ozone reactivity even at very low concentrations, underlining their significance despite very low abundance.

Overall, the results show that while the direct contribution of traffic emissions has declined, other anthropogenic sources are relatively becoming increasingly significant, even within urban environments strongly influenced by traffic. Anthropogenic terpenes have emerged as one of the key compound groups impacting also wintertime atmospheric chemistry. Their importance is expected to be even higher during the warmer months, when both biogenic emissions and increased evaporation from anthropogenic sources enhance their emissions and concentrations in the atmosphere. This will likely further increase their role in oxidative processes and SOA formation.

Data availability. VOC and IVOC concentrations are available in FMI's METIS data repository: https://doi.org/10.57707/fmi-b2share.881r8-32159. Ancillary data (BC, $PM_{2.5}$, O_3, NO, NO_x) can be found from FMI's open data portal: https://en.ilmatieteenlaitos.fi/download-observation.

Author contributions. HH, HT, TR and JN designed the measurement campaign, and TT, KT, ES, TL, AP and HH carried out the measurements and/or participated the data analysis. HH, HT, TR and AP contributed to the funding acquisition and supervision. HH wrote the manuscript. All authors participated in the interpretation of the results, paper review and editing.

Competing interests

None of the authors has any competing interests

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