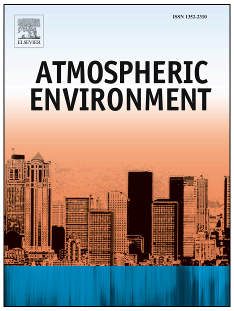

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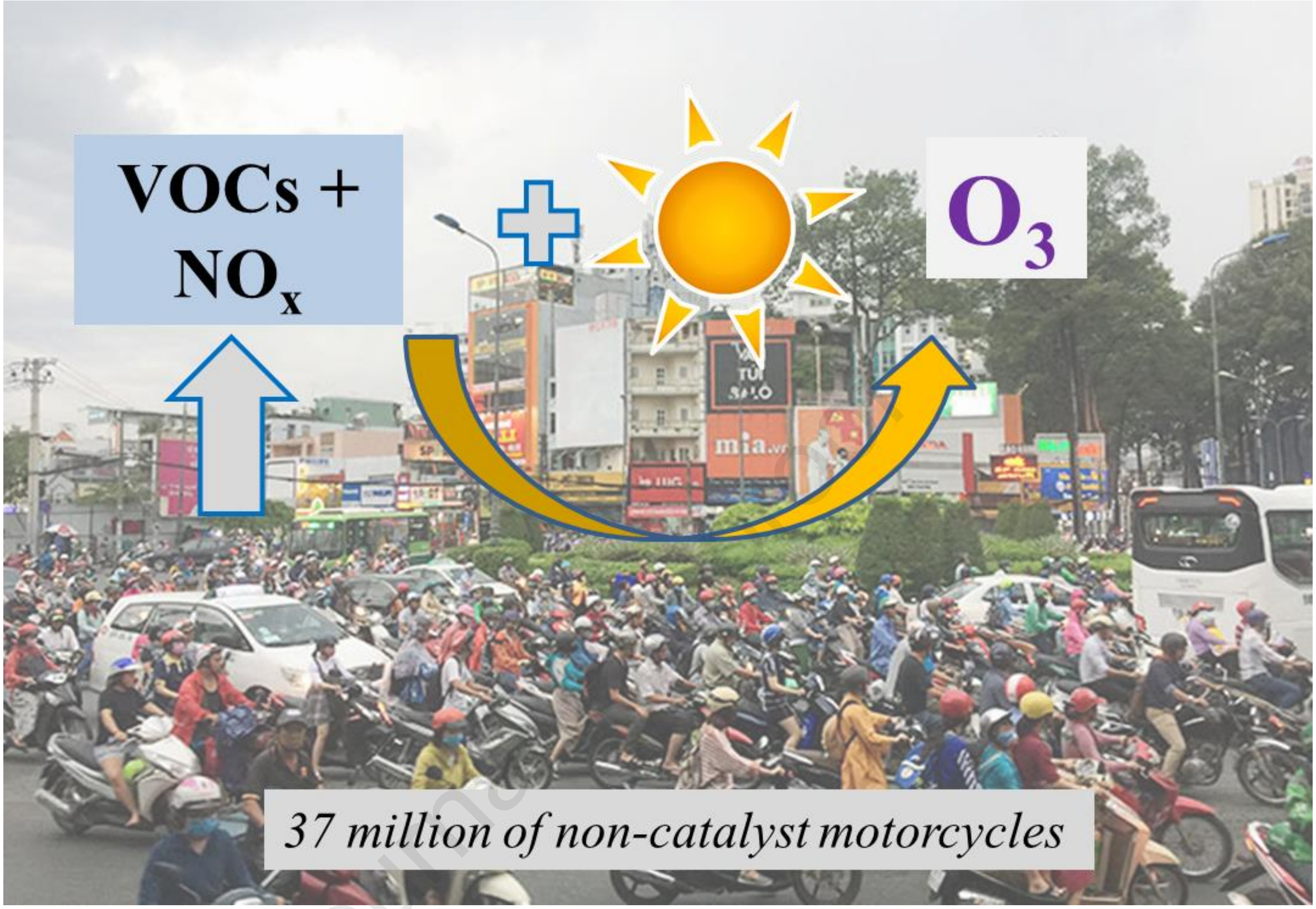
Graphical Abstract



Comprehensive volatile organic compound measurements and their implications for ground-level ozone formation in the two main urban areas of Vietnam

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Abstract

Volatile organic compounds (VOCs) and oxygenated VOCs (OVOCs) were measured in Ho Chi Minh City (HCMC) and Hanoi, the two largest and most populous cities in Vietnam. The purpose of this study is to better understand the VOC atmospheric composition and their role in ground-level ozone formation. Online measurements of a wide range of VOCs and other pollutants were conducted using numerous instruments during different seasons (dry and rainy) in HCMC and Hanoi (spring). Our results show that the mean mixing ratio of total measured VOCs in Hanoi was 80.8 ± 40.7 ppb (mean ± standard deviation), and was similar to that observed during the rainy season (75.2 ± 44.8 ppb) in HCMC. During the dry season campaign in HCMC, which was coincident with the Hanoi campaign, total VOC was around 50% lower (40.7 ± 19.5 ppb), largely a result of increased planetary boundary layer (PBL) height and the direction of the prevailing wind. VOC profiles in both cities were dominated by alkanes (31 – 35%) and OVOCs (27 – 33%) and the proportion of alkenes (13 – 17%) and aromatics (12 – 19%) were comparable. Similarities in diurnal variation for most VOC species (except for isoprene) are seen in both cities with two clear peaks during the morning (7:00 – 8:00 am) and evening (18:00 pm) rush hours, as observed for vehicular-combustion tracers (acetylene and CO). Comparisons of the ambient ratios of paired VOCs, namely *i/n*-pentane, and toluene/benzene, with those reported in motorcycle exhaust, roadside and gasoline samples indicate that motorcycle-related emission is likely a major contributor to VOC pollution. According to the propylene-equivalent concentration (PE conc.) and maximum incremental reactivity (MIR) methods, alkenes and aromatics were determined to be the main contributors to reactivity and ozone potential formation. Furthermore, the initial mixing ratio of VOC species was estimated based on the photochemical age method. The consumed VOCs (initial VOCs minus measured VOCs) has a similar variation trend to ground-level ozone, and a good correlation is observed in HCMC. In contrast, this result was not seen in Hanoi despite relatively high levels of PE conc. and MIR.

Keywords: VOCs, Ozone formation, photochemical reactivity, urban air pollution, Southeast Asia.

1. Introduction

Volatile organic compounds (VOCs) are important trace gases in the atmosphere and include a wide range of chemical compounds, such as non-methane hydrocarbons (NMHCs) and oxygenated-VOCs (OVOCs). Some VOCs are toxic for human health (e.g., benzene) (Colman Lerner et al., 2012). VOCs are important precursors in the formation of ground-level ozone and secondary organic aerosols (SOA) (Atkinson and Arey, 2003; Seinfeld and Pandis, 2016). Ozone is a secondary product which can be formed through photochemical reactions involving VOCs and nitrogen oxides (NOx) in the atmosphere. SOA are a major component of fine particulate matter (PM) (50–85% of the total organic aerosol burden (Jimenez et al., 2009)) and can be produced via gas-phase reactions of VOCs and the subsequent condensation of semi-volatile vapor, as well as by multiphase and heterogeneous processes (Hallquist et al., 2009). Ozone and PM are important air pollutants and have adverse effects on human health, agricultural productivity and climate.

VOCs are emitted into the atmosphere by both anthropogenic and biogenic sources. Large amounts of VOCs in atmosphere are from biogenic emission (primarily isoprene and terpenoids) at global scale (Sindelarova et al., 2014), whereas anthropogenic emission sources are complex and normally dominant in and around urban areas (Cai et al., 2010; Baudic et al., 2016). Urban anthropogenic sources include road-transportation emissions (vehicular exhaust and fuel evaporation), solvent usage, natural gas and liquefied petroleum gas (LPG) leakages, biomass burning, and industrial emissions (Blake and Rowland, 1995; Buzcu and Fraser, 2006; Bon et al., 2011). In addition to these primary emissions, some oxygenated-VOCs (OVOCs) are secondary products, formed in the atmosphere via photochemical reactions (Millet et al., 2015).

A large number of studies have been conducted in urban areas investigating the role of VOCs in local and regional atmospheric chemistry, air quality and their impacts on human health. In addition, VOC studies have been conducted in many regions to provide essential information to policymakers responsible for air quality and pollution abatement (Louie et al., 2013; Li et al., 2015a). These studies have shown that the VOC composition in urban atmospheres is usually dominated by alkanes (Buzcu and Fraser, 2006; Cai et al., 2010; Sakamoto et al., 2018). However, the major contributors to ozone formation are normally found to be alkenes and aromatics species, due to their higher reactivity towards hydroxyl radicals

(OH•) (Hui et al., 2018). In addition, OVOCs account for a significant amount of the total measured VOCs and are also important contributors to ozone formation (Shao et al., 2009). To assess local ozone formation, both propylene-equivalent concentration (PE conc.) (Chameides et al., 1992) and maximum incremental reactivity (MIR) (Carter, 1994) methods are widely used (Hui et al., 2018; Ly et al., 2020). A better understanding of atmospheric composition, emission sources and chemical processing in urban atmospheres is essential for successful ozone and SOA abatement strategies at a given location.

Ho Chi Minh City (HCMC) and Hanoi are the two largest cities in Vietnam, and contribute up to 39% of the country's Gross Domestic Product (GDP), according to General Statistics Office of Vietnam in 2018 (G.S.O, 2019). The climate in HCMC shows a quite different compared to that in Hanoi. In particular, the climate in HCMC is characterized by a tropical monsoon climate with two distinct seasons (dry and rainy), while in Hanoi the city has the warm humid subtropical climate with four distinct seasons (spring, summer, autumn, and winter). With the recent rapid urbanization and industrialization, the population of both emerging cities has increased rapidly, such that by 2018 the populations of Hanoi and HCMC were approximately 8 million and 9 million, respectively (G.S.O, 2019). As a consequence, environmental pollution issues have been gradually rising, with air and water pollution being two of the most serious current problems. Private road-transport is the dominant fraction in the traffic sector in Vietnam. The number of private vehicles has increased significantly, reaching 6.6 and 8.9 million in Hanoi and HCMC in 2019, respectively according to Vietnam Television (VTV, 2019). Motorcycles account for approximately 86% of the total vehicle fleet in the country (VTV, 2019), and are likely to be a major contributor to air pollution. Due to these rapidly growing sources of pollution, air quality has seriously deteriorated in recent years and severe air pollution has strongly impacted on human health (Phung et al., 2016). To address air pollution in Vietnam, a number of studies have been carried out previously. However, most previous studies concerning VOCs focused on the BTEX group (benzene-toluene-ethylbenzene-xylenes) from transport emissions (Truc and Kim Oanh, 2007; Lan and Minh, 2013; Huong Giang and Kim Oanh, 2014). High concentrations of BTEX at the roadside were found in both HCMC and Hanoi. Lan and Minh, (2013) found that motorcycles accounted for 91% of the vehicle fleet and were a major contributor to the high BTEX concentration in HCMC. A similar result was reported by Ly et al., (2020) in Hanoi where motorcycles were also dominant (up to 86% of vehicle volume). One of the first long-term studies of a wide range of VOC species (66 compounds including 50 NMHCs and 16 halogenated hydrocarbons) was conducted by Imamura et al., (2007) in Vietnam, sampling from several sites in both HCMC and Hanoi. Extremely high concentrations of *i*-pentane and toluene were reported and recently confirmed by Ly et al., (2020) in a transport microenvironment. Regarding ambient measurements, the study of VOC pollution in Vietnam is limited. To the best of our knowledge, only one study in Hanoi was reported by Sakamoto et al., (2018) based on one week sampling in ambient air for a wide range of species (50 NMHCs). In general, previous studies have been somewhat limited as they have involved limited numbers of compounds, short sampling periods, manual sampling, and low time resolution (>1 hour). No comprehensive studies of VOCs have been conducted in Vietnam until now. Furthermore, there is no study of the OVOC concentrations in the atmosphere of Vietnam to date.

To better understand VOC pollution in urban areas of Vietnam, measurement campaigns were conducted in the city centers of HCMC and Hanoi as part of the UK-Vietnam 2-Cities project. The main objectives regarding VOCs were (1) to characterize the their atmospheric composition, mixing ratios, chemical reactivity and ozone formation potential, and to compare with other regions; (2) to investigate the temporal variation of VOCs in relation to emission sources, meteorological conditions and photochemical removal; (3) to investigate the role of VOCs in the formation of ground-level ozone by calculating the propylene-equivalent concentration, ozone formation potential, and estimating the initial mixing ratios of VOCs. This work provides the first comprehensive VOC study with wide range and high-resolution measurements of VOCs in the two largest and most populated cities in Vietnam.

2. Measurements

2.1. Sampling campaigns

Intensive online VOC measurements were conducted in the two largest cities in Vietnam. The campaigns were carried out in two distinct seasons in HCMC (rainy season: 27-Sep to 15-Nov 2018, and dry season: 4-Mar to 3-Apr 2019), and during the spring season (7-March to 1-Apr 2019) in Hanoi. The sampling sites (**Fig. 1**) were located in urban areas of HCMC, the largest economic center of Vietnam, and Hanoi, the capital.

HCMC is located in the south of Vietnam, near the Lower Mekong Delta region. It is the most populous city with a population of approximately 9 million in 2018, but more than 14 million if non-registered residents are included (G.S.O, 2019). It also has the largest economy of any city in Vietnam. The sampling site in HCMC (10°45’45” N, 106°40’56” E) was on the roof of an eleven-story building (~ 60 m above ground) of the University of Science, Vietnam National University-Ho Chi Minh City **(Fig. 1**). The two campaigns in Sep – Nov 2018 and Mar 2019 were in the rainy and dry seasons, respectively. Meteorological conditions during the two campaigns will be discussed in **Section 3.1.**

Hanoi is located in the north of Vietnam, the central area of the Red River Delta. The registered population was 8.1 million in 2018, but is more than 10 million if non-registered residents are included (G.S.O, 2019). It is the second largest city in terms of the economy and population. The weather is characterized by a warm humid subtropical climate with four distinct seasons. March (sampling period) is usually cloudy and foggy with average sunshine of about 1.5 hours per day as discussed in **Section 3.1**. The sampling site in Hanoi (21°0'24" N, 105°49'4"E) was on the roof of a seven-story building (~ 30 m from ground) of the Le Hong Phong Political School **(Fig. 1)**.

The sampling sites were selected within downtown areas with a good mix of residential, transport and commercial activities. There are no large-scale point sources such as thermal power plants and major industrial activity within at least 10 km of the sampling locations. The sites and sampling heights were chosen to enable the sampling of air from a wide range of possible sources, including those outside of the cities. The sites had a good 360 degree aspect, being clear of nearby tall buildings and very local pollution sources. Therefore, both sites are considered to be representative of the typical urban air of each city.

2.2. Instruments

Ambient VOCs were continuously sampled and analyzed using several online systems. In HCMC, a gas chromatograph with flame ionization detector (GC-FID) was used for C_2-C_8 non-methane hydrocarbons (NMHCs) and a Proton-transfer-reaction mass spectrometer (PTR-MS) for selected NMHCs and OVOCs. In Hanoi, a dual channel gas chromatograph with flame ionization detectors (DC-GC-FID) was used for the analysis of C_2-C_{10} NMHCs and a Selected Ion Flow Tube - Mass Spectrometer (SIFT-MS) for the analysis of selected NMHCs and OVOCs. The instruments and associated calibration processes deployed at each sampling point are described in the following section. The NMHCs and OVOCs species identified in this study are shown in **Table S1**.

2.2.1. HCMC VOC measurements

At the HCMC site, air was sampled from the top of a 15 m mast that was mounted on the roof of the building (60 m). Air was drawn into the lab through a 3/8” PFA sampling line at a flow of around 10 litres per minute. The individual instruments sampled off this central manifold.

a. Gas chromatography – flame ionization detector (GC-FID)

Twenty-two C_2-C_8 NMHCs (**Table S1**) were automatically measured by the online GC-FID instrument. This instrument is from the University of East Anglia, UK. The instrument is based on a thermal desorption – GC system, comprising two parts: an Agilent 6890 GC-FID and a Markes Unity thermal desorption unit. Briefly, the sampled air was dried by passing it through a reverse flow Nafion dryer before collection and pre-concentration onto a cold trap held at -25°C. The cold trap contained activated carbon (Carboxen 1016 and 1018, 60/80 mesh, Supelco). The sampling flow rate was 30 ml/min. Air was sampled for 20 minutes (giving a 600 ml air sample), before the cold trap was quickly heated to 280°C to desorb the adsorbed NMHCs into the GC equipped with 50 m x 0.32 mm Al_2O_3 PLOT column (Agilent). The duration of the chromatography cycle was 40 min. Therefore, the total time for one sample was approximately one hour. Calibrations were automatically performed every 47 hours using a standard gas mixture containing ~4 ppb of a 32-component ozone precursors mix (National Physical Laboratory - NPL, UK). It is noted that only 21 species were reported in this study because the peaks of *m*- and *p*-xylene do not separate well, and so the sum of them was reported as *m,p*-xylene. The precision of the measurement during the campaigns was calculated to be 5% for most NMHCs.

b. Proton-transfer-reaction mass spectrometer (PTR-MS)

Twelve selected VOCs (Table S1) were also measured by a commercial PTR-MS instrument (IONICON Analytik) in HCMC during both campaigns. This instrument has been intensively deployed in many field measurements (e.g., (Murphy et al., 2010). The instrument is also from the University of East Anglia, UK. The operation principle of this instrument is given in detail elsewhere (Murphy et al., 2010). In this work, we briefly summarize the operational conditions during the field observation in Vietnam. Firstly, air was sampled from the main manifold at a rate of approximately 1 L/min, via ~2 m of ¼" OD PFA tubing. Air was then drawn into the inlet of the PTR-MS via an 1/8" PFA tubing at a flow rate of ~ 100 mL/min. Constant pressure in the drift tube was maintained about 2.2 – 2.3 mbar, and the drift tube field strength (E/N) was kept at 120 Td. The temperatures of the inlet and drift tube were controlled at 40°C. The background signal was periodically determined by passing the air stream through a Platinum-coated glass-wool trap (Shimadzu, TO-14 catalyst) continuously heated to 350°C for 12 cycles, after 80 cycles of measured ambient air. To account for primary ion variability, the signals of the measured VOCs were normalized to the signal of H_3O^+ ion which always guaranteed greater than $3*10^6$ cps. Calibration was carried out approximately weekly by diluting the 0.5 ppmv standard gas mixture (Apel-Riemer Environmental Inc., USA) which contains sixteen VOC species of interest. Concentrations in the range 0 - 4 ppb were prepared by dynamic dilution with VOC-free zero air (BTCA-178, BOC). The identification of compounds and the likely interferences at different m/z values detected by PTR-MS have been studied extensively (de Gouw et al., 2003a; de Gouw et al., 2003b; Warneke et al., 2003). The mass to charge ratio (m/z) and identified VOC species in this study are as follows: m/z 33 for methanol, m/z 42 for acetonitrile, m/z 45 for acetaldehyde, m/z 59 for acetone, m/z 69 for the sum of isoprene and others as discussed below, m/z 71 for the sum of methacrolein and methyl vinyl ketone, (MACR + MVK), m/z 73 for methyl ethyl ketone (MEK), m/z 79 for benzene, m/z 93 for toluene, m/z 107 for the sum of C_8-aromatics, m/z 121 for the sum of C_9-aromatics and m/z 137 for the sum of monoterpenes. The detection limits of various VOCs by PTR-MS were shown in Table S3.

2.2.2. Hanoi VOC measurements

a. Dual channel- gas chromatography – flame ionization detector (DC-GC-FID)

VOC mixing ratios were measured online using a dual channel GC-FID system (Hopkins et al., 2003; Hopkins et al., 2011). The system comprised a commercially-available autosampler and preconcentrator (CIA Advantage and Unity 2 respectively) supplied by Markes International coupled to a home-built water removal trap and a gas chromatograph with flame ionization detectors (Agilent 7890). The ambient air was drawn at a constant flow rate (50 ml/min) through the water removal trap (an 80 ml glass vessel held at -30°C) to freeze-out and remove any water from the sample stream before being passed onto an “ozone precursors trap” (Markes International) maintained at −30 °C. The trap contained two different adsorbents with differing trapping efficiencies in order to retain VOCs with a wide range of volatilities. Air samples were acquired in a constant flow of 50 mL/min, during 10 minutes of pre-concentration giving an overall volume of 500 ml. After acquisition, the trap was rapidly heated at a rate of 40°C per second up to 250 °C, to transfer the collected analytes into the GC-FID via a heated transfer line (200 °C) in a flow of ultra-pure helium as carrier gas. The trap was held at the maximum temperature for 6 minutes in order to assure the complete desorption of the sample.

Up to 30 target compounds were separated during a run of approximately 40 minutes. The GC system was configured such that samples were split in near-equal portions between two different columns, separating the VOCs by volatility, into two fractions. The more volatile portion was analyzed using a PLOT (Porous Layer Open Tubular) column (50 m x 0.53 mm x 10 μm alumina/Na_2SO_4) while the less-volatile fraction was separated on a methyl polysiloxane DB-5 column (60 m x 0.23 mm x 1 μm). Upon injection of the sample into the GC system, the oven was held at 40 °C for 3 minutes, then warmed to 110 °C at 10 °C per minute, before being heated up to 200 °C at 11 °C per minute and finally maintained at this temperature for 15 minutes.

The identification and quantification of 30 VOCs was performed using a certified NPL ozone-precursors mix standard of 4 ppb concentration. Peak identifications were performed by retention time (RT), which was frequently verified and occasionally corrected for drift. Detection limit (DL) and quantification limit (QL) were obtained for each hydrocarbon and are shown in Table S2. Blank measurements were performed using ambient air which had been passed through a heated (400 °C) platinum catalyst to oxidize and remove any VOCs contained therein. Samples of a target gas (a mixture of low concentration VOCs) were injected once a day in order to ensure the quality and linearity of the instrument measurements. The repeatability of the analytical system was tested using the standard gas by successive injections of the same concentration. The procedure allowed the peak area variation coefficient (VC) for each hydrocarbon in the standard.

b. Selected-Ion Flow-Tube Mass Spectrometer (SIFT-MS)

A Voice200 SIFT-MS (Syft Technologies, Christchurch, New Zealand) was deployed in Hanoi to measure a total of 20 organic and inorganic compound mixing ratios (Wagner et al., 2021). The instrument was operated with a flow tube temperature of 120°C, a sample flow rate of 100 sccm, pressure of 460 mTorr, a flow tube of 50 V, and a constant nitrogen carrier gas flow of 25 sccm (Research grade, BOC). The microwave plasma ion source, which acts on an air/water mix at a pressure of approximately 300 mTorr, generates three reagent ions H_3O^+, NO^+, and O_2^+. The reagent ions pass through an array of electrostatic lenses and the upstream quadrupole mass filter which sequentially pass the reagent ions individually into the flow tube where they ionize compounds in the sample gas. During acquisition the SIFT-MS sequentially sampled a total of 29 mass-to-charge ratios which included the primary ions: H_3O^+ at *m/z* 19 including its first and second water clusters (m/z 37, 55 respectively), NO^+ at *m/z* 30 including its first water cluster (m/z 48) and O_2^+ at *m/z* 32. The instrument scanned for an additional 25 product ion *m/z* values characteristic of 22 gas phase compounds. The suite of selected masses (**Table S4**) was measured in selected ion monitoring mode (SIM) with a dwell time of 0.15 s per *m/z* which resulted in a total measurement cycle of 4.6 s. The SIM acquisition lasted for 50 minutes per hour.

The instrument background was assessed for five minutes of each hour by sampling zero air from an in house-built palladium alumina-based zero air generator heated to 380℃ in SIM mode. The five-minute average background mixing ratio was subtracted from the ambient mixing ratio measurements of the corresponding hour. The mixing ratio limit of detection (LOD) was approximated from two standard deviations of the 1 min background measurement (in normalized counts per second, ncps) for a given hour divided by the corresponding sensitivity (ncps/ppbv). Ensemble averages of the applied background and LOD mixing ratios are shown in **Table S4**. Sensitivities for 12 compounds detected by SIFT-MS were determined daily from automated calibrations performed using an in house developed dilution unit. This was using a 1 ppm gravimetrically prepared standard containing methanol, ethanol, acetonitrile, acetone, butadiene, benzene, toluene and xylene, trimethylbenzene, methacrolein, methyl ethyl ketone and isoprene in ultrahigh purity nitrogen (NPL) diluted with ambient humidity zero air. Multipoint calibrations were performed up and down the concentration range of 0, 0.5, 1, 5, 10 and 20 ppb and zero air measurements were performed before and after sampling for each calibration.

2.2.3. Auxiliary measurements

Carbon monoxide (CO) was measured at both sites using a TA 3000 CO analyzer (AMETEK Process Industries) in Hanoi, and a model 48i (Thermo Scientific, USA) in HCMC. For TA 3000 CO analyzer, a standard mixture containing 1 ppm of CO from the National Physical Laboratory (NPL, UK) was sampled every 1-2 days to ensure stability of the instrument and quantify the data reported. The 48i CO analyzer was weekly calibrated using a CO standard mixture of 10 ppm. Ozone was measured using a UV photometric analyzer (49i, Thermo Scientific, USA) at both sites. The meteorological data including temperature, relative humidity, pressure, wind speed, and wind direction were recorded by an automatic weather station (Davis Vantage Pro Weather Station and Ogasawara-Keiki Co., Ltd) at each sampling site. Planetary boundary layer (PBL) height data was downloaded from ERA5, the fifth generation reanalysis from ECMWF (European Centre for Medium-Range Weather Forecasts) (Hersbach et al., 2018). Rainfall and sunshine hours data were from General Statistics Office of Vietnam (2019).

The 168-hour backward trajectories ending at the two sampling sites were run every 1-hour for all campaigns using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (http://www.arl.noaa.gov/HYSPLIT.php) (Stein et al., 2015). The arrival height of the incoming air masses was chosen at 100 m as representing well-mixed air and the height of sampling tower. To evaluate the impact of air mass transport on VOC pollution in two cities, backward trajectories in each campaign were further clustered using Euclidean distance method from “Splitr” package. Number of clusters was changed from two to six clusters. A visual inspection based on a difference in length, shape and the start location of 168-hour backward trajectories was used to determine a number of clusters. Then three clusters were decided to represent for air mass classification.

2.3. Data analysis

The raw measurements from different instruments were averaged to the sampling time resolution (hourly) of each GC-FID sample before any further analysis. Data analysis was performed using R language in which the “Openair” package was deployed for plotting the graphs and preparing data (Carslaw and Ropkins, 2012) and “Splitr” package for backward trajectory calculation.

3. Results and Discussion

3.1. Meteorological conditions

In HCMC, the measurement campaign was divided into two periods, corresponding to the rainy (27-Sep to 15-Nov 2018) and dry (4-Mar to 3-Apr 2019) seasons. As shown in **Table 1**, the average monthly rainfall of 370.4 (mm per month) in the rainy period is significantly larger than that of 31.6 (mm/month) in the dry period. There were insignificant variations in temperature, but relative humidity in the rainy season was 87.0%, much higher than that of 65.4% in the dry season. The wind speed and wind direction also show significant differences. **Figure 2** depicts the wind rose plots of wind speed and wind direction at the two sampling sites. At the HCMC site, the average wind speed during the rainy campaign was 2.32 ± 0.95 m/s, significantly lower than that of 3.42 ± 0.99 m/s during the dry campaign (**Fig. 2a,b**). The prevailing winds during the rainy season in southern Vietnam (May-October) are normally from the south-west, and during the dry season (November-April) the monsoon flow switches to the NE-SE sector. In 2018, the change in wind regime occurred in late September which resulted in air arriving at the sampling site from all wind sectors and a stronger influence from the S-SE-E sector than expected. During the rainy campaign, the dominant wind sectors were east-southeast (18%), south-southeast (16%) and east (14%), but with some influence from westerly and northerly air flow. The wind direction during the dry campaign was almost exclusively from the east-southeast (21%), south-southeast (38%) and south (21%). Notably, from these directions, the sampling site is closer to the sea and rural areas than other directions, meaning that the air arriving in HCMC is likely to be less polluted than in other wind sectors. The average planetary boundary layer (PBL) height in the rainy campaign was 379 ± 359 m, approximately half that of 805 ± 500 m in the dry season (**Table 1**).

In Hanoi, the measurements were conducted between 7-March and 1-Apr 2019. The meteorological conditions are also summarized in **Table 1**. In comparison to HCMC, the average temperature (22.3 ± 3.4 °C) was lower but relative humidity (85.3 ± 9.3%) was comparable during the spring campaigns. Despite the high humidity average values, no significant rain events occurred in March (accumulated precipitation 15.1 mm/month). The average monthly total hours of sunshine (44.6 hours) was quite small, and also much lower than in HCMC (**Table 1**). Several cloudy and foggy days were observed during the campaign. **Figure 2c** shows the wind rose from data obtained in Hanoi during the field campaign. The mean wind speed was 1.96 ± 0.93 m/s and the percent of calm periods accounted for 8%. The wind was strongly impacted by the north-northeast wind direction (30%). The average PBL height of 420 ± 248 m was significantly lower than that obtained in HCMC (805 m) during the same period of the year. Higher PBL height, wind speed and temperature were often observed at midday at both sites but the maxima depended on seasons/sites **(Fig. 3)**. For example, the temperature in HCMC peaks earlier in the rainy season (10:00 am) than in the dry season (13:00 pm). The variations in meteorological conditions between the two cities (HCMC vs. Hanoi) and the two sampling periods (rainy vs. dry in HCMC) will have an impact on the mixing ratios and photochemical reactions of the measured VOCs.

Figure 4 shows mean 168-h backward trajectory clusters (Euclidean distance) arriving at the monitoring sites calculated from the HYSPLIT model. Having one of the longest atmospheric lifetimes of the VOCs measured (2 months), ethane was used for assessing the potential impact of long-range transport on pollution levels in the 2 cities. In HCMC rainy campaign, trajectories in cluster C1 mainly originated from southwestern directions (Gulf of Thailand), while those in cluster C2 and C3 were from northern directions (China mainland) and from northeastern directions (western Pacific Ocean), respectively. Clusters C1 (2.20 ppb) and C2 (2.42 ppb) during the rainy campaign were associated with higher ethane concentrations, compared to that of cluster 3 (1.80 ppb). Back trajectories in cluster C1 were generally shorter suggesting suitable conditions for the build-up of local emissions, whilst cluster C2 contained air masses that could have been influenced by mainland China before arriving at the measurement site. This could explain the higher ethane concentrations in these clusters. The average ethane concentration for cluster C3 was lowest because most air masses in cluster 3 travelled mainly over the sea and would be less likely to pick up terrestrial emissions. Back trajectories in the dry campaign were generally similar to that in cluster C3 during the rainy campaign which mainly originated from northeastern and eastern directions (western Pacific Ocean). As a result, the ethane concentrations in the three dry season clusters ranged from 1.60 to 1.74 ppb showed no statistically significant difference (Fig. 4d). In Hanoi, trajectories in cluster C1 mainly originated from northern directions (China mainland), while those in cluster C2 were characterized by northwestern directions originating from the cold Siberian high-pressure. Trajectories in cluster C3 originated from northeastern directions (China coastal areas). The cluster analysis based on back trajectories shows that the origin of sampled air masses had a strong impact on the observed ethane concentrations (Fig. 4e,f). Mean ethane concentrations for clusters C1 and C2 were 4.96

and 4.11 ppb, significantly higher that of 3.05 ppb for cluster 3. As seen in Fig. 4e, air masses in cluster C1 and C2 had passed over mainland China before arriving at the measurement site. In contrast, cluster C3 contained air masses that experienced a significant marine influence, highlighting the impact of marine air masses in reducing the air pollution in Hanoi.

3.2. VOC pollution in urban Vietnam

In this study, the term total VOCs is defined as the sum of all measured non-methane hydrocarbons (NMHCs), including alkanes, alkenes, aromatics and alkyne, and oxygenated-VOCs (OVOCs). **Figure 5** shows the hourly mixing ratio variation of various VOC groups (alkanes, alkenes, aromatics, acetylene and OVOCs), ozone, and CO measured at the HCMC and Hanoi sites. The mean, standard deviation and range of the measured VOC mixing ratios are summarized in **Table S5**. We note that the number of VOC species measured at the two sites was not exactly the same, so where comparisons are made between the different sites and seasons, an identical set of VOCs is used. For the data analysis, the particular instrument used for each VOC is noted in **Table S5**. In general, the GC data was used for the NMHCs whilst the PTRMS and SIFT-MS data were used for the OVOCs and acetonitrile.

3.2.1. Ambient mixing ratios and chemical speciation in HCMC

The mean mixing ratio of total VOCs observed in the rainy campaign was 75.2 ± 44.8 ppb, much higher than that in the dry season with a value of 40.7 ± 19.5 ppb (Table S5). The hourly mean mixing ratios during the rainy and dry seasons varied from 8.0 to 347.0 ppb and from 4.5 to 253.2 ppb, respectively (Table S5). In general, the rainy mixing ratio of each VOC group was around double that observed in the dry season. For instance, the mean measured alkane mixing ratios in rainy and dry seasons were 23.3 ± 14.8 ppb and 14.4 ± 7.6 ppb, respectively. A similar difference was observed for CO which averaged 0.96 ± 0.65 ppm and 0.60 ± 0.28 ppm in the rainy and dry seasons, respectively. These results indicate the strong seasonality of VOC and CO levels and potential influencing factors will be discussed in Section 3.3. **Figure 6** shows the relative proportions of the different VOC groups. The percentage contributions are broadly similar in the 2 campaigns, with alkanes (31 – 35%) and OVOCs (27 – 33%) making the greatest contribution to total VOCs, accounting for around 60%. Aromatics (16 – 19%) and alkenes (13 – 16%) shared almost equal proportions. Acetylene accounted for a small amount (3 – 5%).

Regarding individual species, C_2-C_5 alkanes were amongst the most abundant NMHCs, with *i*-pentane having the highest concentration compared to other NMHCs. The *i*-pentane concentrations in the rainy and dry seasons were 8.64 ± 5.97 ppb and 5.37 ± 3.54 ppb, respectively. Toluene was the second abundant compound and it was the dominant species among the quantified aromatics accounting for 40% and 50% in the rainy and dry seasons, respectively. Ethene and propene were the dominant species among the measured alkenes, and together accounted for 58% (rainy) and 70% (dry) of total alkenes. Among the measured OVOCs, methanol had the highest concentration with mean values of 9.64 ± 6.95 ppb (rainy) and 4.16 ± 1.71 ppb (dry). Acetone, MEK, and acetaldehyde also made a significant contribution to the measured OVOCs concentration. The mean isoprene concentrations in the rainy and dry seasons were 0.34 ± 0.27 ppb and 0.32 ± 0.30 ppb (Table S5), respectively and there was statistically insignificant seasonal variation (*t*-test, $p > 0.05$) in isoprene concentrations.

3.2.2. Ambient mixing ratio and chemical speciation in Hanoi

The mean mixing ratio of total VOCs in Hanoi was 80.8 ± 40.7 ppb, and the hourly mean mixing ratios ranged from 11.8 to 245.3 ppb (Fig. 5 and Table S5). Compared with other VOC groups, OVOCs presented the highest mean mixing ratios (34.5 ± 17.9 ppb) accounting for 43% of the total VOCs, in which ethanol and methanol are the most abundant species (mean mixing ratios of 13.4 and 12.9 ppb, respectively). Alkanes (21.5 ± 11.0 ppb, 27%) was the second most abundant group, followed by alkenes (11.5 ± 7.7 ppb, 14%), aromatics (8.2 ± 6.0 ppb, 10%) and acetylene (4.5 ± 3.4 ppb, 6%). The dissimilar profile when compared with HCMC is mainly due to the inclusion of ethanol in Hanoi, which represent 16.6% of the total. Therefore, if we exclude ethanol from Hanoi data, the percentage contribution of each VOCs group is quite similar to that obtained in HCMC (Fig. 6).

Ethene and acetylene presented the highest concentrations with values of 5.32 ± 3.91 ppb and 4.50 ± 3.40 ppb, respectively; followed by *i*-pentane (4.30 ± 2.94 ppb). The concentration of ethane in Hanoi was relatively high (4.16 ± 1.52 ppb) in comparison to that observed in HCMC, especially when air masses had passed over mainland China as shown previously (Fig. 4e). Similarly to HCMC, toluene (2.95 ± 2.46 ppb) was the most abundant species among the measured aromatics. The average isoprene concentration in Hanoi was 0.68 ± 0.52 ppb, significantly higher than that observed in HCMC (Table S5). Comparing the two cities, during the same period (Mar 2019) the total VOC mixing ratio was around twice as high in Hanoi as in HCMC. However, the springtime levels in Hanoi were similar to those observed in HCMC during the rainy season, showing that both cities experience similar levels of pollution, depending partly on the time of year. Clearly, VOC pollution in Hanoi was more severe during spring, which may be due to a combination of prevailing winds (import of background pollution), PBL height and the stable meteorological conditions (as discussed in Section 3.1).

In summary, high mixing ratios of primary NMHCs such as ethene, acetylene, *i*-pentane and toluene were observed in both urban atmospheres, indicating that their origins were probably from anthropogenic sources (e.g., vehicular exhaust including burned and unburned emission, gasoline evaporation, and solvent usage).

3.2.3. Comparison to other Asian cities

In order to get snapshot of the current levels of VOC pollution in urban areas of Vietnam, we compare our VOC concentrations with those recently measured in two other major Asian cites; Beijing, China (unpublished data) and Delhi, India (Stewart et al., 2021). In addition, two recent studies of a wide range of VOCs in ambient air (Sakamoto et al., 2018) and roadside (Ly et al., 2020) in Hanoi are used for further comparison. Twenty-one VOC species accounting for 94% and 82% of the total measured VOCs concentration in HCMC and Hanoi were selected for comparison. **Table 3** shows the mean VOC concentrations measured in HCMC and Hanoi together with those observed in the other studies/places.

The total concentration of the eighteen NMHCs in HCMC was comparable to that observed in Beijing. For instance, the concentrations of 46.8 ppb (rainy/2018) and 27.2 ppb (dry/2019) in HCMC were similar to those of 48.9 ppb (in winter/2016) and 24.2 ppb (in summer/2017) in Beijing. The total concentration of these species in Hanoi was 37.6 ppb in Mar/2019, mid-way between the winter and summer levels in Beijing. However, the total concentrations in both Vietnamese cities were much lower than those observed in Delhi during the pre-monsoon/2018 (60.3 ppb) and post-monsoon/2018 (238.4 ppb). Our total NMHC concentrations are in agreement with those reported in a previous ambient study performed in Hanoi in September 2015 (32.6 ppb) (Sakamoto et al., 2018). However, higher NMHC concentrations were reported at a roadside site in Hanoi (Ly et al., 2020) in December 2014 and January 2015 with total value of 161.6 ppb. Additionally, high BTEX concentrations at the roadside were also reported in previous studies in Hanoi (Truc and Kim Oanh, 2007) and HCMC (Lan and Minh, 2013; Huong Giang and Kim Oanh, 2014). A higher concentration at roadside close to a major source of NMHCs is expected. The sampling locations in this study were chosen in order to sample a wider footprint of potential emissions.

Comparison based on the total concentrations can provide a snapshot of the current state of VOC pollution in the various cities. In reality, the concentration and VOC will vary greatly depending on a number of factors including local meteorology, sampling location relative to emission sources, etc. However, even if traffic emissions are the main source of VOCs, the exact chemical composition of those emissions will depend strongly on the make-up of the vehicle fleet and types of fuel in use. Ethane, propane, and *i*-pentane are abundant species in CNG (compressed natural gas), LPG (liquid petroleum gas) and gasoline, respectively. As seen in **Table 3**, relatively high concentrations of *i*-pentane and toluene, compared to other NMHCs, were seen in both Vietnamese cities. This profile is similar to that reported in ambient air in Hanoi (Sakamoto et al., 2018). In contrast, the ambient air in Beijing was characterized by high concentrations of ethane and propane which suggests a greater contribution from CNG and LPG fuels, even though gasoline has been identified as the main fuel in Beijing (Li et al., 2017). In Delhi, LPG leakage was reported to be the main source of propane and butanes, as the result LPG usage contributed up to 32% of the source profile of NMHCs, which was only slightly lower than that of gasoline (38%) (Stewart et al., 2021). Apart from ethane and propane, other NMHCs including pentanes, most alkenes, BTEX and acetylene during the summer campaign in Beijing were lower than those measured in the Vietnamese cities **(Table 3)**. Ethene and acetylene during the winter campaign in Beijing were relatively high compared to those in Vietnam, probably due to the greater emissions and more stable weather conditions during the wintertime. Due to the effect of weather conditions during the post-monsoon season in Delhi, the concentration of all species was significantly higher than in Vietnam. However, except for C2-C4 alkanes in pre-monsoon, other species in Delhi are comparable to, or lower than those measured in HCMC and Hanoi. This comparison with two Asian megacities (i.e., Beijing and Delhi) shows that the concentrations and VOC distribution of the most abundant NMHCs in Vietnamese urban areas are comparable to those in Beijing, China, but lower than in Delhi, India. However, the chemical composition profiles have significant differences.

The ambient VOC profiles in both HCMC and Hanoi were also compared to those previously measured at an urban roadside (Imamura et al., 2007; Ly et al., 2020), and a commercial gasoline station (Imamura et al., 2007). Higher concentrations of *i*-pentane and toluene in the VOC profile were also observed in those studies, indicating that the measured ambient VOCs in Vietnam are strongly impacted by gasoline usage. Concerning the vehicular fleet in Vietnam, motorcycles represent the dominant vehicle fraction, accounting for more than 80% of transportation mode followed by cars (10%) (Lan and Minh, 2013; Ly et al., 2020). Most motorcycles have a four-stroke engine and are not equipped with catalyst converters. Higher VOC emission by non-catalyst motorcycles is expected and it was identified as the main contributor to VOC emission on-road in Hanoi (Ly et al., 2020). VOC profiles from motorcycles have been reported in China and Taiwan from chassis dynamometer tests (Tsai et al., 2003; Liu et al., 2008; Dhital et al., 2019). Similarities were also found between these studies.

To further explore the importance of motorcycles in VOC pollution in urban Vietnam, the ratios of *i*-pentane/*n*-pentane and toluene/benzene are compared to those reported in roadside studies (Imamura et al., 2007; Ly et al., 2020), gasoline (Liu et al., 2008; Lan and Minh, 2013), and motorcycle exhaust gas (Liu et al., 2008; Dhital et al., 2019). To exclude the effect of photochemical reactions, we only use early morning data (4:00 to 7:00 am). It is noted that *i*-pentane is well-correlated with all C_2-C_4 alkenes and other traffic-related species such as acetylene, CO and benzene, with correlation coefficients (r) > 0.8 ($p < 0.01$) as shown in **Fig. S1**. **Figure 7a** shows the correlation between *i*-pentane and *n*-pentane for each dataset. A strong correlation is observed between the species ($r > 0.96$, $p < 0.01$). The slopes of the regression line during the rainy and dry seasons in HCMC were 2.8 and 2.9, respectively, which is slightly higher than that of 2.4 in Hanoi. These ratios are within a range of motorcycle exhaust gas (2.4) (Dhital et al., 2019), gasoline (3.5) and roadside (3.7) measured during 2000 – 2005 in Vietnam (Imamura et al., 2007). However, these ratios are lower than that reported in nine roads in Hanoi, which had an average ratio of 4.8 (Ly et al., 2020). Regarding the correlation between toluene and benzene, good correlation coefficients are observed of 0.7 to 0.9 (Fig. 7b). The slopes of the regression line in HCMC during the rainy and dry seasons are 2.9 and 2.2, respectively, whereas the ratio value in Hanoi is 2.5. These ratios fall within a range from gasoline (2.9) to motorcycle exhaust (2.0), roadside samples (1.9, measured during 2000 – 2005, and 2.1, during Dec/2014 –

Jan/2015). These findings suggest that motorcycle-related emission is a major contributor to VOC pollution in urban areas of Vietnam.

3.3. Temporal variation and influencing factors

3.3.1. Diurnal variation in both cities

The temporal variation in VOCs is mainly governed by three factors: meteorological conditions, photochemical processes, and emission sources. Acetylene, a well-known tracer of primary traffic combustion was selected for reference (Borbon et al., 2013). A comparison of the diurnal profile of acetylene concentrations and that of traffic at both cities is shown in Fig. S2. Vehicle volume was obtained from previous studies (Hien et al., 2019). The diurnal profile of acetylene was similar to that of traffic, with two clear peaks corresponding to the morning and evening traffic rush hours, around 7:00 am and 18:00 pm in both cities. A small peak occurring at 11:00 am during the lunchtime is also evident, particularly during the dry season in HCMC and in Hanoi, and occurs before a drop in car and motorcycle activity. The lunchtime period in Vietnam is quite long (almost two hours) and many activities take place at this time which will involve an increase in traffic. The diurnal profile of acetylene was also compared to that of two other tracer gases, namely CO and ethene (**Fig. S2**). Large similarities in the diurnal variation of all three combustion-produced gases are seen in both cities, and significant reductions in their mixing ratios during the weekend are also observed (**Fig. S2**). Therefore, acetylene is a good tracer for primary traffic emission in this study.

Figure 8 shows the normalized to midnight (average concentrations) diurnal profiles of selected VOC species for the three field campaigns. Acetylene was selected as an inert tracer of combustion (k_{OH} = 7.8×10^{-13} $\mathrm{cm^3.molecule^{-1}.s^{-1}}$) and its profiles are embedded in each graph (shaded greys areas). The mixing ratio of various NMHCs in HCMC had a pronounced diurnal variation with two obvious peaks during the morning (7:00 am) and evening (18:00 pm) rush hours, and they were similar for the two seasons (Fig. 8a-c in rainy, 8e-g in dry periods). The pattern of diurnal variation was similar to that of acetylene, indicating that traffic-related emissions are one of the main sources of NMHCs in HCMC, as would be expected for a large city. However, other sources also seem to contribute to the daily cycle of specific NHMCs. For example, the diurnal variation of propane (Fig. 8a,e, blue line) shows the maxima occurred earlier (6:00 am) in the morning and later (19:00 pm) in the evening. LPG leakage was reported as one of the main sources of propane and butanes in urban areas (Cai et al., 2010; Bon et al., 2011) where LPG was used as the main fuel in LPG vehicles and household fuel. In Vietnam, there are no LPG vehicles, but the use of this fuel for daily cooking is widespread and could therefore account for this pattern. The molar ratio of propane and butanes contained in household fuel is usually between 50/50 and 30/70, while their molar ratios in ambient air in the rainy and dry seasons are 0.61 and 0.62 respectively, which is closer to a 40/60 ratio. Moreover, propane correlated more strongly with butanes (r = 0.91), than with acetylene (r = 0.62) and CO (r = 0.66) (**Fig. S1**).

After reaching the morning maxima, the mixing ratio of NMHCs decreased quickly which could be related to: (1) the decrease in primary emissions, (2) the increase in photochemical loss rates, and (3) the increasing atmospheric boundary layer height (dilution). During daytime, higher temperatures, wind speed and PBL height result in greater dilution and dispersion, leading to lower NMHC mixing ratios. The lowest daytime mixing ratio of most NMHCs (except isoprene) occurred around midday, which was coincident with the typical ozone maximum (**Fig. 3d)**. Photochemical removal also plays a role in controlling the diurnal variation of many VOCs, especially for compounds with a shorter lifetime (e.g., alkenes) (Borbon et al., 2013). To explore the role of photochemistry on the daily cycle we compared the daytime minima of some reactive species. As shown in Fig. 8b,f,k, the daytime minimum of most alkenes was the same magnitude regardless of their OH reactivity. This pattern was also observed in other urban areas such as São Paulo, Brazil (Dominutti et al., 2016). Although the increasing magnitude of the ozone concentration from its minimum to maximum on a diurnal basis was similar to that obtained for the evolution of PBL height, we cannot conclude that the role of photochemistry was more important than the PBL height variation during the daily cycle. Diurnal profiles of most VOCs, even for very reactive species as aforementioned, tend to go up and down simultaneously, which could be explained by the PBL height variation.

In urban atmosphere, although isoprene is primarily emitted from vegetation especially during the high light flux period, its concentration can also be affected by vehicle exhaust (Borbon et al., 2001). As shown in Fig. 8b,f, the diurnal variation of isoprene in HCMC showed a typical biogenic emission profile with a broad peak in the mid-afternoon (15:00). A similar profile can be seen for both seasons, although the mixing ratios during mid-afternoon peak were clearly higher by factor of 1.3 in the dry season. There are very few trees in the vicinity of the sampling site and it is likely that the isoprene mixing ratios observed in HCMC were impacted by the biogenic emission from the Can Gio Mangrove forest to the south of HCMC (Fig. S3d). Moreover, the minor peaks seen in early morning (7:00 am) could relate to traffic emissions. To better understand the contribution between biogenic and anthropogenic sources of isoprene in HCMC, the correlations between isoprene and acetylene were examined. Strong correlation during the early morning (4:00 am to 7:00 am) was obtained with a correlation coefficient (r) of 0.84 ($p < 0.01$), but only moderate correlation was seen for all day data, with r of 0.48 ($p < 0.01$). This result indicates that isoprene in HCMC has a major biogenic origin, with a smaller contribution from traffic.

The OVOCs have a mixture of primary and secondary sources and consequently their diurnal profiles (Fig. 8d,h) are different from those of the NMHCs which have only primary emission sources. The OVOCs can be divided into three separate groups: (1) carbonyls (acetaldehyde, acetone and MEK); (2) methanol; and (3) MVK+MACR, (secondary products of isoprene oxidation). The diurnal variations of the carbonyls show a single broad peak in the morning, with maxima dependent on the individual compound. For example, the diurnal variation of acetaldehyde and acetone reached a maximum around 8:00 – 9:00 am in the rainy season, and 9:00 – 11:00 am in the dry season. These maxima are later than those observed for typical primary pollutants, and the daytime mixing ratios decrease more slowly as a result of the balance between secondary production and dilution processes. The maxima of acetaldehyde and acetone were later during the dry season and similar to the maximum seen in ozone. In addition, there are no obvious peaks during evening rush hours suggesting that these two carbonyl compounds in HCMC are less impacted by traffic-related emissions. Methanol peaked at 6:00 am in the rainy season and around 11:00 am in the dry. The diurnal profile of methanol shows lower variation than the carbonyls. Globally, biogenic emissions are a major source of methanol, but in urban areas anthropogenic sources may also contribute to its measured concentration. To explore the possible sources of methanol, a polar plot is shown in Fig. S3e. Methanol clearly shows a different pattern to that of acetylene (combustion tracer) and isoprene (biogenic tracer). High methanol concentrations were observed when the wind direction was from west to north. It is interesting to note that the top ten industrial zones in HCMC are located in these directions, suggesting that the methanol concentration observed at the urban site is likely impacted by industrial sources. Similarly, MEK reached maxima at 5:00 - 6:00 am in both seasons. The MEK polar plot is similar to the one of methanol, suggesting that industrial emissions of MEK are an important source of MEK in HCMC. The difference in daily cycles between methanol and MEK is that the MEK concentration reduced significantly during daytime, especially at high PBL height and wind speed conditions. This can be explained by the contribution of other source (e.g., biogenic) to methanol during the daytime. As major products of isoprene oxidation, the diurnal variation of MVK+MACR was concurrent with the isoprene profile (Fig. 8d,h), and the polar plot of MVK+MACR was also similar to that of isoprene.

The normalized diurnal profiles of various VOCs in Hanoi are also shown in Fig. 8i-m. Diurnal variations of most NMHCs in Hanoi exhibit a large similarity with those observed in HCMC, except for isoprene. Two clear peaks occurred during the morning and evening rush hours, and the trend was similar to the acetylene profile (shaded area). This result confirms the likely dominant contribution of traffic emissions to ambient concentrations of most NMHCs in Hanoi. As also seen in HCMC, the diurnal profile of propane shows a little difference compared to acetylene with an earlier and broader peak in the morning (6:00 - 11:00 am). In addition, the molar ratio of propane/butanes was 0.97 closed to 50/50 ratio in LPG fuel. High correlation (r = 0.86) between propane and butanes, but weaker correlation (r = 0.53) between propane and acetylene was obtained suggesting that propane and butanes had similar source, and were likely impacted by household LPG fuel, similar to HCMC.

The diurnal profile of isoprene in Hanoi is quite different to that observed in HCMC. As shown in Fig. 8k, the variation of isoprene was more typical of a traffic-related source being similar to acetylene. The high correlation between isoprene and acetylene during the morning data (4:00 am to 7:00 am) rush hours (r = 0.88) was comparable to that of all day data (r = 0.84). The polar plots of isoprene also showed a large similarity to that of acetylene (Fig. 4Sa,d). The analysis indicates that the isoprene mixing ratio observed in Hanoi was strongly affected by traffic emission, with less impact from the biosphere. This may partly be due to the lower temperatures and cloudy conditions in Hanoi during the sampling period, which would have reduced biological emissions.

Unlike in HCMC, most OVOCs in Hanoi had a diurnal variation with two pronounced peaks, although the maxima were often different from the traffic-related NMHCs (Fig. 8m). For example, the diurnal pattern of most OVOCs exhibited a broad peak around 10:00 am and a sharper peak during the evening rush hour (17:00 pm). The morning peak of MVK coincided with that of acetylene; however, the shape is quite different with MVK concentration increasing from midnight, in common with MEK and acetone. Whilst the evening peak of OVOCs can be explained by the contribution of primary traffic emissions and a shallower boundary layer, the broad morning peak seen several hours after the main traffic peak suggests significant secondary (photochemical) production of these compounds. Similar to several NMHCs, daytime minima of OVOCs occurred around 13:00 pm which was not observed in HCMC. This result indicates that the secondary production of several OVOCs in Hanoi was not strong enough in order to offset the impact of PBL height evolution.

Compared to other large cities , e.g., Mexico City (Bon et al., 2011), Los Angeles and Paris (Borbon et al., 2013), São Paulo (Dominutti et al., 2016), Delhi (Stewart et al., 2021), and Beijing (Li et al., 2019) the diurnal variation of NMHCs observed in the two Vietnamese cities shows some interesting differences. A minimum mixing ratio of NMHCs was usually observed during the night due to a significant reduction in primary emission sources in Vietnamese cities, while a minimum in Beijing or Mexico City occurred during mid-day as a result of photochemical removal and the increase in dilution/dispersion. A relatively high nighttime concentration compared to that during mid-day was explained by the effect of shallow PBL during the night in those cities (Bon et al., 2011; Borbon et al., 2013; Dominutti et al., 2016). Overall, on a diurnal basis, a strong local emission had greater contribution to the morning and evening VOC peaks, whilst the lowest mixing ratio of most VOCs occurring during night-time could be attributed to a significant reduction of emission strength. The low mixing ratio of most VOCs during midday was a combination of a reduction in primary emission sources, an increase in PBL height and photochemical removal.

3.3.2. Seasonal variation in HCMC

In general, the measured mixing ratios of most VOC groups during the rainy season were higher than those in dry season in HCMC (Table S5). Regarding VOC groups, significant reduction ranged from acetylene (23%) to OVOCs (56%), in which total VOCs mixing ratios decreased 46% on average between two seasons. The primary tracer CO was also reduced by 38%, similar to the reduction in total alkanes. Mean ozone concentration was also lower during the dry season (~13%). Ozone is a secondary pollutant and its atmospheric levels and production depend on both the level of its precursors, and local and synoptic meteorological factors. Among the NMHCs, alkenes had the lowest decrease ratio (31%), especially for reactive anthropogenic alkenes, being isoprene the lowest with ~ 6% reduction. Assuming that human activities and the local urban emissions are similar in both seasons, it is likely that ambient concentrations are strongly influenced by meteorological conditions. Temperature and relative humidity were similar in both seasons and the effect of rainfall can also be excluded due to the very low solubility of most VOCs and the higher concentrations observed during the rainy season. Among the meteorological factors, wind and planetary boundary layer (PBL) varied significantly between two seasons as shown in Section 3.1. Significant enhancements in wind speed and PBL height were observed in the dry season with 47% and 112% increments, respectively. Lower wind speeds and PBL height in the rainy season favor the accumulation of pollutants emitted from the surface, resulting in increasing levels of pollution. Furthermore, the prevailing wind during the dry season was from the south and southeast (150-200°) which corresponds to the shortest distance from the South China Sea (~40 km) to the sampling site. Emissions from urban areas would be diluted by the clean air from the sea. In contrast, the wind direction during the rainy campaign was more varied with contributions from all directions (**Fig. 2a**).

In addition to prevailing meteorological conditions, a regional emission is a possible factor influencing the mixing ratio of several VOC species observed at the sampling site. Table 2 lists the top ten VOC species with the highest reduction factors between two seasons. Some of these are used in industrial process as solvents or raw materials. MEK had the highest reduction (63.1%), and it is commonly used in industry as solvent. The top eight species in table 2, from MEK to acetaldehyde, all had a similar pollution rose (refer to Fig S3e for methanol) with higher concentrations with stronger wind speed, and a wind direction from the west to north. This indicates that industrial activity could be an important source for several OVOCs and aromatics in HCMC.

3.4. The role of VOCs in O_3 formation

Figure 5 shows the hourly variation of ozone mixing ratios at both sites. The hourly mean mixing ratios of ozone in HCMC and Hanoi ranged from 0.3 to 146.8 ppb and 0.2 to 79.2 ppb, respectively (Table S5). In HCMC, the mean 8-hour mixing ratio exceeded the Vietnamese national standard (60 ppb) on twenty two days during the rainy campaign, but only three days during the dry and Hanoi campaigns. Figure 3 shows the diurnal profiles of O_3 mixing ratio and temperature at both sites. Higher nighttime concentration of O_3 was observed in Hanoi and HCMC during the dry season compared to that in rainy season. The expected diurnal cycle is observed for ozone during all three campaigns, but clear differences in the time at which the peak ozone value occurs are evident in Fig. 3d. The maximum ozone concentrations are observed in the morning in HCMC during the rainy season (9:00 – 10:00 am), whereas later peaks are observed during the dry season (12:00 – 14:00 pm) and in Hanoi (13:00 – 14:00 pm). These differences are consistent with the peak temperatures observed for those campaigns, as shown in Fig. 3c, indicating that temperature is an influencing factor in ozone formation.

In order to assess the role of VOCs in ozone formation, the initial mixing ratio of VOCs was estimated by the photochemical age method (equation 1) (de Gouw et al., 2005; Warneke et al., 2007). Because most VOCs can be oxidized during transport from emission sources to receptor sites, the initial mixing ratio of VOCs is defined as the mixing ratio from the fresh emission before VOCs undergo any change due to oxidation. The photochemical age method is based on a pair of VOCs, which have a large difference in their rates of reaction with OH radicals, the primary loss mechanism for most VOCs. Several assumptions have to be made before this method can be applied. In this study, we chose the pair of *m,p*-xylene (18.7 cm^3. $molecule^{-1}$ s^{-1}) and benzene (1.22 cm^3 $molecule^{-1}$ s^{-1}) for the HCMC site and 1,2,4-trimethylbenzene (32.5 cm^3 $molecule^{-1}$ s^{-1}) and benzene for the Hanoi site. The NMHCs chosen were very well correlated (Fig. S5). Diurnal variation of *m,p*-xylene to benzene ratios, and 124-TMB to benzene ratios show that lower ratio appears in daytime. The initial mixing ratios of *m,p*-xylene to benzene, and 124-TMB to benzene were estimated by choosing 97.5 percent data below those values. Then, the initial emission ratios $(X/B)_0$ were set to 2 and 1.2 during the rainy and dry seasons in HCMC and 0.9 in Hanoi. As it can be noted in Fig. 2, higher wind speeds and the contribution of winds from the northwest are mainly observed during the rainy season. This dissimilar pattern, could suggest the increase of *m,p*-xylene ambient concentrations and its emission ratios during the rainy season which suggest the contribution of industrial sources, located in the northwest of the city.

$$[VOC_i]_t = [VOC_i]_0 \times \exp(-k_i \times [OH] \times \Delta t) \qquad (1)$$

Where $[VOC_i]_t$ is the measured mixing ratio of $VOCi$; $[VOC_i]_0$ is the initial mixing ratio of VOC_i; k_i is the reaction rate constant for the reaction of VOC_i with OH radicals; $[OH]$ is the average OH radical concentration which is set to 5×10^6 molecules cm^{-3}; Δt is the photochemical age which is calculated by the following equation (2):

$$\Delta t = \frac{1}{[OH] \times (k_X - k_B)} \times \left[\ln\left(\frac{[X]}{[B]}\right)_{t=0} - \ln\left(\frac{[X]}{[B]}\right)_{t=t} \right] \qquad (2)$$

Where X and B are *m,p*-xylene and benzene concentrations, respectively, chosen as the pair of primary VOCs for Δt calculation; $([X] / [B])_{t=0}$ and $([X] / [B])_{t=t}$ are the initial and measured ratios of *m,p*-xylene to benzene; $[OH]$ is also set to 5×10^6 molecules cm^{-3}; k_X and k_B are the reaction rate constants of *m,p*-xylene (18.7×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) and benzene (1.22×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) towards OH radicals (Atkinson and Arey, 2003).

The estimated photochemical ages (Δt) at the HCMC site in rainy and dry seasons, and at the Hanoi site were 2.1 ± 0.9 (h) and 1.3 ± 0.7 (h), and 2.1 ± 1.8 (h) respectively. When the mean wind speeds in HCMC during rainy and dry seasons were 2.32 ± 0.95 and 3.42 ± 0.99 m/s, respectively (Table S5), and wind speed in Hanoi was 1.96 ± 0.93 m/s, the average travel distances of air mass were simply calculated within 15 – 18 km, consistent with location of the sampling sites within the city center. This result also indicates that the measured VOCs at the receptor sites were strongly affected by surrounding areas.

The photochemical age method shows that VOCs losses during daytime were mainly due to the reaction with OH radicals, thus daytime data from 7:00 am to 17:00 pm were used to estimate the initial mixing ratio. The initial mixing ratio of isoprene was not estimated because the concentrations of MVK and MACR (the oxidation products of isoprene) were not measured individually. Table S6 shows the results obtained for the photochemical age calculation. The estimated initial mixing ratio of total NMHCs during daytime was 75.5 ± 39.6 ppb in rainy and 36.9 ± 14.7 ppb in dry seasons in HCMC, and 56.5 ± 31.3 ppb in Hanoi. The measured mixing ratios of NMHCs were lower than the initial mixing ratios as shown in Table S6. Among the VOC groups, alkenes showed the largest difference in initial and measured mixing ratios because they are very reactive species.

The consumption of VOCs is calculated from the difference between initial and measured mixing ratios as also given in Table S6. In HCMC, the consumed mixing ratio of VOCs was 28.9

± 20.4 ppb in rainy season three times higher than the one estimated in the dry season (9.6 ± 6.8 ppb). Smaller consumed mixing ratios of VOCs observed in dry season are likely due to a smaller their initial mixing ratios. Figure 9 shows the time series of measured NMHCs, consumed VOCs and ozone at the two sampling sites. The trend of consumed VOCs was similar to that of O_3 (Fig. 9a,c). In addition, a significant correlation ($r = 0.66 – 0.68$, $p < 0.05$) between the consumed VOC and O_3 mixing ratios during daytime was obtained in HCMC (Fig. 9b,d), whereas no correlation between the measured VOC and O_3 mixing ratios was seen. In contrast, weak correlation ($r = -0.2$, $p < 0.05$) was obtained between consumed VOC and O_3 in Hanoi (Fig. 9f). A consumed VOC mixing ratio of 17.5 ± 11.5 ppb was relatively high compared to that estimated in dry season in HCMC, but the O_3 mixing ratio was still lower. The difference might be attributed to the weather conditions between two cities as discussed in Section 3.1. In addition, because ozone levels are also highly dependent on the concentration of nitrogen oxides (NOx) which were not measured during the campaign, future study should be conducted to address the phenomenon in Hanoi.

3.5. Propylene-equivalent concentrations

To assess the potential impact of individual VOC species on ozone formation in urban Vietnam, the propylene-equivalent concentration (*PE conc.*) proposed by (Chameides et al., 1992) and maximum incremental reactivity (MIR) by (Carter, 1994) were applied. Both methods are useful to evaluate the ozone formation related to different VOC species. Photochemical formation of ozone is generally initiated by the reaction of VOCs with OH radicals to produce the initial organic peroxy (RO_2) radicals, which consequently promotes the formation of ozone. The formation rate of RO_2 radicals vary in the chemical activity of the particular VOC. The PE concentration was used to assess the photochemical reactivity of VOCs, whereas ozone formation potentials (OFP) were calculated to measure more directly the contribution of VOCs to ozone formation.

The PE concentration reflects the reactivity of VOCs towards OH radicals normalized to the OH reactivity of propylene. The *PE conc.(i)* for each VOC species *i* is calculated by the following equation (3) in ppbC:

$$PE\ conc.(i) = conc.(i) \times \frac{k_i}{k_{C_3H_6}} \quad (3)$$

Where, *conc.(i)* is the concentration of VOC species *i* (in ppbC); k_i and $k_{C_3H_6}$ are reaction rate constants with OH radicals of VOC species *i* and propylene (cm^3 molecule^{-1} s^{-1}). These *k* values are obtained from (Atkinson and Arey, 2003) and shown in Table S5.

Table 4 shows the top ten most important VOCs for ozone formation, the majority of which are alkenes and aromatic compounds. A notable exception is *i*-pentane in HCMC, which is listed in the top ten (rank 7). Figure 6 shows the PE concentration of each VOC group and their relative contribution to total PE concentrations. Because acetylene and acetonitrile are relatively low-reactivity gases, the PE concentration of these was negligible. In HCMC, the total PE concentration was 107.7 ± 72.6 ppbC and 68.6 ± 38.8 ppbC in the rainy and dry seasons, respectively (Fig. 6e). The proportion of alkenes to total PE concentration was much lower in the rainy season (39% in rainy *vs.* 54% in dry), although the absolute alkenes PE concentration in the rainy season were slightly higher than in dry (Table S5). The reason for this is that the relative concentration of other groups was slightly higher during the rainy season. The second largest proportion in total PE concentration was represented by aromatics, which accounted for 43% (45.8 ± 34.4 ppbC) in the rainy period and 29% (20.2 ± 11.9 ppbC) in the dry period (Fig. 6e). This result suggests that the role of aromatics in atmospheric photochemical processes during the rainy period was more significant than during the dry season in HCMC. The alkanes and OVOCs had lower contributions at around 10% each (Fig. 6a,b). Furthermore, during the rainy period in HCMC, the contribution of aromatics increased the total PE concentration, especially from *m,p*-xylene and toluene. The mixing ratios of these species were likely impacted by industrial emissions due to the more frequent north-west winds seen during the rainy campaign.

The total PE concentration in Hanoi was 121.5 ± 76.2 ppbC, which was similar to HCMC during the rainy season but much higher than during the dry one (Fig. 6). The PE concentration also indicates that, during the spring period, the VOC contribution to air pollution was more significant in Hanoi than in HCMC. In Hanoi, the alkenes played a predominant role in the reactivity of total VOCs, with maximum values of 59.4 ± 35.5 ppbC, accounting for 49% of the total PE concentration. The proportion of aromatics to total PE concentration was estimated to be 30% (36.9 ± 31.0 ppbC). While alkanes and OVOCs were dominant in absolute concentration, their contributions to the PE concentration were only 10% for each group, similar to that observed in HCMC.

Due to their significant role in chemical reactivity, the contribution of individual alkene and aromatic species is evaluated in more detail. Figure 10 shows the PE concentration of various alkene/aromatic species/groups as a function of total VOC mixing ratios at the two sites. For the alkenes group, C_4-alkenes are the sum of all measured butene species, and the C5 alkenes are the sum of *trans*-2-pentene, n-pentene and 1,3-butadiene. Isoprene is separated from the C5 alkenes due to its important role in photochemical reactivity. Monoterpenes were found in the top ten species so were included this analysis. In HCMC, C_4-alkenes (butenes, 31%) were the main contributors to alkene PE concentration, closely followed by C_5-alkenes (22%), isoprene (16%), and monoterpenes (15%). The proportions of ethene and propene to reactivity were relatively small, with values of 7% and 10%, respectively. Notably, the sum contributions of isoprene and monoterpenes were relatively high (31% in HCMC, and 27% in Hanoi) although the sampling sites were located in the city center. Beside their origin from biogenic sources, both chemicals can be directly emitted from several combustion sources (e.g., traffic emission) in urban areas (Borbon et al., 2001). In Hanoi, C_5-alkenes (pentenes) were the dominant species contributing to alkene PE concentration, accounting for up to 39%. A similar proportion of C4 alkenes (butenes, 23%) and isoprene (22%) was observed. Although ethene and propene were the most abundant of the individual alkenes, they showed the lowest reactivity (4.5% and 6.5%, respectively).

The aromatics also play an important role in the chemical reactivity. Figure 10c,d shows the contribution of individual compounds/groups of aromatics at the different mixing ratios of total VOCs. Although toluene and *m,p*-xylene are important species regarding individual contribution to total aromatic PE concentration (Table 4), the sum of C9 aromatics has the highest PE concentration (rank 1) in both cities. As shown in Fig. 10c,d, the proportion of each aromatic family exhibits some differences between the two cities. In Hanoi, C_9-aromatics contributed a significant amount to the aromatics PE concentration (58%), whilst in HCMC C_8-aromatics were the major contributor, contributing 45% to total aromatics PE concentration. C_8-aromatics (27%) in Hanoi and C_9-aromatics (33%) in HCMC were the second highest contributors, higher than that of toluene with values of 14% in Hanoi and 21% in HCMC. Due to its lower reactivity, benzene contributed only a small fraction in both cities (ca. 1%).

3.6. Ozone formation potential

Ozone formation potential (OFP) reflects the maximum ozone production which can be produced from a particular VOC. OFP is estimated by multiplying the MIR coefficients and the measured VOC concentrations as shown in equation (4) for VOC species i (µg/m^3):

$$OFP(i) = conc.(i) \times MIR(i) \quad (4)$$

Where, *conc.(i)* is the concentration of VOC species *i* (µg/m^3); *MIR(i)* is the maximum incremental reactivity coefficient of VOC species *i* which is obtained from (Carter, 1994) and given in Table S5. MIR expressed in unit of grams of ozone generated per gram of VOC (g O3/g VOCs)

The top ten VOC species as well as their contribution to OFP are given in Table 5. Figure 6 shows the OFP by chemical groups and their relative contribution to total OFP. The total OFP in HCMC during the rainy season was 515.8 ± 356.4 µg/m^3, slightly higher than that of 471.1 ± 297.7 µg/m^3 in Hanoi. The lowest total OFP was observed in HCMC during the dry season with value of 281.9 ± 151.7 µg/m^3. As with the PE concentration, alkenes and aromatics were the main contributors to the total OFP, whilst alkanes contributed only a relatively small amount (Fig. 6). The contributions of OVOCs in total OFP ranged from 12% in the dry season in HCMC to 18% in Hanoi.

In the rainy season, aromatics (47%) played a predominant role in OFP, almost two-fold higher than that of alkenes (26%) (Fig. 6). Several aromatics, such as ethylbenzene, toluene and *m/p*-xylene were not only impacted by traffic emission but also by industrial activities when the wind blew from the north westerly sector (see Section 3.3.2). In contrast, during the dry season in HCMC the proportions of alkenes and aromatics to OFP were almost comparable (36 – 38%). An equal share between alkenes and aromatics was also observed in Hanoi (Fig. 6).

The contributions of each VOC to OFP are further analyzed to identify the main VOC species in ozone formation. The 10 most abundant species at each site and period are shown in Table 5. These 10 VOCs accounted for more than 70% of the total OFP. Although some differences can be found in the rank order, most VOCs are the same at both sites and include ethene, propene, *trans*-2-pentene, toluene, C8 and C9 aromatics, *i*-pentane and acetaldehyde.

Alkenes and aromatics are dominant in ozone formation in urban Vietnam, showing a consistency with data obtained in other Asian cities such as Beijing (Li et al., 2015b), Nanjing

(Shao et al., 2016) and Wuhan (Hui et al., 2018). Ethene, propene, toluene, xylene isomers and C9 aromatics were commonly in the top ten species contributing to OFP. Isoprene was also a dominant contributor to OFP in Hanoi, similar to the aforementioned studies, but it was out of the top ten species in HCMC. However, it was noted that isoprene played a key role in photochemical reactivity (Propylene Equivalence) as reported in all studies. For alkanes, the most striking difference was *i*-pentane which played a significant role in ozone formation in urban Vietnam (rank 6 in HCMC, rank 11 in Hanoi). However, propane and butanes dominated the alkane contribution to ozone formation in the other cities (Li et al., 2015b; Shao et al., 2016; Hui et al., 2018). As mentioned previously, motorcycle-related emission (exhausted gas and evaporation) with high *i*-pentane was likely a major VOC source in Vietnam. Therefore, our results highlight the substantial contribution of motorcycle-related emission sources in the atmospheric VOC chemistry in urban areas of Vietnam.

4. Conclusion

In this study, intensive online measurements of a wide range of VOCs, including 33 NMHCs (C_2-C_{12}), 6 OVOCs, monoterpenes and acetonitrile were conducted for the first time in two most populous cities of Vietnam. We conducted two campaigns in HCMC, one in the rainy and one in the dry season, and one campaign in Hanoi during March, coincident with the dry season in HCMC. We present here a detailed evaluation about composition, spatio-temporal variability and the role of VOCs in ozone formation.

The mean mixing ratios of the measured VOCs in HCMC rainy and dry seasons, and in Hanoi were 75.2 ± 44.8 ppb and 40.7 ± 19.5 ppb, and 80.8 ± 40.7 ppb, respectively. The VOC pollution in the urban atmosphere of Vietnam was relatively high, as comparable with Beijing. A remarkable seasonal variation was seen in HCMC, where VOC mixing ratios in the rainy season were around twice as high as those in the dry season. Meteorological factors including winds and PBL height were determined as major influencing factors in VOC seasonal variation, controlling the dispersion and dilution processes. Large similarities in pronounced diurnal variation for most NMHC species were observed in both cities (except for isoprene), which are also similar to those of the combustion tracers (acetylene and CO), with two clear peaks during the morning (7:00 am) and evening (18:00 pm) rush hours. The observed diurnal profiles of NMHCs show some interesting differences compared to those obtained in other cities in the world, with minima occurring during the night-time due to a significant reduction of primary emissions. This result indicates that strong local emissions impacted on VOC pollution in Vietnam. In addition, the presence of industry-originated species (such as methanol, MEK) in HCMC was observed under the influence of north-west wind direction. Consequently, diurnal profiles of OVOCs show a significant difference between the two cities and from the primary VOC species.

Regarding VOC composition, both cities were characterized by a contribution of alkanes (31 – 35%) ~ OVOCs (27 – 33%) > aromatics (12 – 19%) ~ alkenes (13 – 17%) > acetylene (3 – 7%) > acetonitrile (ca. 1%). The levels of acetonitrile suggest that none of the two cities were impacted by significant biomass burning emissions during the measurement periods. The VOC distribution is broadly similar to that observed in other urban locations with some interesting differences. For example, we observed particularly high mixing ratios of *i*-pentane and toluene. This profile in urban ambient air is similar to those observed at the urban roadside site and based on a comparison of the ratios of *i/n*-pentane and toluene/benzene. We conclude that motorcycle-related emissions strongly impact on the VOC composition in Vietnam. In consequence, controlling the motorcycle exhaust and reducing the number of private motorcycles is likely an effective strategy for improving air quality in Vietnam.

The propylene-equivalent (PE) concentration and ozone formation potential (OFP) were estimated to assess the photochemical reactivity and the contribution to ozone formation. Alkenes and aromatics dominated the reactivity, accounting for 76 – 83% of total VOC reactivity at both sites. C_4 and C_5-alkenes (excluded isoprene) were the largest contributors to the total alkene's reactivity, reaching together up to 50%. The OFP results also show that alkenes and aromatics were dominant at both sites, accounting together for 70% of total OFP. During rainy season at HCMC, the OFP of aromatics dominate over alkenes, being two-fold higher and indicating that aromatics have a significant contribution in ozone formation. Toluene, *m,p*-xylene, C_9-aromatics and *i*-pentane were commonly determined as the largest contributors to VOC reactivity and OFP. All VOC species undergo chemical loss from emission sources to receptor sites; therefore, to further explore the role of VOCs in ozone formation, we estimate the initial and consumed mixing ratios of VOCs during the daytime. These results show that similar variations and significant correlations between the consumed VOC and ozone mixing ratios were obtained in HCMC. However, this result was not seen in Hanoi. Finally, it is suggested that additional measurements and a sophisticated photochemical model would be required to elucidate the ozone formation.

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Table captions

Table 1. Average meteorological conditions during the measurement campaigns in HCMC and Hanoi

Table 2. The top ten VOC species with the highest reduction (%) between rainy and dry campaigns in HCMC

Table 3. Comparison of selected VOCs (ppb) with other studies/places

Table 4. Propylene – equivalent concentrations (ppbC) for the top ten VOC species in HCMC and Hanoi

Table 5. Ozone formation potential (OFP) (µg/m^3) for the top 10 most abundant species and VOC groups in HCMC and Hanoi

Table 1. Average meteorological conditions during the measurement campaigns in HCMC and Hanoi

Parameters / **Sites**	**HCMC**		**Hanoi**
	Rainy (27-Sep to 15-Nov 2018)	Dry (4-Mar to 3-Apr 2019)	7-March to 1-Apr 2019
Wind speed (m/s)	2.32 ± 0.95	3.42 ± 0.99	1.96 ± 0.93
Temperature (°C)	31.3 ± 3.8	31.6 ± 3.9	22.3 ± 3.4
Relative humidity (%)	87.0 ± 12.7	65.4 ± 13.7	85.3 ± 9.3
PBL height (m)	379 ± 359	805 ± 500	420 ± 248
Sunshine hours (hour/month)	161.6	238.1	44.6
Rainfall (mm/month)	370.4	31.6	15.1

Table 2. The top ten VOC species with the highest reduction (%) between rainy and dry campaigns in HCMC

Rank	Species	Reduction (%)
1	MEK	63.1
2	Ethylbenzene	61.3
3	Toluene	59.7
4	C_9-Aromatics	57.9
5	Methanol	56.8
6	Acetone	56.2
7	*m,p*-Xylene	55.9
8	Acetaldehyde	52.5
9	Propane	45.5
10	n-Butane	44.9

Table 3. Comparison of selected VOCs (ppb) with other studies/places

Sites	**HCMC (rainy)**	**HCMC (dry)**	**Hanoi (spring)**	**Hanoi (ambient)**	**Hanoi (roadside)**	**Beijing (summer)**	**Beijing (winter)**	**Delhi (pre-monsoon)**	**Delhi (post-monsoon)**
Periods	Sep-Nov/2018	Mar/2019	Mar/2019	Aug/2015	Dec/2014-Jan/2015	May-June/2017	Nov-Dec/2016	May-June/2018	Oct/2018
Refs	This study			Sakamoto et al., 2018	Ly et al., 2020	Unpublished data		Stewart et al., 2021	
Ethane	2.08	1.67	4.16	1.16	4.2	**3.57**	**9.68**	**6.15**	**32.02**
Propane	3.69	2.01	3.78	2.45	3.4	**6.20**	**7.33**	**19.91**	**43.15**
n-Butane	3.77	2.28	2.58	2.13	4.9	**2.89**	2.97	**7.89**	**39.74**
i-Butane	2.36	1.3	1.47	1.06	2.2	0.96	1.34	5.62	20.77
n-Pentane	2.75	1.79	1.89	**2.81**	10.6	1.07	1.22	1.55	6.76
i-Pentane	**8.64**	**5.37**	**4.3**	**5.59**	**50.9**	2.48	2.23	4.39	17.54
Ethylene	**5.06**	**2.84**	**5.32**	1.67	7.7	1.39	**8.29**	4.25	21.62
Propene	1.45	0.96	1.29	2.3	5.1	0.32	1.43	1.11	6.26
1-Butene	0.45	0.3	0.57	0.79	1.6	0.15	0.39	0.31	1.74
trans-2-Butene	0.49	0.4	0.26	2.48	1.2	0.13	0.25	0.15	1.28
cis-2-Butene	0.46	0.37	0.24	0.24	2.9	0.11	0.22	0.16	1.21
Isoprene	0.34	0.32	0.68			0.67	0.10	1.1	0.9
Acetylene	2.4	1.8	**4.5**			1.23	6.17	2.41	10.4
Benzene	1.97	1.16	1.29	2.33	12.8	0.57	1.77	1.36	6.67
Toluene	**6.43**	**2.59**	2.95	**4.76**	**27.4**	1.66	2.02	2.55	18.38
m,p-Xylene	2.36	1.04	1.14	1.56	**15.9**	0.58	1.89	0.7	4.93
o-Xylene	1.03	0.61	0.55	0.59	6	0.25	0.72	0.33	2.42
Ethylbenzene	1.11	0.43	0.67	0.7	4.8		0.86	0.33	2.64
Methanol	9.64	4.16	12.89			14.90	9.61	26.95	60.08
Acetaldehyde	4.38	2.52	3.15						
Acetone	5.75	2.08	2.59			3.09	8.32	6.3	14.3
Alkanes	23.3	14.4	18.2	15.2	76.2	17.2	24.8	45.5	160.0
Alkenes	7.9	4.9	7.7	7.5	18.5	2.1	10.6	6.0	32.1
Aromatics	12.9	5.8	6.6	9.9	66.9	3.1	7.3	5.3	35.0
NMHCs	**46.8**	**27.2**	**37.6**	**32.6**	**161.6**	**24.2**	**48.9**	**60.3**	**238.4**

Notes: Bold and underlined text indicates the top three VOCs in each study.

Table 4. Propylene – equivalent concentrations (ppbC) for the top ten VOC species in HCMC and Hanoi

Site	**HCMC rainy (Sep-Nov 2018)**			**HCMC dry (Mar 2019)**			**Hanoi (Mar 2019)**		
Rank	Species	Conc.	(%)	Species	Conc.	(%)	Species	Conc.	(%)
1	C_9-Aromatics	15.6	14.5	*trans*-2-Pentene	8.0	11.6	C_9-Aromatics	21.9	18.0
2	*m,p*-Xylene	13.4	12.5	C_9-Aromatics	6.6	9.6	*trans*-2-Pentene	17.0	14.0
3	Toluene	9.6	9.0	Isoprene	6.2	9.1	Isoprene	13.1	10.8
4	*trans*-2-Pentene	6.6	6.1	Monoterpenes	5.9	8.6	*m,p*-Xylene	6.5	5.3
5	Isoprene	6.5	6.0	*m,p*-Xylene	5.9	8.6	1-Pentene	6.3	5.2
6	Monoterpenes	6.3	5.9	*trans*-2-Butene	3.9	5.7	MVK	5.7	4.7
7	*i*-Pentane	5.9	5.5	Toluene	3.9	5.6	Toluene	4.4	3.6
8	Acetaldehyde	5.0	4.6	*i*-Pentane	3.7	5.4	Propene	3.9	3.2
9	*trans*-2-Butene	4.8	4.4	*cis*-2-Butene	3.2	4.7	Acetaldehyde	3.6	3.0
10	Propene	4.3	4.0	Propene	2.9	4.2	1,3-Butadiene	3.3	2.7

Table 5. Ozone formation potential (OFP) (µg/m^3) for the top 10 most important species and VOC groups in HCMC and Hanoi

Site	**HCMC rainy (Sep-Nov 2018)**			**HCMC dry (Mar 2019)**			**Hanoi (Mar 2019)**		
Rank	Species	OFP	(%)	Species	OFP	(%)	Species	OFP	(%)
1	*m,p*-Xylene	74.3	14.4	*m,p*-Xylene	32.6	11.6	C_9-Aromatics	70.0	14.9
2	Toluene	64.5	12.5	C_9-Aromatics	25.9	9.2	Ethene	44.3	9.5
3	C_9-Aromatics	59.5	11.6	Toluene	25.6	9.1	*m,p*-Xylene	36.0	7.7
4	Acetaldehyde	42.4	8.2	Ethene	23.7	8.4	Ethanol	33.7	7.2
5	Ethene	42.3	8.2	Acetaldehyde	20.8	7.4	*trans*-2-Pentene	32.6	6.9
6	*i*-Pentane	32.5	6.3	*i*-Pentane	20.1	7.2	Acetaldehyde	31.7	6.8
7	*o*-Xylene	28.6	5.6	*o*-Xylene	16.5	5.9	Toluene	29.5	6.3
8	Propene	23.0	4.5	*trans*-2-Pentene	15.5	5.5	Propene	20.5	4.4
9	MEK	15.2	3.0	Propene	15.3	5.4	1-Pentene	18.3	3.9
10	*trans*-2-Pentene	12.8	2.5	*trans*-2-Butene	9.0	3.2	Isoprene	17.2	3.7

Figure captions

Fig. 1. Location of sampling sites in Hanoi and HCMC during field campaigns.

Fig. 2. Wind rose plots at the two sampling sites: (a) rainy and (b) dry campaigns in HCMC, and (c) in Hanoi

Fig. 3. Diurnal variation of (a) PBL height, (b) wind speed, (c) temperature, (d) O_3 mixing ratio, and (e) CO mixing ratio. HCM.rainy (green), HCM.dry (red) and HN (blue) denote the sampling campaign in rainy, and dry in HCMC and in Hanoi, respectively. The shaded area indicates the 95 % confident interval.

Fig. 4. Mean backward trajectory clusters (left) and mean ethane mixing ratio by cluster (right) from (a-b) rainy and (c-d) dry campaigns in HCMC, and (e-f) in Hanoi. Box shows the 25th, 50th and 75th percentiles; whiskers show the minimum and maximum values. Black dot represents the outlier values.

Fig. 5. Time-series of hourly mixing ratios of VOCs (left), and O3 and CO (right). Five VOCs categories include alkanes, alkenes, aromatics, OVOCs and acetylene. (a – b) in rainy and (c – d) in dry campaigns in HCMC, and (e – f) in Hanoi. The VOC data from the correspondent instruments was identified in Table S5.

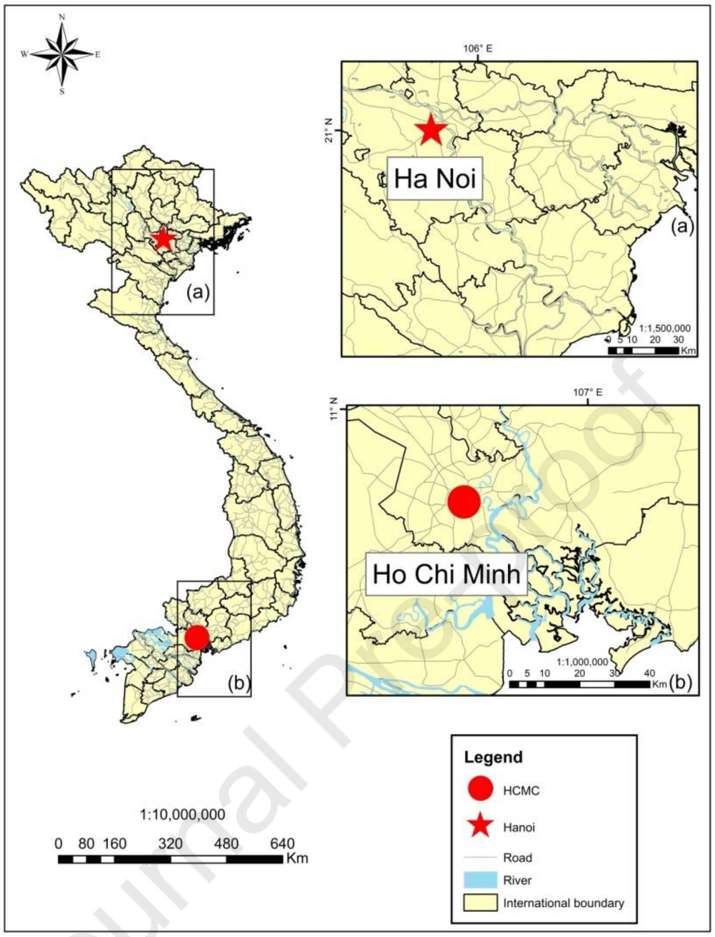
Fig. 6. (top panel) Proportion (%) of VOC groups (a) rainy and (b) dry campaigns in HCMC, and (c) in Hanoi. (bottom panel) Comparison of (d) absolute VOC concentrations, (e) propylene-equivalent concentrations, and (f) ozone formation potential by chemical groups measured in HCMC (rainy and dry campaigns) and in Hanoi. For comparison purposes, ethanol data from Hanoi were excluded from the calculation.

Fig. 7. Comparison of (a) *i/n*-pentane and (b) toluene/benzene ambient ratios estimated in this study with those obtained in motorcycle exhaust (Dhital et al., 2019), liquid gasoline in Vietnamese market (Imamura et al., 2007), urban roadside from 2000 to 2005 (Imamura et al., 2007), and urban roadside during Dec/2014 – Jan/2015 (Ly et al., 2020). For *i*/n-pentane ratios: $y = 2.8x + 0.3$, $r = 0.96$ in rainy; $y = 2.9x – 0.1$, $r = 0.97$ in dry; and $y = 2.4x – 0.3$, $r = 0.99$ in Hanoi. For toluene/benzene ratios: $y = 2.9 x + 0.4$, $r = 0.70$ in rainy; $y = 2.2x – 0.2$, $r = 0.90$ in dry; $y = 2.5x – 0.8$, $r = 0.84$ in Hanoi

Fig. 8. Normalized to midnight diurnal variations of representative VOCs. The same column indicates for the same campaign, and the same row indicates for the same chemical groups. Left (a-d) and middle (e-h) panels show for rainy and dry campaigns in HCMC, and right panel (i-m) for Hanoi. (a, e, i) alkanes; (b, f, k) alkenes; (c, g, l) aromatics; and (d, h, m) OVOCs. Legend is shown the same as the first figure in the same row. The VOC data from the correspondent instruments was identified in Table S5. Acetylene (shaded area) was plotted in all figures for comparison purpose.

Fig. 9. Time-series of the mixing ratios of measured total VOCs, consumed VOCs and O_3 (left) and scatterplots of O_3 and consumed VOC mixing ratios (right). (a-b) in rainy and (c-d) in dry campaigns in HCMC, and (e-f) in Hanoi.

Fig. 10. The PE concentrations with different alkene and aromatic species/groups as a function of total VOCs mixing ratio: (left panel) for Alkenes (a) HCMC and (b) Hanoi; and (right panel) for Aromatics (c) HCMC and (d) Hanoi. *Notes*: C_4-alkenes are the sum of *trans*-2-Butene, 1-Butene, and *cis*-2-Butene. C_5-alkenes are the sum of *trans*-2-Pentene, 1-Pentene, and 1,3-Butadiene. Isoprene is shown separately itself. C_8-Aromatics are the sum of xylenes and ethylbenzene. C_9-Aromatics in Hanoi are the sum of 1,3,5-Trimethylbenzene (TMB), 1,2,4-TMB, 1,2,3-TMB. The VOC data from the correspondent instruments was identified in Table S5.



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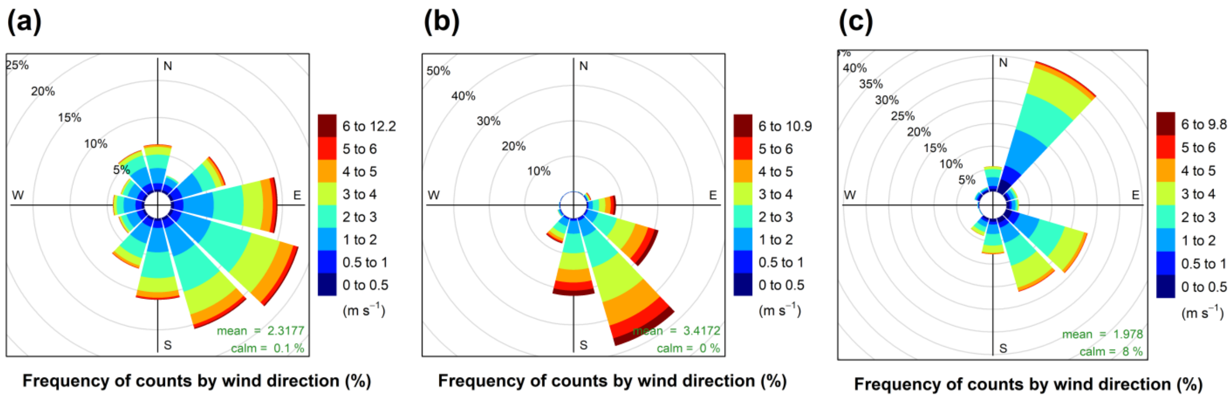

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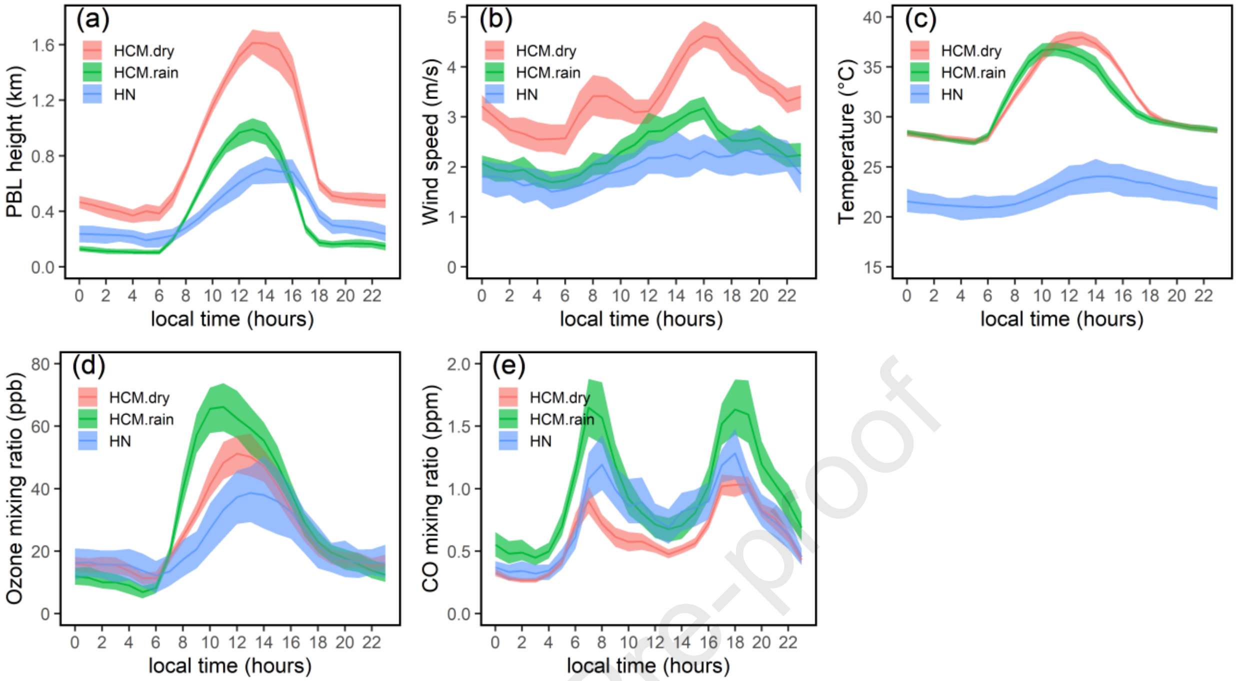

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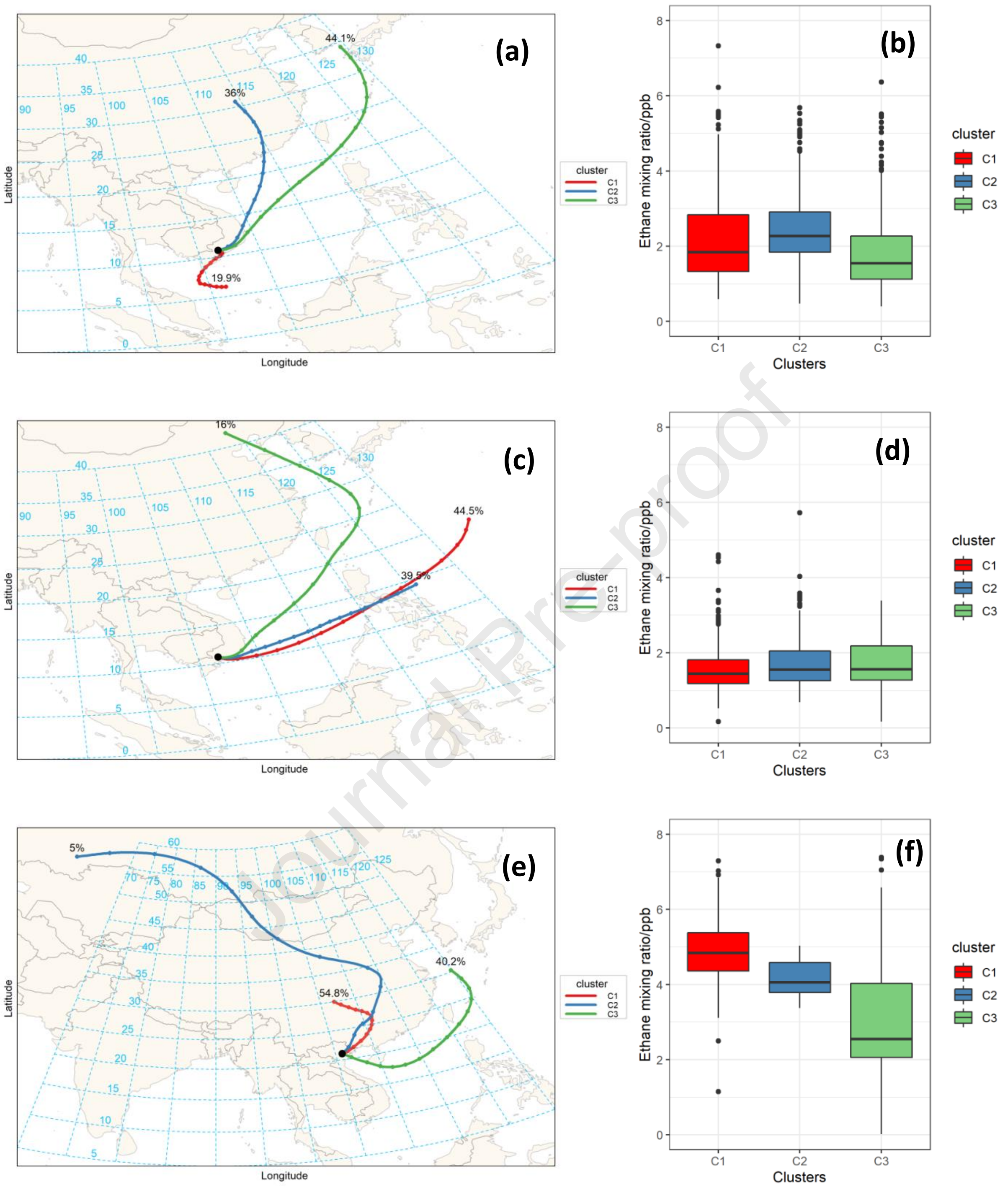

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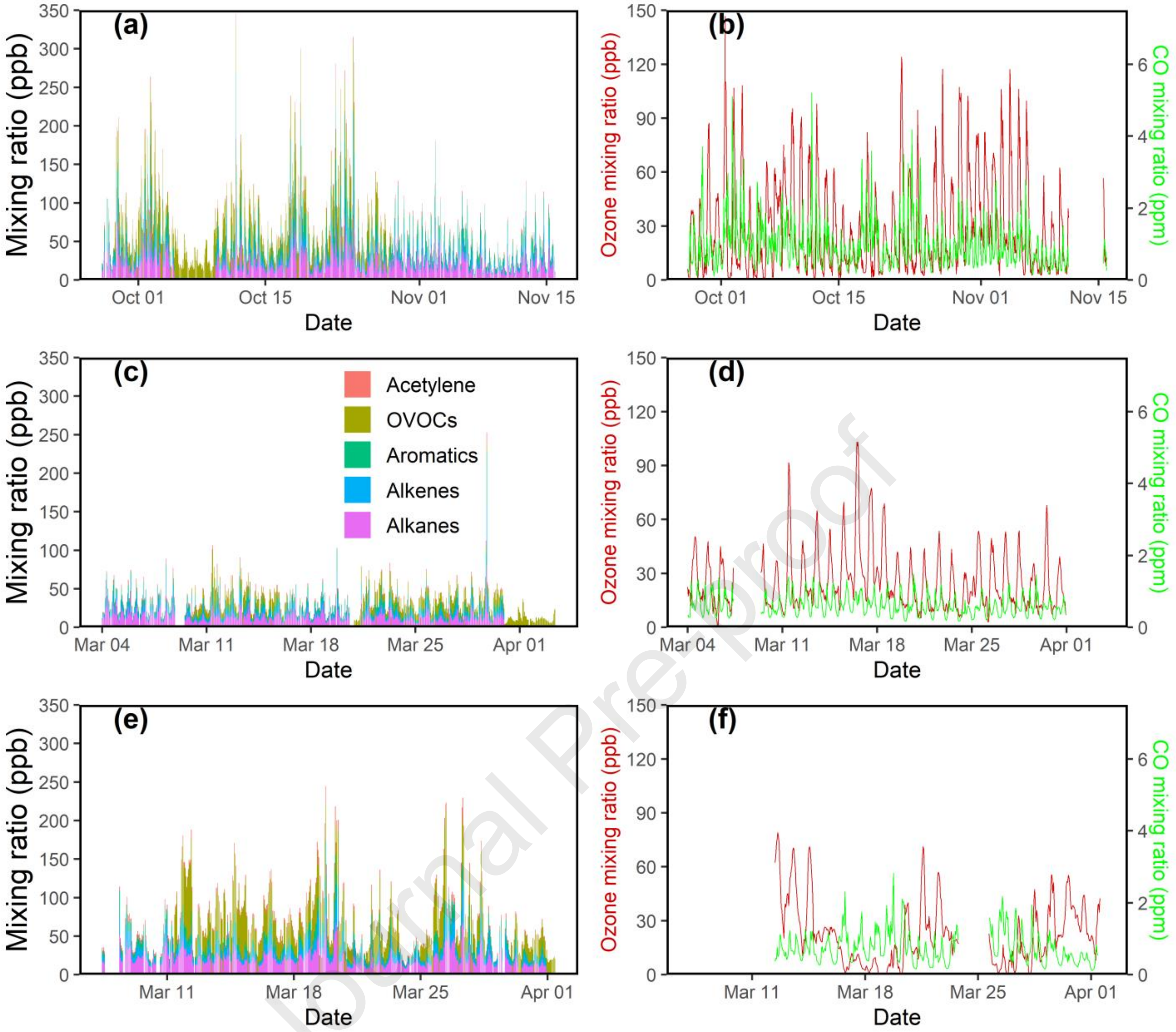

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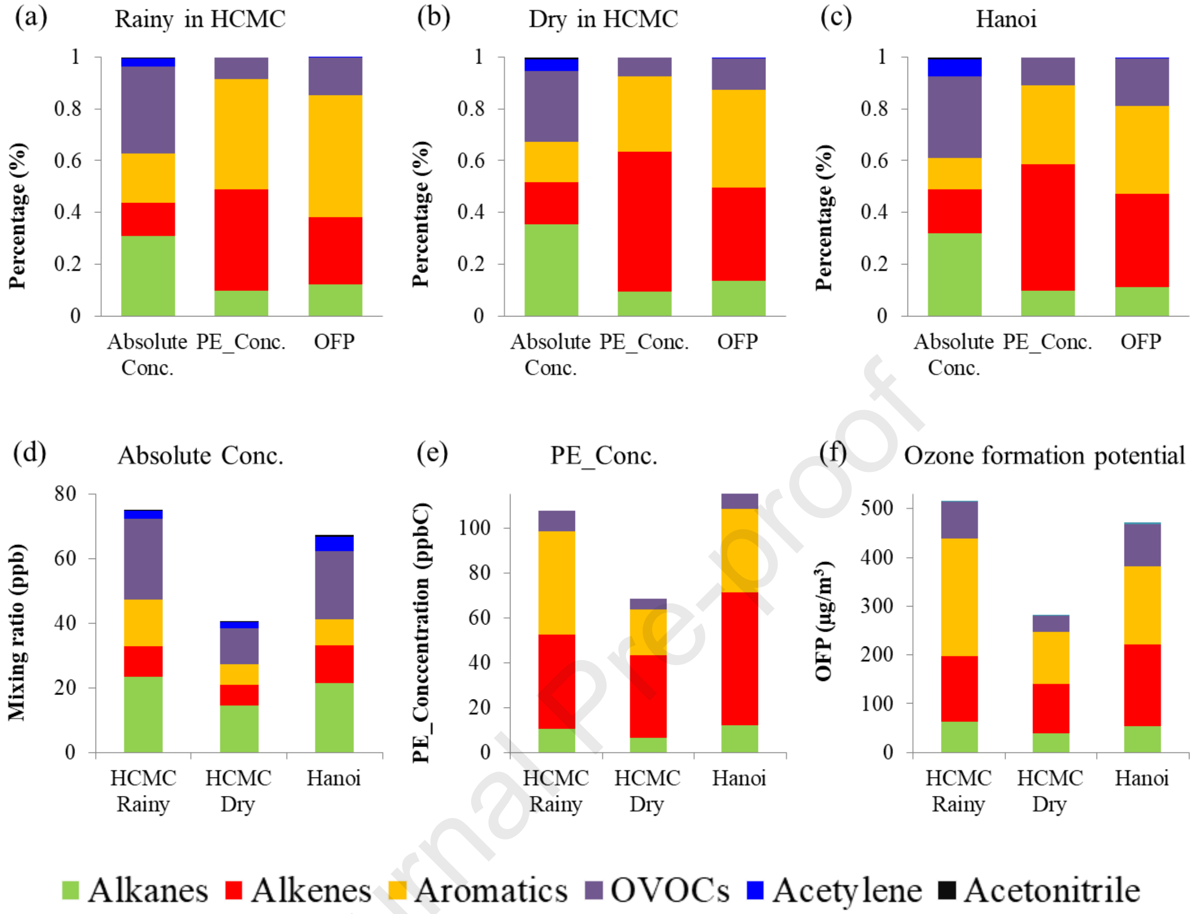

Fig. 6. (top panel) Proportion (%) of VOC groups (a) rainy and (b) dry campaigns in HCMC, and (c) in Hanoi. (bottom panel) Comparison of (d) absolute VOC concentrations, (e) propylene-equivalent concentrations, and (f) ozone formation potential by chemical groups measured in HCMC (rainy and dry campaigns) and in Hanoi. For comparison purposes, ethanol data from Hanoi were excluded from the calculation.

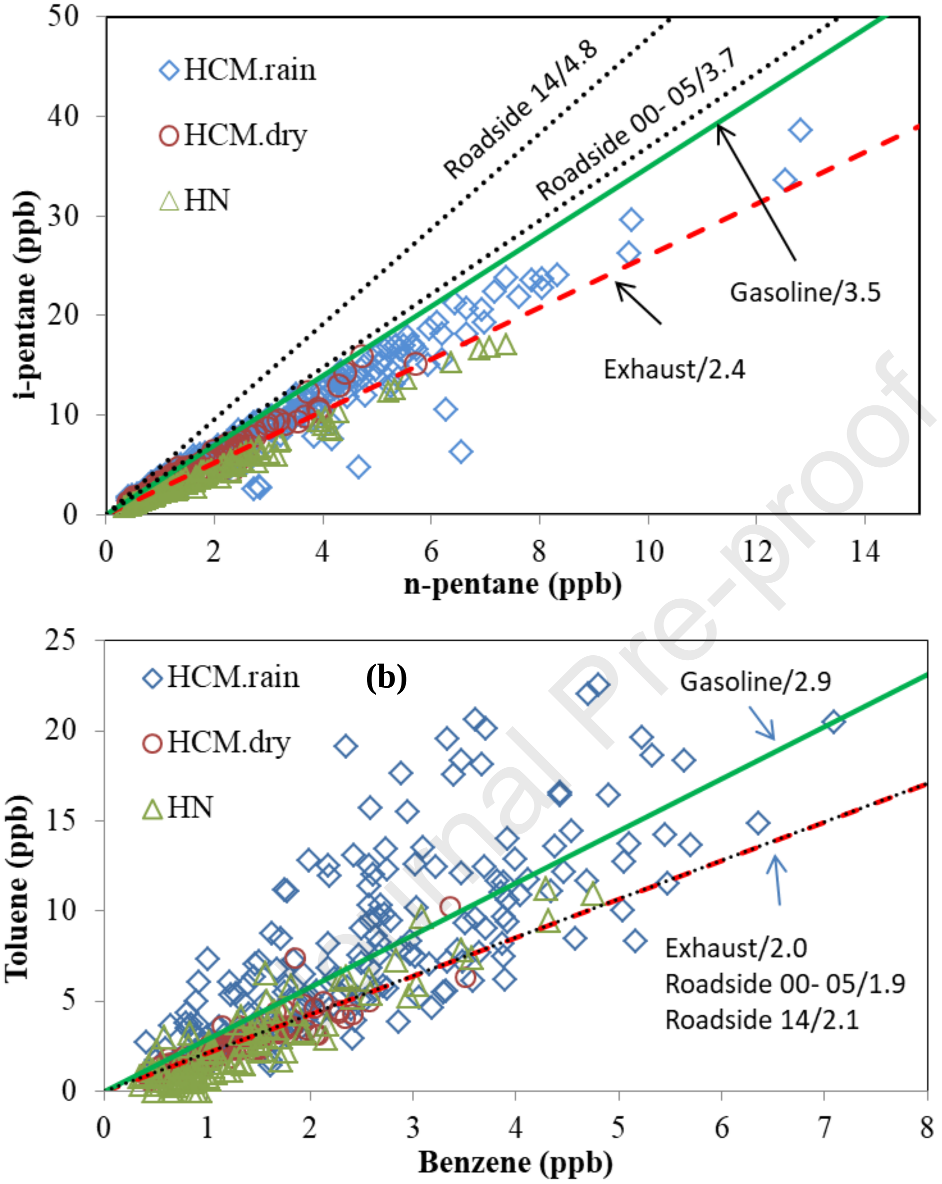

Fig. 7. Comparison of (a) *i*/*n*-pentane and (b) toluene/benzene ambient ratios estimated in this study with those obtained in motorcycle exhaust (Dhital et al., 2019), liquid gasoline in Vietnamese market (Imamura et al., 2007), urban roadside from 2000 to 2005 (Imamura et al., 2007), and urban roadside during Dec/2014 – Jan/2015 (Ly et al., 2020). For *i*/n-pentane ratios: y = 2.8x + 0.3, *r* = 0.96 in rainy; y = 2.9x – 0.1, *r* = 0.97 in dry; and y = 2.4x – 0.3, *r* = 0.99 in Hanoi. For toluene/benzene ratios: y = 2.9 x + 0.4, *r* = 0.70 in rainy; y = 2.2x – 0.2, *r* = 0.90 in dry; y = 2.5x – 0.8, *r* = 0.84 in Hanoi

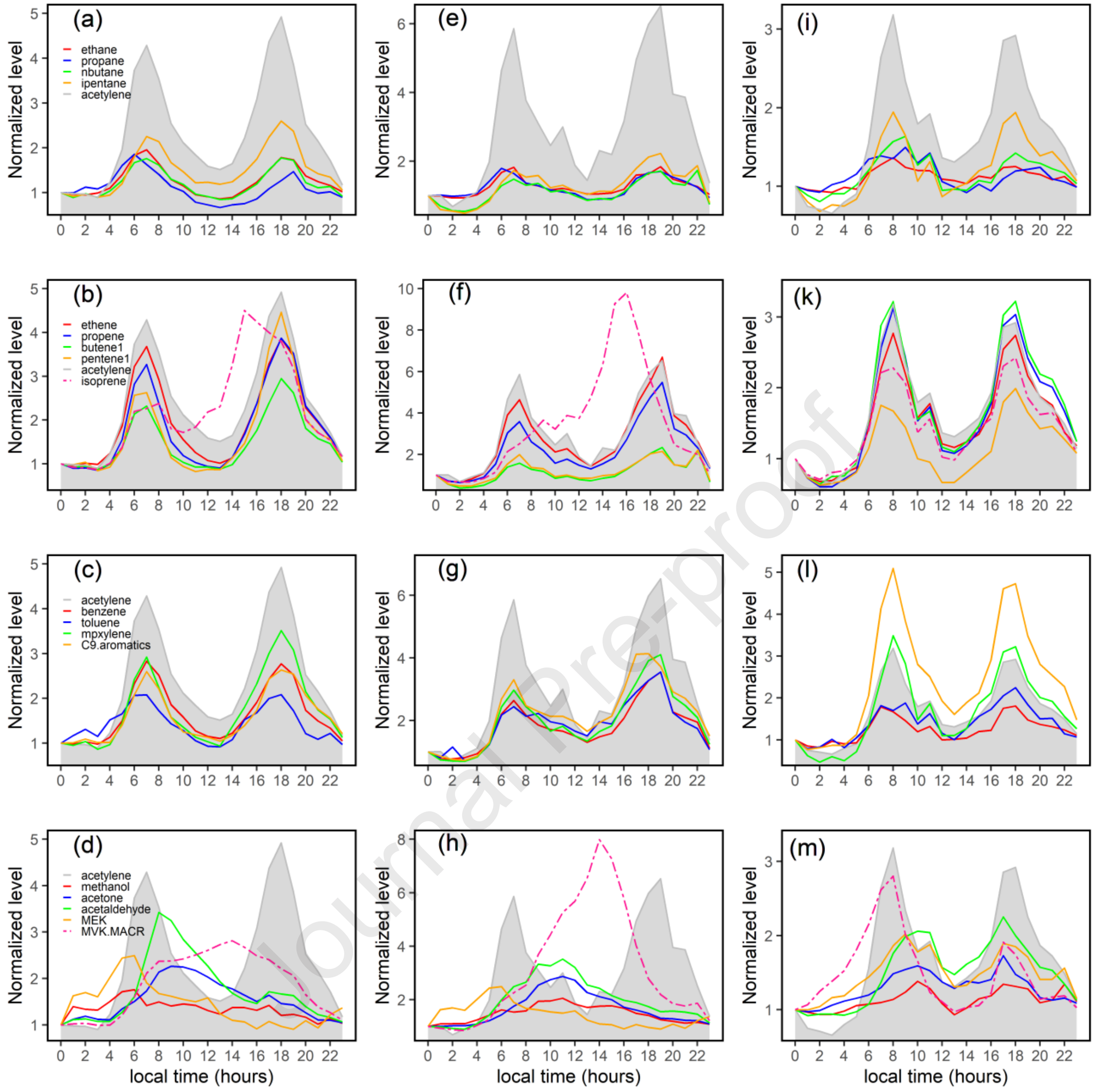

Fig. 8. Normalized to midnight diurnal variations of representative VOCs. The same column indicates for the same campaign, and the same row indicates for the same chemical groups. Left (a-d) and middle (e-h) panels show for rainy and dry campaigns in HCMC, and right panel (i-m) for Hanoi. (a, e, i) alkanes; (b, f, k) alkenes; (c, g, l) aromatics; and (d, h, m) OVOCs. Legend is shown the same as the first figure in the same row. The VOC data from the correspondent instruments was identified in Table S5. Acetylene (shaded area) was plotted in all figures for comparison purpose.

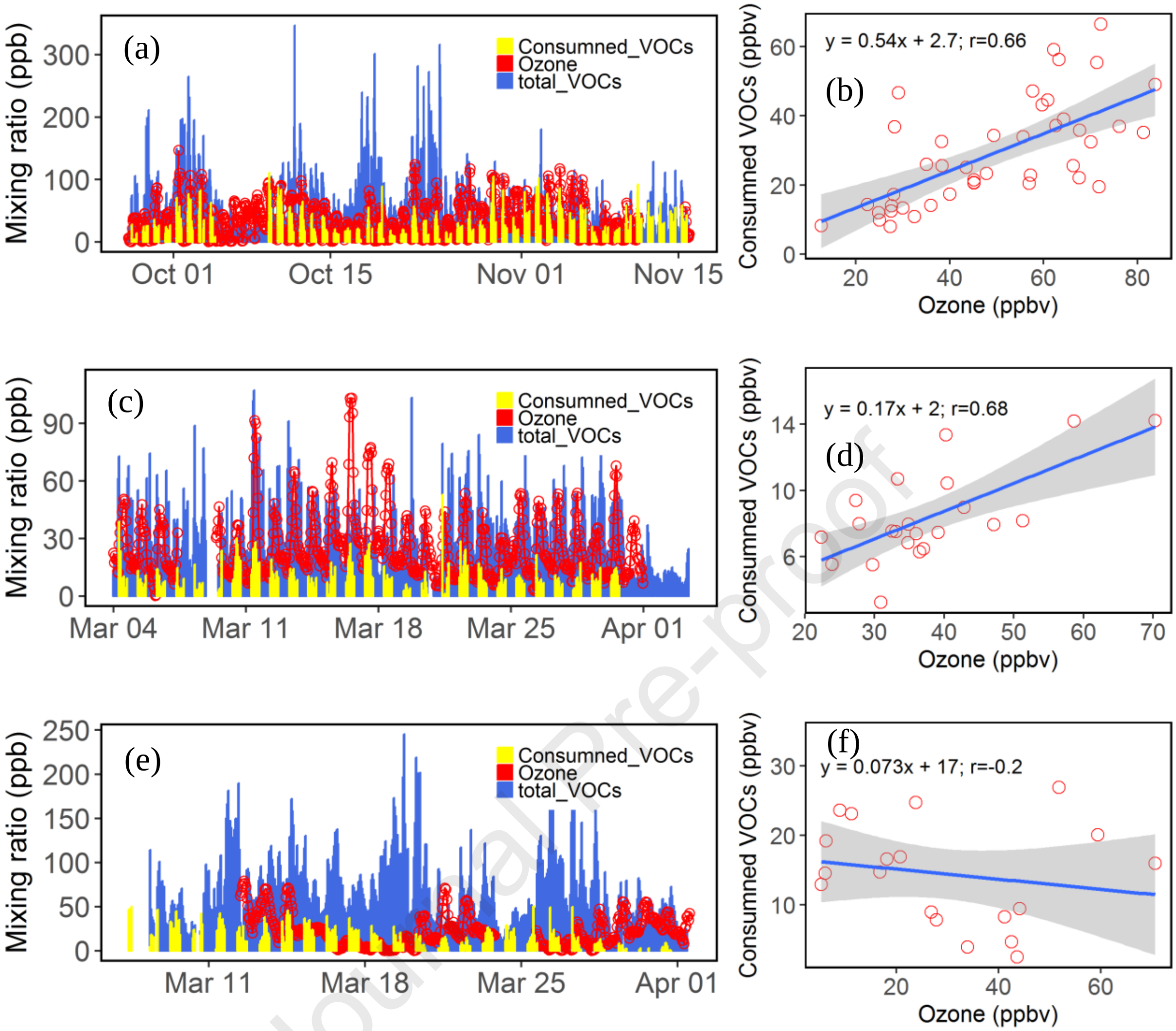

Fig. 9. Time-series of the mixing ratios of measured total VOCs, consumed VOCs and O_3 (left) and scatterplots of O_3 and consumed VOC mixing ratios (right). (a-b) in rainy and (c-d) in dry campaigns in HCMC, and (e-f) in Hanoi.

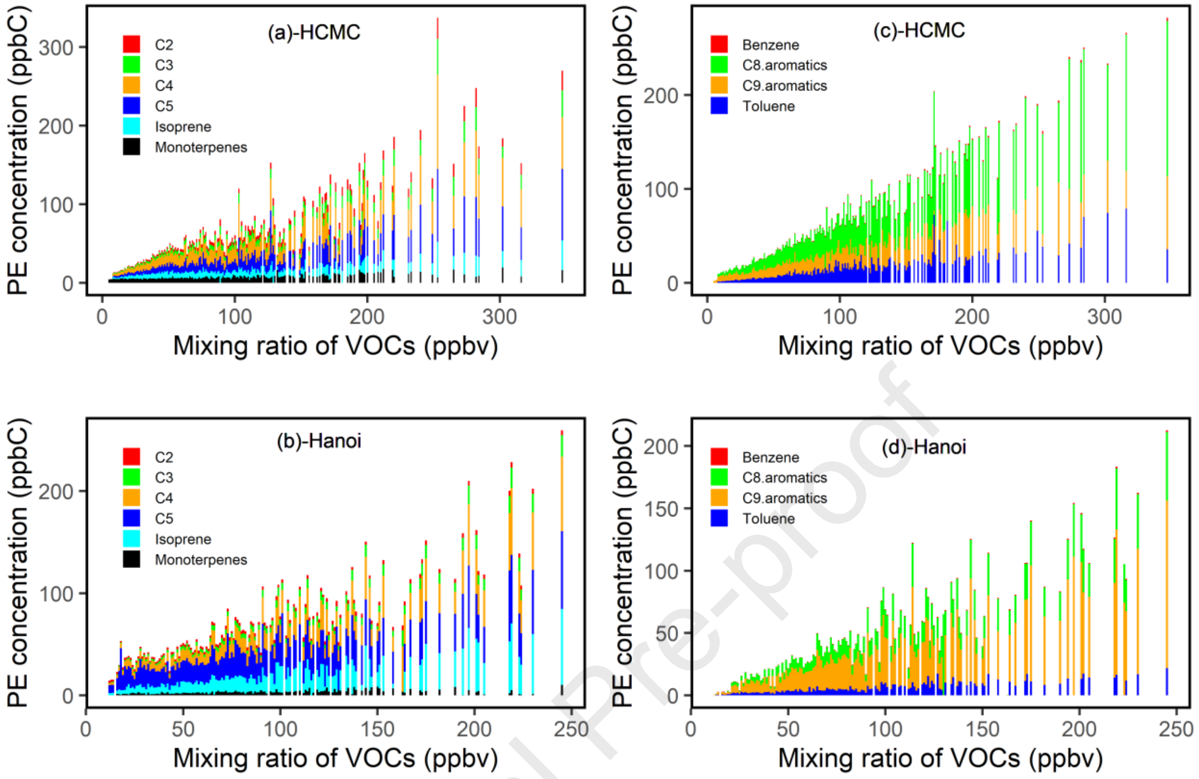

Fig. 10. The PE concentrations with different alkene and aromatic species/groups as a function of total VOCs mixing ratio: (left panel) for Alkenes (a) HCMC and (b) Hanoi; and (right panel) for Aromatics (c) HCMC and (d) Hanoi. *Notes*: C_4-alkenes are the sum of *trans*-2-Butene, 1-Butene, and *cis*-2-Butene. C_5-alkenes are the sum of *trans*-2-Pentene, 1-Pentene, and 1,3-Butadiene. Isoprene is shown separately itself. C_8-Aromatics are the sum of xylenes and ethylbenzene. C_9-Aromatics in Hanoi are the sum of 1,3,5-Trimethylbenzene (TMB), 1,2,4-TMB, 1,2,3-TMB. The VOC data from the correspondent instruments was identified in Table S5.

Highlights

- Extensive VOC evaluation including composition, spatio-temporal variability and their role in surface ozone formation are investigated for the first time in Vietnam
- Ambient VOC levels are strongly impacted by motorcycle-related emissions
- Variability in VOC levels are ruled by wind pattern and planetary boundary layer height
- Alkenes and aromatics dominated the potential ozone formation.
- Higher levels of ethane were observed from air masses passing over China mainland

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: