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Semi-Quantitative Characterization of Volatile Organic Compounds in Indoor and Outdoor Air Using Passive Samplers: A Case Study of Milan, Italy

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Abstract

This study presents a semi-quantitative characterization of volatile organic compound (VOC) concentrations and their emission sources in indoor and outdoor environments across four residential and laboratory sites in Milan, Italy, during the summer of 2024. Radiello® passive samplers (Fondazione Salvatore Maugeri in Padova, Italy) were employed for VOC collection, followed by gas chromatography–mass spectrometry analysis. The semi-quantitative mean total VOC (TVOC) concentration was 220.8 ± 195.4 µg/m^3 for the outdoor air and slightly higher at 243.6 ± 134.3 µg/m^3 for the indoor air, resulting in an indoor-to-outdoor relative ratio of 1.10. The outdoor VOC profile was dominated by hydrocarbons, accounting for 80.3% ± 4.6% (173.2 ± 143.8 µg/m^3) of TVOCs, followed by aromatic hydrocarbons at 13.3% ± 5.5% (37.2 ± 49.7 µg/m^3). Indoors, hydrocarbons also predominated, representing 34.1% ± 15.2% (95.2 ± 80.1 µg/m^3) of the TVOCs, followed by terpenes at 20.7% ± 15.5% (49.0 ± 46.4 µg/m^3). Other VOC groups contributed smaller fractions in both environments. The emission profiles from cleaning and personal care products were assessed semi-quantitatively to determine their relative percentage contributions to the indoor VOCs. Source attribution was further supported by diagnostic relative ratios—benzene/toluene, toluene/benzene, and (m + p)-xylene/ethylbenzene—which provided insight into dominant emission sources and photochemical aging.

Keywords: volatile organic compounds; urban air quality; indoor air quality; household products; gas chromatography–mass spectrometry; passive sampling; Radiello samplers; Milan

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1. Introduction

Air pollution represents one of the most critical global environmental and public health challenges of the 21st century. According to the World Health Organization (WHO), air pollution is responsible for approximately 7 million premature deaths annually. Moreover,

over 90% of the global population resides in areas where air quality fails to meet WHO standards [1,2]. Volatile organic compounds (VOCs) are key contributors to air pollution, significantly affecting both air quality and human health [3].

VOCs play a key role in atmospheric chemistry. They contribute to the formation of secondary organic aerosols (SOAs) through interactions with atmospheric oxidants such as hydroxyl radicals (•OH), ozone (O_3), and nitrate radicals (•NO_3). This process leads to the formation of fine particulate matter ($PM_{2.5}$ and PM_{10}), which is linked to severe health issues, including respiratory and cardiovascular diseases, and an increased risk of premature mortality [4–7]. Moreover, VOCs are integral to the development of photochemical smog; their reaction with nitrogen oxides (NO_x) under sunlight produces ground-level O_3, which exacerbates respiratory conditions such as asthma, chronic obstructive pulmonary disease (COPD), and acute respiratory distress syndrome (ARDS) [8,9]. Certain classes of VOCs, including halogenated compounds, contribute to stratospheric O_3 depletion through photodissociation, releasing reactive halogen species that catalyze O_3 destruction, thus increasing the risks of skin cancer and cataracts [10,11].

VOCs are omnipresent in both outdoor and indoor environments, originating from a variety of natural and anthropogenic sources. Natural sources, such as vegetation, forest fires, volcanic activity, and oceanic processes, continuously emit VOCs into the atmosphere, contributing to the global VOC burden [4,12]. However, human activities are responsible for a significant portion of toxic VOC emissions. Overall, vehicle emissions, industrial processes, solvent use, and biomass burning, among others, contribute to approximately 25% of the total global VOC burden [4,13,14]. In indoor environments, major sources of VOC emissions include construction materials, wall paints, furniture, and household products [15–17]. The health effects that result from VOC exposure range from acute symptoms such as throat irritation and headaches to long-term conditions including liver damage, respiratory diseases, and an increased risk of cancer [15,18,19]. Addressing these health risks requires comprehensive monitoring and understanding of VOC sources and concentrations.

Although VOCs have been extensively studied in outdoor and indoor environments worldwide, there is a lack of detailed investigation specifically focused on Milan, Italy. Despite Milan's high urbanization, traffic density, and industrial emissions, comprehensive VOC monitoring addressing both indoor and outdoor environments is scarce. To address this gap, this study presents a semi-quantitative characterization of VOC concentrations and emission profiles across five selected sites in Milan during a two-month period (June–July 2024), with parallel indoor and outdoor sampling. A key feature of this work is the use of the relative indoor-to-outdoor (I/O) VOC ratios as indicators to distinguish between indoor and outdoor sources for different VOC groups, complemented by established diagnostic VOC ratios in outdoor air—benzene/toluene (B/T), toluene/benzene (T/B), and ($m + p$)-xylene/ethylbenzene (X/E)—which help to further differentiate specific emission sources and photochemical aging. Furthermore, this study provides the semi-quantitative percentage distribution of VOC emissions originating from cleaning and personal care products used in the monitored indoor environments. This important aspect, which has frequently been neglected in previous research, offers valuable insight into indoor VOC source contributions, thereby enhancing the understanding of indoor air quality dynamics.

We identified a wide range of VOC chemical classes, including hydrocarbons such as long-chain alkanes linked to diesel-related compounds [4]; aromatic hydrocarbons, including benzene, toluene, ethylbenzene, and xylenes (BTEX) and others, primarily associated with vehicular emissions [4]; cyclic siloxanes, such as octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5), noted for their environmental persistence and bioaccumulation concerns [20,21]; and other VOC groups, including terpenes, aldehydes, ketones, ethers, alcohols, esters, and halogenated VOCs. Several of the detected compounds are known or suspected to cause adverse health effects, including carcinogenicity and endocrine disruption. By capturing this comprehensive VOC profile and applying source attribution analyses, this study fills a critical knowledge gap for Milan by providing essential data to support future absolute quantification studies, long-term monitoring, health risk assessments, and seasonal variation analyses.

Although comprehensive data on VOC characterization and quantification in Milan remain scarce, historical studies have shown that benzene concentrations in the city were substantially higher in previous decades. For example, Fustinoni et al. [22] reported a mean outdoor benzene concentration of 53 μg/m^3, with an average total BTEX concentration in outdoor air of 408 μg/m^3. Later, Lai et al. [23] documented a mean outdoor benzene concentration of approximately 12 μg/m^3 and an indoor concentration of 9 μg/m^3 during the 1996–2000 period. More recently, Collivignarelli et al. [24] observed an outdoor benzene concentration ranging from 1.5 to 4.0 μg/m^3 during 2016–2018, based on ARPA Lombardia air quality monitoring data. Together, these findings demonstrate a pronounced decline in benzene and BTEX concentrations over the past three decades, reflecting the effectiveness of emission control measures. In our study, the semi-quantitative mean benzene concentration measured during the summer was 2.5 μg/m^3 for outdoor air and 0.6 μg/m^3 for indoor air. The corresponding mean semi-quantitative total BTEX concentration was 26.44 μg/m^3 for outdoor air, confirming the marked and consistent long-term reduction.

Milan is located within the Po Valley, surrounded by the Alps to the north and the Apennines to the south. Its geography is characterized by low wind speeds, particularly during winter, with temperature inversions and frequent ground-based thermal inversions being especially common during this season. These mesoscale meteorological conditions reduce vertical mixing and favor the accumulation of pollutants near the surface, leading to wintertime concentrations that are often substantially higher than those observed in summer [25]. Consequently, the semi-quantitative concentrations reported in this study, derived from summer measurements, may underestimate the potential annual mean exposure. The mean annual semi-quantitative concentrations could be even higher if we had included data collected in winter.

Passive air samplers (PASs) provide a cost-effective and practical tool for long-term VOC monitoring in both indoor and outdoor environments. Compared with active sampling methods, PASs offer advantages such as lower maintenance costs, ease of use, independence from external power sources, and silent operation [12,26]. While active samplers rely on controlled airflow and provide high-resolution temporal data, delivering information about episodic VOC concentrations over short periods, PASs may underestimate episodic peaks but provide reliable estimates of average VOC concentrations through time-integrated sampling. Due to the time-integrated nature of passive air sampling, short-term peak concentrations are averaged over the entire sampling period, thus minimizing their influence on the reported VOC concentrations. This characteristic makes them especially suitable for assessing long-term exposure trends and spatial variations. Their ability to operate continuously in remote or inaccessible locations further supports their applicability in extended air quality studies [26–29].

Based on geometric configuration, PASs are categorized into axial and radial samplers, each with distinct operational characteristics. Axial samplers have longer diffusion paths and smaller cross-sectional areas, resulting in lower uptake rates. In contrast, radial samplers have a larger diffusive surface and shorter diffusion paths, and their 360° symmetrical geometry allows analytes to access the sorbent material from all directions, increasing the uptake rate and enabling more uniform VOC absorption. However, a higher sampling rate does not necessarily translate into greater sampling efficiency, which also depends on compound-specific diffusion behavior and the physicochemical properties of the sorbent [12,30–32]. The selection between these configurations depends on factors such as the study objectives, target compounds, and environmental conditions.

For this study, Radiello® passive/diffusive samplers were selected for their ability to effectively capture a wide range of VOCs. The highly adsorptive activated charcoal allows the collection of both polar and non-polar VOCs, ensuring a comprehensive assessment of indoor and outdoor air quality. According to Fuselli et al. [33] and the Radiello® manual, VOCs collected on these samplers remain stable for up to 6 months when the cartridges are properly sealed and stored at 4 °C—the analyte content remains unaltered during this period. This stability ensures the reliability of the collected data during storage and transport prior to analysis. Their performance is further supported by European regulatory frameworks for VOC monitoring, reinforcing their suitability for scientific air quality assessments [34,35].

PASs are widely used for VOC monitoring worldwide. Key studies that have used PASs include one by Mukerjee et al. [36], who investigated VOC distributions near a petroleum refinery in South Philadelphia, United States, and one by Vallecillos et al. [26], who conducted a multi-year VOC monitoring study near petrochemical industries in Tarragona, Spain. These studies, among others, confirm the reliability and broad applicability of PASs for long-term VOC assessment in diverse urban and industrial environments. Building on this foundation, we employed PASs to assess VOCs in both outdoor and indoor air in Milan, integrating passive sampling with gas chromatography–mass spectrometry (GC-MS) for accurate identification and semi-quantitative analysis. We expect our findings to contribute to a better understanding of VOC dynamics in Milan's urban environment, supporting the development of targeted air quality management strategies.

2. Materials and Methods

2.1. Sampling Sites

Milan, located in northern Italy, is the most populous city in the country, with approximately 5 million residents [37]. As a major European metropolis, Milan presents a complex urban landscape shaped by intensive commercial activity, a strong manufacturing base, and a dense transportation network. These characteristics make it a strategically relevant location for investigating VOC concentrations and their emission sources.

To obtain a comprehensive semi-quantitative characterization of VOCs in both indoor and outdoor air and to identify their potential sources, air sampling was carried out at five carefully selected sites across Milan. These locations were selected to represent a range of urban and suburban environments, including high-traffic areas, quieter residential zones, and sites with significant green space. The selection aimed to capture the heterogeneity of urban background levels and traffic-related VOC emissions across the city. The monitoring sites were selected by prioritizing accessibility and safety to ensure the integrity and reliability of the data collection process. Precautions were taken to protect the sampling equipment from environmental or human interference. The study also adhered to ethical standards by obtaining prior informed consent from property owners or occupants when necessary.

The sampling locations included one laboratory and four residential apartments, as described below. Figure 1 presents the spatial distribution of these sites, along with representative satellite imagery from Google Maps.

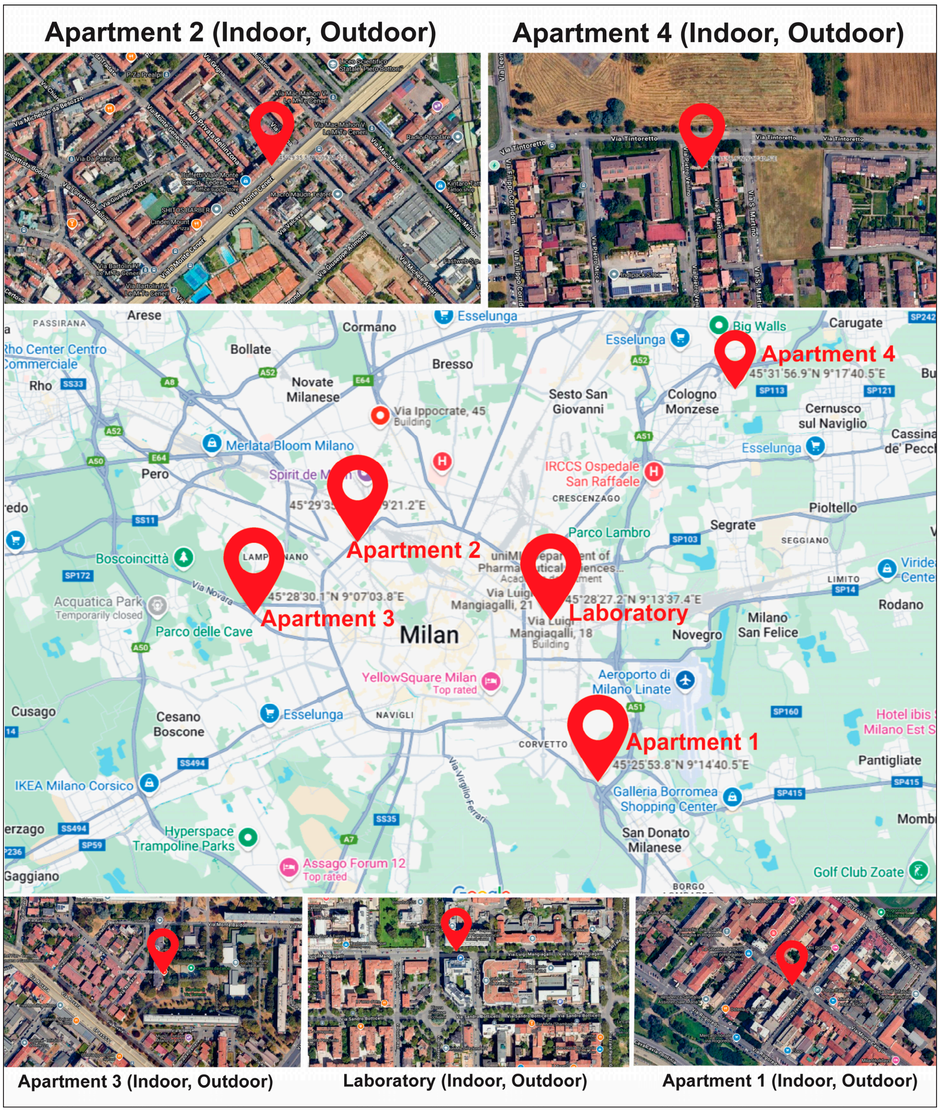

Figure 1. The map shows the locations of the indoor and outdoor volatile organic compound sampling sites across the metropolitan area of Milan, Italy.

1. Laboratory (latitude: 45.474220, longitude: 9.227056): This site is located in a mixed-use area comprising residential and institutional buildings. Outdoor sampling was carried out in the laboratory courtyard, approximately 200 m from a major road, allowing the capture of both urban background levels and traffic-related emissions.
2. Apartment 1 (latitude: 45.431622, longitude: 9.244577): This site is situated in a densely populated residential area with high traffic intensity. Sampling was performed 50 m from a busy road, enabling the assessment of traffic-influenced VOC concentrations in a highly urbanized setting.
3. Apartment 2 (latitude: 45.493200, longitude: 9.155900): This site is located in a residential setting with elevated traffic volumes. The sampling point was 20 m from a primary road, providing data representative of urban VOC exposure hotspots.
4. Apartment 3 (latitude: 45.475016, longitude: 9.117718): This site lies in a residential neighborhood characterized by greater green coverage and lower traffic density relative to the other locations. It offers a useful contrast to the more polluted urban sites, reflecting VOC concentrations in a relatively cleaner microenvironment.
5. Apartment 4 (latitude: 45.53248, longitude: 9.29457): This site is positioned in a suburban residential zone with moderate traffic influence. Sampling was con-

ducted 100 m from the nearest roadway, representing VOC exposure levels typical of suburban conditions.

2.2. Chemicals and Standard Solutions

Dichloromethane (DCM, ≥99.8%, stabilized with amylene; Merck KGaA, Darmstadt, Germany) was employed as the extraction solvent for VOC desorption from the Radiello® cartridges. A homologous series of *n*-alkanes ranging from C_8 to C_{20} (40 mg/L in hexane; Sigma-Aldrich, Merck KGaA, Darmstadt, Germany) was used to calculate the retention indices (RIs) to support compound identification via gas chromatography.

For accurate identification and semi-quantitative determination, individual external standards of selected VOCs were prepared in DCM. Compounds were identified by using the NIST Mass Spectral Library, applying a minimum match probability threshold of ≥85% to ensure reliable spectral confirmation. The selected VOC standards included toluene (≥99.5%), *m*-xylene (≥99.5%), *p*-xylene (≥99.5%), (±)-citronellal (≥95%, racemic mixture), (R)-(+)-limonene (≥99%, enantiomerically enriched), γ-terpinene (≥97%), α-pinene (≥98.0%), (-)-β-pinene (≥99%), (-)-β-citronellol (≥98.5%, enantiomerically enriched), (-)-terpinen-4-ol (≥95%), cineole (≥99%), terpineol (60–85%, mixture of positional isomers), butyl acetate (≥99.7%), and dibutyl phthalate (≥98.0%). All reference compounds were purchased from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany), except cineole, which was sourced from Janssen Chimica (Geel, Belgium).

Given the semi-quantitative scope of this study, full calibration curves were not developed for each compound. Instead, a single-point calibration approach was adopted for most VOCs. Limonene was selected as a representative compound for multi-point calibration, prepared in concentrations ranging from 0.000189 to 0.30312 mg/L, consistently yielding a correlation coefficient (R^2) > 0.995. For all other compounds, semi-quantitative estimations were performed based on single-concentration standards, under the assumption of comparable detector responses.

Where analytical standards were not available, estimated response factors (RFs) were calculated using structurally related compounds, including alkanes (C_8–C_{20}) and available standards, to improve the reliability of semi-quantitative estimations in the absence of analytical standards for all detected compounds. This approach enabled the calculation of approximate concentrations for unidentified VOCs based on their relative detector responses.

However, there are several limitations associated with this semi-quantitative characterization method. First, the lack of certified analytical standards for many VOCs detected in both outdoor and indoor air limits the accuracy of the quantification. Additionally, the absence of equipment to measure environmental factors, such as temperature, humidity, and airflow, at the sampling sites introduces further uncertainty, because these factors can influence the uptake rates of VOCs by PAS, potentially causing variability and bias in the results. The main disadvantage of this method is that it provides relative quantification of concentrations rather than absolute concentration values, which are necessary for accurate health risk assessments of the detected VOCs. Moreover, the limited number of sampling sites in Milan and the absence of duplicate samplers at each location may reduce the reliability of the data. Furthermore, sampling was only conducted during the summer, which limits the capture of seasonal variations. Considering Milan's location within the Po Valley, winter meteorological conditions such as temperature inversions and limited air circulation may lead to elevated VOC concentrations compared to those measured in summer [25]. This method is typically used when the study objectives focus on relative semi-quantitative characterization of VOCs, rather than precise absolute quantification.

Future studies should overcome these limitations by implementing on-site monitoring of environmental parameters to allow precise sampling rate corrections, increasing the number of sampling sites with duplicates, and extending monitoring across all seasons to capture temporal variability. Additionally, the application of absolute quantification methods is essential to enhance the accuracy and reliability of VOC measurements. Expanding both spatial and temporal coverage will improve the understanding of VOC dynamics and strengthen the foundation for accurate health risk assessments, particularly for regulated VOCs.

2.3. Sampling Methods and Sample Preparation

Radiello® passive/diffusive samplers developed by the Fondazione Salvatore Maugeri in Padova, Italy, were used to assess VOCs in both outdoor and indoor air in Milan, Italy. These samplers utilize a cylindrical adsorbing cartridge housed within a white diffusive body, supplied by Sigma-Aldrich (Merck KGaA, Darmstadt, Germany)). VOC sampling is facilitated by diffusion across a microporous polyethylene membrane that is 1.7 mm thick, with an average pore size of 25 ± 5 µm and a length of 18 mm. VOCs are adsorbed onto an activated charcoal cartridge housed within a stainless-steel net cylinder, which features a 100-mesh grid and a diameter of 5.8 mm, and is filled with approximately 530 ± 30 mg of activated charcoal with a particle size range of 35–50 mesh [35].

Sampling was conducted from June to July 2024, a period marked by elevated temperatures and increased traffic emissions, to capture potential variations in VOC concentrations. Indoor samplers were placed in residential apartment hallways (40–70 m^2) at a height of 1.5–2 m, ensuring coverage of major living areas as well as centrally within the laboratory. Outdoor samplers were placed 20–30 m from indoor sites, at an elevation of 2–4 m, housed in polypropylene shelters to protect against rain and direct sunlight, following the manufacturer's recommendations to avoid weather-induced contamination. Each Radiello® sampler was pre-conditioned and calibrated according to the manufacturer's guidelines prior to use to ensure precision and reliability [35].

The frequency of cartridge replacement was determined based on the expected VOC concentration variability. Indoor cartridges were replaced every 14 days, reflecting the typically higher and more variable VOC concentrations in indoor environments, influenced by internal pollution sources [15]. Conversely, outdoor cartridges were replaced every 28 days, reflecting generally more stable VOC concentrations in outdoor environments, as reported previously [4]. This approach ensured the collection of reliable and representative data from both indoor and outdoor settings. A total of 20 indoor and 10 outdoor samplers were employed.

This sampling duration is consistent with the Radiello® manual, which recommends an exposure period of up to 30 days for long-term monitoring. According to the manufacturer's specifications, the breakthrough volume for Radiello® samplers with a white diffusive body and solvent extraction is 70,000–80,000 $\mu g/m^3$, substantially higher than the maximum total VOC semi-quantitative concentration observed in this study (about 570 $\mu g/m^3$). This large safety margin ensures that breakthrough and saturation effects are negligible [35]. Furthermore, Zimmerman et al. [38] confirmed that these samplers maintain VOC stability within their sorption capacity and acceptable relative percent difference (%Bias) limits for up to 1 month of exposure. While some compounds may degrade beyond 1 month, most remain stable for up to 12 months, supporting the appropriateness of a 4-week sampling interval. Some VOCs may react or polymerize during sampling, potentially affecting their measured concentrations, a known limitation of passive VOC sampling [39,40].

At the end of the sampling period, each cartridge was carefully sealed in a glass tube and transported to the laboratory, where it was stored at 4 °C and analyzed within 72 h to preserve the adsorbed VOCs. For desorption, 2 mL of DCM was added directly into the glass tube containing the cartridge, with gentle stirring for 30 min at room temperature. Then, the extract was transferred to a vial for GC-MS analysis. DCM was chosen over carbon disulfide (CS_2), as recommended by the manufacturer, due to its superior efficacy in VOC extraction, thus ensuring more reliable and accurate results [41].

Rigorous quality control measures were implemented to ensure the reliability of the data, including blank and negative controls. Blank controls were analyzed before each measurement set to detect potential contamination from DCM. Negative controls involved placing 2 mL of DCM in a glass tube with a new Radiello® cartridge, which was incubated for 30 min with periodic agitation. This step was carried out to detect any contamination from the sample preparation environment. Additionally, each sample was analyzed twice using a semi-quantitative method to assess consistency and accuracy.

2.4. VOC Emissions from Cleaning and Personal Care Products

VOC emissions were assessed from 17 household cleaning detergents and 21 personal care products, which were commonly used at the indoor sampling locations during the monitoring period. The primary aim of this analysis was to determine semi-quantitatively the relative abundance and category distribution of VOCs emitted from these products. This procedure enabled the identification of potential emission sources and their relative contributions to the indoor VOC burden observed at the sampling sites.

For each product, a 10 mL aliquot was transferred into a 300 mL glass jar, into which a Radiello® cartridge was placed within a white diffusive body. The jars were hermetically sealed and heated in a water bath at 50 °C for 1 h to promote the volatilization of VOCs into the headspace, where they were subsequently adsorbed by the cartridge. After the exposure period, VOCs were desorbed using 2 mL of DCM for 30 min, following the procedure described in Section 2.3. The extracts were analyzed by GC–MS using the same analytical method applied to air samples (see Section 2.5).

2.5. GC-MS Analysis

VOCs were analyzed using a SCION 436-GC gas chromatograph equipped with a single quadrupole mass spectrometer (Bruker Corporation, Techcomp, Fulton, MD, USA), operated at the Department of Environmental Science and Policy, University of Milan, Italy. A Zebron ZB-SemiVolatiles capillary column (30 m long × 0.25 mm internal diameter × 0.25 µm film thickness; Phenomenex, Bologna, Italy) was used for chromatographic separation. It was selected for its excellent peak capacity and low bleed characteristics, making it suitable for the resolution of a broad spectrum of VOCs. The carrier gas was high-purity helium delivered at a constant flow rate of 1.0 mL/min to maintain retention time reproducibility and optimal peak symmetry. The temperature gradient of the GC oven was optimized for compounds of varying volatility: an initial hold at 35 °C for 5 min to retain highly volatile analytes, followed by a ramp to 90 °C at 5 °C/min, and holding at that temperature for 3 min to optimize the resolution of mid-volatility compounds. Finally, the temperature was increased to a final temperature of 280 °C at 10 °C/min, and held there for 3 min to elute less volatile, higher-molecular-weight species. The total chromatographic runtime was 41 min.

Samples (2 µL) were injected in splitless mode, with an injector temperature maintained at 240 °C. This technique was employed to maximize analyte transfer to the column and to improve the detection sensitivity of trace-level compounds. The mass spectrometer operated in electron ionization mode, with an ion source temperature of 230 °C and a quadrupole temperature of 150 °C. Mass spectra were acquired over a scan range of m/z 35–500 amu, encompassing the expected mass range of indoor, outdoor, and product-derived VOCs. This configuration ensured high sensitivity and reproducibility for the detection of both low- and high-molecular-weight VOCs, aligning with current analytical standards for environmental VOC profiling.

3. Results and Discussion

3.1. Overview of Detected VOCs

We conducted a semi-quantitative characterization of VOCs in both indoor and outdoor air at five monitoring sites in Milan, Italy. The concentration of each VOC group detected in the sample air is expressed as micrograms per cubic meter ($\mu g/m^3$). We considered the following VOC groups: hydrocarbons, aromatic hydrocarbons, terpenes, organosiloxanes, alcohols and ethers, aldehydes and ketones, esters, and halogenated compounds. The VOCs within each group generally share similar physicochemical properties and emission sources. This classification facilitated our interpretation of VOC distribution patterns and supported preliminary source attribution by linking chemical groups to known emission sources. It also allowed us to perform a comparative assessment of indoor and outdoor VOC compositions, revealing the combined impact of ambient pollution and emissions from indoor product use on air quality. Details on the calculation method for VOC concentrations are provided in the Supplementary Material (Table S1; Equations (S1)–(S3)).

3.2. Semi-Quantitative Characterization of VOCs in Outdoor and Indoor Air

Figure 2 shows the semi-quantitative mean concentrations for each VOC group in outdoor and indoor air. Because the sampling sites differed substantially in the types and concentrations of VOCs, the results of the quantitative analyses are expressed as the mean with the standard deviation. In this context, the standard deviation reflects the variation between different sites rather than repeated measurements from the same site. This distinction is important for interpreting the magnitude of the deviations observed.

In the outdoor air, hydrocarbons were the dominant chemical group across all five sites, with a mean concentration of 173.2 ± 143.8 $\mu g/m^3$, accounting for 80.3% ± 4.6% of the total volatile organic compounds (TVOCs). Aromatic hydrocarbons were the second most abundant group (37.2 ± 49.7 $\mu g/m^3$, 13.3% ± 5.5% of TVOCs), followed by terpenes (2.7 ± 3.2 $\mu g/m^3$), esters (2.2 ± 1.1 $\mu g/m^3$), alcohols and ethers (1.7 ± 1.3 $\mu g/m^3$), halogenated compounds (1.5 ± 1.3 $\mu g/m^3$), organosiloxanes (1.2 ± 1.4 $\mu g/m^3$), and aldehydes and ketones (1.1 ± 1.6 $\mu g/m^3$).

Among the individual VOC species detected in outdoor air, tetradecane showed the highest semi-quantitative mean concentration (59.8 ± 28.1 $\mu g/m^3$), followed by dodecane (52.1 ± 56.3 $\mu g/m^3$) and hexadecane (16.8 ± 11.1 $\mu g/m^3$). Other major contributors included tridecane (16.1 ± 25.6 $\mu g/m^3$), (m + p) xylenes (13.8 ± 24.7 $\mu g/m^3$), decane (10.6 ± 22.1 $\mu g/m^3$), ethylmethylbenzenes (8.1 ± 14.5 $\mu g/m^3$), toluene (6.1 ± 2.5 $\mu g/m^3$), pentadecane (5.8 ± 6.8 $\mu g/m^3$), and 2,2,4-trimethylpentane (4.6 ± 2.6 $\mu g/m^3$). These 10 compounds collectively accounted for 84.1% ± 9.7% of outdoor TVOCs. Table S2 presents a full list of VOCs detected outdoors, along with the semi-quantitative concentration for all samples.

The mean semi-quantitative TVOC concentration in outdoor air across all sites was 220.8 ± 195.4 $\mu g/m^3$. Among the monitored locations, the mean semi-quantitative TVOC concentration of Outside Apartment 2 was notably higher compared with the other outdoor sites. This elevated concentration is primarily attributed to the high traffic density in the area, contributing to increased levels of specific alkanes (*n*-decane, *n*-dodecane, *n*-tridecane, *n*-tetradecane, and other linear alkanes) and alkylbenzenes (benzene, toluene, ethylbenzene, m + p xylene, and ethylmethylbenzenes), which are consistent with emissions from gasoline and diesel combustion. This finding aligns with previous research linking heavy traffic to elevated VOC concentrations [4,42,43].

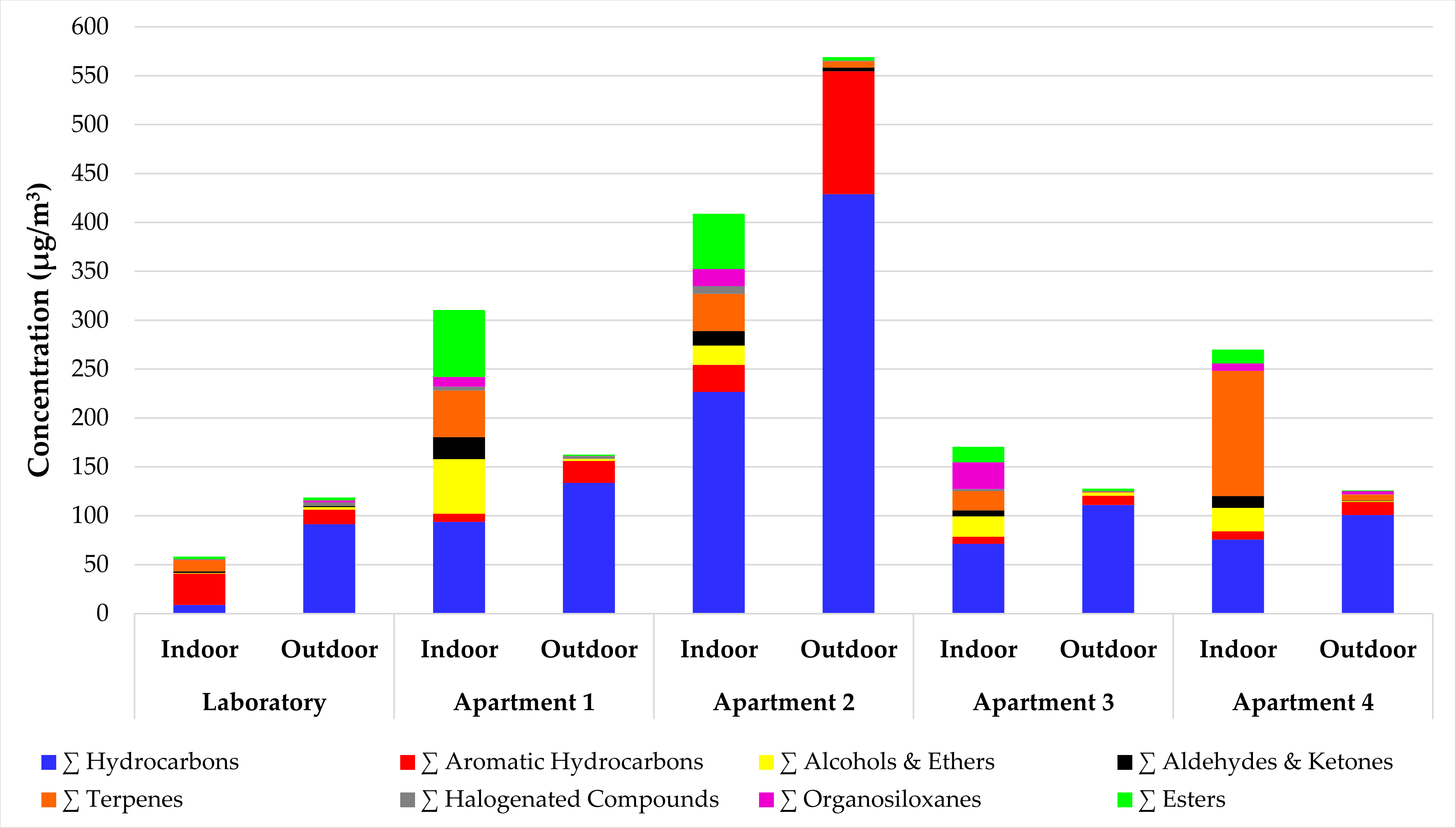

Figure 2. The stacked bar chart shows the mean semi-quantitative concentrations (µg/m^3) of the volatile organic compound groups across five indoor and outdoor environments in Milan.

Considering the five indoor air monitoring sites, hydrocarbons were again the most abundant group (95.2 ± 80.1 μg/m^3), accounting for 34.1% ± 15.2% of TVOCs. Terpenes were the second most abundant group (49.0 ± 46.4 μg/m^3, 20.7 ± 15.5% of TVOCs), followed by esters (31.5 ± 28.9 μg/m^3), alcohols and ethers (24.2 ± 19.9 μg/m^3), aromatic hydrocarbons (16.8 ± 12.1 μg/m^3), organosiloxanes (12.6 ± 10.2 μg/m^3), aldehydes and ketones (11.4 ± 8.1 μg/m^3), and halogenated compounds (2.9 ± 3.2 μg/m^3).

The 10 most abundant VOCs identified indoors were tetradecane (29.2 ± 22.8 μg/m^3), dodecane (17.3 ± 13.3 μg/m^3), limonene (13.2 ± 9.0 μg/m^3), *n*-butyl acetate (11.9 ± 13.1 μg/m^3), decamethylcyclopentasiloxane (10.3 ± 9.7 μg/m^3), hexadecane (10.0 ± 14.3 μg/m^3), α-pinene (9.7 ± 11.1 μg/m^3), β-linalool (9.7 ± 11.8 μg/m^3), toluene (9.1 ± 7.6 μg/m^3), and 1-butoxy-2-propanol (8.1 ± 5.5 μg/m^3). Collectively, these compounds accounted for 53.9% ± 7.3% of indoor TVOCs. Table S3 provides a full list of VOCs detected indoors, along with their semi-quantitative concentrations.

The mean semi-quantitative indoor TVOC concentration was 243.6 ± 134.3 μg/m^3, which was on average 10% higher than the outdoor concentrations. Overall, the I/O ratio was 1.10. Thus, the indoor TVOC concentration was 10% higher compared with the outdoor TVOC concentration. This higher indoor TVOC concentration is consistent with a previous study [44]. However, the laboratory and Apartment 2 sites showed a higher mean outdoor semi-quantitative TVOC concentration relative to the mean indoor semi-quantitative TVOC concentration.

Apartment 2 exhibited the highest indoor semi-quantitative TVOC concentrations, driven by the continuous infiltration of outdoor pollutants through open windows, amplified by its proximity to a major traffic route. Due to elevated ambient temperatures during the monitoring period, apartment windows and doors were routinely left open throughout the day and into the night, facilitating unfiltered exchange with the outdoor environment. This led to the indoor accumulation of traffic-related VOCs. In this case, open-window ventilation did not improve indoor air quality but instead facilitated the intrusion of outdoor pollutants. This finding aligns with previous studies showing that polluted outdoor air can infiltrate indoor environments, increasing indoor pollution levels, particularly in areas near major roads [45,46]. Conversely, in the laboratory, where windows remained closed and mechanical ventilation was used, the indoor semi-quantitative VOC concentrations were lower than those outdoors. This underscores the effectiveness of controlled ventilation systems in managing indoor air quality, particularly in high-traffic urban environments.

3.3. I/O VOC Ratios as Indicators of Source Attribution

We calculated the I/O ratio for each VOC group. This diagnostic tool is widely used to identify dominant emission sources. Moreover, the use of relative I/O ratios based on VOC group concentrations minimizes the influence of short-term variability in individual compound concentrations. An I/O ratio greater than 2.0 typically suggests a predominance of indoor sources, whereas a ratio close to 1.0 ± 0.2 implies an outdoor origin. Intermediate values (1.2–2.0) indicate mixed contributions from both environments [18]. Table 1 presents a summary of the relative I/O ratio for each of eight VOC groups across all sampling sites.

We observed notable variations in the I/O ratios across the VOC groups and sampling locations. Hydrocarbons and aromatic hydrocarbons consistently exhibited an I/O ratio < 1.0, indicating a dominant contribution from outdoor sources. This pattern aligns with the elevated outdoor concentrations observed at traffic-influenced sites and supports the interpretation that vehicular emissions, via infiltration and natural ventilation, are major contributors to indoor levels of these compounds.

Table 1. Indoor-to-outdoor (I/O) ratios of volatile organic compound chemical groups across all monitoring sites.

Groups of VOCs	I/O Ratio									
	Laboratory	Sources	Apartment 1	Sources	Apartment 2	Sources	Apartment 3	Sources	Apartment 4	Sources
Hydrocarbons	0.1	O	0.70	O	0.53	O	0.64	O	0.75	O
Aromatic Hydrocarbons	2.14	I	0.37	O	0.22	O	0.76	O	0.64	O
Alcohols and Ethers	0.27	O	28.19	I	nd *	I	6.77	I	28.98	I
Aldehydes and Ketones	1.30	I and O	nd *	I	3.98	I	nd *	I	20.81	I
Terpenes	77.73	I	227.19	I	5.97	I	26.09	I	20.78	I
Halogenated Compounds	0.07	O	1.58	I and O	10.82	I	4.07	I	nd **	O
Organosiloxanes	0.17	O	32.52	I	nd *	I	75.64	I	2.44	I
Esters	1.01	O	49.91	I	15.73	I	6.31	I	19.96	I

* nd—not detected in outdoor air; ** nd—not detected in indoor air.

Interestingly, aromatic hydrocarbons in the laboratory environment showed an I/O ratio > 2.0, pointing to a strong indoor source. This can likely be attributed to the use of high-purity solvents during laboratory procedures, which considerably elevate indoor concentrations of these compounds.

For the other VOC groups, including alcohols and ethers, aldehydes and ketones, terpenes, halogenated compounds, organosiloxanes, and esters, the I/O ratio was usually >2, indicating a primary indoor origin. These VOC groups are typically emitted from cleaning agents, personal care formulations, and a variety of consumer products frequently used in indoor environments. However, some sites exhibited more complex source profiles. For example, halogenated compounds in Apartment 1 and aldehydes and ketones in the laboratory showed an intermediate I/O ratio, indicating mixed sources. In these cases, both outdoor infiltration and indoor activities contributed significantly to the indoor VOC concentrations. These findings underscore the importance of considering outdoor air quality when evaluating indoor VOC concentrations, as many outdoor-derived compounds are transported into indoor spaces through different pathways.

3.4. Diagnostic VOC Ratios in Outdoor Air: B/T, T/B, and X/E

The B/T, T/B, and X/E ratios are widely used diagnostic tools to assess the origin of VOCs and to evaluate the photochemical aging of air masses. The B/T ratio is frequently employed to estimate the contribution of VOC sources. A B/T ratio of 0.23–0.66 is typically associated with mobile sources, especially vehicular exhaust, whereas a B/T ratio < 0.23 suggests that stationary sources, such as fuel evaporation or industrial emissions, are dominant. Conversely, a B/T ratio > 0.66 implies a mixed contribution from both mobile and stationary sources [47]. The T/B ratio, which complements the B/T ratio, helps differentiate between traffic and solvent-related emissions. A T/B ratio < 2.0 typically reflects fresh traffic emissions. A T/B ratio of 2.0–5.0 indicates mixed influence from vehicles and industrial activities involving solvent use, while a T/B ratio > 5.0 has been associated with significant contributions from industrial sources or solvent evaporation. These T/B thresholds are adapted from previous studies conducted in urban environments [48,49]. In urban environments, the X/E ratio generally ranges from 2.5 to 2.9, reflecting relatively fresh emissions. Conversely, an X/E ratio < 2.5 suggests that air masses have undergone substantial photochemical aging [50]. An X/E ratio of 2.8–4.6 has been strongly associated with vehicular traffic, a major contributor to urban VOCs [51].

The calculated mean relative B/T, T/B, and X/E ratios for each outdoor sampling site are presented in Table 2. The mean was 0.39, 2.69, and 2.72, respectively. These values suggest that vehicular traffic is the predominant source of VOCs in the ambient environment. The B/T ratios fall within the typical range associated with vehicle exhaust (0.23–0.66), while the T/B ratios indicate mixed contributions from traffic and solvent-related industrial activities. The mean X/E ratio (2.72) points to relatively fresh emissions with moderate photochemical aging.

Table 2. Site-specific outdoor volatile organic compound ratios of benzene to toluene (B/T), toluene to benzene (T/B), and (m + p)-xylene to ethylbenzene (X/E) at the monitored locations in Milan, Italy.

Location	B/T	T/B	X/E
Laboratory	0.42	2.36	2.77
Apartment 1	0.38	2.60	2.90
Apartment 2	0.55	1.83	3.56
Apartment 3	0.31	3.26	2.52
Apartment 4	0.29	3.41	1.85
Mean ratio	0.39	2.69	2.72

Notably, Apartment 2 exhibited the highest X/E ratio (3.56), reinforcing its classification as a traffic-influenced site. In contrast, Apartment 4 showed the lowest X/E ratio (1.85), indicating the presence of more aged air masses, likely due to photochemical degradation and atmospheric dispersion.

Although both vehicular traffic and industrial solvent-related activities contribute to ambient VOCs in Milan, the overall emission profile is clearly dominated by vehicular sources. Local variations reflect differences in proximity to roads and urban density, with urban areas more affected by fresh traffic emissions, while the suburban site exhibits signs of aged air masses.

3.5. Semi-Quantitative Comparison Between VOC Emissions from Consumer Products and VOCs Detected in Indoor and Outdoor Air

Figure 3 presents the semi-quantitative percentage distribution of VOCs emitted from household cleaning detergents and personal care products used at the monitoring sites in Milan. For comparison, the figure also shows the average percentage composition of VOC groups identified in both indoor and outdoor air across all sampling locations. The values represent the relative contribution of each VOC group to the total detected compounds, providing an integrated view of product emission profiles and ambient VOC composition.

Based on the results, the predominant contributors to indoor VOC emissions are consumer products, particularly cleaning detergents and personal care products. The most abundant compound groups emitted from these products include terpenes, alcohols and ethers, and esters. This pattern is consistent with previous studies highlighting these products as major indoor VOC sources [17,52–55]. In contrast, hydrocarbons and aromatic hydrocarbons detected indoors are primarily attributed to outdoor air infiltration. These groups are typically associated with vehicular traffic and combustion-related sources, and their presence indoors reflects the transport of pollutants from the ambient outdoor environment. This interpretation is further supported by the I/O ratios (see Section 3.3), which emphasize the contribution of outdoor-origin VOCs to indoor air composition.

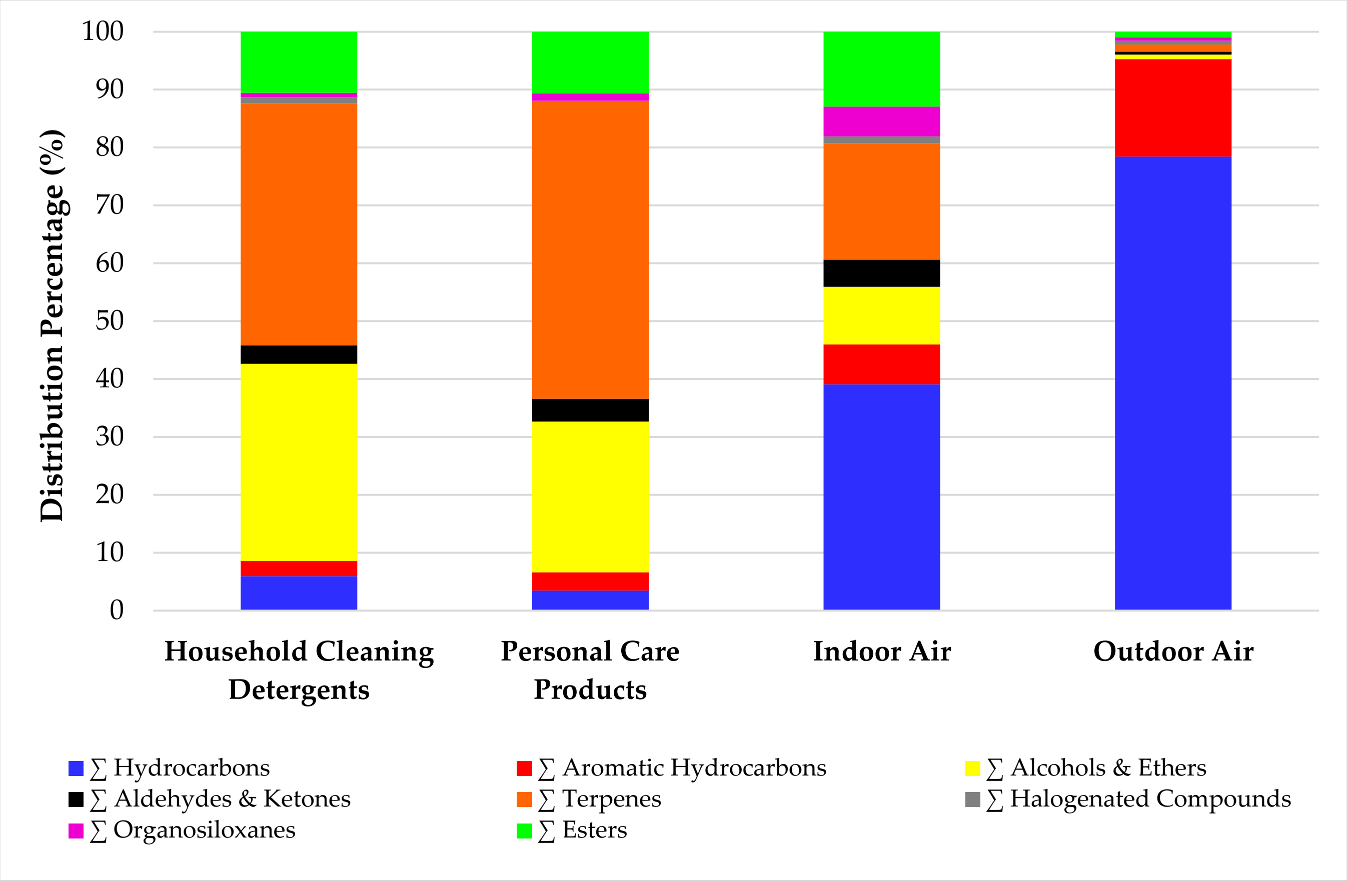

Figure 3. The bar chart shows the average percentage distribution of volatile organic compound groups emitted from consumer products and detected in indoor and outdoor air at the monitored sites.

3.6. TVOC Concentrations in Milan and Comparison with Global Cities

Table 3 presents the mean semi-quantitative concentrations of TVOCs in both outdoor and indoor air in Milan, alongside reported values from selected international cities. We calculated the mean semi-quantitative TVOC concentrations for Milan by determining the total concentrations at each monitoring site (indoor and outdoor) and then using these values to calculate the arithmetic mean across all sites. This approach provides a relative overview of the local urban TVOC burden. Note that the referenced studies differ significantly in terms of sampling locations, durations, protocols, analytical methods, and especially the timing of data collection. While we conducted our study during the summer, some of the cited studies either reported data limited to specific seasons, with sparse measurement from the summer or covered much longer monitoring periods that span multiple seasons. These temporal differences complicate direct comparisons, as seasonal variations and monitoring duration can substantially affect the concentrations. Furthermore, the concentrations reported here are semi-quantitative estimates, in contrast to the absolute values presented in other studies in Table 3. Therefore, direct comparisons should be made cautiously, considering these methodological differences. Despite these limitations, the comparative assessment offers a valuable relative perspective on TVOC variability at both local and international scales.

In Milan, the mean semi-quantitative TVOC concentrations were relatively elevated compared with several other urban centers. For example, the outdoor TVOC concentration in Milan exceeds the concentrations reported in Calgary (42 μg/m^3), Ghent (24.5 μg/m^3), and Ulsan (28.1 μg/m^3), likely reflecting higher vehicular traffic and urban density. Similarly, the indoor TVOC concentration in Milan is higher than what was reported in La Plata (112.5 μg/m^3) and Ghent (152 μg/m^3), underscoring the contribution of indoor sources, including consumer products and infiltration of outdoor air. However, the indoor TVOC concentration in Milan is lower than the concentrations found in highly polluted environments such as Ajman (3092.2 μg/m^3) and Dubai (594.8 μg/m^3). Cities such as Çanakkale (500–550 μg/m^3) and Harbin (411 μg/m^3) also have higher indoor TVOC concentrations, so Milan is placed in the intermediate range of indoor air pollution. These findings highlight the significant influence of local factors, such as traffic emissions, industrial activities, building ventilation, climatic conditions, and population density, on urban VOC concentrations.

Table 3. The mean semi-quantitative total volatile organic compound concentrations (μg/m^3) in indoor and outdoor air in Milan, compared with values reported in selected global cities.

City/Country	Type of Air	TVOC Concentration (μg/m^3)	References
Milan/Italy	Outdoor	220.8	Present study
	Indoor	243.6	
Ghent/Belgium	Outdoor	24.5	[56]
	Indoor	152	
Slovakia	Indoor	519.7	[57]
Squinzano/Italy	Outdoor	420	[58]
	Indoor	303	
Ajman/United Arab Emirates	Outdoor	114	[59]
	Indoor	3092.16	
Dubai/United Arab Emirates	Indoor	594.77	[60]
Çanakkale/Turkey	Indoor	500–550	[61]
Schleswig-Holstein/Germany	Indoor	289	[62]
Harbin/China	Indoor	411	[63]
Addis Ababa/Ethiopia	Indoor	289	[64]
La Plata (Buenos Aires)/Argentina	Outdoor	44.51	[46]
	Indoor	112.46	
Calgary, Alberta/Canada	Outdoor	42	[65]
Beijing/China	Outdoor	119	[66]
Ulsan, Korea	Outdoor	28.1	[67]
Nsukka, Nigeria	Outdoor	71	[19]
	Indoor	115; 254	

Although we have provided relative quantification of VOCs rather than absolute concentrations, the identified VOC profile still warrants attention due to potential human health impacts, particularly regarding BTEX compounds because of their established or potential carcinogenicity, as classified by authoritative regulatory agencies. Benzene is classified as carcinogenic to humans (Group 1) by both the U.S. Environmental Protection Agency (USEPA) and the International Agency for Research on Cancer (IARC). Ethylbenzene is classified as Group 2B, indicating it is possibly carcinogenic to humans, while toluene and xylenes are classified as Group 3, meaning they are not classifiable regarding their carcinogenicity to humans [17,68,69].

The relative mean outdoor benzene concentration, averaged across all sampling locations, was approximately 2.5 μg/m^3. At two sampling sites, this semi-quantitative estimate slightly exceeded the reference limit of 3.4 μg/m^3 established by Directive (EU) 2024/2881 [70]. However, these figures should be interpreted as indicative relative estimates rather than precise absolute concentrations due to methodological limitations inherent in achieving full absolute quantification.

Some of the cyclic siloxanes detected in this study, such as decamethylcyclopentasiloxane (D5) and octamethylcyclotetrasiloxane (D4), have been linked to adverse effects on the endocrine and reproductive systems, with potential impacts on immune function as well as liver, lung, and kidney health. These compounds raise concerns regarding their disruption potential and bioaccumulation. Specifically, D4 meets the criteria for persistence, bioaccumulation, and toxicity, while D5 is classified as highly persistent and bioaccumulative, though its toxicity remains uncertain [20,21].

VOCs emitted by air fresheners are recognized as potentially toxic or hazardous under U.S. federal regulations and USEPA guidelines, with some compounds classified as carcinogens. These emissions contribute significantly to indoor VOC levels in monitored environments [71,72].

Importantly, although we have presented relative semi-quantitative estimates, the mean indoor TVOC concentration in Milan exceeded the 200 $\mu g/m^3$ threshold proposed by Mølhave [73], above which discomfort or adverse health effects may occur in residential environments. Three of the four monitored apartments surpassed this threshold. Despite the relative nature of the data, these findings highlight the presence of VOC mixtures that raise concerns about indoor air quality and underscore the need for mitigation strategies in urban residential settings. These relative findings emphasize the importance of ongoing VOC monitoring in both outdoor and indoor environments, which should be complemented by absolute quantitative measurements to accurately assess population exposure to VOCs.

4. Conclusions

We have provided a comprehensive semi-quantitative characterization of VOCs in indoor and outdoor environments in Milan, Italy, over a two-month summer period in 2024. Based on a Radiello® PAS and GC-MS, we found that the mean indoor TVOC concentration exceeded the mean outdoor TVOC concentration. Specifically, the relative mean I/O ratio was 1.10, indicating that indoor VOC concentrations were approximately 10% higher. This suggests that indoor spaces, even under natural ventilation conditions, act as reservoirs for VOCs due to continuous emissions from consumer products and infiltration from outdoor sources.

Hydrocarbons were the dominant VOC group in both environments, although the distribution patterns varied. In outdoor air, hydrocarbons and aromatic hydrocarbons comprised most of the VOCs, followed by terpenes, esters, alcohols and ethers, halogenated compounds, organosiloxanes, and aldehydes and ketones. Indoor air was dominated by hydrocarbons and terpenes, followed by esters, alcohols and ethers, aromatic hydrocarbons, organosiloxanes, aldehydes and ketones, and halogenated compounds.

The B/T, T/B, and X/E ratios confirmed that vehicular traffic is the primary contributor to outdoor VOCs in Milan, with secondary influences from industrial solvent use and photochemical aging. Indoor VOC sources were mainly linked to emissions from consumer products, particularly cleaning and personal care products, with additional contributions from outdoor air infiltration, highlighted by the alignment between product emissions and indoor VOC profiles. Importantly, the mean indoor TVOC concentration in three of the four monitored apartments exceeded the health-based threshold of 200 $\mu g/m^3$ proposed by Mølhave [73], raising concerns about indoor air quality and the potential need for mitigation strategies in residential settings.

The Radiello® PAS demonstrated their effectiveness for integrated, long-term monitoring of VOCs in both indoor and outdoor environments. They offer a reliable, low-maintenance tool for exposure assessment. Nonetheless, certain limitations must be acknowledged. The semi-quantitative nature of the analysis, which relied on relative RFs and RIs, introduces uncertainty in absolute concentration values. The limited number of sampling sites also constrained spatial representativeness. Furthermore, our restriction to a single summer season limits its applicability to other climatic periods. Future studies should include year-round and spatially diverse monitoring to better capture seasonal and geographical variability in VOC emissions, thereby improving exposure assessments and mitigation planning.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/atmos16091088/s1, Equations (S1)–(S3): Calculation of volatile organic compound concentrations; Table S1. Manufacturer-specified sampling rates (Q) for Radiello® passive samplers under standard conditions (25 °C and 1013 hPa). The values have been reproduced from the Radiello® Manual; Table S2: List of volatile organic compounds detected in outdoor air across five locations in Milan, Italy, during monthly sampling campaigns in June and July 2024. The semi-quantitative concentrations are reported for each campaign, along with the mean concentrations over the full monitoring duration at each site; Table S3: List of volatile organic compounds detected in indoor air across five locations in Milan, Italy, based on biweekly sampling campaigns conducted in June and July 2024 (two samples per month). Semi-quantitative concentrations are reported separately for each month, along with overall mean concentrations for the full monitoring period at each site [35,74].

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