Anthropogenic VOC in Abidjan, southern West Africa: from source quantification to atmospheric impacts

Pamela Dominutti[1*], Sekou Keita [2,3], Julien Bahino[2,3], Aurélie Colomb[1], Cathy Liousse[2], Veronique Yoboué[3], Corinne Galy-Lacaux[2], Eleanor Morris[4], Laëtitia Bouvier[1], Stéphane Sauvage[5] and Agnès Borbon[1]

[1] Université Clermont Auvergne, CNRS, Laboratoire de Météorologie Physique (LaMP), F-63000 Clermont-Ferrand, France.

[2] Laboratoire d'Aérologie, Université Paul Sabatier Toulouse 3 - CNRS, Toulouse, France

[3] Laboratoire de Physique de l'Atmosphère (LAPA)- Université Felix Houphouët-Boigny, Abidjan, Côte d'Ivoire

[4] Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK

[5] IMT Lille Douai, Sciences de l'Atmosphère et Génie de l'Environnement (SAGE), Douai, France

**Now at Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK*

Correspondence to P. Dominutti (pamela.dominutti@york.ac.uk) + A. Borbon (agnes.borbon@uca.fr)

Abstract

Several field campaigns were conducted in the framework of the Dynamics-Aerosol-Chemistry-Cloud Interactions in West Africa (DACCIWA) project to measure a broad range of atmospheric constituents. Here we present the analysis of an unprecedented and comprehensive dataset integrating up to fifty-six volatile organic compounds (VOCs) from ambient sites and emission sources. VOCs were collected on multisorbent tubes in the coastal city of Abidjan, Côte d'Ivoire, in winter and summer 2016 and later analysed by gas chromatography coupled with flame ionization and mass spectrometer detectors (GC-FID and GC-MS) at the laboratory.

The comparison between VOC emission source profiles and ambient profiles suggests the substantial impact of two-stroke motorized two-wheel vehicles and domestic fires on the composition of Abidjan's atmosphere. However, despite high VOC concentrations near-source, moderate ambient levels were observed (by a factor of 10 to 4000 lower), similar to the concentrations observed in northern mid-latitude urban areas. Besides photochemistry, the reported high wind speeds seem to be an essential factor that regulates air pollution levels in Abidjan.

Emission ratios (ΔVOC/ΔCO) were established based on real-world measurements achieved for a selected number of representative combustion sources. Maximum measured molar mass emissions were observed from two-wheel vehicles, surpassing other regional sources by two orders of magnitude. Local practices like waste burning also make a significant contribution to VOC emissions, higher than those from light-duty vehicles by 1.5 to 8 orders of magnitude. These sources also largely govern the VOC's atmospheric impacts in terms of OH reactivity, secondary

organic aerosol formation (SOAP) and photochemical ozone creation potential (POCP). While the contribution of aromatics dominates the atmospheric impact, our measurements reveal the systematic presence of anthropogenic terpenoids in all residential combustion sectors. Finally, emission factors were used to retrieve and quantify VOC emissions from the main anthropogenic source sectors at the national level. Our detailed estimation of VOC emissions suggests that the road transport sector is the dominant source in Côte d'Ivoire, emitting around 1200 Gg yr^{-1} of gas-phase VOCs. These new estimates are 100 and 160 times larger than global inventory estimations from MACCity or EDGAR (v4.3.2), respectively. Additionally, the residential sector is largely underestimated in the global emission inventories, by a factor of 13 to 43. Considering only Côte d'Ivoire, these new estimates for VOCs are three to six times higher than the whole of Europe. Given the significant underestimation of VOC emissions from transport and residential sectors in Côte d'Ivoire, there is an urgent need to build more realistic and region-specific emission inventories for the entire West African region. This might be not only true for VOCs but for all atmospheric pollutants. The lack of waste burning, wood fuel burning and charcoal burning and fabrication representation in regional inventories also needs to be addressed, particularly in low-income areas where these types of activities are ubiquitous sources of VOC emissions.

Keywords: VOCs, emission inventories, West Africa, air pollution, emission ratios.

1. Introduction

The West Africa region, located to the north of the Gulf of Guinea, is one of the most populated areas in Africa with more than 300 million inhabitants in 2016 (United Nations, 2017). The population has increased by a factor of five since 1950, making West Africa the fastest growing region in the world. Furthermore, future projections indicate population densities in developing countries will continue to increase. The impact in Africa will be particularly high, with projections indicating that the population of the continent could represent 40% of the world's population by 2100 (United Nations, 2017). The unplanned explosive growth of urban centres in the region is a significant issue, with water access, air pollution, health problems and unregulated emissions being identified as major concerns.

These emissions can produce diverse effects on atmospheric chemistry which are enhanced by severe photochemical conditions and dynamic atmospheric interactions. The atmospheric composition over West Africa is affected by air masses transported from remote sources, i.e., aerosol dust from the Sahara Desert, biomass burning plumes and local urban pollution (Knippertz et al., 2017; Mari et al., 2011). Observations performed during the AMMA (African Monsoon Multidisciplinary Analysis, West Africa, 2005-2006) campaign showed that air quality issues are predominantly related to traffic and combustion emissions (Mari et al., 2011). Residential emissions in southern West Africa (SWA) are attributed to charcoal and wood burning as they are primary sources of domestic energy, widely used for cooking and heating activities. Regional biomass burning is a significant source of carbonaceous aerosols and volatile organic compounds (VOCs) that can have effects on public health and climate through the formation of secondary pollutants (Gilman et al., 2015; Knippertz et al., 2015b; Sommers et al., 2014).

Additionally, in most of the southern West Africa cities, traffic emissions are major sources of air pollution (Assamoi and Liousse, 2010). The road transport sector is largely disorganized due to the underdevelopment of road networks and to the absence of a regulation policy for public transportation (Assamoi and Liousse, 2010). As a result, two-wheel vehicles are widely used in the cities for short-distance travel, replacing public transport. Furthermore, the

vehicle fleet has increased in the last year, which is characterized in most cities by a large number of old vehicles (Keita et al., 2018). Over the next few years, African emissions from the combustion of fossil fuels, biofuels, and refuse are expected to increase considerably and could represent about 50% of the global emissions of organic carbon (Knippertz et al., 2017; Liousse et al., 2014). However, emission estimates are uncertain and detailed emission inventories are still required for a better estimation of their impacts on climate change and health over this highly sensitive region (Knippertz et al., 2017).

VOCs include a large number of species which can affect air quality by producing secondary pollutants such as ozone and secondary organic aerosols (Seinfeld and Pandis, 2006). Given the reactive nature of VOCs (Atkinson and Arey, 2003), VOC emissions need to be disaggregated by species or species groups for a better representation of their chemical features, and to access their impacts on the secondary formation processes. As VOCs are significant pollutants present in urban atmospheres, in-situ VOC observations are necessary to directly assess exposure and to improve the prediction of secondary product formation.

Several field campaigns have been conducted in the last twenty years all over the world with the purpose of characterizing VOC species to better understand their emission sources and fate (Bechara et al., 2010; Bon et al., 2011; Borbon et al., 2013; Brito et al., 2015; Dominutti et al., 2016; Kumar et al., 2018; Salameh et al., 2015; Wang et al., 2014; Warneke et al., 2007). In particular, VOC field observations have been intensely used as constraints for the development of reliable emission inventories (Borbon et al., 2013; Boynard et al., 2014; Gaimoz et al., 2011; Niedojadlo et al., 2007; Salameh et al., 2016b). Some of these studies pointed out significant discrepancies between inventory estimations and emission ratios derived from ambient measurements, implying some limitations in the accurate modelling of VOCs impacts. For northern mid-latitude cities, discrepancies up to a factor of 10 for VOC emissions have been observed (Borbon et al., 2013; Boynard et al., 2014). Such discrepancies are expected to be even more substantial in places of the developing world with high anthropogenic pressures like Africa and South America (Huang et al., 2017). For Africa in particular, the emission inventories frequently used are those developed for global scales due to the lack of observations, which involve numerous uncertainties (Keita et al., 2018; Liousse et al., 2014). While global emission inventories commonly estimate the total mass of speciated VOCs, they fail in reproducing the spatial and temporal variability of VOC emission speciation. Indeed, the emission composition can change depending on the emission source, fuel quality, combustion technologies, and main regional practices (Huang et al., 2017). The use of activity data and emission factors derived from local measurements of regional-specific sources may help to reduce the uncertainties in those emission inventories. In a recent study calculated the emission factors (EFs) of different compounds and activities in southern West Africa (Keita et al., 2018). A comparison of the emissions calculated from the EFs with those observed from the EDGARv4.3.2 (Huang et al., 2017) inventory showed a marked discrepancy (factor of 50 difference) for fifteen VOCs species (3 alkanes, 8 aromatics, isoprene and 3 monoterpenes) in Côte d'Ivoire. That study emphasised the importance of considering African anthropogenic emissions at regional scales. Due to the scarcity of suitable data, the uncertainties in the observations cannot currently be assessed and more detailed studies are required to quantify these uncertainties. Characterization and quantification of the emissions is crucial for improving our understanding of the contributions of anthropogenic and natural sources to the atmospheric composition over southern West Africa, and for assessing their impact on public health and air quality conditions.

Several intensive field campaigns in the framework of the Dynamics-Aerosol-Chemistry-Cloud-Interactions in West Africa (DACCIWA) project were conducted in 2015 and 2016 (Knippertz et al., 2015a). Here, we present the results obtained from the VOC field campaigns at different sites, including ambient and near-source measurements, in one of the major southern West Africa cities: Abidjan in Côte d'Ivoire. Abidjan is the economic capital of Côte d'Ivoire with a population of 6.5 million (in 2016), representing more than 20 % of the population of the country (United Nations, 2017). Along with autonomous districts, Abidjan encompasses an area of 2119 km^2 and is distinguished by remarkable industrialization and urbanization. In summer, West Africa is influenced by monsoon phenomenon which is mainly driven by the surface pressure contrast between the relatively cold waters of the tropical Atlantic Ocean and the Saharan heat low (Knippertz et al., 2017). This seasonal circulation characterized the wet (summer) and dry (winter) periods in the region. During the dry season (November to February), most of the region is dominated by dry northeasterly winds from the Sahara and the precipitation is confined to the coast, where the sea-breeze circulation provides humid air and produces near-surface convergence. Then, the monsoon starts its development and southwesterly moist winds begin to enter deeper into the continent producing more clouds and precipitation between July and August. The strong pressure and temperature gradients between the Atlantic Ocean and the Sahara drive the strong monsoon flow northward along with southwesterlies, reaching higher latitudes up to 20° N (Knippertz et al., 2015b).

Speciated VOCs were collected during DACCIWA using sorbent tubes, and then analysed and quantified at the laboratory applying different gas chromatography techniques. These data provide the first constraints for the construction of a regional emission inventory and for understanding the role of anthropogenic VOC emissions in regional atmospheric chemistry.

This work aims to establish and analyse the spatial distribution of VOC concentrations and VOC speciated profiles of primary anthropogenic sources in Abidjan by performing sampling under real-conditions. These sources include traditional and regional-specific ones, such as road transportation (gasoline and diesel emissions from different vehicles), charcoal fabrication, and burning emissions from domestic cooking fires, landfill waste, and hardwood fuel. This new dataset provides substantial information enabling the quantification of VOC emissions for several sources in Côte d'Ivoire. These source profiles are analysed and contrasted with those provided by global emission inventories. Finally, the impact on air quality due to the use of regional-specific sources is assessed in terms of reactivity and secondary pollutant formation.

2. Materials and Methods

As part of the DACCIWA project, intensive field campaigns were performed in 2015 and 2016, focusing for the first time on the most populated southern coastal region of West Africa. The DACCIWA campaign had an emphasis on atmospheric composition, including air pollution, health impacts and cloud-aerosol interactions (Knippertz et al., 2015a). Here we present new results from intensive ambient measurements in Abidjan and an extended VOC speciation from source emission measurements. These results are part of the activities developed under the workpackage 2 (WP2) - Air Pollution and Health - which aims to link and quantify emission sources, air pollution and related health impacts over different urban sources in West Africa (Knippertz et al., 2015a).

2.1 Sampling

The field campaigns were conducted in Abidjan, Côte d'Ivoire during summer and winter according to the strategic directions of the DACCIWA WP2. Two types of cartridges were deployed for VOC measurements: single sorbent cartridge made of Tenax TA 60-80 mesh (250 mg) or multi-sorbent cartridges made of Carbopack B (200mg) and Carbopack C (200 mg (carbotrap 202) purchased from Perkin Elmer). The combination of different sorbent materials allowed the sampling of 10 aromatics (C_6-C_9), 22 n-alkanes (C_5-C_{16}), 10 monoterpenes, 7 aldehydes, isoprene, and other oxygenated compounds. All compounds are reported in Table S1. Before the sampling, cartridges were conditioned by flowing purified nitrogen, at a rate of 100 mL min^{-1} for 5 hours at 320°C.

Firstly, ambient VOC were collected to analyse their spatial distribution in Abidjan. Ambient measurements were performed at nine sites, which are shown in Figure 1. The distribution of the sampling locations was selected according to the primary source locations. They include urban background sites and areas impacted by residential, road transport, domestic fires, waste burning and industrial activities. The characteristics and geographical location of each site are reported in Table 2. The ambient campaigns were conducted during the dry season (February 2016). Samples were collected every 2 days at different times of the day (from 6 a.m. to 8 p.m.) by using a manual pump (Accuro 2000, Dräger) at 100 sccm (standard cubic centimetres per minute) flow rate. One single sorbent tube was exposed six times at each sampling location. In total, 3.6 L of air were collected at each site for a single 600 mL volume each time. Details on the sampling strategy are reported in Table S3.

Secondly, direct source emission measurements were performed to obtain VOC emission profiles from the main anthropogenic sources in Abidjan. The sources include traditional ones like road transportation, and southern West Africa specific ones such as domestic waste burning, charcoal fabrication, charcoal burning as well as wood fuel burning (Table1). Despite that part of these measurements for a limited number of VOC (fifteen species including 3 alkanes, 8 aromatics, 3 terpenes and isoprene) and particles were discussed somewhere (Keita et al., 2018), we improve the VOC database extended to 56 VOC species measured in the follow source emissions:

- For road transportation, analysis of different vehicle exhaust measurements was carried out. Samples integrate five road transportation sub-categories: heavy-duty diesel vehicles (HDDV, trucks, and buses – 3 samples on Tenax and 3 samples on Carbopack tubes), light-duty diesel vehicles (LDDV, diesel cars, 2 samples on Tenax tubes), light-duty gasoline vehicles (LDGV, gasoline cars, 2 samples on Tenax tubes), two-wheel two-stroke (TW2T, 3 samples on Tenax and 3 samples on Carbopack tubes) and two-wheel four-stroke (TW4T, 3 samples on Tenax and 3 samples on Carbopack tubes) vehicles. Differences in fuel type (gasoline and diesel) and the fleet age have been considered. In African countries, two-wheel vehicles (two-stroke or four-stroke engines) frequently use a mixture of oil and gasoline derived from smuggling, which is characterized by high pollutant emissions (Assamoi and Liousse, 2010).
- Regarding domestic waste burning (WB), samples were obtained (5 samples on Tenax tubes) at the official domestic landfill site located to the east of Abidjan (AD, Figure 1 and Table 2). The sampling was performed inside the waste burning plume to integrate the different combustion processes involved.
- Charcoal burning (CH) and wood fuel burning (FW) are common cooking and heating practices in African urban areas. Wood fuel burning emissions were obtained by measuring the fire plume of tropical African hardwood, specifically Hevea (*Hevea brasiliensis*). Wood and charcoal were burned in two types of stoves traditionally used in the southern West Africa region for cooking, which are made of metal and baked earth.

The measurements included all the combustion phases (Keita et al., 2018) (4 samples on Tenax and 3 samples on Carbopack tubes).

- The charcoal making (CHM) profile was obtained by measuring emissions from traditional kilns, that use different types of dense wood. The kiln was covered with a layer of leaves and another one of soil of about 10 cm thickness. The smoke was sampled through holes made in the CHM kiln, which are located in the horizontal plane, and provide the air circulation for the pyrolysis propagation (Keita et al., 2018) (2 samples one on Tenax and one on Carbopack tubes).

All samples were obtained in the emission plume at around 1–1.5m from the source, except for vehicles where samples were taken at the tailpipe outlet while the vehicle's engine was idling. Carbon monoxide (CO) and carbon dioxide (CO_2) measurements were also performed on the emission sources together with the VOC measurements. For this, the QTRAK-7575 sensor (TSI, Keita et al., 2018) was used to measure real-time CO_2 and CO gas concentrations. CO is measured by using an electrochemical sensor with a sensitivity of 0 to 500 ppm with ±3% accuracy. CO_2 concentrations are obtained by using a non-dispersive infrared detector with a sensitivity of 0 to 5000 ppm with an accuracy of ±3 %. The instrument was calibrated in the laboratory prior to each emission measurement These concentrations were used for the estimation of EF values from different samples, which were later averaged for every source category. Details on the sampling strategy at emission are reported in Table S4.

2.2 Analytical instrumentation

Duplicate measurements were performed and analysed in two different laboratories to investigate the reproducibility of analytical techniques and to acquire a wider range of VOC species. The analysis of the Tenax TA tubes was performed at the *Laboratoire de Météorologie Physique* (LaMP, Clermont-Ferrand, France) using a gas chromatograph mass spectrometer system (GC/MS, Turbomass Clarus 600, Perkin Elmer®) coupled to automatic thermal desorption (Turbomatrix ATD). Each tube was desorbed at 270°C for 15 min at a flow rate of 40 mL. min^{-1} and pre-concentrated on a second trap, at -30°C containing Tenax TA. After the cryofocusing, the trap was rapidly heated to 300°C (40° s^{-1}) and the target compounds were flushed into the GC. Due to the high loads in some samples, an inlet and outlet split of 5 mL min^{-1} and 2 mL min^{-1} were set up, respectively. The analytical column was a PE-5MS (5% phenyl – 95% PDMS, 60m×0.25mm×0.25µm) capillary column (Perkin Elmer) and a temperature ramp was applied to guarantee the VOCs separation (35°C for 5 minutes, heating at 8°C min^{-1} to 250°C, hold for 2 minutes). The mass spectrometer was operated in a Total Ion Current (TIC) from 35 to 350 m/z amu. Chromatography parameters were optimized to enable good separation of fifteen identified compounds by a complete run of 34 minutes on each cartridge. Calibration was performed by analysing conditioned cartridges doped with known masses of each compound, present in certified standard low-ppb gaseous standard, purchased from the National Physical Laboratory (NPL, UK; 4 ppb ±0.8 ppb). That method provided the separation and identification of 16 compounds, from C_5 to C_{10} VOCs, including 8 aromatics, 3 monoterpenes, 4 alkanes and isoprene. The limit of detection lies between 1.10 ppt (1,2,3-trimethylbenzene) and 22.6 ppt (2-methylpentane). The global uncertainty is estimated between 5% and 38%.

Carbopack tubes analysis was carried out by applying a gas chromatography-flame ionization detector (ATD-GC-FID, Perkin Elmer) system at the *SAGE Department (IMT Lille Douai*). The cartridges were previously thermo-desorbed at 350°C for 15 minutes with a helium flow of 20 mL min^{-1}. This method allowed the separation and

identification of up to 56 compounds, from C_5–C_{16} VOCs, including 7 aldehydes, 4 ketones, 10 monoterpenes and 6 long-chain alkanes from C_{12} to C_{16}. More details on the analytical technique can be found elsewhere (Ait-Helal et al., 2014; Detournay et al., 2011). VOCs can be classified according to their saturation concentration, C^*, which indicates their volatility (Ait-Helal et al., 2014; Epstein et al., 2010; Robinson et al., 2007). Here, C_{12}–C_{16} alkanes are classified as VOC of intermediate volatility, since given their C^* values are between 10^3 µg m^{-3} $<C^*<10^6$ µg m^{-3} (Ait-Helal et al., 2014). The detection limits lie between 1 ppt to 13 ppt (hexadecanal) and the global uncertainty varies between 3.7% and 32.6% as detailed elsewhere (Detournay et al., 2011; Keita et al., 2018).

The application of both methods allowed the comparison of common compounds that were measured at ambient sites and sources (benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, trimethylbenzenes, n-heptane, iso-octane, n-octane, α-pinene, β-pinene, limonene, isoprene) and the performance analysis of the analytical techniques. Furthermore, the combination of different sorbent tubes and analytical strategies allowed the quantification of a higher number of VOC species, and therefore, a more extensive analysis of source contributions.

2.3 Metrics and calculations

Different calculations were implemented to assess the VOC emissions and their impacts in Abidjan. Here we provide the mathematical basis for each investigated parameter. Firstly, the emission factors (EF) were computed for the whole extended VOC database (56 compounds) following the methodology described in Keita et al. (2018). EFs combined with regional statistics were later used for the estimation of VOC emissions in Côte d'Ivoire for each source category. Secondly, the emission ratios (ER) of each VOC species related to CO for all the emission sources were established. Finally, the reported ERs were used to evaluate the impacts on atmospheric reactivity by applying commonly used metrics.

2.3.1 Emission factors and quantification of VOC emissions

VOC emission factors were estimated from the concentrations measured for all the emission sources, 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 emission factor of the specific VOC in gram per kilogram of burned fuel (g kg^{-1}); ΔVOC = $[VOC]_{emission} - [VOC]_{background}$ is the VOC mixing ratio in the emission and background air respectively, in parts per billion by volume (ppbv), MW_{VOC} is the molar weight of the specific VOC (in g mol^{-1}), 12 is the molar weight of carbon (g mol^{-1}) and *fc* is the mass fraction of carbon in the fuel analysed. The *fc* values used were obtained from the literature and applied to each source. The EF for selected fifteen VOCs were already published and more details about the method can be found elsewhere (Keita et al., 2018). Here we applied the same method for the whole VOC database, including 56 compounds directly measured from the emission sources. For this, VOC emissions were estimated using the emission factors obtained from near-source measurements along with the statistical International Energy Agency (IEA) activity data, available for the different sources). Equation 1 was used to compute the emission factors, considering all the VOC species measured and including the mass fraction of each fuel (fc) obtained from the literature. Additionally, the differences in fuel type and the fleet age have been considered, as well as the fleet distribution by calculating the equivalent vehicular fleet. For the road transport sector, the equivalent fleet means were calculated considering the fleet characteristics in Côte d'Ivoire, as detailed in Keita et al. (2018). These

calculations were based on the information given by the Direction Generale des Transports Terrestres in Côte d'Ivoire, which considered that 60% of vehicles are old models and 77% of the total fleet is composed by light-duty vehicles. Regarding two-wheel vehicles, 60% of them are two-stroke engines and only 40% of the total are considered as recent vehicles (SIE CI, 2010). In the residential profile, we integrated the emissions measured from charcoal making, charcoal burning and wood fuel burning sources, commonly observed at residential sites in Abidjan. Afterwards, the mean road transportation and residential profiles for Côte d'Ivoire were computed and compared with two referenced global inventories, EDGAR v4.3.2 and MACCity (Granier et al., 2011; Huang et al., 2017).

2.3.2 Molar mass emission ratios

Emission ratios (ER) were obtained by dividing each VOC mixing ratio by carbon monoxide (CO) mixing ratios as follows:

$$ER = \frac{[\Delta VOC]\ ppbv}{[\Delta CO]\ ppmv} \quad (2)$$

We selected CO as a combustion tracer because most VOCs and CO are co-emitted by the target sources. Furthermore, ratios to CO are regularly reported in the literature for biomass burning and urban emissions (Baker et al., 2008; Borbon et al., 2013; Brito et al., 2015; Gilman et al., 2015; de Gouw et al., 2017; Koss et al., 2018; Wang et al., 2014) which are useful constraints for further comparisons. Emission ratios were calculated in ppbv of VOC per parts per million by volume (ppmv) of CO, which is similar to a molar ratio (mmol VOC per mol CO). Molar mass (MM) emission ratios were also computed following Gilman et al. (2015). MM is the VOC mass emitted (μg m^{-3}) per ppmv CO, obtained from equation 2 and converted by using the VOC molecular weight (MW) (g mol^{-1}) and the molar volume (24.86 L at 1 atm and 30°C). Table S1 includes the emission ratios obtained for each VOC and MW values used.

2.3.3 VOC-OH reactivity

The OH reactivity was estimated to evaluate the potential contribution of each measured VOC to the photochemical processing. VOC-OH reactivity represents the sink reaction of each VOC with the hydroxyl radical (OH) and is equal to

$$VOC_{OH\ reactivity} = ER\ x\ k_{OH}\ x\ CF\ , \quad (3)$$

where ER is the emission ratio for each VOC related to CO (ppbv per ppmv), k_{OH} is the second-order reaction rate coefficient of VOC with the hydroxyl radical (x10^{-12} cm^3 $molecule^{-1}$ s^{-1}) and CF is the conversion factor of molar concentration (2.46×10^{10} molecule cm^{-3} $ppbv^{-1}$ at 1 atm and 25°C) (Gilman et al., 2015). k_{OH} values for all VOC species were obtained from Atkinson and Arey (2003) and the NIST Chemical Kinetics Database (Manion et al., 2015).

2.3.4 Ozone Formation Potential

The oxidation of VOCs is often initiated by the reaction with the hydroxyl radical (·OH), which in the presence of NO_x ($NO+NO_2$) leads to the photochemical formation of O_3. The ozone formation potential represents the ability of each VOC to produce tropospheric ozone and it was calculated as follows:

$$VOC\_ozone\ formation\ potential = ER\ x\ POCP, \quad (4)$$

where the ER is the emission ratio of each VOC related to CO (ppbv of VOC per ppmv of CO) and POCP is the photochemical ozone creation potentials developed in previous studies (Derwent et al., 2007; Jenkin et al., 2017). POCP values were obtained by simulating a realistic urban mass trajectory with the Master Chemical Mechanism (MCM). This model estimates the change in ozone production by incrementing the mass emission of each VOC (Derwent et al., 1998). POCPs for an individual VOC are estimated by quantifying the effect of a small increase in its emission on the concentration of the formed modelled ozone, respective to that resulting from the same increase in the ethene emission (POCP value for ethene is, therefore, 100). In this study, POCP values were analysed on VOC family basis obtained from a recent study (Huang et al., 2017), or adapted from individual POCP values.

2.3.5 Secondary organic aerosol (SOA) formation potential

The SOA formation potential represents the propensity of each VOC to form secondary organic aerosols and is equal to

$$SOA\_VOC\ formation\ potential = ER\ x\ SOAP\ , \quad (5)$$

where ER is the emission ratio for each measured VOC related to CO (ppbv of VOC per ppmv of CO) and SOAP is a non-dimensional model-derived SOA formation potential (Derwent et al., 2010; Gilman et al., 2015). All SOAP values represent the modelled mass of organic aerosol that were formed per mass of VOC reacted on an equal mass emitted basis relative to toluene. Toluene was selected as the reference compound due to its well-known emissions and it is usually documented as a critical anthropogenic SOA precursor (Derwent et al., 2010).

ER, k_{OH} and SOAP values for each VOC and each source are detailed in Table S1. In the absence of SOAP values for specific compounds, we estimated the values (indicated in Table S1, referred as [a]) by using those of comparable compounds based on similar chemical properties, as suggested in the study of Gilman et al. (2015).

2.4 Ancillary data

Meteorological observations were provided by the NOAA Integrated Surface Database (ISD; https:// www.ncdc.noaa.gov/isd for more details). Daily rainfall, air temperature, and wind speed and direction measurements were recorded at the Abidjan Felix Houphouet Boigny Airport. Figure 1 gives the geographical location of the meteorological station and ambient sampling locations.

3. Results and discussion

3.1 Local meteorological conditions

Meteorological data from Abidjan, Côte d'Ivoire, are reported in Figure 2. Weekly accumulated precipitation and weekly air temperature means were analysed during 2016. Meteorological conditions in Abidjan are also affected by the monsoon phenomenon which establishes two well defined seasons: a wet season between March and August and a dry season from November to February. The weekly mean air temperature observed was between 24.6 and 29.4°C, reaching a maximum during the beginning of the wet season (Figure 2). The precipitation pattern shows an increased rate during the monsoon period; however, negative anomalies were observed this year compared with the previous

ones (Knippertz et al., 2017). Observed wind patterns during the field campaign showed a predominant contribution from the southwesterly sector with maximum speed during daytime up to 13 m s^{-1}. The high wind speed records reported in Abidjan are higher than those observed in other polluted urban atmospheres (Dominutti et al., 2016; Salameh et al., 2016a; Zhang et al., 2014).

3.2 VOCs in Abidjan atmosphere

Our analysis relies on the fifteen VOC species already listed in Keita et al. (2018, only for emission sources) and these were measured in both ambient air and at emission sources. The VOCs include 8 aromatic hydrocarbons, 3 monoterpenes, 3 alkanes, and isoprene which span a wide range of reactivity and represent the various types of VOC expected to be released by fossil/non-fossil fuel combustion and biogenic emissions.

3.2.1. Ambient concentrations and spatial distribution

The ambient concentration sum of the fifteen quantified VOCs ranged from 6.25 to 72.13 µg m^{-3} (see size-coded pie chart, Figure 3). Higher VOC concentrations were reported in KSI, BIN CRE and PL sites (Figure 3). The predominant VOCs are toluene (4.18 ± 3.55 µg m^{-3}), m+p-xylene (4.05 ± 3.41 µg m^{-3}), iso-octane (2.59 ± 3.37 µg m^{-3}), benzene (1.00 ± 0.41 µg m^{-3}), ethylbenzene (0.93 ± 0.86 µg m^{-3}) and limonene (0.77 ± 0.76 µg m^{-3}). Overall, anthropogenic VOCs dominated the ambient composition by a factor of 5 to 20 compared to biogenic ones. BTEX (benzene, toluene, ethylbenzene, and m+p and o-xylenes), a subgroup of aromatic VOCs, usually makes up a significant fraction of the VOC burden in urban atmosphere (Borbon et al., 2018; Boynard et al., 2014; Dominutti et al., 2016). They are emitted by fossil fuel combustion from transport and residential sources as well as evaporation processes such as fuel storage and solvent uses (Borbon et al., 2018). Here their contribution ranged from 35% to 76% of the total VOC burden measured at the ambient sites. Therefore, the following discussion will only focus on BTEX as representative of all measured anthropogenic VOC patterns. Figure 3 shows the spatial distribution of the total VOC concentrations at each site and detailed by the BTEX composition. Firstly, a spatial heterogeneity of the total measured VOC concentration (total values on pie chart, Figure 3) is depicted in the Abidjan district. This spatial heterogeneity has been already pointed out by recent studies performed in Abidjan for other atmospheric pollutants (Bahino et al., 2018; Djossou et al., 2018). While a spatial heterogeneity was also observed in aerosol concentrations (Djossou et al., 2018), maximum aerosol concentrations were reported near domestic fires (similar to KSI) and landfill sites (AD), showing a different pattern than the one observed for the VOC concentrations. Besides the dilution processes, the spatial distribution of total VOC concentrations seems to be related to the proximity of emission sources, affecting ambient VOC concentrations in the different sampling locations. For example, higher total VOC concentrations were mainly observed in the central urban area (like KSI, CRE and PL) where the density of emission sources increases.

Second, m+p-xylene and toluene dominate the ambient distribution of BTEX, ranging from 9 to 27 % and 8 to 31 % of the total VOC, respectively. BTEX composition is consistent between PL, CRE, BIN and KSI sites with high VOC loads while an enrichment in benzene concentrations is observed at FAC, ABO, ZYOP, AT and AD sites (from 16% to 30% contribution). The BTEX composition can be affected by emissions and chemistry. The toluene-to-benzene ratio is a useful indicator of either traffic and non-traffic source or chemistry effects. On the one hand, the toluene-to-benzene at PL, CRE, BIN and KSI sites is higher than 4 which suggests the influence of sources other than traffic

like industrial sources. On the other hand, the toluene-to-benzene lie between 0.8 and 1.9 at lower VOC load sites (FAC, ABO, ZYOP, AT and AD) (Brocco et al., 1997; Heeb et al., 2000; Muezzinoglu et al., 2001). These values are closer to the one usually observed at traffic emissions. There is no visible effect of chemistry here especially on higher aromatics like C8-aromatics with a shorter lifetime whose contribution stays almost constant regardless of the site.

The mean ambient concentrations observed in Abidjan for alkanes and aromatics were compared with those observed in other cities worldwide (Figure 4). On one hand, mean concentrations in Abidjan depicted lower values when compared with those measured in other cities (Figure 4). Keita and co-workers (2018) pointed out the high emissions observed in Abidjan sources. In their study, road transport and wood burning VOC emission factors spanned 2 to 100 orders of magnitude, respectively, when compared with those from the literature. Our ambient observations suggest that wind speed have an important role in the mixing and dilution of the anthropogenic emissions leading to low VOC concentrations in the Abidjan atmosphere. As it was pointed out in the meteorological description, the proximity of Abidjan to the ocean and the intrusion of the sea-breeze circulation can facilitate the dispersion processes and, consequently, the urban emissions dilution. Indeed, Deroubaix et al. (2019) analysed the regional dispersion of urban plumes from southern West Africa coastal cities, i.e. Abidjan, where the inland northward transport of anthropogenic coastal pollutants along with biomass burning emissions were observed.

On the other hand, a reasonably good agreement in the relative composition of alkanes and aromatics is observed, showing the same distribution in most cities, except for Karachi where higher contributions of heptane and benzene were measured (Barletta et al., 2002). Observed concentrations of hydrocarbons result from primary emissions, chemical processing and dilution in the atmosphere. Dilution affects equally all the compounds by decreasing absolute levels without altering their composition. Chemistry can be neglected because the transport time between major urban sources and receptor sites is usually less than the compound lifetimes (here the shortest lifetime for trimethylbenzene is 4.3h). Finally, only emissions are expected to significantly alter the hydrocarbon composition. However, the composition is the same regardless of the location. Such commonality suggests that the urban hydrocarbon composition worldwide is controlled by emissions from fossil fuel combustion and, gasoline powered vehicle in particular (see also next section). Finally, the ambient hydrocarbon distributions in Abidjan are noticeably similar to other northern mid-latitude megacities, suggesting that emissions from fossil fuel combustion for alkanes and aromatics dominate over other regional-specific sources. These results are also consistent with previous studies comparing different database worldwide without including an African city like Abidjan (Borbon et al., 2002; Dominutti et al., 2016; von Schneidemesser et al., 2010). Even if emissions can be different in intensity (number of vehicles for instance), the hydrocarbon composition seems to be similar in the different urban atmospheres.

3.2.2. Ambient composition vs. emission source profiles

A comparative approach was carried out between ambient and source measurement compositions with the purpose of detecting emission source fingerprints in ambient VOC profiles. Figure 5 shows the relative mass contribution of VOC profiles observed at the nine urban sites together with those obtained from the emission sources. While a noticeable variability in the contribution of emission sources is observed, smoother differences are depicted between the ambient sites. This result reinforces the similar BTEX profiles discussed in the section 3.2.1, where the mixing and dilution process were suggested as the main drivers in the control of ambient emissions. Trimethylbenzenes (124-

TMB, 135-TMB, and 123-TMB), mainly observed in road transport emissions, display a dissimilar profile showing higher fractions from sources than ambient sites (Figure 5). These differences might be related to the short lifetime of these compounds (around 4 hours), with a reaction rate ranging from 1.8 to 8.8 x10^{-15} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003). Their reactivity implies a faster reaction in the atmosphere and losses of these species from the emission to the receptor.

On the other hand, in most of the cases, ambient profiles showed higher contributions of alkanes, monoterpenes and isoprene, likely associated with the contribution from different anthropogenic and biogenic sources. The presence of terpenes and isoprene in the profile of all emission sources is notable, mainly in those associated with domestic burning processes, such as charcoal, waste and wood fuel burnings (Figure 5). The terpene emissions from biomass burning were already identified in several studies as they are common species emitted by combustion processes (Gilman et al., 2015; Simpson et al., 2011). Additional studies based on African biomass emissions also reported concentrations of limonene and α-pinene higher than isoprene (Jaars et al., 2016; Saxton et al., 2007).

For the selected VOC species, aromatic compounds represent the higher fraction from ambient and source profiles, contributing from 31 to 75% (Figure 5). Comparing the same VOC species in emission sources versus ambient profiles, we found a similarity with the two-wheel vehicle and domestic fire profiles like wood fuel burning and charcoal burning sources. Nevertheless, the VOC ambient profiles obtained from the sites did not show a contrasted difference despite the differences in the activities conducted nearby.

3.3. Molar mass of measured VOC emissions in Abidjan.

Here we compare the composition and magnitude of anthropogenic emissions as a function of molar mass emission ratios as described in section 2.3.2, which is a readily calculated property used to quantify anthropogenic emissions (Gilman et al., 2015). For this analysis, our expanded VOC database of 56 species was considered, including 12 terpenes, VOCs of intermediate volatility (IVOCs from C_{12}–C_{16} n-alkanes), ketones and aldehydes (>C_6) compounds for all sources (Table 1 and Table S1). Species groups were classified according to GEIA groups (Huang et al., 2017) according to the chemical function of each VOC family (Table S2). In this way, molar masses were also grouped by VOC family from individual values (Table S1). Since the VOCs of intermediate volatility (IVOCs) do not have a specific classification, they were integrated in the group of heavy alkanes (VOC6). Note also that the most volatile fraction of OVOC which usually represents the major fraction, is not represented here in the VOC22 and VOC23 categories. The associated contribution should be analysed as the lower expected limit. Figure 6 shows the contribution of VOC groups to the measured molar mass and the total molar mass of each source, while Figure 7a-d (upper panel) compared the magnitude of measured molar masses for the four leading sectors. As already described in the previous section, the distribution reported in Figure 6 reveals the predominance of aromatic molar masses (VOC13-VOC17), ranging from 26 % to 98 %. The prevalence of these compounds is predominantly observed in gasoline-fuelled vehicles, like gasoline light-duty (LDGV) and two-wheel (TW) vehicles and diesel light-duty vehicles (LDDV). Alkanes (VOC5+VOC6) also comprise a noticeable molar mass fraction, dominating in two-wheel two-stroke vehicle, heavy-duty vehicle and charcoal related sources (by 40, 47 and 53%, respectively).

A considerable IVOCs contribution from the emission of heavy-duty vehicles was observed, with IVOCs dominating the VOC6 fraction by 30% (considering that VOC6 represents 47% of the total emissions from this source).

Interestingly, and as already discussed in Section 3.2.2, monoterpenes (VOC11) comprised 11%, 13% and 22% contribution in wood fuel burning, heavy-duty vehicle and waste burning sources, respectively (FW, HDDV and WB, Figure 6 and Figure 7b-c). Terpenes in biomass burning sources were already pointed out as the most significant emitted compounds together with furans and aromatics in chamber experiments (Koss et al., 2018). Nevertheless, to the extent of our knowledge, their presence in road transport or open waste burning emissions remains unexplored. Regarding OVOCs (VOC22), they were observed in a smaller fraction (less than 7%) apart from heavy-duty vehicles, which contributes to 11% of the total measured molar mass. Previous studies have reported OVOCs as the main fraction in biomass burning emissions (Akagi et al., 2011; Gilman et al., 2015; Yokelson et al., 2013). Moreover, Sekimoto and co-workers also analysed the VOC emission profiles depending on the pyrolysis temperature, showing enrichment of terpenes and non-aromatic oxygenates under high-temperature conditions and an increase in oxygenated aromatics under low-temperature fires (Sekimoto et al., 2018). Comparing the burning-related sources such as wood fuel burning with previous studies, a lower total measured molar mass was observed in our study than those obtained in the US fuels, by a factor of 33 to 117 (Gilman et al., 2015). In that work, Gilman and co-workers have shown that OVOCs represent 57 to 68% of the total measured molar mass. A different pattern is observed in this study, likely related to the limitation of VOC species measurements by the sampling method deployed, which allows the collection of a limited number of aldehydes ($>C_6$) and other oxygenated compounds as well. Thus, our total molar mass estimation for the sources in Abidjan should be considered as lower limit since additional contributions could be expected from other unknown emitted VOCs, such as OVOCs, alkenes and nitrogenated VOCs.

Four sources (TW2T, HDDV, WB, and CH) that represent the leading sectors in the region (road transportation, waste burning, and charcoal burning emissions) were selected, in order to analyse the magnitude of emissions as a function of molar mass and their potential impacts related to African emissions (next section). Figure 7 (a-d) shows the relative composition and the total molar mass of the measured VOC ($\mu g\ m^{-3}$) emitted per ppmv of CO. Two-wheel two-stroke vehicles (TW2T) disclosed the highest molar mass emissions ($4680 \pm 512\ \mu g\ m^{-3}\ ppmv\ CO^{-1}$, Figure 7a-d). TW2T emissions were 10 to 200 times higher than any other source here analysed, such as heavy-duty vehicle ($458\pm60\ \mu g\ m^{-3}\ ppmv\ CO^{-1}$), wood fuel burning ($31.5\pm2.50\ \mu g\ m^{-3}\ ppmv\ CO^{-1}$), charcoal burning ($43.8\pm6.37\ \mu g\ m^{-3}\ ppmv\ CO^{-1}$) and light-duty vehicle ($137.5\pm20\ \mu g\ m^{-3}\ ppmv\ CO^{-1}$) emissions (Figure 6). While aromatics (VOC13-VOC17) seem to dominate the molar mass fraction for most sources, their contributions are dissimilar, dominated by benzene (VOC13) and toluene (VOC14) in burning-related sources, and by xylenes (VOC15) and trimethylbenzenes (VOC16) in traffic-related ones.

3.4 Implications on atmospheric reactivity

The estimation of the impact on atmospheric chemistry of measured VOC emissions is based in the three metrics described in the Section 2.3.

3.4.1 OH reactivity of measured VOC emissions

Figure 7(e-h) shows the fractional contributions and total VOC-OH reactivity per ppmv of CO for the selected sources. The highest total reactivity is observed from the emissions of two-wheel two-stroke vehicles (TW2T, $488 \pm 43\ s^{-1}\ ppmv\ CO^{-1}$), outpacing other sources by a factor of 7 to 170. This disclosed difference is related to the high

ERs observed for the more reactive species, like terpenes (VOC11) and C_8- and C_9-aromatics (VOC15 and VOC16, respectively). Terpenes (VOC11) and aromatics (VOC13-VOC17) altogether are the dominant sink of OH, contributing to 47 to 87% of the total calculated OH reactivity. Individually, terpenes governed the OH reactivity in open waste burning emissions (76%) and heavy-duty diesel vehicles (60%) (Figure 7f-g). When compared with other sources, a singular profile is observed for charcoal burning emissions where aldehydes (VOC22, 13%) and heavier alkanes (VOC6, 28%) have higher contribution than in other emission sources. The modest presence of alkenes in the VOC-OH fractional analysis, well-known for their high reactivity effects, is related to the limitation of the sampling method which does not allow the collection of light alkene species. We might expect a high contribution of alkenes adding to the terpene burden.

3.4.2 Ozone formation potential of measured VOC emissions

Overall, the fractional ozone formation distribution is dominated by aromatics (VOC13 to VOC17) in all sources, by 38 to 63%. Alkanes (VOC6) represent a significant contribution in charcoal burning, heavy-duty diesel vehicles, and two-wheel two-stroke vehicles, accounting for 45, 28 and 26%, respectively. It is important to note the terpenes (VOC11) contribution, coming not only from burning sources but also from the road transportation sector (Figure 7i-l). Aldehydes (VOC22) are well-known due to their high reactivity in the atmosphere (Atkinson and Arey, 2003; Sommariva et al., 2011), and some of these species have shown a large impact on ozone formation and chemistry. In our estimation, we can observe the contribution of these compounds mainly from diesel (HDDV) and charcoal burning sources (CH). The total potential ozone was calculated for each source, showing most of the time a dominant contribution from two-wheel two-stroke vehicles (80 343 POCP ppmv CO^{-1}), which is 13, 24 and 150 times higher than the potential impact in ozone formation derived from heavy-duty vehicles, waste burning and charcoal burning emissions, respectively.

3.4.3 SOA formation potential of measured VOC emissions

Figure 7 (m-p) shows the composition and mean SOA formation potentials of VOC families emitted by each selected source. As can be expected, charcoal burning has the lowest SOAP values (335 SOAP per ppmv CO^{-1}), compared with two-wheel two-stroke vehicle, heavy-duty vehicle and waste burning sources, whose SOAPs values are 147, 10 and 9 times greater, respectively. Globally, aromatics (VOC13-VOC17) governed the SOA formation in our estimations, by 72 to 98%. Interestingly, terpenes (VOC11) represented a minor contribution in the SOA formation, presenting a SOAP index lower than for aromatic species. It represents approximately 20% of the SOAP for toluene (VOC14). Despite the well-known role of terpenes as SOA precursors (Ait-Helal et al., 2014), the method used here is not able to correctly quantify their contributions to SOA formation. The differences between SOAP values and measured aerosols yield were already pointed out by Gilman and co-authors (Gilman et al., 2015), who performed some sensitivity tests in order to harmonize SOAP and aerosols yields. We performed the same analysis here, adjusting the SOAP terpene values to be 10% higher. The results in total SOAP per ppmv of CO did not show considerable increases in any of the sources, expanding the total SOAP up to 1%. Similar results were observed for fractional distribution, so that the changes in terpenes SOAPs (VOC11) did not show any substantial change in the VOC contribution for SOA formation. These findings are in agreement with those identified in the study of Gilman

et al. (2015), suggesting an underestimation in the fractional contribution of terpenes to the potential formation of organic aerosols over southern West Africa region.

3.5 Quantification of VOC emissions

Anthropogenic VOC emissions were quantified by considering the complete VOC dataset, which includes the 56 compounds analysed, aldehydes, IVOCs and terpenes species. Mean residential emissions are also integrated and compared with those from the EDGAR v4.3.2 inventory. Additionally, we incorporate the residential and road transport profiles provided by the MACCity inventory (Granier et al., 2011), available in the ECCAD-GEIA database (http://eccad.aeris-data.fr). The main differences between both global inventories are related to the speciation level of VOCs families. MACCity considers all the aromatics in the same VOC group; thus, we provide here the sum of VOC13 to VOC17 families (Table S2) to compare it with the aromatics group from our quantification.

Figure 8 exhibits the speciated emissions calculated for Côte d'Ivoire along with those provided by the two emission inventories. Globally, the discrepancies already highlighted in the previous analysis are exacerbated by introducing the complete VOC database. Calculated residential emissions are greater by a factor of 14 and 43 when compared with EDGAR v4.3.2 and MACCity, respectively (Figure 8a). In terms of composition, the main differences observed are related to the VOC22 group (aldehydes). This group discloses a higher contribution by a factor of 5 in the EDGAR inventory, accounting for 64% of the total emission. There is also a disparity in the contribution from aromatics (sum of VOC13 to VOC17) and alkenes (VOC12), which reveals a more substantial influence in the MACCity profile (58% and 22%, respectively) (Figure 8a). This disparity could be related to the few VOC species that were analysed for the VOC12 group in our study. Nevertheless, aromatics dominate the fractional contribution in our calculated emissions (39%), especially toluene (VOC14) and C_8-aromatics (VOC15) (11% and 10%, respectively). Alkanes (>VOC6 alkanes) show a more significant contribution in the residential profile, in which IVOCs contribute 20% of the total calculated alkanes obtained by our estimations.

Regarding the road transportation sector, total calculated emissions are higher than the global inventories by a factor of 100 and 160 for EDGAR and MACCity, respectively (Figure 8a). A moderate agreement is observed with speciation (Figure 8b). Aromatics and alkanes are the main contributions for all profiles in different proportions. Our estimates report the most significant contributions in C_8-aromatics (VOC15), C_9-aromatics (VOC16) and toluene (VOC14), with a 25, 14 and 10% contribution, respectively (Figure 8c and Figure 9). In comparison, EDGAR v4.3.2 shows a contribution of 9% for VOC15, 3.5% for VOC16 and 13% for VOC14 (Figure 9). Road transport profiles also reproduce the anomalies in the VOC12 (alkenes) contribution observed in the residential sector, presenting greater emissions in the global inventories. The comparison between both inventories also depicted considerable discrepancies, of a factor of 3.

A similar profile is observed for heavier alkanes (VOC6) which present an analogous contribution between our estimation and EDGAR emissions (34 and 37%, respectively; Figure 8b). Nevertheless, the alkanes (VOC5+VOC6) contribution in the MACCity profiles prevails over road transport emissions accounting for 62% of the total emissions.

Interestingly, terpenes and isoprene emissions can be denoted in both sectors in the Côte d'Ivoire calculated emissions (VOC11 and VOC10). Despite the reduced contribution of these species (9% in residential and 4% in road transport), the underestimation of them in the emissions from anthropogenic sources could have consequences for atmospheric

chemistry. Since the reactivity is specific for each VOC, the inaccuracies in the speciation could also have implications on the estimation of their impacts. Specifically for terpenes (VOC11), it can be noted their high contribution in the k_{OH} reactivity, accounting for 42% in the residential sector and 28% in road transport sector reactivities (Figure 8c). Even though the total OH reactivity in all profiles is rather similar, the alkenes fraction in this study is not well-represented which could increase the contribution in terms of reactivity.

Figure 9 also displays the residential and road transportation profiles obtained from Côte d'Ivoire, compared with EDGAR v4.3.2 profiles for Europe. Noticeably in our estimations, road transport and residential sectors presented comparable total emissions, whereas those from the EDGAR inventory were different by a factor of 8 (86.1 vs 12.1 Gg year^{-1}, respectively). Similar disagreements are also observed when comparing EDGAR total emissions for Europe with Côte d'Ivoire, where the former presents larger emissions (198 vs 86 and 433 vs 12 Gg year^{-1}, respectively). We highlight here the substantial differences in total emissions, outpacing those estimated for Europe by a factor of 3 for road transport and by a factor of 6 for residential sector (433 and 198 Gg year^{-1}, respectively). The lack of measurements and source profile data in Africa was previously pointed out in the development of EDGAR inventory, which led to considering the priority of this region for future inventory improvements (Huang et al., 2017). Even though our VOC database is not extensive for all the species emitted by the sources analysed, the incorporation of new VOC species reinforces the usefulness of *in situ* measurements under real conditions to derive realistic emission factors and subsequent estimates of representative emission profiles.

3.6 Anthropogenic emissions of terpenes, IVOCs and aldehydes in southern West Africa

As previously highlighted, terpenes commonly emitted by biogenic sources were observed in the emissions from anthropogenic sources. Global emission inventories wholly neglect these emissions; however, they could have considerable effects in the atmospheric chemical processing, by producing secondary pollutants in the atmosphere. Figure 10a shows the fractional distribution of terpenes in several analysed emission sources. The main contributions are associated with the emissions from waste burning (47%), two-wheel vehicle (20%), wood fuel burning (17%) and charcoal making (14%) sources. The total annual emissions estimated for these compounds, which represents 334 Gg year^{-1} and 11% of the total emissions, cannot be neglected when compared with the emission of other well-known anthropogenic VOC, i.e. C_9-aromatics. Evaluating the distribution of terpene species among the emission sources permits a different pattern to be noted (Figure 11). While terpene emissions from road transport are mainly dominated by α-ocimene and α-terpinolene, limonene and isoprene are mainly emitted by wood-burning sources. The main wood types burnt in Côte d'Ivoire are Hevea (*Hevea brasiliensis)* and Iroko (*Milicia excelsa*), which are widely used in urban domestic fires for cooking, heating and other services (Keita et al., 2018). In our study, we only present the results obtained from Hevea, a tropical African hardwood, characterised as a species that emits monoterpenes (Bracho-Nunez et al., 2013; Wang et al., 2007). The principal monoterpene compounds naturally emitted by Hevea species are sabinene, limonene, and α-pinene (Bracho-Nunez et al., 2013). The isoprene emissions from non-isoprene emitting species were already observed in biomass burning studies, which indicates that isoprene is formed during the combustion process (Hatch et al., 2015).

As it can be noted in Figure 11, isoprene emissions are also impacted by vehicles, mainly two-wheel sources, and camphene and β-pinene emissions by heavy-duty vehicle sources. The anthropogenic sources of isoprene have been documented in urban areas, mainly associated with traffic emissions (Borbon et al., 2001; von Schneidemesser et al.,

2011). However, to the best of our knowledge, no previous studies have ever analysed the presence of monoterpenes from road transportation sources. α-pinene and β-pinene emissions are dominated by charcoal burning fires, which also contribute in some fraction to the emissions of isoprene and limonene. In contrast, charcoal making emissions are dominated by γ-terpinene and isoprene. The results from biomass burning sources provided here were obtained from non-controlled experiments, which did not allow the evaluation of differences between the emissions from each combustion phase (pyrolysis, flaming and smouldering). Further investigation is needed in order to develop a better understanding of these differences and to characterization the different combustion phases.

VOCs of intermediate volatility are suspected to be efficient precursors of SOA (Seinfeld and Pandis, 2006 and references therein). However, as it was discussed in the section 3.4.3, our method was not able to resolve the differences between VOC families and most SOAP was assigned to aromatic compounds (up to 98%). Figure 10b reports the fractional contribution and total emissions of IVOCs. Charcoal making, wood fuel burning, heavy-duty diesel vehicles, and two-wheel vehicles represent the primary sources of these compounds, accounting for 58, 15, 12 and 11% of the total, respectively. Despite their lower emissions compared with aromatics or terpenes, IVOCs are estimated to account for 80 Gg year^{-1} of emissions in Côte d'Ivoire. A recent study observed that fine particles in Abidjan are three times higher than the World Health Organization recommended concentrations (Djossou et al., 2018). Hence, a better understanding of the aerosol precursors and formation processes is essential for the later reduction of their concentrations in the urban atmosphere.

Oxygenated compounds were previously indicated as essential species in the emissions from burning sources (Gilman et al., 2015; Hatch et al., 2015; Koss et al., 2018; Wiedinmyer et al., 2014). In addition, oxygenated compounds like non-aromatics were dominant in the burning emission sources including a range of functional groups, of which alcohols and carbonyls were the most abundant (Koss et al., 2018; Stockwell et al., 2015). Figure 10c shows that aldehyde emissions are mainly governed by charcoal making, two-wheel vehicle and wood burning sources (Figure 10c). In our study the quantified aldehydes represent only 5.5% of the total emissions of the country (170 Gg year^{-1}). However, they can be essential compounds concerning reactivity and ozone formation. Hence, further analysis of oxygenated compounds together with furans and other nitro-oxygenated compounds needs to be addressed in future campaigns, in order to improve not only the quantification of these compounds but also provide a better identification of the African tracers from biomass burning processes.

4. Summary and conclusions

This study reports for the first time a chemically detailed range of VOCs including C_5-C_{16} alkanes, monoterpenes, alkenes, aromatics and carbonyls compounds by using sorbent tubes during an intensive field campaign in Abidjan, southern West Africa. We present here an original dataset integrating main emission sources and ambient measurements from nine representative sites, and covering the urban spatial distribution of VOCs in Abidjan. The spatial distribution and composition of VOC in ambient air in Abidjan reveals the effect of local burning and traffic emissions. The highest concentrations were observed near domestic fires, landfill waste fires and traffic sites, in agreement with the results reported in previous studies, when gas-phase and aerosols pollutants were measured.

The calculation of emission ratios is an important metric to evaluate the estimates provided by global emission inventories. Emission ratios from regional-specific emission sources were established here and later used for the analysis of fractional molar mass contribution and the estimation of potential VOC OH reactivity, ozone and

secondary organic aerosol formation. The distribution of VOC emissions (magnitude and composition) was different for each evaluated source. Two wheel and heavy-duty vehicle sources presented the most significant total molar mass emissions, while charcoal burning was the lowest. The sources related to burning processes, such as waste and wood burning, also presented significant contribution to VOCs emissions. These sources represent common activities present in Abidjan and might contribute a large quantity of VOC emissions to the southern West Africa region.

Regarding VOC speciation, molar mass contributions were mostly dominated by aromatic and alkane compounds. Since few alkene species were quantified, aromatics ruled both ozone and SOA formation potential. However, the SOA metrics applied here were not able to accurately analyse the other important SOA precursors contribution, such as monoterpenes. Nevertheless, monoterpenes can contribute significantly to VOC OH reactivity from some sources like waste burning, and the alkane species can significantly contribute to the total reactivity.

In order to estimate the magnitude of VOC emissions in Côte d'Ivoire, emission factors were determined from the *in-situ* VOC database. Road transportation and residential profiles were obtained and compared with those reported in global emission inventories (MACCity and EDGAR). Our results revealed a discrepancy of up to a factor of 43 and 160 for residential and transport profiles when compared with both referenced inventories. The high levels of VOC emissions obtained for Côte d'Ivoire outpace European emissions by up to a factor of 6. Interestingly, monoterpene emissions were observed in anthropogenic emission sources from biomass burning to road transportation sources, contributing to up to 340 Gg $year^{-1}$. These compounds are generally missing in the global anthropogenic emission profiles, which would underestimate their impacts on air quality. This underestimation is not only expected for Côte d'Ivoire but for all West Africa countries.

This study, in the framework of the DACCIWA project, allowed us for the first time to identify and quantify several VOCs in ambient air and at emission sources in Abidjan, Côte d'Ivoire. Our results provide significant constraints for the development of more realistic regional emission inventories. A continuous effort is needed to collect new emission data and ambient measurements in West African countries for all critical atmospheric pollutants.

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Data availability.

All data used in this study is available on the AERIS Data and Service Center, which can be found at http://baobab.sedoo.fr/DACCIWA.

Competing interests. The authors declare that they have no conflict of interest.

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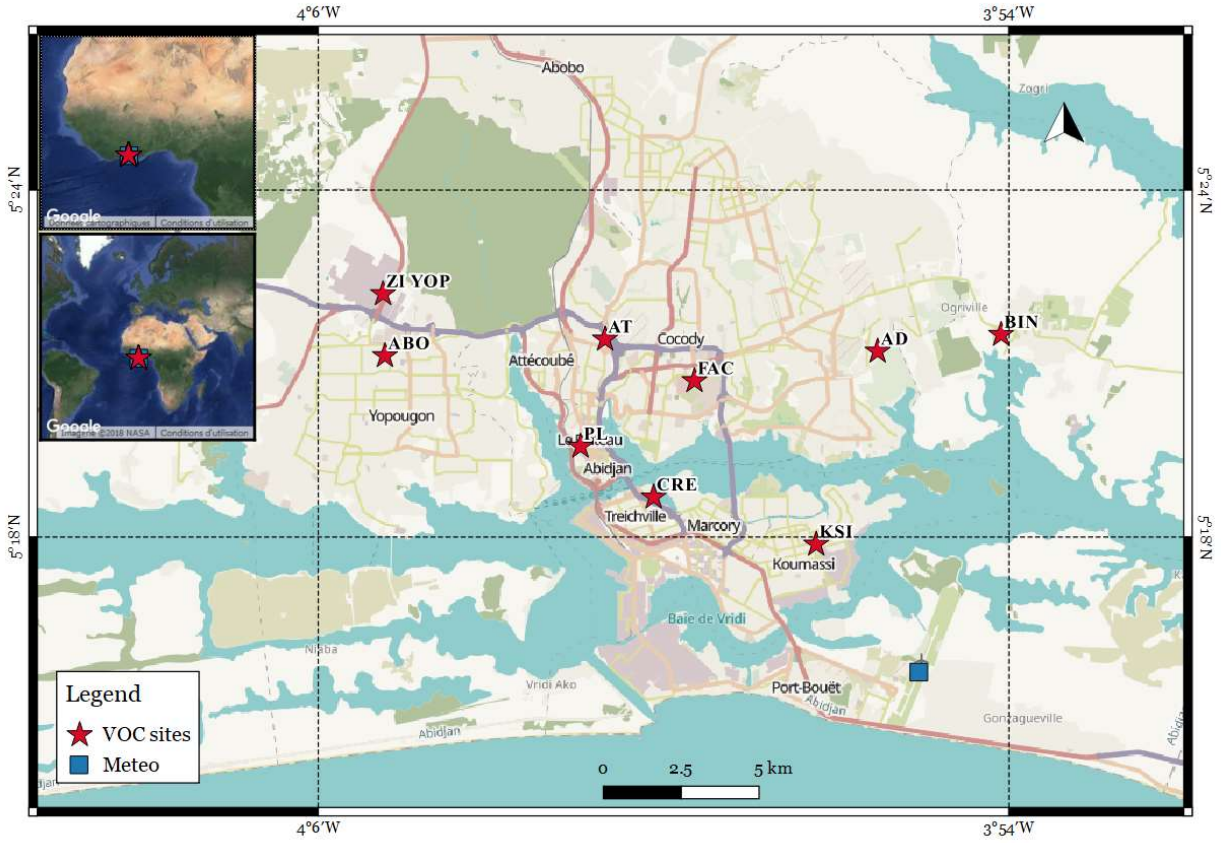

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966 **Figure 1**. Geographical location of Abidjan, Côte d'Ivoire and spatial distribution of ambient VOC measurements.
967 Red stars indicate the VOC measurement sites and the blue square represents the meteorology site. More
968 information about the ambient site is detailed in Table 2. Map: ©OpenStreetMap contributors (OpenStreetMap
969 contributors, 2015)

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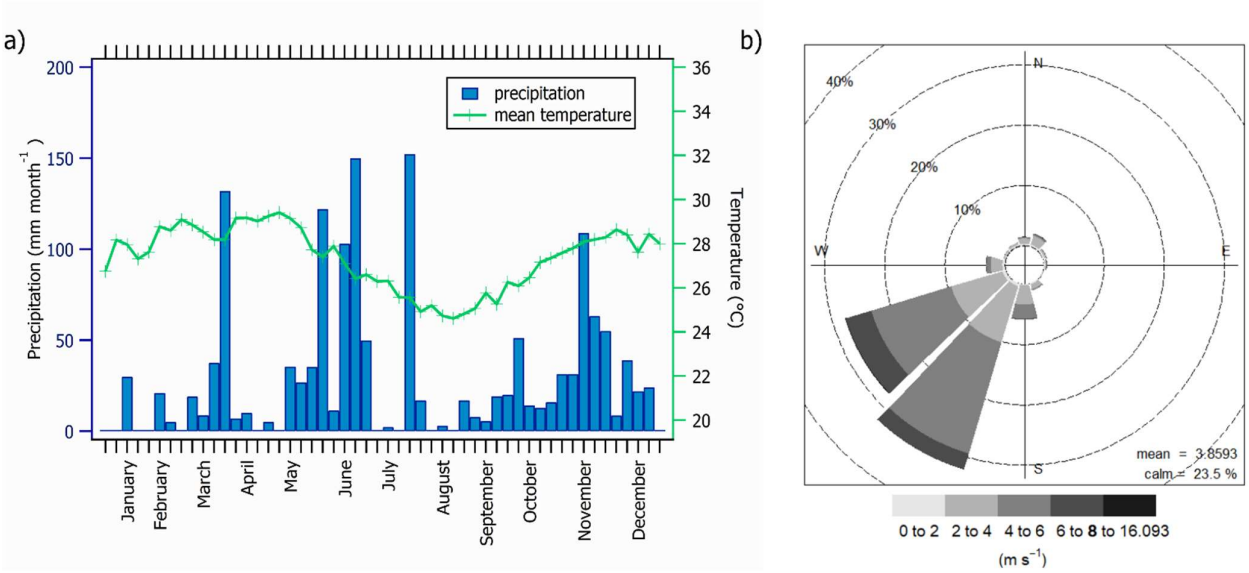
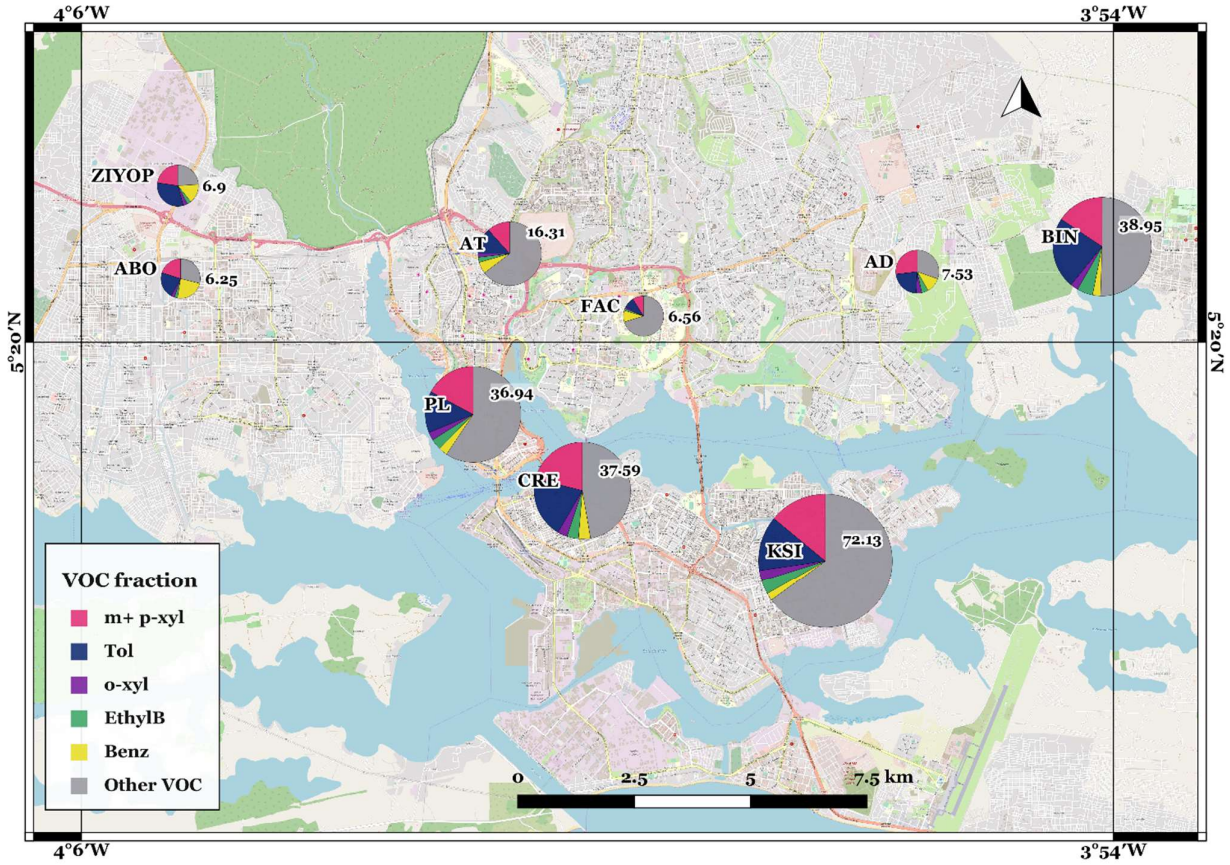


Figure 2. Meteorological data observed in Abidjan, Côte d'Ivoire. The figure represents a) the weekly accumulated precipitation (in mm month^{-1}) and weekly mean air temperature (in °C) and b) the wind speed (in m s^{-1}) and direction observed (deg), during the field campaigns (2016). Data was downloaded from the National Centers for environmental information site (NCDC), NOAA and recorded at Abidjan International Airport (see location in Figure 1).



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979 **Figure 3.** Spatial distribution of VOCs measured at ambient sites in Abidjan, size-coded by the sum of VOCs (in
980 µg m^{-3}) and color-coded by the relative contribution of BTEX compounds (% in mass), namely m+p-xylene (m+p-
981 xyl), toluene (Tol), o-xylene (o-xyl), ethylbenzene (EthylB), benzene (Benz), and other VOC. Values shown in
982 each pie-chart represent the total VOC concentration measured at the sampling point. Ambient site names and
983 characteristics are presented in Table 2. Map: ©OpenStreetMap contributors (OpenStreetMap contributors, 2015)

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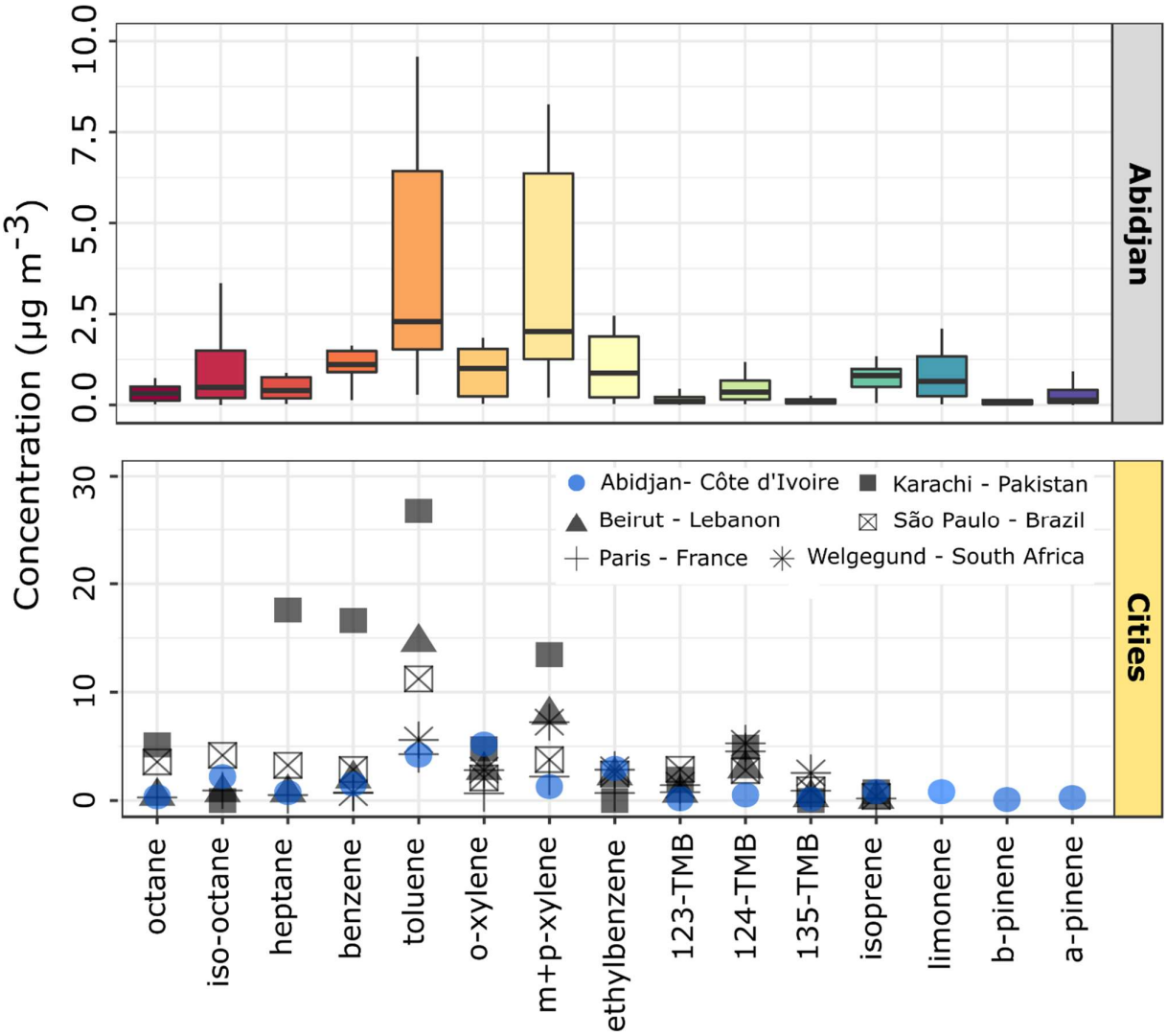


Figure 4. Boxplot showing the VOC concentrations (µg m^{-3}) at Abidjan ambient sites (upper panel). The middle line in each box plot indicates the median (50th percentile), the lower and upper box limits represent the 25th and 75th quartiles, respectively, and the whiskers the 99% coverage assuming the data has a normal distribution. The lower panel shows the mean concentrations reported in other cities worldwide, such as Abidjan - Côte d'Ivoire (this study), Paris - France (AIRPARIF, 2016), São Paulo - Brazil (Dominutti et al., 2016), Beirut - Lebanon (Salameh et al., 2014), Karachi - Pakistan (Barletta et al., 2002) and Welgegund - South Africa (Jaars et al., 2014).

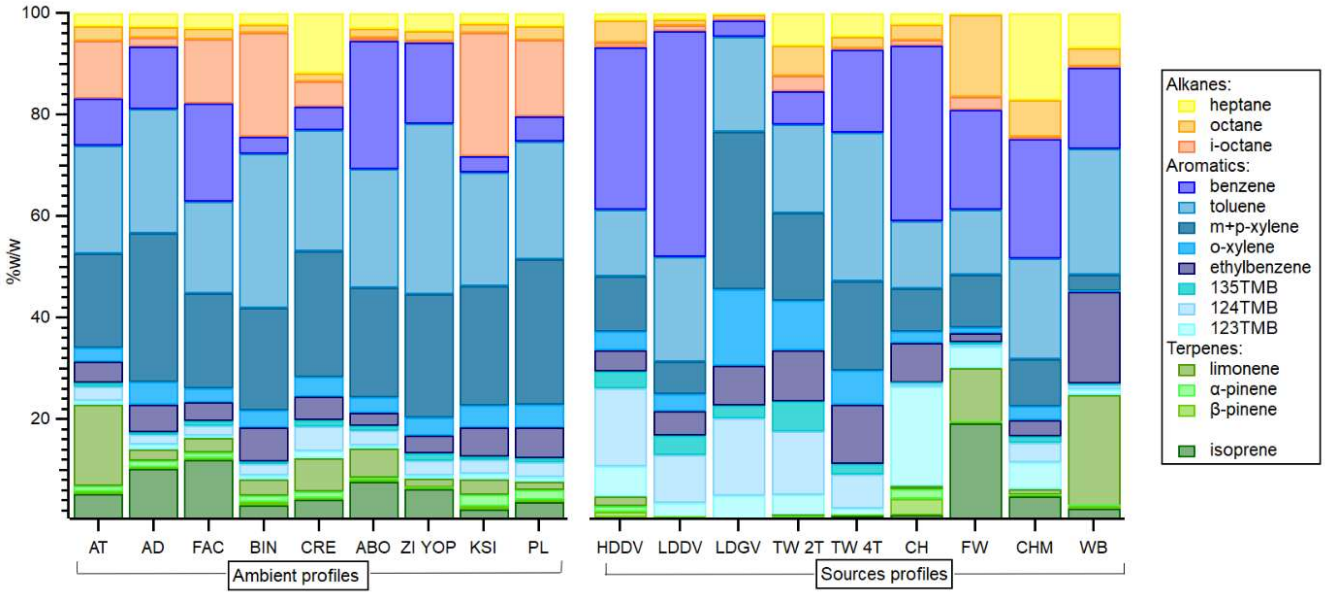


Figure 5. Relative concentration comparison between ambient measurements and emission source profiles of VOCs measured in Abidjan, Côte d'Ivoire. Orange and yellow based colours represent the contributions of alkanes, blue based colours aromatics, and green-based colours terpenes and isoprene.

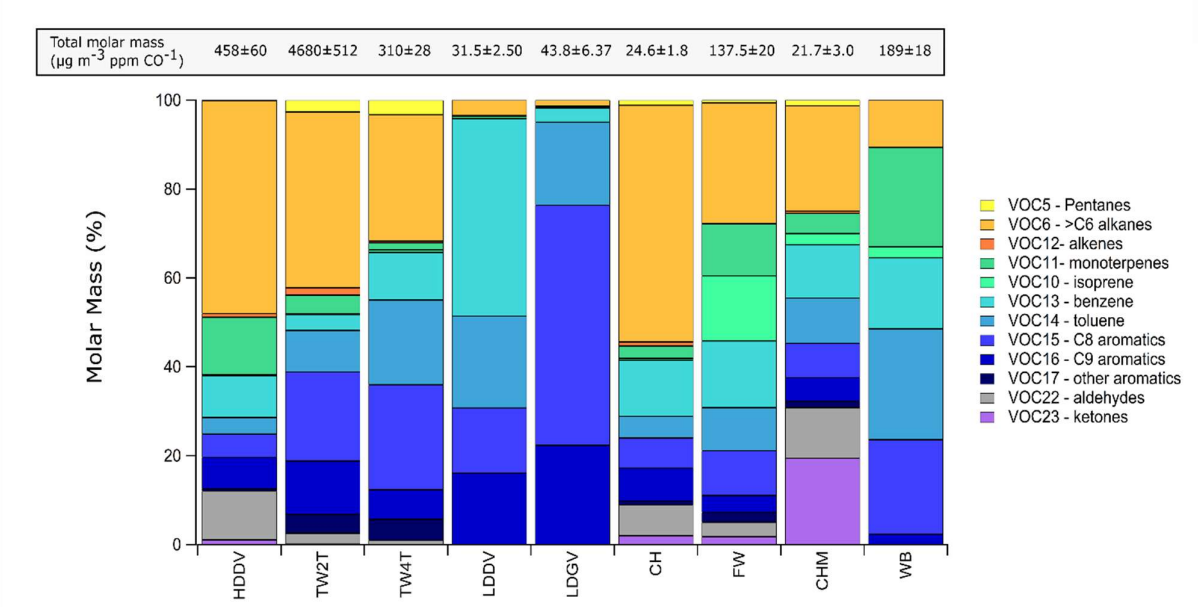


Figure 6. Contribution of VOC reported in Table S1 to the measured molar mass of anthropogenic sources analysed in Abidjan, aggregated in VOC families (Table S2). The emission sources under analysis are heavy-duty diesel vehicles (HDDV), two-wheel two-stroke vehicles (TW2T), two-wheel four-stroke vehicles (TW4T), light-duty diesel vehicles (LDDV), light-duty gasoline vehicles (LDGV), charcoal burning (CH), wood fuel burning (FW), charcoal making (CHM) and waste burning (WB). Values in the upper panel represent the total measured molar mass (in µg cm^{-3} ppm CO^{-1}) of the respective anthropogenic source.

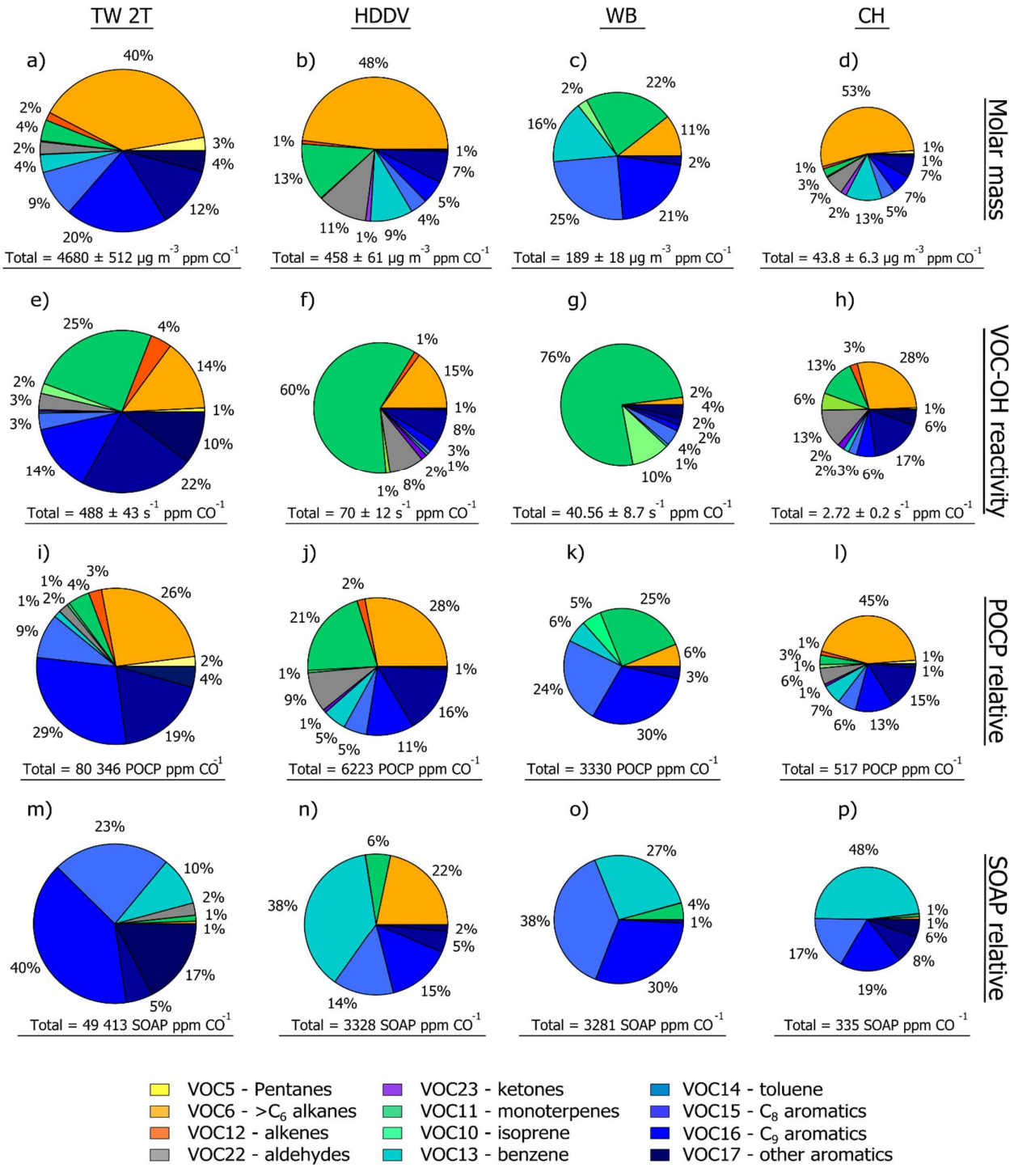


Figure 7. Contributions of VOC emission ratios to (a)–(d) the measured molar mass, (e)–(h) OH reactivity, (i)–(l) relative ozone formation potential POCP and (m)-(p) relative SOA formation potential, aggregated in VOC families. Absolute totals for each source are shown below each pie chart in the respective units.

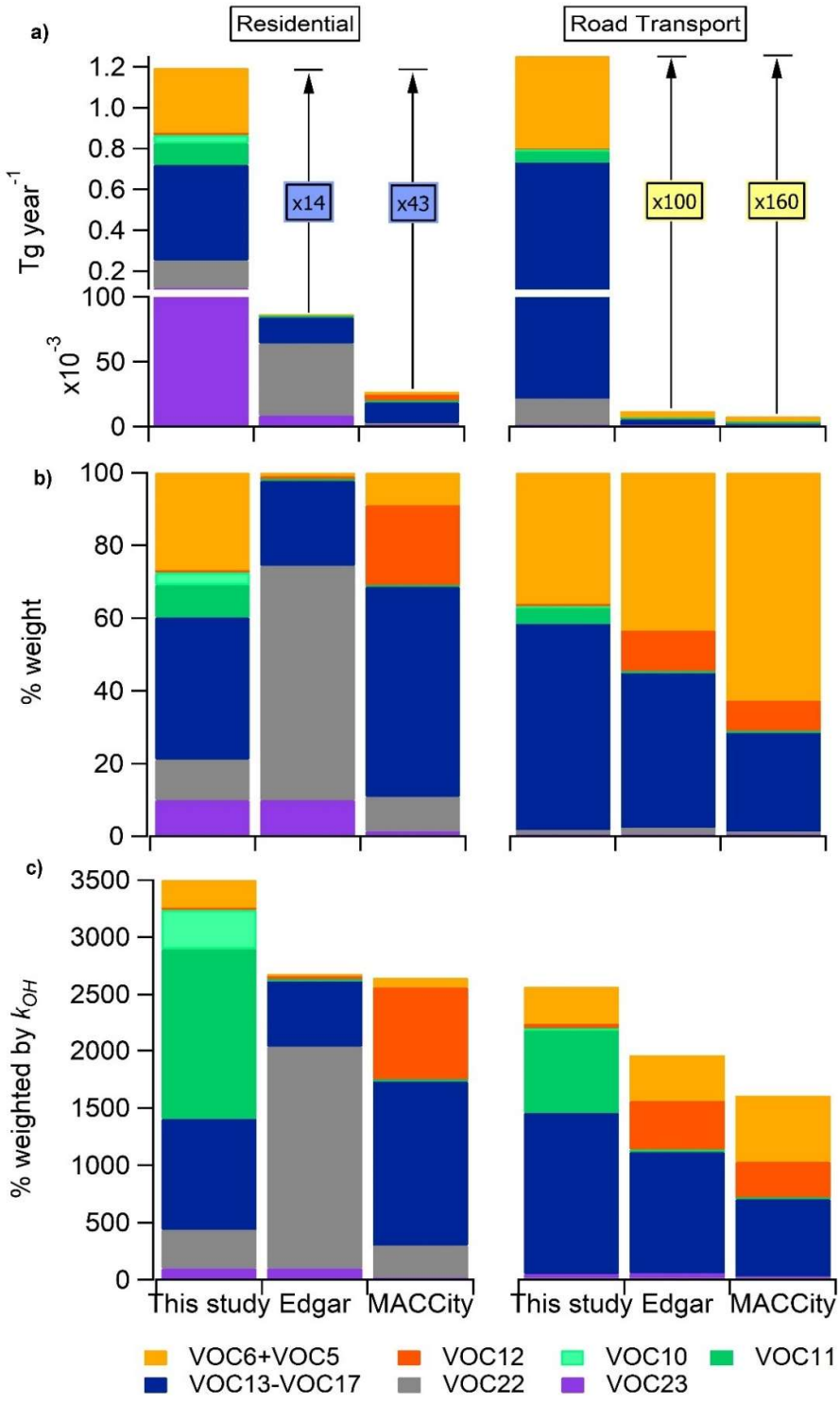


Figure 8. Comparison of VOC emission profiles for Côte d'Ivoire from the emissions estimated from the measurements of this study and the EDGAR v4.3.2 (Huang et al., 2017) and MACCity inventories (Granier et al., 2011). The profile analysis integrates road transportation and residential sectors based on the sector activity for 2012. a) absolute emissions, in Tg year^{-1}, b) relative mass contribution, and c) relative mass reactivity, considering 100 Tg of emissions weighted by the k_{OH} reaction rate calculated for each VOC family.

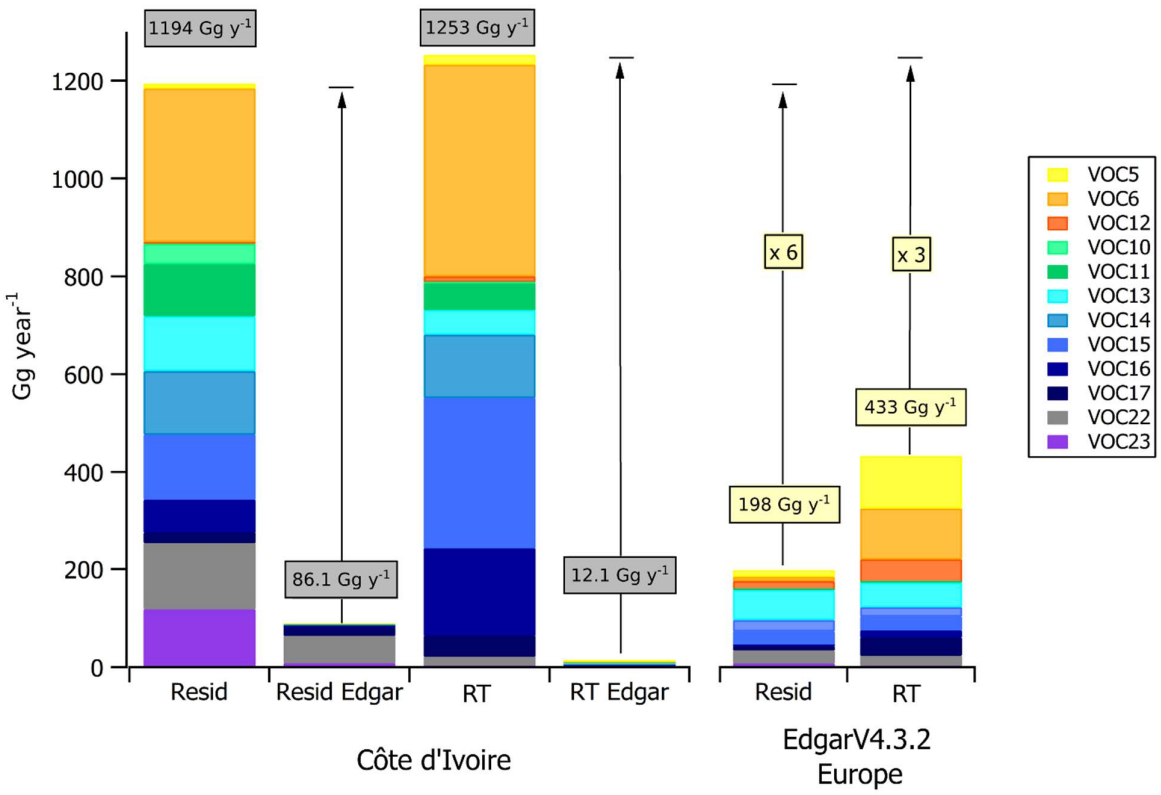


Figure 9. VOC emission profiles considering all the VOC families calculated from the measurements of our study and compared with the global EDGAR v4.3.2 inventory (Huang et al., 2017). The comparison integrates road transportation (RT) and residential (Resid) sectors in Côte d'Ivoire and Europe for the year 2012. Absolute emissions are expressed in Gg year^{-1} for each VOC group.

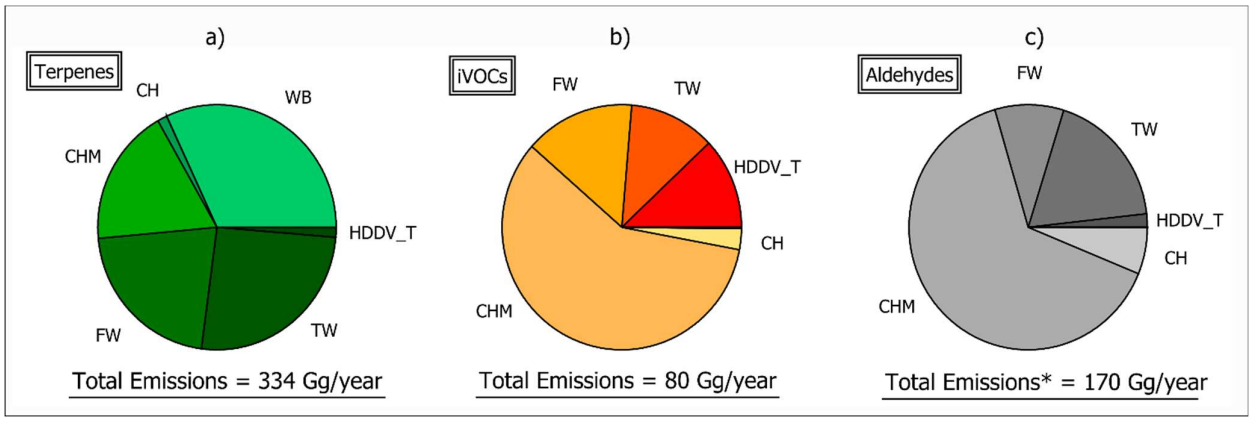
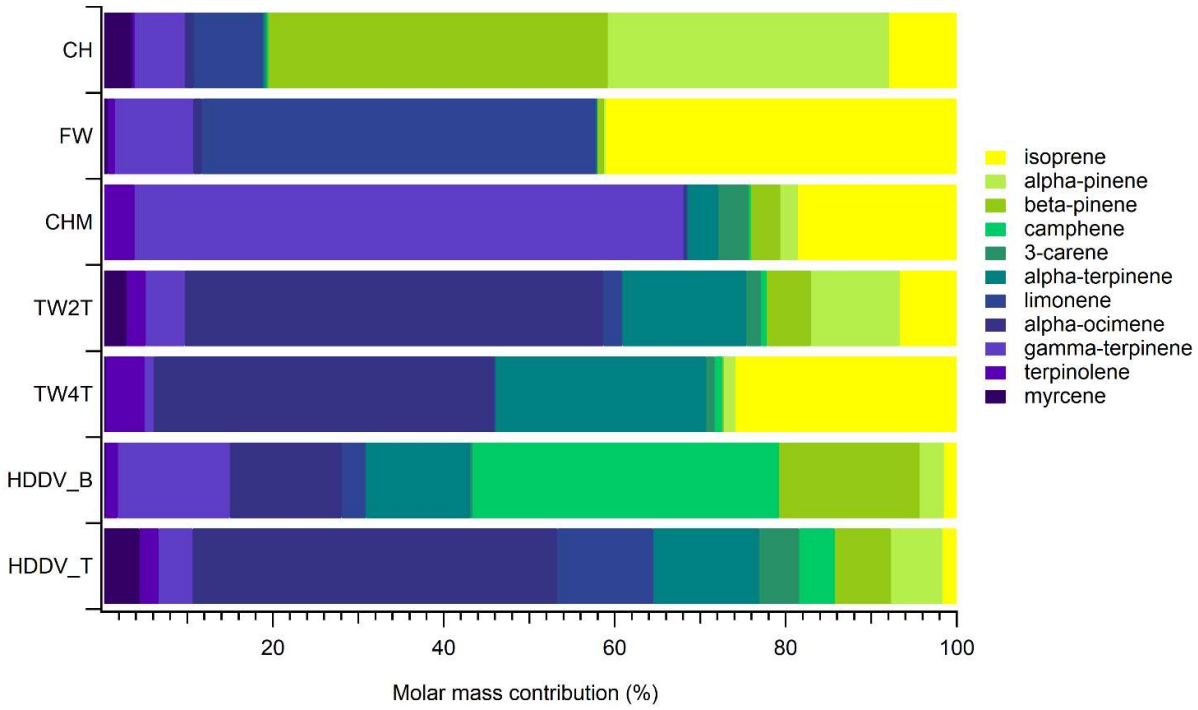


Figure 10. Total estimated emissions and relative distributions in the anthropogenic sources measured in Côte d'Ivoire for the VOC family a) Terpenes, b) IVOCs and c) Aldehydes (* for aldehydes species $>C_6$).



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1042 **Figure 11**. Distribution of monoterpenes and isoprene in the emission sources measured in Abidjan. The values
1043 represent the percentage of each terpenoids over the total emission estimated for these species.

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List of Tables

Table 1. Description of the emission sources measured and evaluated in Abidjan, Côte d'Ivoire.

Reference	Sub-group	Description	source	type
HDDV		Heavy-duty diesel vehicles	Diesel emissions	Road Transport
	HDDV-T	Diesel trucks	Diesel emissions	Road Transport
	HDDV-B	Diesel buses	Diesel emissions	Road Transport
LDDV		Light-duty diesel vehicles	Diesel emissions	Road Transport
LDGV		Light-duty gasoline vehicles	Gasoline emissions	Road Transport
TW	TW2T	Two-wheel two-stroke	a mixture of smuggled oil and gasoline	Road Transport
	TW4T	Two-wheel four-stroke	a mixture of smuggled oil and gasoline	Road Transport
CH		Charcoal	Charcoal burning	Residential
FW		Wood fuel burning	*Hevea brasiliensis*	Residential
CHM		Charcoal making	Charcoal fabrication	Residential
WB		Waste burning	Domestic landfill burning	Waste burning

Table 2. Geographical location and characteristics of ambient measurement sites in Abidjan, Côte d'Ivoire

ID	Site location	Longitude	Latitude	Activity
AT	Adjame	04°01'04"W	05°21'14"N	Traffic site. Site near a gbaka public transport station; regular traffic jams; obsolete public transport vehicles (gbaka, shared taxis and buses); human activities
AD	Akouédo	03°56'16"W	05°21'12"N	Landfill waste burning Uncontrolled landfill, continuous waste burning of all types of waste
FAC	Cocody	03°59'27"W	05°20'42"N	Residential. University residences; electric vehicles; new personal vehicles; use of liquefied petroleum gas (LPG) for cooking
BIN	Bingerville	03°54'07"W	05°21'30"N	Urban Background Far from traffic, near to Ebrié Lagoon
CRE	Treichville	04°00'10"W	05°18'41"N	Green urban area, Near to Ebrié Lagoon; windy
ABO	Abobo	04°04'10"W	05°26'08"N	Traffic + residential Townhall, near to the big market of Abobo. Old communal taxis and minibuses in a crowded crossroad, human activities
ZI YOP	Yopougon	04°04'52"W	05°22'12"N	Industrial area Heavy industries (cement plants) and light industries (agro-industries, plastic and iron processing, pharmaceutical and cosmetics industries); heavy goods vehicles, traffic jams
KSI	Koumassi	03°57'20"W	05°17'52"N	Domestic fires + traffic Residential site mainly influenced by domestic activities, fire-wood, and charcoal; old vehicles.
PL	Plateau	04°01'26"W	05°19'33"N	Traffic/administrative City center, crossroad with traffic jams; light-duty vehicles, near the train station