Evaluating major anthropogenic VOC emission sources in densely populated Vietnamese cities.

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Abstract

Volatile organic compounds (VOCs) play an important role in urban air pollution, both as primary pollutants and through their contribution to the formation of secondary pollutants, such as tropospheric ozone and secondary organic aerosols. In this study, more than 30 VOC species were continuously monitored in the two most populous cities in Vietnam, namely Ho Chi Minh City (HCMC, September-October 2018 and March 2019) and Hanoi (March 2019). In parallel with ambient VOC sampling, grab sampling was used to target the most prevalent regional-specific emission sources and estimate their emission factors (EFs).

Emission ratios (ERs) obtained from ambient sampling were compared between Vietnamese cities and other cities across the globe. No significant differences were observed between HCMC and Hanoi, suggesting the presence of similar sources. Moreover, a good global agreement was obtained in the spatial comparison within a factor of 2, with greater ER for aromatics and pentanes obtained in the Vietnamese cities.

The detailed analysis of sources included the evaluation of EF from passenger cars, buses, trucks, motorcycles, 3-wheeled motorcycles, waste burning, and coal-burning emissions. Our comparisons between ambient and near-source concentration profiles show that road transport sources are the main contributors to VOC concentrations in Vietnamese cities.

VOC emissions were calculated from measured EF and consumption data available in Hanoi and compared with those estimated by a global emission inventory (EDGAR v4.3.2). The total VOC emissions from the road transport sector estimated by the inventory do not agree with those calculated from our observations which showed higher total emissions by a factor of 3. Furthermore, the inventory misrepresented the VOCs speciation, mainly for isoprene, monoterpenes, aromatics, and oxygenated compounds. Accounting for these differences in regional air quality models would lead to improved predictions of their impacts and help to prioritise pollution reduction strategies in the region.

Keywords: emission ratios, regional emission sources, global inventories, Southeast Asia

1. Introduction

The World Health Organization (WHO) defines poor air quality as the most significant single environmental health risk and attributed 4.2 million deaths to ambient air pollution exposure in 2021(WHO, 2021). 75 % of those air pollution-related deaths occur in low-middle income countries, such as those in Asia (Lelieveld et al., 2018).

Among the various pollutants present in the troposphere, volatile organic compounds (VOCs) play a crucial role in urban air pollution and include a large number of species. Although VOCs can be emitted from both anthropogenic and biogenic sources, the former is the primary source in urban areas. Once released into the atmosphere, VOCs can undergo several chemical reactions (oxidation) due mainly to the hydroxyl radical (·OH) and ozone during the day and with the nitrate radical at night. This leads to the formation of secondary oxygenated VOCs (OVOC) (Atkinson, 2000; Goldstein and Galbally, 2007), tropospheric ozone (Seinfeld and Pandis, 2006), and secondary organic aerosols (Fuzzi et al., 2006; Hester and Harrison, 1995; Koppmann, 2007).

Many primary pollutants are known to be decreasing in urban areas in the northern mid-latitudes, including those related to vehicle emissions (Uherek et al., 2010). For example, some studies have shown a decrease in VOC and carbon monoxide (CO) concentrations by almost two orders of magnitude over the past five decades in Los Angeles (Warneke et al., 2012), USA. In the United Kingdom, long-term measurements also show significant decreases for VOC and CO (up to 26 % and 12 %, respectively (von Schneidemesser et al., 2010), a downward trend that is also reflected in emission inventories (EIs). Figure S1 shows the total annual anthropogenic VOC emissions estimated in the Emissions Database for Global Atmospheric Research (EDGARv4.3.2 global inventory https://edgar.jrc.ec.europa.eu/dataset_ap432_VOC_spec, Huang et al., 2017). According to the inventory, total VOC emissions have decreased significantly over the past 40 years in the United States and Europe, with totals of 7 and 10 Tg yr^{-1}, respectively, in 2012. In developing countries, however, VOC emissions have been steadily increasing over that time period, with the Southeast Asia (SEA) region reaching up to 8 Tg yr^{-1} in 2012, surpassing those from Europe.

Accurately quantifying the spatial and temporal distribution of emissions is a challenge, even more so in the developing world (e.g., SEA region), where ambient measurements and local emissions data are scarce. EIs in these regions typically combine bottom-up and top-down approaches to estimate emissions, using emission factors (EFs) from northern mid-latitudes countries (such as the European Environment Agency - European Monitoring and Assessment Programme (EMEP/EEA)), together with any regional or national activity data. In consequence, uncertainties from many data sources are aggregated in the overall estimation of the magnitude and speciation of emission. Several studies have reported emission inventory (EI) assessment in developed countries using ground or aircraft-based measurements of ambient pollutants (Borbon et al., 2013; Kim et al., 2011; Wilde et al., 2021). For example, urban emission ratios (ERs) of various VOCs to a combustion tracer (CO, acetylene) are commonly used to constrain and assess regional EIs in urban areas (Borbon et al., 2013, 2022; Coll et al., 2010; Warneke et al., 2007). Recent studies reveal significant discrepancies when contrasting

observations and inventories of VOC emissions, by several orders of magnitudes mainly for the road transportation sector (Borbon et al., 2013; Dominutti et al., 2019; Salameh et al., 2016a; Thera et al., 2019). Furthermore, the misrepresentation of VOCs speciation in global inventories was also revealed when compared with in-situ observations, as in the case of Sao Paulo, Brazil (Dominutti et al., 2020).

Vietnam is one of the fastest-growing economies in the SEA, and the country has undergone rapid population growth, with more than 96 million inhabitants in 2019 (General Statistics Office, 2020; General Statistics Office of Vietnam, 2020). Such rapid growth has led to the deterioration of air quality, with exposure to ambient air pollution being one of Vietnam's most important unknown public health risks (Phung et al., 2016). However, short-term studies conducted in Vietnam have shown that vehicular emissions, biomass burning, and secondary formation processes are important sources of fine particulate matter ($PM_{2.5}$) and other pollutants (Hai and Kim Oanh, 2013; Hang et al., 2014; Hien et al., 2019). Indeed, the transport sector is still increasing, with motorcycles accounting for 86% of the total vehicle fleet in the country. Ho Chi Minh City (HCMC) and Hanoi are the most densely populated cities in Vietnam, with an estimated 9 and 8 million inhabitants in 2019, respectively (General Statistics Office, 2020). Hanoi, the capital of Vietnam, typically experiences several air pollution episodes each year. Recent studies in HCMC have also shown poor air quality and PM concentrations surpassing the WHO air quality recommendations (Hien et al., 2019).

Despite the potential impacts of air pollution in Vietnam, a limited number of studies have conducted long-term air quality or emission source measurements to better tackle air pollution and its related health effects. Although some inventories have been developed at local and regional scales in Vietnam, their uncertainties are unknown, and the speciation of VOCs is generally not taken into account (Ho and Clappier, 2011; Trang et al., 2015; Tung et al., 2011). The paucity of observations in the SEA region is an important limitation when it comes to developing accurate EIs. Therefore, *in-situ* observations can be a powerful tool to help improve EIs that consider the specificity of regional emission sources. Furthermore, a better understanding of emission sources and air pollutants also provides direct indications of population exposure to air pollution and valuable information for policymakers in developing abatement policies.

Herein we present our findings from the “A Two City study of Air Quality in Vietnam” project that took place in the two most densely populated cities in Vietnam. We evaluate urban VOC emission sources using detailed *in-situ* observations comprising comprehensive near-source and ambient VOC measurements at urban sites.

2. Materials and methods

Intensive field campaigns were conducted in 2018 and 2019 in Hanoi and HCMC. The main purpose of the project was to better understand the key drivers for air pollution under different synoptic conditions and how they are affected by different types of longer-range transportation of pollutants.

Hanoi, located in the north of Vietnam, is the country's second-largest city in terms of economy and population (Fig 1). It has a warm and humid subtropical climate with four distinct seasons (Nguyen, 2009). The month of March (sample period) is generally cloudy and hazy, with an average of about 1.5 hours of

clear-sky sunshine per day (Hien et al., 2022). HCMC, located in the south of Vietnam (Fig 1), generally experiences more solar irradiance throughout the year. It has two distinct seasons, a dry season from December to April and a wet season from May to November (Nguyen, 2009) with an average of 7.7 and 5.3 hours per day clear-sky conditions, respectively (Hien et al., 2022).

2.1 Sampling strategy

Online VOC observations were made from roof top locations in Hanoi and HCMC and are described in detail by Hien et al. (2021). Both sampling locations were near busy highways that experienced a large volume of light and heavy-duty vehicle traffic (Figure 1). Intensive field campaigns were carried out in HCMC in September-October 2018 (Hien et al., 2022) and simultaneously in both cities in March 2019. In Hanoi, direct source emission measurements were also carried out to obtain VOC emission profiles from selected sources. The study targeted the main anthropogenic sources in the city and are thought to be representative of other urban locations in Vietnam.

2.2 Online ambient measurements

A detailed description of the on-line observations of VOCs are included in Hien et al. (2021). Briefly, VOCs in Hanoi were measured using an online dual-channel Gas Chromatograph coupled with Flame Ionization Detection (DC-GC-FID, Agilent 7890) and a Selected-Ion Flow-Tube – Mass Spectrometer (SIFT-MS Voice 2000). A total of 40 compounds (some of them grouped into similar families, i.e. monoterpenes, C_8 and C_9 aromatics) were reported and shown in table S2 of the Supplementary Information. A similar setup was deployed in HCMC, where a dual GC-FID and a Proton Transfer Reaction – Mass Spectrometer (PTR-MS) were used to measure more than 30 VOCs. Concurrent observations of carbon monoxide (CO) and ozone concentrations were made to support VOCs data analysis and their interpretation. More details can be found in the Supplementary Information. In this work, we revisited and reanalysed the ambient VOC data obtained in Hanoi and HCMC (Hien et al., 2022) together with source emissions measurements performed in Hanoi.

2.3 Source emission measurements

Direct source emission measurements were carried out to obtain VOC emission profiles from Hanoi's main anthropogenic sources. Samples were collected using 1.2-liter evacuated canisters (dual-valve electropolished stainless-steel canisters) and later analyzed using the DC-GC-FID described in section 2.2 to quantify up to thirty-eight VOC species (including eleven alkanes, eight alkenes (including isoprene), eight aromatics, eight terpenes, and acetylene). All the canister samples were analysed within a day of their collection to assure the preservation and stability of VOCs measured.

Measurements of CO and carbon dioxide (CO_2) were simultaneously made at the emission sources using a QTRAK-7575 sensor (TSI) (Keita et al., 2018). The instrument relies on an electrochemical sensor with a

range between 0.1 and 500 ppm for the CO measurements with an accuracy of ± 3%. CO_2 concentrations were obtained using a non-dispersive infrared detector ranging between 0.1 and 5000 ppm (accuracy of ± 3%). The sensor was calibrated in the laboratory before each emission measurement using a cylinder of ambient air and following the procedures detailed in a previous study (Keita et al., 2018). The CO and CO_2 concentrations obtained were used to estimate EF from different samples and sources.

Emission sources were targeted to investigate emissions from the road transportation sector and domestic waste combustion, coal burning, and cook fuel burning emissions considering the specific practices in the SEA (Cao et al., 2016, Hai and Kim Oanh, 2013; Hang et al., 2014; Hien et al., 2019, Sakamoto et al., 2018) (Table S1). The samples were obtained in emission plumes, approximately 1 m from the source.

- Road transportation: The most common vehicle types were chosen for investigation: heavy-duty vehicles (diesel vehicles including trucks and public buses - five samples); light-duty vehicles (two samples of each diesel and non-diesel cars); three-wheeled motorcycles (3W, three samples); and four-stroke motorcycles (4S motorcycles, five samples). Differences in fuel type (petrol, ethanol content, and diesel) and fleet age were also considered. All transport-related samples were taken while the vehicle engine was idling.
- Waste burning (WB): samples were obtained near the road in spontaneous fires ignited by locals (two samples). Sampling was carried out within the waste combustion plume integrating the different combustion processes involved.
- Charcoal burning (CB) is a common cooking practice, from morning until late evening, at food stalls in Hanoi and other Vietnamese urban areas. The samples were collected within the smoke plume of the food stands.

2.4 Data analysis

2.4.1 Calculation of emission ratios

To establish VOC enhancement emission ratios from ambient measurements (referred to as ER in this work), the chemical removal of reactive compounds must be considered. The VOC enhancement ER refers to the ratio of a selected VOC to a vehicular tracer compound (CO or acetylene) in fresh emissions without undergoing photochemical processing. Air masses reaching the sampling site contain emissions from various sources. Those close to the sampling site will be dominated by primary emissions and therefore suitable for ER calculations, while other sources, further away, may have had sufficient time for chemical processing to have occurred which could perturb the ER calculation.

CO and acetylene (C_2H_2) are combustion tracers commonly used in the literature (Borbon et al., 2013; Dominutti et al., 2020; Salameh et al., 2016b; Warneke et al., 2007) due to their relatively low reactivity in the atmosphere (k_{OH} = 1.4 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} and 0.90 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} respectively) (Atkinson and Arey, 2003). Overall, we found better correlation coefficients for VOC versus C_2H_2 (Figure S4c, S5c, and S6c). Nevertheless, we used both tracers to ensure rigor of the calculations and because ratios to CO are most

regularly reported in the literature for urban and traffic emissions (Borbon et al., 2013; Dominutti et al., 2020; de Gouw et al., 2017; Salameh et al., 2016b; Simpson et al., 2014b; Thera et al., 2019; Wang et al., 2014), which provide valuable constraints for further comparisons.

A commonly applied method to determine these ratios is the Linear Regression Fit (LRF) which uses the slope of the scatter plot between a selected VOC and a tracer (Dominutti et al., 2020; Warneke et al., 2007). To evaluate the effects of chemical transformation on the observations, the scatterplots are coloured by morning and nighttime ambient measurements. In cases where photochemistry is sufficient to perturb the correlation, we would expect to see differences between those periods since photochemistry will be more prevalent during the daytime (Borbon et al., 2013; de Gouw et al., 2017). No significant difference was observed between the nighttime and daytime VOC data (Figure S2) which suggests photochemistry does not affect the data presented here. This is further supported by the strong correlation between benzene and 1,2,4-trimethyl benzene. These compounds are known to be co-emitted by urban sources, but have vastly different lifetimes in the atmosphere (k_{OH} (benzene) = 1.4 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, k_{OH} (124-TMB) = 33 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}). If chemical processing were impacting the data then we would expect to see a more rapid decrease in 1,2,4-trimethyl benzene and a curvature in the scatter plot. These results indicate that the distance and time between the primary emission and sampling point are short enough for the chemical processing of VOCs in both cities to be insignificant and would not affect the ER calculations.

Consequently, we applied the LRF method to all the data obtained without filtering to determine enhancement ER. Good correlations were also obtained between CO and acetylene at both sites, suggesting their emission from similar sources (Figure S2). Thus, enhancement ERs were calculated as parts per billion by volume (ppbv) of VOC per parts per million by volume (ppmv) of CO and per ppbv of C_2H_2 (Table S2).

2.4.2 Calculation of emission factors

The EFs were estimated from the concentrations measured from all the emission sources. EFs can be determined using the carbon balance method (Ferek et al., 1998; Keita et al., 2018; Radke et al., 1991; Ward and Radke, 1993). The amount of carbon emitted into the atmosphere from each source allows an estimate of the amount of fuel burned during the combustion processes. As a result, EFs are obtained using the method developed by Keita et al. (2018) as follows:

$$EF(VOC) = \frac{\frac{\Delta VOC}{\Delta CO + \Delta CO_2} x\, MW_{VOC}}{12} x\, fc\, x\, 10^3 \quad (1)$$

where EF (VOC) is the specific emission factor of the VOC in gram per kilogram of burned fuel (g kg^{-1}); ΔVOC = [VOC] emission − [VOC] background are the mixing ratio of the VOC in the emission and background atmosphere, respectively, in ppbv, MW_{VOC} represents the molar weight of each specific VOC (in g mol^{-1}), 12 denotes the molar weight of carbon (g mol^{-1}), and *fc* is the carbon mass fraction in the fuel responsible for emissions, which were obtained from the literature and applied to each source (Ban-Weiss et al., 2010; IEA-AMF, 2019; Keita et al., 2018; Lundin et al., 2013). Thus, EFs for each VOC specific to each

emission source were estimated using equation (1). In order to obtain total VOC emissions, the equivalent vehicular fleet was calculated by integrating the differences in fuel type, fleet age, and distribution. The average VOC EFs are detailed in Table S3.

For the road transport sector, the average equivalent fleet was calculated considering the fleet characteristics in Hanoi and Vietnam. For example, in Hanoi, 96% of the total fleet comprises light-duty vehicles, 89% is composed of motorcycles (General Statistics Office, 2020). Fuel types and vehicle standards in Vietnam have changed over the past decade. For example, in 2017, new cars and motorcycles had to meet the EURO 4 and EURO 3 standards, respectively (Huu and Ngoc, 2021; Le and Yang, 2022; Vietnam, 2011). Most of these motorcycles are four-stroke engines, but only 6% are equipped with catalysts (Ly et al., 2020a), and 35% of the vehicle fleet did not meet any EURO standard (Kim Oanh et al., 2012). A similar vehicular fleet composition is reported at the national level, with a dominant fraction of motorcycles accounting for around 90% of the fleet. Octane rating (RON, research octane number) measures the fuel's ability to withstand an explosion caused by its premature combustion in the combustion chamber. Aromatic compounds like benzene are added to gasoline to meet the required octane rating, limited to 2.5% in 2017 by a Vietnamese government regulation (Vietnam, 2009).

In 2015, Hanoi introduced the 5% ethanol-blended gasoline, E5 RON 92, which replaced the RON 92 in 2018. After the conversion, consumers gradually adopted this fuel, bringing the E5 RON 92 gasoline usage rate up to 45% of total gasoline consumption in Hanoi (PVOIL, 2018)**.** However, this consumption percentage dropped to 38% in 2019 due to its higher prices than RON 95 (Evnexpress, 2019).

2.4.3 Comparison with a global emission inventory

We estimate the total annual emission of thirty-eight VOCs from the EF obtained near sources in Hanoi. Additionally, the EFs were crossed with the activity data available from International Energy Agency (IEA) for the different sources in Vietnam. The total emission obtained from our estimations was then compared to the global VOC inventory, EDGAR v4.3.2 (http://edgar.jrc.ec.europa.eu/, last accessed 15/05/2022). For comparison purposes, VOC species were aggregated into fifteen VOC families (VOC2 to VOC16), as detailed in the inventory. The VOCs emissions related to Hanoi urban area integrate 7 points of the inventory grid, covering a spatial resolution of 0.1° x 0.1° each (EDGAR database, Huang et al., 2017). Finally, our total VOC and VOC group estimations from the road transport sector are compared to the annual total VOC emissions provided by the EDGAR inventory for Hanoi.

3. Results and discussion

3.1 VOC concentrations in Vietnam

The mixing ratios of different VOC species measured in both Vietnamese cities are discussed in a recently published article (Hien et al., 2022), where the VOC profiles in both cities were dominated by alkanes (31–35%) and OVOCs (27–33%), followed by alkenes (13–17%) and aromatics (12–19%) in similar proportion.

Even though a similar contribution of VOC groups has been found during sampling periods and cities, significant differences were observed in the mixing ratios measured at HCMC during the two sampling periods (Figure S5a, S6a). Average VOC mixing ratios, nighttime (22:00–5:00 LT), and daytime (10:00–18:00 LT) levels measured at Hanoi (2019) and HCMC (2019) and HCMC (2018) are presented in the SI (Figures S4a, S5a, and S6a respectively). Hanoi's highest average mixing ratios were obtained for OVOCs (ethanol and methanol), C_6–C_9 aromatics, i-pentane, C5-alkenes, and acetylene. The highest average mixing ratios in HCMC were observed for C_7-C_9 aromatics, i-pentane, and C_2-C_4 alkenes. OVOCs also presented high concentrations, particularly during 2018 measurements. Generally, greater concentrations were observed during the rainy season at HCMC (2018, Figure S6). These differences indicate that local meteorology and regional dynamics impact air pollution in HCMC. The concentration ratios between daytime and nighttime averages give a good idea about emission sources and atmospheric photochemical processing (Figure S4b, S5b, S6b). As can be seen, higher concentration ratios (by a factor of 1.5 or more) were observed for traffic-related VOCs such as heavy alkanes (C_7-C_8), ethene, propene, 1,3-butadiene, acetylene, C_8- and C_9-aromatics (also SIFT-MS m/z 107 and m/z 121) at Hanoi. A similar profile was also detected in HCMC in 2019, with higher diurnal concentrations of alkenes and aromatics. The main differences between the cities are related to the OVOC concentration ratios, which presented higher diurnal values at HCMC for methanol (PTR-MS m/z 33), acetaldehyde (m/z 45), and acetone (m/z 59). The concentration ratios observed in HCMC in 2018 showed a similar profile with a higher contribution of the same species except for toluene and methanol; however, day-to-night ratios were lower than those observed in 2019. These concentration ratios suggest higher VOC emissions during the day being offset by a deeper mixing layer compared to nighttime, resulting in relatively constant mixing ratios between day and night.

Isoprene was much higher during the day at HCMC because its biogenic emissions are light- and temperature-dependent. This result is also observed for the mixing ratios of isoprene-oxidation products (MVK+MACR, m/z71), which also presented a higher contribution during daytime at HCMC. Substantial seasonal differences are observed in HCMC, with day-to-night ratios higher by a factor of 3 during the dry season. Isoprene showed a strong correlation with CO and acetylene at Hanoi but a weak correlation at HCMC during both sampling periods. On the one hand, these results indicate a higher contribution of the biogenic sources of isoprene in HCMC due to more sunshine and warmer temperatures. On the other hand, the strong correlation in Hanoi evidences the contribution of anthropogenic sources of isoprene as reported previously (Borbon et al., 2001; dos Santos et al., 2022).

Figure S3 displays the average mixing ratio concentrations of a selected number of VOC measured in Hanoi and HCMC and compared with those reported in the literature for other cities worldwide. The distribution of VOC in Hanoi and HCMC is similar to those observed in other megacities. Despite this distribution agreement, the average mixing ratios of most VOCs were higher in the Vietnamese cities compared to those in the other megacities (by a factor of 1.2 to 14).

3.2 Seasonal and spatial variability of ER in Vietnam

As previously discussed, some seasonal differences were observed in the VOC concentrations at HCMC between the two field campaigns performed in 2018 and 2019. In order to determine if seasonality also affected ERs, the two campaigns were evaluated separately. Figure 2 shows the ERs of VOC relative to CO and acetylene obtained at HCMC for each compound measured during each season and then grouped into compound types, namely: aromatics, alkanes, alkenes, CO, acetylene, and OVOCs. No strong seasonality was observed for either approach and similar ERs were observed at HCMC within a factor of 2, except for isobutene, which exhibited a higher ER in 2018 by a factor of 4. Other minor differences are observed for isoprene (with higher ER in 2019) and some oxygenated compounds (butanone, acetone, and methanol higher in 2018).

The stability of ER over the year indicates that ERs are not strongly affected by seasonality and that emission sources do not change over the year in HCMC. These results are in line with those observed in previous studies in Beirut (Salameh et al., 2015) and Sao Paulo (Dominutti et al., 2020), where no intense seasonality was observed in the ER.

In the case of Hanoi, measurements were only performed in 2019, not allowing the analysis of seasonality. The spatial distribution of ER in Vietnam is analyzed by comparing the ER obtained in both cities during the same period. Figure 3 shows the average ER obtained relative to acetylene and CO in both cities during the 2019 campaign. Higher ER of CO, acetylene, and octane have been observed in Hanoi than in HCMC, suggesting differences in the fuel used or the contribution from other sources, such as domestic fuel combustion. In recent years, Vietnam has started a transition toward cleaner fuels, banning RON 92 and encouraging the use of biofuels, such as ethanol-containing fuels (E5 RON92) or RON 95 gasoline. However, this shift to new fuels is not completely adopted by the population, and most vehicles are still fueled with gasoline as opposed to the recent ethanol-containing fuels. Therefore, the greater octane ratios observed in Hanoi could be related to the greater consumption of RON 92 in the city than in HCMC during this study. This could also explain Hanoi's larger ratios observed for acetylene and CO.

Other VOC species also show slightly higher differences than a factor of 2 in the comparison between the Vietnamese cities. As is the case of some alkenes (pentene, cis-2-butene, trans-2-pentene and isoprene) and oxygenated VOCs (methanol and butanone). The differences in the alkenes could be associated with the difference in seasonality since those compounds present a higher sensibility to photochemical reactions and evaporative processes which are dependent on ambient temperature and solar radiation. In the case of oxygenated VOCs, they could be related to the influence of other emission sources.

Nevertheless, despite the minor discrepancies observed, a good agreement in the ER between both cities is globally observed within a factor of 2. These similarities indicate that similar emission sources regulate the release of VOCs in the two most populous cities of Vietnam, with a high contribution of vehicular-related emission, even if the presence of other VOC sources cannot be neglected.

3.3 Comparison of Vietnamese ER with other places worldwide

This section compares the average VOC/CO ERs obtained in both Vietnamese cities in 2019 with other places worldwide. This choice was made based on the availability of ER reported from other studies, which mainly calculate the ER relative to CO. Figure 4 shows the ER obtained at Hanoi and HCMC versus those obtained at Sao Paulo (Dominutti et al., 2020), Beijing, and Beirut (Salameh et al., 2016a; Wang et al., 2014), as those cities are all within developing countries, at different stages of development.

Generally, a good consistency (within a factor of 2) is observed between ER in all the cities evaluated. There are, however, several larger-scale differences which highlight interesting features in the emissions occurring in each of the cities investigated. Some aromatics, such as trimethyl benzenes, presented higher ER at Hanoi. In the case of Beijing, higher OVOCs (methanol and acetone) are observed in the ER compared to both cities and light alkanes (propane and ethane) compared to HCMC. However, more significant ER of C_9-aromatics, iso-pentane, n-octane, and 1,3-butadiene are revealed in Vietnamese cities (Figure 4). Compared to Beirut, a similar result is obtained, with greater ER of C_9-aromatics, n-octane, and isoprene observed at Hanoi.

The ethane and propane enrichment in Sao Paulo (by a factor of 4 to 7) and Beirut revealed a stronger influence of LPG and/or NG emissions, which is also observed in Hanoi compared to HCMC. In a previous study, the influence of emissions from China was observed to affect the ambient concentrations of ethane and propane in Hanoi during our sampling campaign in 2019 (Hien et al., 2022). Thus, the influence of the long-range transport of these species could have an impact on the differences in ER observed in both Vietnamese cities. Nevertheless, this contribution could also change over the year under the influence of different air masses. Longer-term measurements are then needed to better characterise the contribution from these sources.

The lower ER of ethanol observed in Hanoi than in Sao Paulo could be related to the difference in fuel formulation in both countries and the fleet composition. In Hanoi, the incorporation of ethanol in fuels is relatively recent and not fully adopted by all vehicles. In contrast, in the Brazilian city, different biofuels are available and consumed more significantly by the fleet. Similarly, the higher ERs observed for aromatics and pentanes in Vietnamese cities indicate the specificities of local fleet composition and technologies and the fuels used in the country.

An additional comparison between Hanoi, HCMC, and other cities can be found in Figure S8. A moderate consistency with northern mid-latitude cities (Los Angeles and Paris) was found, especially for aromatics and alkenes. However, there are significant differences for alkanes (except octane) and oxygenated with higher ER obtained in the northern cities by factors of 2 to 13 and 2 to 11, respectively. These differences could be related to the lower levels of CO observed in Vietnamese cities, resulting in lower ERs. Furthermore, diesel-powered cars are more frequently used in European cities, with heavy alkanes and toluene making larger contributions. ERs reported in Mecca (Simpson et al., 2014a) presented a good agreement when compared with those obtained in Vietnam, but still higher contributions of light alkanes (C_2-C_4) and alkenes are reported in the Middle East city.

This evaluation discloses the differences in the spatial variability of VOC ER, with the lower impact of those NG/LPG-related compounds and similar to higher contribution of traffic-related ones, indicating that specific fleet/fuel characteristics could have consequences in the ER observed in Vietnam.

3.4 VOC Emission profiles from combustion sources

Figure 5 compares the average relative species concentration profiles to the total VOC mass measured from different emission sources together with samples from a traffic site and the profile from the ambient site where online measurements were obtained in Hanoi.

The comparison between the ambient and traffic sites reveals quite a good agreement, with higher contribution observed for acetylene, toluene, monoterpenes, and ethene near traffic emissions. Except for acetylene, all the other species have atmospheric lifetimes of less than two days, and a lower contribution in the ambient site can be expected. In contrast, a higher contribution of light alkanes is observed in the ambient site, suggesting the contribution of non-traffic related sources, such as cooking emissions using LPG/NG, in the release of these compounds. The average profiles of each emission source reveal differences between them and are mainly related to the fuel burned and the age of the vehicles. They all, however, present a chemical profile dominated by pentanes, light alkenes, acetylene, and aromatics. In the case of heavy-duty vehicles (buses and trucks), the profiles between the diesel vehicles agree well albeit with some differences in the toluene contribution (higher contribution in the truck profile).

Light-duty vehicles can burn all types of fuels in Hanoi, including different grades of petrol (for example, RON 95 and E5 RON 92) and diesel, consequently, we have selected a range of vehicles to capture this diversity. It can be noted that passenger cars fueled with diesel have a toluene contribution which represents more than 50 % of the total VOCs measured, followed by ethene. For ethanol and petrol-fueled passenger cars, a good agreement (R^2= 0.82 - 0.97) is observed between both profiles, with a higher contribution of toluene in gasoline-fueled cars.

Motorcycles dominate the vehicular fleet in Hanoi (89%) and Vietnam (86%) and should, therefore, have an impact in terms of emissions by the road transport sector. Most are 4-stroke motorcycles, and only a small fraction have a catalytic converter (Ly et al., 2020a). Light alkanes, mainly pentanes, dominate the VOC profiles from motorcycles emissions and reveal a more significant contribution of heavy alkanes from older motorcycles. Motorcycles were found to emit a large amount of acetylene which, given the large number of motorcycles in the city, may explain the high levels measured at the ambient site (Figure 5). For 3-wheeled motorcycles, most used for transporting goods, a similar profile is observed to those from diesel vehicles, with a higher contribution of butanes in their emissions.

Regarding other combustion sources, we have also measured the emissions from coal-burning and waste-burning sources. Their profiles are quite different since the emissions will depend on the age of the coal or the

content of waste being burned. In general, a higher contribution of heavy alkanes is observed (>C_6 alkanes) in waste burning, providing a different signature to the coal combustion source.

Interestingly, monoterpenes were systematically detected in all the emission sources in different content, contributing up to 11% to the total VOC mass measured (Figure 5). The presence of monoterpenes, traditionally perceived as a solely biogenically released compound, has already been discussed in a recent study in West Africa, where monoterpenes represent 20 and 47% of road transport and waste-burning sources, respectively (Dominutti et al., 2019).

Generally, a higher contribution of light alkanes than heavy ones is noticed, with pentanes representing the largest fraction of total VOC mass, responsible for up to 34% of emissions. These results align with the ambient profile, and the ER observed in Hanoi and HCMC, where C_9 aromatics and pentanes presented the most significant contribution in ambient air dominated by iso-pentane, pentane, propene, and aromatic compounds (Imamura et al., 2006; Ly et al., 2020a; Sakamoto et al., 2018).

We believe the emission sources investigated here give a representative view of emissions from the transport sector in Vietnam, representing the diversity of the vehicle fleet in the country. To the best of our knowledge, this is the first time a detailed study combining emission sources and continuous ambient VOC measurements has been developed in Vietnam and even the SEA region.

3.5 VOC emission factors from the road transport sector

Emission factors (EFs) are defined as the amount of a pollutant emitted per kilogram of burned fuel. Previous studies have shown that during fuel combustion, approximately 95% of carbon is emitted into the atmosphere as CO_2 and CO (Chen et al., 2007; Hall et al., 2012; Keita et al., 2018). The EF calculation method estimates the released amount of carbon from CO and CO_2 concentrations, hinting at a minor misestimation of EF values (Dominutti et al., 2019; Hall et al., 2012; Keita et al., 2018; Pant and Harrison, 2013; Yokelson et al., 2007). Therefore, we compare here the ER obtained from continuous ambient measurement with the EF observed from emission sources (coal burning, trucks, diesel, and petrol cars, motorcycles, buses, etc.) (Figure 6). This comparison allows us to investigate which profiles fitted best with the VOC ratios in ambient air, considering that ER represents all the combustion sources (mainly traffic-related ones) affecting the atmospheric composition in the urban area.

Overall, both datasets have consistency, with the main discrepancies in truck emissions. This difference could be related to the low fraction of trucks in the urban areas, representing approximately 1% of the fleet during rush hours (Ly et al., 2020b). A relatively good agreement between ambient ER and petrol (R^2 = 0.64) and diesel (R^2 = 0.75) passenger car emissions is observed (Figure 6). Diesel cars denote higher emissions of benzene and 123-TMB within the aromatics, isopentane and n-heptane for alkanes, and slightly higher contribution of propene and isobutene in the alkene group. Petrol cars, however, present only minor differences with ambient ER but greater emissions of 123-TMB and pentenes. Buses' profile was relatively consistent with the ER, with two

main differences observed: the pretty significant contribution of 123-TMB and the low levels of n-heptane. As for motorcycles, higher isopentane and 224-TMP and lower toluene ethylbenzene, propane, and butane emissions are depicted (Figure 6). A poor contribution of toluene is also displayed in the emission profile of coal burning. These results suggest that the high ratios of toluene and C_9-aromatics in Hanoi are mainly related to the emissions from cars and buses diesel-fueled vehicles. The higher levels of pentenes are associated with the emission from petrol-fueled cars and motorcycles, which are largely the most significant contributors to pentanes emissions in Hanoi. This agrees with the profile obtained in another recent study in Hanoi, where a good accord was observed between near-road traffic ambient measurements and motorcycle emissions (Sakamoto et al., 2018).

3.6 Road Transport emission estimations and comparison with a global emission inventory

This section evaluates the differences in the magnitude of VOC emissions and speciation between observations and estimation from global inventories for the road transport sector in Hanoi. For that, the composition of the circulating fleet was considered, as well as the consumption of gasoline and diesel in the city. Additionally, a downscaling of the road transport emissions of the global inventory was performed, integrating an extended region around the city of Hanoi.

Figure S9 illustrates the VOC relative contribution of the road transport profile obtained from observations and that estimated by the global inventory. Substantial differences are observed in chemical speciation between both profiles, except for ethane (VOC2), propane (VOC3), and benzene (VOC13). Aromatics and alkanes are the main contributors in both profiles but in different proportions. Our estimates disclose the most significant contributions in pentanes (VOC5), C_8 aromatics (VOC15), and C_9 aromatics (VOC16), with 17.5 %, 12 %, and 11%, respectively. In comparison, EDGAR reports a contribution of 6% for VOC5, 3 % for VOC15, and 1.5% for VOC16 (Figure S9). Discrepancies are also associated with heavy alkanes' contribution (>C6 alkanes, VOC6), which dominated the road transport profile of the inventory, counting for 54% of the total VOCs. These dissimilarities between the profiles could be related to the compounds considered for the speciation of the groups. In our estimation, VOC6 (2,3- methyl pentanes, n-hexane, n-heptane, octane, and 2,2,4- trimethyl pentane), VOC12 (1-butene, trans-2-butene, isobutene, cis-2-butene, pentene, trans-2-pentene and 1,3- butadiene) are integrated by a fixed number of species, while those of the inventory combine several unknown species. Due to this limitation in the number of VOCs accounted, we have removed those groups for the following comparisons.

Figure 7 displays the absolute VOC emissions (in Tn $year^{-1}$), estimated by the EDGAR inventory and our measurements. Significant differences are noted for several species, including pentanes (VOC5), acetylene (VOC 9), aromatics (VOC14-VOC16), isoprene (VOC10), and monoterpenes (VOC11) (Figure S9,7). Overall, our results show that except for VOC 7 and VOC8, all the VOC groups present higher emissions than the estimations of EDGAR.

As mentioned before, pentanes presented the highest VOC levels in both cities, and they also dominated the emission profile (23%), 3.5 times higher than the inventory estimation (Figure 7a). Aromatics also display an underestimation by a factor of 2.5 to 9 (VOC14, 15 and 16). This discrepancy is likely due to the EFs used in the inventory estimation not being representative of the local characteristics of the Vietnamese fleet. These differences are substantial, with total aromatics found to be three times higher than those calculated by the EDGAR inventory.

Isoprene and monoterpenes (VOC10 and 11) are the groups depicting the greatest underestimation, by a factor of 47 in the case of isoprene and entirely absent for monoterpenes (Figure S9,7b). Despite biogenic emissions dominating the global contribution of isoprene, it can also be released by traffic-related sources, as documented in previous studies, which can exceed the biogenic ones depending on the season (Borbon et al., 2001; Brito et al., 2015; dos Santos et al., 2022). There is an increasing volume of evidence about the presence of monoterpenes in anthropogenic emissions. Recent studies have evaluated the contribution of these species from personal care and volatile consumer products, suggested as the main emission sources in northern urban areas (Coggon et al., 2021; Gkatzelis et al., 2021; McDonald et al., 2018). In addition, the presence of monoterpenes in roadside concentrations has been highlighted in a recent study in Hanoi, where ocimene related-compounds reach up to 0.95 ppb and show a similar trend to traffic-related tracers (Ly et al., 2020a). The strong correlations of acetylene and CO with isoprene and its presence in emission profiles of several sources in Hanoi reinforce its emission from anthropogenic sources (Figure S2). Nevertheless, the contribution from other sources cannot be neglected. Ethanol and other oxygenated compounds, such as aldehydes, are not present in the road transport profile of the inventory. The introduction of ethanol-blended fuels in Vietnam was done after the development of the inventory, which could explain its absence in the profile. A recent study in Sao Paulo has shown that oxygenated VOCs can contribute considerably to the traffic-related emission profiles where ethanol or other biofuels are frequently burned (Dominutti et al., 2020). Unfortunately, our study did not include the evaluation of EF for oxygenated VOCs, and they should be included in future studies in Vietnam.

Regarding the total calculated VOC emissions, a discrepancy by a factor of 3 (more than 6000 Tn $year^{-1}$) is disclosed between the estimation and the observations (Figure 7d). Even if these differences are not as substantial in other places (i.e., West Africa), they can have implications on the oxidative capacity of the atmosphere at the regional scale. Furthermore, since major underestimations are related to highly reactive VOCs, such as alkenes, monoterpenes, and aromatics, the inaccuracies in the speciation could also have consequences on the estimation of their impacts on the formation of secondary pollutants.

The scarcity of source profile measurements and long-term ambient data in regions such as the SEA, reinforces the need for further research on VOCs and their representation in EIs. Our results provide relevant information on individual EFs of VOC from in situ observations, which can help develop accurate EIs in the SEA region.

3.7 Limitations of this study and recommendations

This study focused on VOC ERs established from ambient measurements and EFs estimated from individual sources in Vietnam, limiting our study in some aspects. Despite the advantages offered in the measurement of online VOCs in urban traffic sites, focus on the transport sector limits the discussion on the contribution from other potential sources that may be relevant for other urban sites in Vietnam but less dominated by traffic. In addition, other sources such as industrial, biomass burning, residential, ship transportation, and volatile consumer products should be assessed to have a complete picture of the VOC emissions in Vietnam and to better evaluate population exposure to air pollution.

We recommend that future studies include an expanded number of vehicles to better estimate the uncertainties from the measurements obtained. Moreover, our measurements were performed under real-world but also uncontrolled conditions. Therefore, further work should include the estimation factors from controlled emission chambers, mainly for estimating coal and other burning emissions.

Restrictions in access to data were found during our research, mainly due to the lack of reliable information available. The estimation of total emissions can benefit from improving the availability of activity data from consumption and source characteristics to develop more reliable EIs.

Finally, long-term VOC data was unavailable over the year and these observations would help evaluate the contribution of VOC emission sources over the whole year in Vietnam.

4. Conclusions

This work presents, for the first time, a comprehensive study on EFs and ERs of ambient VOC and total VOC emissions from the road transport sector in Vietnam. Our ER estimations show no substantial differences between the dry and rainy seasons in HCMC and a relatively homogeneous spatial distribution within the two cities (Hanoi and HCMC), suggesting that similar emission sources are presented in both areas.

Globally, the comparison with other cities worldwide shows a reasonable consensus with higher emissions ratios in Hanoi than in other places. These findings disclose the differences in the global variability of VOC ER, with a higher contribution of traffic-related ones, indicating that specific fleet characteristics and fuels could impact the ER observed in Vietnam.

The total VOC emissions calculated for the road transport sector were compared with a downscaled global inventory. Substantial differences are observed in chemical speciation between the two profiles. Our estimates reveal the most significant contributions in pentanes, C_8 aromatics, and C_9 aromatics, while heavy alkanes' contribution dominated the road transport profile of the inventory. Oxygenated compounds are not represented in the inventory for the area, as well as isoprene and monoterpenes depict the more contrasting underestimation by a factor of 47. Regarding absolute VOC emissions, a discrepancy of a factor of 3 between

inventory and our estimations in Hanoi is observed. Those discrepancies could have consequences on the estimation of the effects that road transport can have on regional air quality.

Thus, at a local and regional level, comprehensive measurements integrating ambient levels and regional-specific sources are of great interest in providing more reliable information to improve the VOCs magnitude and speciation of emission estimations in the SEA region.

Author contributions.

PAD conceptualized and drafted the paper, analysed the data and produced the figures with help from JRH, HAL, GLF, SK, and DEO. Experimental design and project planning was carried out by DEO, HTT and HAL. Field measurements were performed by PAD, JRH, MS, GPM, DHH, GLF, and DEO. Reviewing and editing were carried out by JRH, HAL, DEO and GLF.

Declaration of competing interest.

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 study.

Acknowledgments.

This study was funded by the RCUK (Research Councils UK)- NAFOSTED (Vietnam National Foundation for Science and Technology Development) Newton Fund Research Partnership under grant number NE/P014771/1.

Acknowledgement is made to Dr Katie Read from the Atmospheric Measurement and Observation Facility (AMOF), National Centre for Atmospheric Science (NCAS) for the support of the ozone and carbon monoxide measurements. The authors would like to kindly thank the dedicated efforts of Nguyen Viet Thanh, Nguyen Doan Thien Chi and Tran Anh Ngan for collecting samples and participating in the field campaigns.

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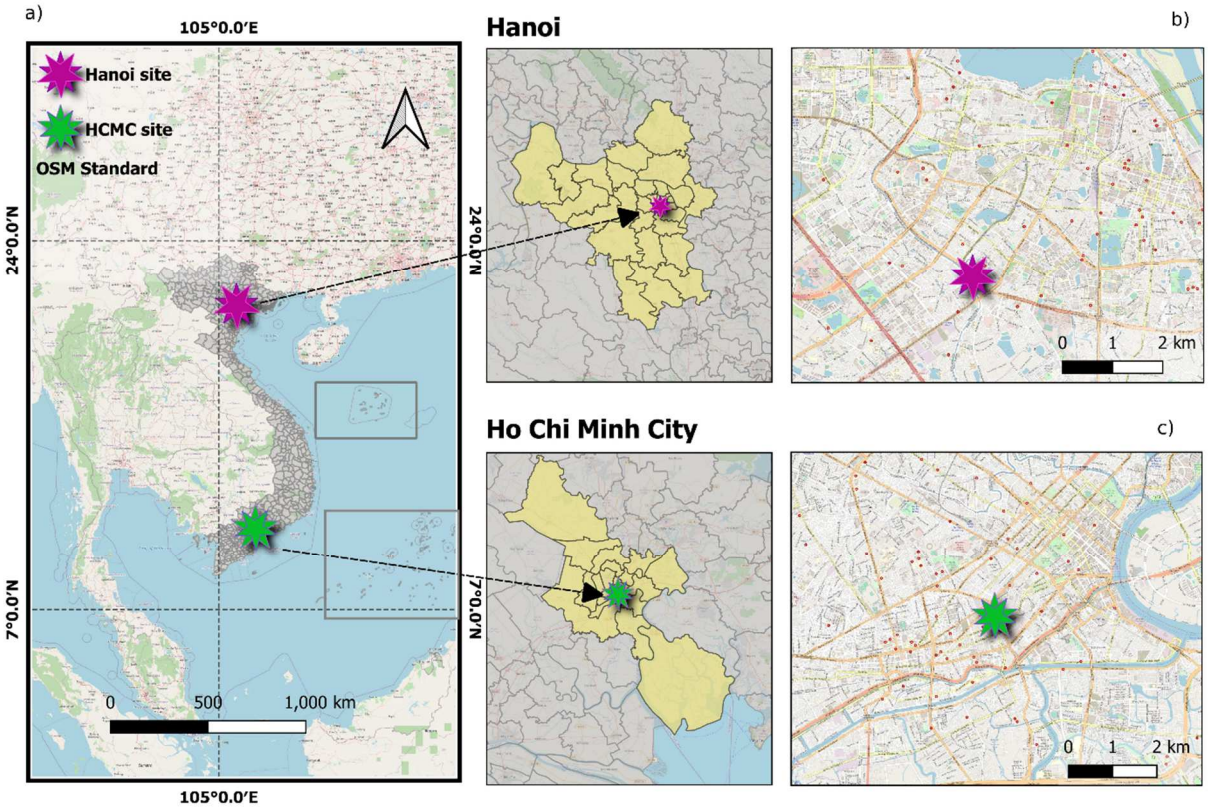


Figure 1. Location of sampling points in Hanoi (purple star) and HCMC (green star) and their location in Vietnam. © OpenStreetMap contributors, 2021. a) location of Hanoi and HCMC in Vietnam, b) location of the sampling point in Hanoi and zoom to the Hanoi sampling area and c) location of the sampling point in HCMC and zoom to the HCMC sampling area.

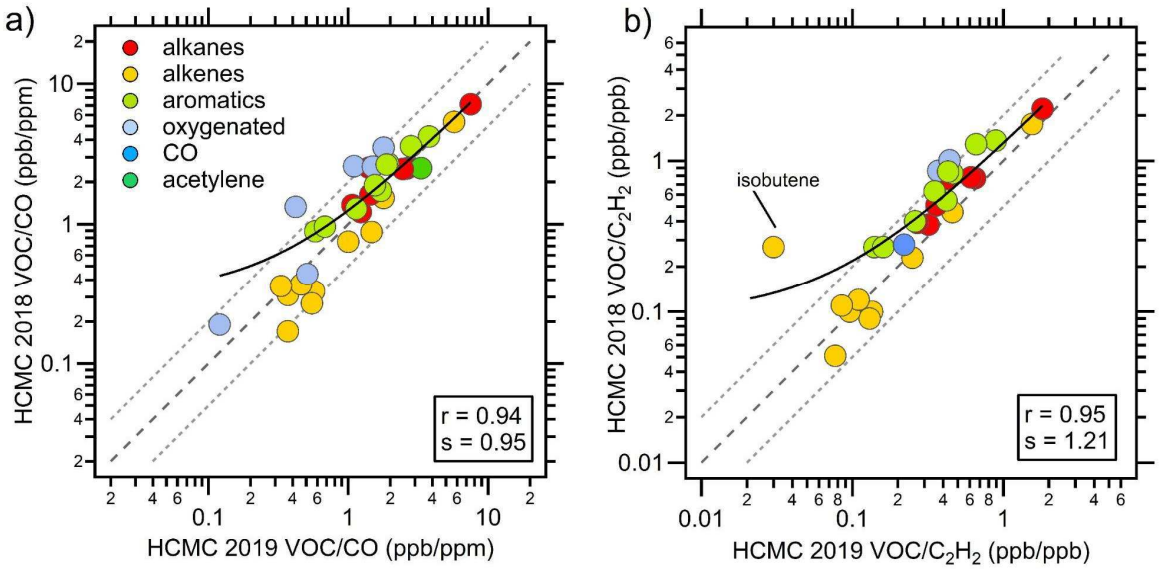
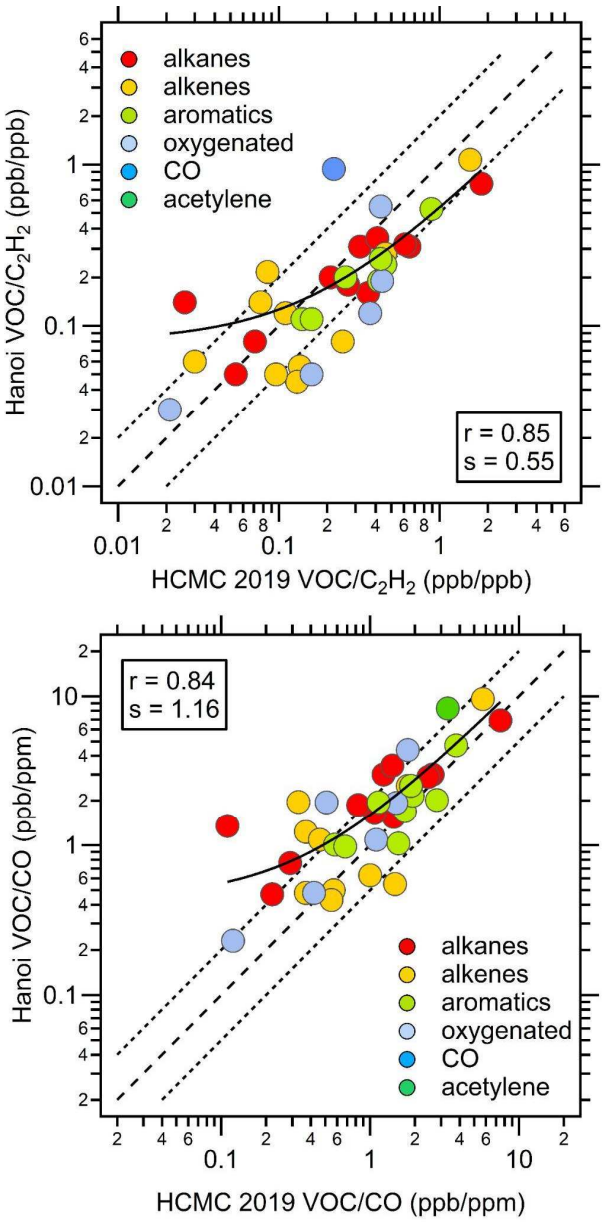


Figure 2. Seasonal average emission ratios of VOC/CO (a) and VOC/C_2H_2 (b) obtained in HCMC in 2018 and 2019, during rainy and dry seasons, respectively. Color-coded markers represent VOC families. The solid line represents the 1:1 relationship between sampling sites compared, and the dashed lines represent the difference within a factor of 2.



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805 **Figure 3. Average emission ratios of VOC/C_2H_2 (a) and VOC/CO (b) were derived for each VOC species at both**
806 **sampling sites in Hanoi and HCMC for 2019. Color-coded markers represent VOC families, the solid line**
807 **represents the 1:1 relationship between sampling sites compared, and the dashed lines represent the difference by**
808 **a factor of 2.**

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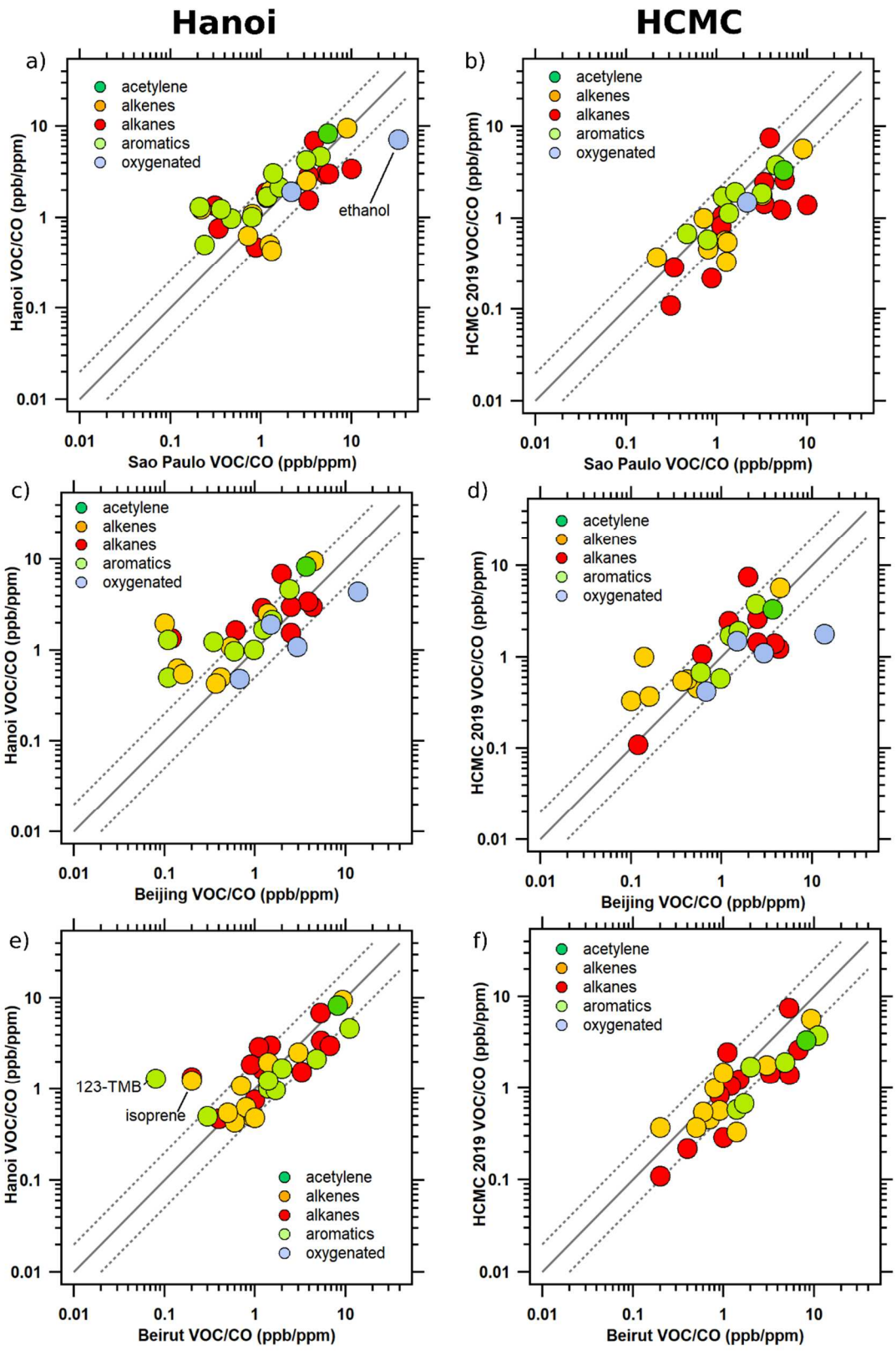
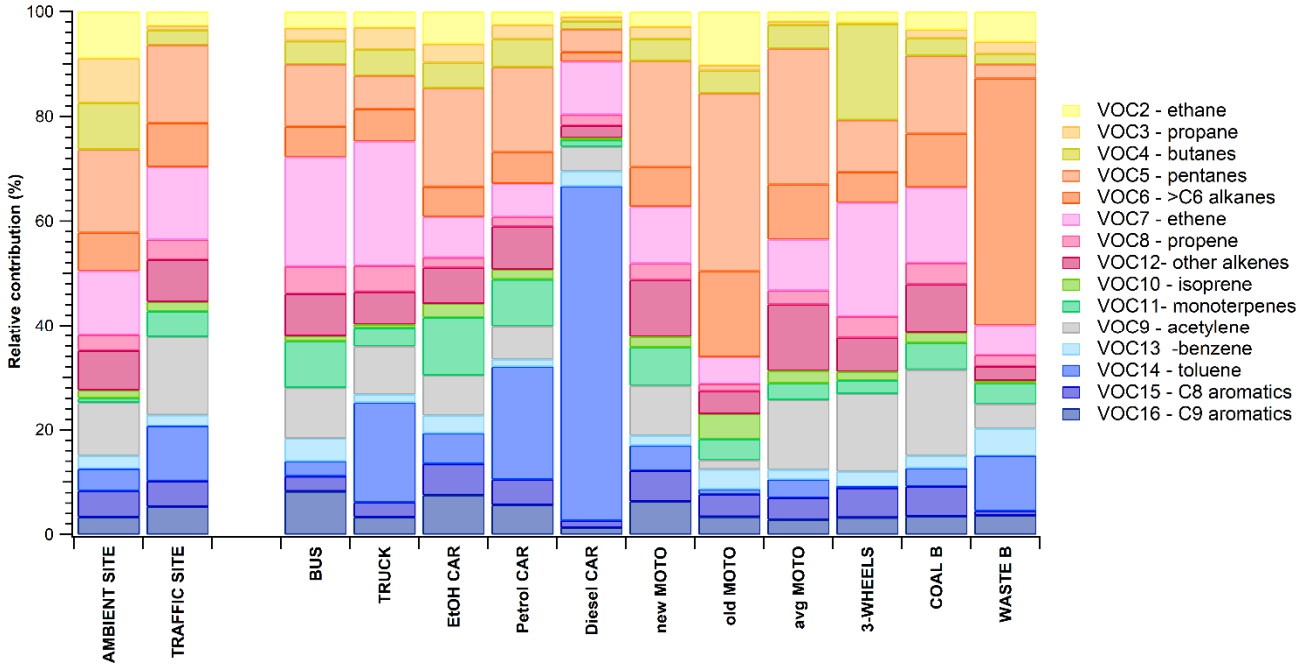


Figure 4. Comparison of VOC to CO (ppb/ppm) emission ratios obtained at urban sites in Hanoi and HCMC and compared with those reported in the literature for a)-b) Sao Paulo, c)- d) Beijing, and e)- f) Beirut.



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815 **Figure 5. The relative contribution of VOC group concentrations from emission sources to the total VOC**
816 **mass measured and compared to the ambient and near-road traffic site profiles observed in Hanoi.**

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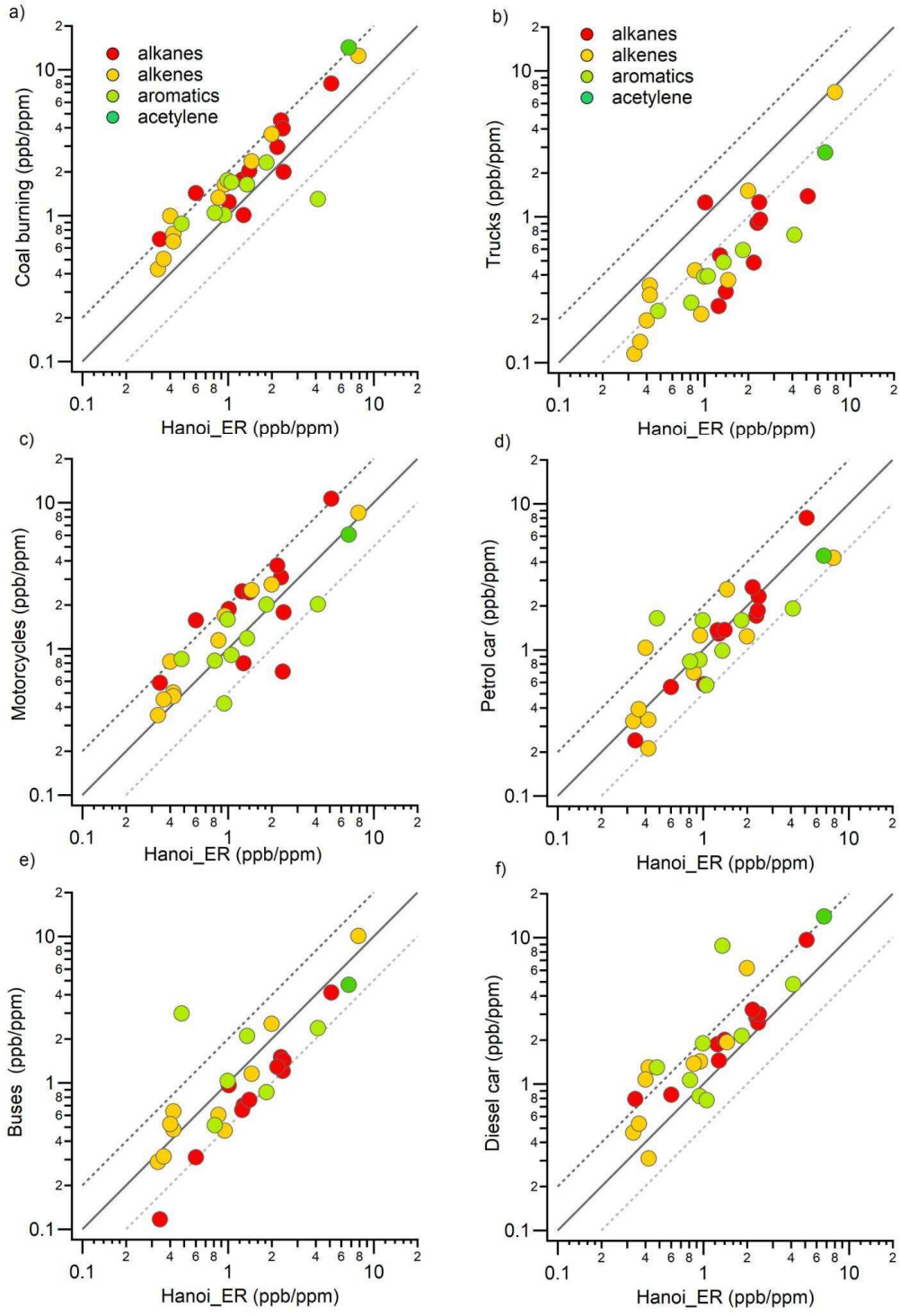

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820 **Figure 6. Emission ratios comparison between the LRF method from ambient measurements and the**
821 **averaged ones obtained near-source emissions in Hanoi for a) coal burning, b) trucks, c) motorcycles,**
822 **d) petrol cars, e) buses, and f) diesel cars.**

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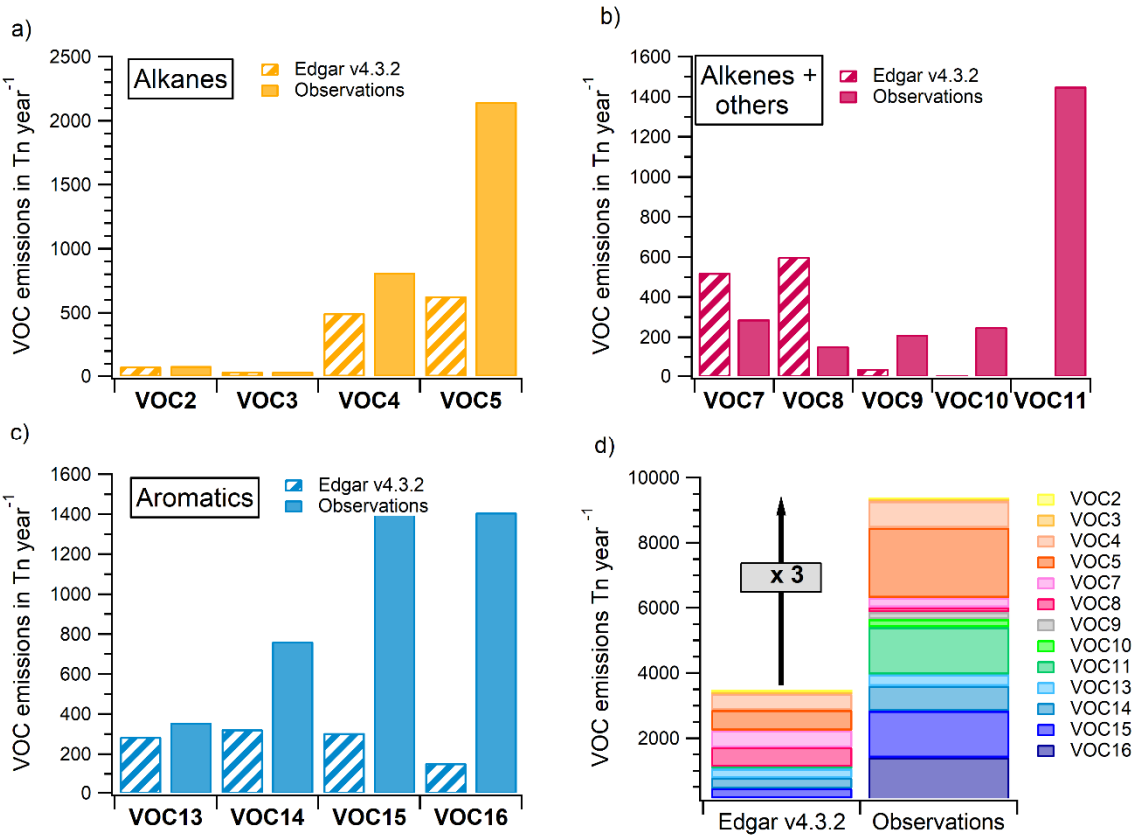

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825 **Figure 7. Absolute VOC emissions from the road transport sector estimated by the global inventory,**
826 **EDGAR4.3.2, and our emission factors in Hanoi. a), b), and c) represent the emissions per group of VOC**
827 **(alkanes, alkenes+others, and aromatics) estimated by the inventory in stripped bars and by our EF in**
828 **solid bars. d) represent the total VOC emissions comparison between both estimations. Colors represent**
829 **the VOC group following the methodology used in the inventory. Only the VOC groups with species in**
830 **common were considered in this evaluation.**

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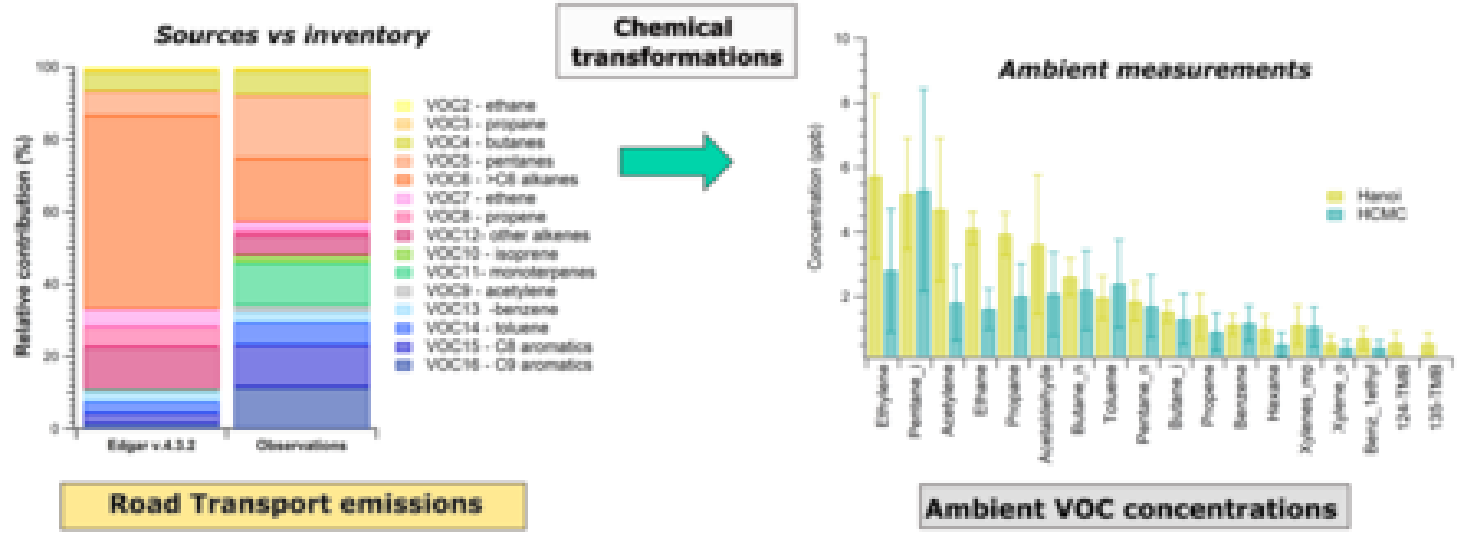
Sources vs inventory
Relative contribution (%)
100
80
60
40
20
0
Edgar v.4.3.2
Observations
VOC2 - ethane
VOC3 - propane
VOC4 - butanes
VOC5 - pentanes
VOC6 - >C6 alkanes
VOC7 - ethene
VOC8 - propene
VOC12- other alkenes
VOC10 - isoprene
VOC11- monoterpenes
VOC9 - acetylene
VOC13 -benzene
VOC14 - toluene
VOC15 - C8 aromatics
VOC16 - C9 aromatics
Chemical transformations
Ambient measurements
Concentration (ppb)
10
8
6
4
2
Hanoi
HCMC
Ethylene
Pentane_i
Acetylene
Ethane
Propane
Acetaldehyde
Butane_n
Toluene
Pentane_n
Butane_i
Propene
Benzene
Hexane
Xylenes_m+p
Xylene_o
Benz_1ethyl
124-TMB
135-TMB
Road Transport emissions
Ambient VOC concentrations